Synthesis and Kinetic Study of CeO$_2$ and SiO$_2$ Supported CuO Catalysts for CO Oxidation

by

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Shaikh Tofazzel Hossain

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ABSTRACT

Shape- and size-controlled CeO$_2$ and SiO$_2$ have been used in many catalysis applications. This research focused on the low-temperature CO oxidation for the automotive exhaust system. After starting a car, it needs to increase the temperature of catalytic convertor to achieve full CO conversion. Toxic gas from the car pollutes the environment till the car reaches the required temperature. Thus, the preparation of efficient catalyst is much needed to lower the CO conversion temperature. This work especially focused on the correlation of the effect of catalyst supports’ kind and morphology with their catalytic activity. Copper nitrate and copper carbonate precursors for wet impregnation method and copper nitrate for thermal decomposition method have been used to impregnate CuO onto hydrothermally prepared CeO$_2$ nanorods. Several characterization techniques, such as X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and hydrogen temperature programmed reduction ($\text{H}_2$-TPR) have confirmed the presence of three different copper species (α, β, and γ) interacting with CeO$_2$ nanorods while forming oxygen vacancies in CeO$_2$ lattice by compensating the charges between copper and cerium.

Cu-O-Ce solid solutions and CuO impregnated on CeO$_2$ nanorods catalysts (CuO/CeO$_2$) with various compositions have been prepared using thermal decomposition and hydrothermal methods, to understand the distribution effect of copper species on low temperature CO oxidation. A series of temperature programmed reduction-temperature programmed oxidation (TPR-TPO) thermal cycling studies have been conducted to
understand the interactions between three assigned copper species (α, β, and γ) with CeO₂ support and the corresponding catalytic performance of the catalysts.

The effect of support reducibility and reduction treatment has been studied in SiO₂ nanospheres and CeO₂ nanorods supported CuOₓ (0≤x≤1) catalysts on CO oxidation. CuO nanoparticles have been impregnated on SiO₂ nanospheres and CeO₂ nanorods using thermal decomposition method and then the samples have been oxidized in air at different temperatures (400-600 °C). The sample oxidized at 400 °C has also been further reduced under hydrogen atmosphere to compare the effect of thermal treatment (oxidation vs. reduction treatments) on the catalytic activity. In comparison to SiO₂ nanospheres supported CuOₓ catalysts, both CuO/CeO₂ and reduced CuOₓ/CeO₂ catalysts exhibited superior catalytic performance in terms of CO conversion and low-temperature hydrogen consumption. The enhanced activity of CeO₂ nanorods supported CuOₓ catalysts has been correlated strongly to the surface defects on CeO₂ nanorods and interfacial structures.

In addition, in a novel design of co-supported scaffold structure catalyst, CeO₂ nanorods and SiO₂ nanospheres have been mixed in various ratios and 10 wt% CuO nanoparticles have been impregnated onto CeO₂-SiO₂ composite support using thermal decomposition method. Agglomeration of CeO₂ nanorods have been stopped by introducing SiO₂ nanospheres in the catalyst system, and this design can increase the chance to expose more CeO₂ surface to CuO nanoparticles in order to form higher amount of surface defects (incorporation of Cu ions and oxygen vacancies) and lead to higher synergistic interaction between CuO and CeO₂. H₂ TPR and CO oxidation
experiments suggested an enhanced low-temperature catalytic performance for 1:1 ratio mixture of CeO$_2$ and SiO$_2$ due to a strong interfacial interaction among SiO$_2$-CeO$_2$-CuO.

For kinetic study, 5%CO-95%He and O$_2$ gases have been used to reduce and oxidize CuO/CeO$_2$ catalyst respectively at a constant temperature of 400 °C (isothermal process). Mathematical formulas for power law, diffusion, nucleation and contraction models have been used to compare with the experimental data collected during the reduction and oxidation process of the catalyst to determine the best fitted reaction mechanism.
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# Table of Contents

Chapter 1: Introduction .......................................................................................................................... 1  
1.1. Background .................................................................................................................................. 1  
1.2. Problem statement ......................................................................................................................... 3  
1.3. Literature review .......................................................................................................................... 4  
1.3.1. Heterogeneous catalysis ........................................................................................................... 4  
1.3.2. Cerium oxide ........................................................................................................................... 9  
1.3.3. Silicon oxide ............................................................................................................................ 12  
1.3.4. Copper oxide ........................................................................................................................... 15  
1.3.5. Supported CuO catalysts .......................................................................................................... 19  
1.3.6. Reaction rate and mechanism for CO oxidation ......................................................................... 26  
1.4. References ................................................................................................................................... 30  

Chapter 2: Experimental ........................................................................................................................ 42  
2.1. Synthesis methods ......................................................................................................................... 42  
2.1.1. Hydrothermal method .............................................................................................................. 42  
2.1.2. Wet impregnation method ........................................................................................................ 42  
2.2. Instrumentation ............................................................................................................................ 44  
2.2.1. X-ray diffraction (XRD) ............................................................................................................ 44  
2.2.2. Raman spectroscopy ............................................................................................................... 45  
2.2.3. Transmission electron microscopy (TEM) ................................................................................ 47  
2.2.4. X-ray photoelectron spectroscopy (XPS) ................................................................................ 48  
2.2.5. BET surface area ...................................................................................................................... 49  
2.2.6. Temperature programmed techniques ....................................................................................... 50  
2.2.7. Pulse chemisorption ................................................................................................................ 53  
2.2.8. Catalytic activity characterization for CO oxidation ................................................................. 55  
2.2.9. Thermogravimetric analysis (TGA) ......................................................................................... 56  

Chapter 3: Effect of impregnation methods on CO oxidation over CeO₂ nanorods supported CuO catalysts .............................................................................................................................. 58  
3.1. Introduction ................................................................................................................................... 58  
3.2. Experimental .................................................................................................................................. 59  
3.2.1. Catalyst preparation .................................................................................................................. 59  
3.2.2. Catalyst Characterizations ......................................................................................................... 61  
3.3. Results and Discussions ................................................................................................................. 61  
3.3.1. XRD ......................................................................................................................................... 61
List of Figures

Figure 1.1. Simulated heterogeneous catalyst-support. ...................................................... 2
Figure 1.2. Various ways of interaction of the catalyst with the support. ......................... 2
Figure 1.3. The mechanism of heterogeneous catalysts’ surface reactions: (a) Langmuir-Hinshelwood, (b) Rideal-Eley, and (c) Precursor mechanism........................................... 5
Figure 1.4. CO oxidation reaction over Au-TiO$_2$ catalysts. Reprinted with permission from Science [26]. ............................................................................................................... 8
Figure 1.5. CO oxidation reaction over Au-CeO$_2$ catalysts. Reprinted with permission from Kim et al. [27]. Copyright (2012) American Chemical Society. ......................... 9
Figure 1.6. Atomic structure of CeO$_2$ unit cell. ............................................................. 9
Figure 1.7. Typical TEM images of CeO$_2$ nano-octahedra (a), nanocubes (b), and nanorods (c). Structural simulated model of a CeO$_2$ nano-octahedra (d), nanocubes (e), and nanorods (f). Reprinted with permission from Wiley [31]. ........................................ 11
Figure 1.8. Structural change of CeO$_2$ during redox reactions........................................ 12
Figure 1.9. Various methods to synthesized different types of silica nanospheres. Reprinted with permission from Elsevier [40]................................................................. 14
Figure 1.10. SEM images of silica nanospheres synthesized using Stober method with variable MeOH/TEOS ratios before and after calcination. Reprinted with permission from Elsevier [40]........................................................................................................ 15
Figure 1.11. Atomic structure of CuO (a) and Cu$_2$O (b) unit cells................................. 16
Figure 1.12. TEM and HRTEM images (left), and STEM images with EDX mapping (right) of CuO-CeO$_2$ catalysts with various morphologies. Reprinted with permission from Zabilsky et al. [65]. Copyright (2015) American Chemical Society. ................. 21

Figure 1.13. TEM and HRTEM images of CuO/CeO$_2$ nanopolyhedra, nanorods and nanocubes. Reprinted with permission from Wiley [60]. ................................................. 22

Figure 1.14. TEM, HRTEM, STEM and HRSTEM images of CuO/CeO$_2$ nanorods (left) and STEM-EDX mapping of CuO/CeO$_2$ nanorods (right). Reprinted with permission from Yao et al. [66] and Chen et al. [67]. Copyright (2014 and 2015) American Chemical Society.............................................................. 22

Figure 1.15. Schematic illustration of proposed mechanism for H$_2$ and CO oxidation reaction over CuO/CeO$_2$ catalysts. .............................................................. 23

Figure 1.16. TEM images of CuO on hollowSiO$_2$ (a-c) and EDX mapping of CuO on hollowSiO$_2$ (d-h). Reprinted with permission from Nature [71]. ................................. 25

Figure 1.17. TEM images of CuO on hollow SiO$_2$ spheres. Reprinted with permission from Springer [72]. .............................................................. 26

Figure 1.18. Reaction coordinate diagram of an arbitrary reaction with and without the catalyst. ..................................................................................... 27

Figure 1.19. Mechanism for CO oxidation over metal oxide supported catalysts. LH model (a-c), LFS model (d-f), and MVK model (g-h)................................................... 29

Figure 2.1. Autoclave in the furnace......................................................... 43

Figure 2.2. Schematic representation of wet impregnation method.................. 43

Figure 2.3. (a) Bragg's law, (b) X-ray diffraction setup.............................. 45

Figure 2.4. (a) Elastic and inelastic scattering, (b) Raman spectroscopy setup.... 46
Figure 2.5. Schematical representation of TPR process ........................................... 52
Figure 2.6. Calibration curves of TPR for standard Cu$_2$O sample ......................... 52
Figure 2.7. Schematic representation of CO oxidation process using gas chromatograph .................................................................................................................. 55
Figure 3.1. XRD patterns of (a) CeO$_2$ nanorods, various CuO/CeO$_2$ catalysts and CuO nanopowders, (b) Magnified XRD patterns of various CuO/CeO$_2$ catalysts............ 62
Figure 3.2. Raman spectra of CeO$_2$ nanorods, different CuO/CeO$_2$ catalysts and CuO nanopowders. .................................................................................................................... 64
Figure 3.3. XPS spectra of various CuO/CeO$_2$ catalysts. ........................................ 66
Figure 3.4. TEM images of (a) CeO$_2$ nanorods, (b) CuO/CeO$_2$-CNP, (c) CuO/CeO$_2$-CCP, (d) CuO/CeO$_2$-TD ............................................................................................................ 68
Figure 3.5. HRTEM images of single CeO$_2$ nanorod (a and b), CuO/CeO$_2$-CNP (c and d), and single CuO nanoparticle (e). Calculated FFT of CuO nanoparticle (f). Inset of (a): calculated FFT of CeO$_2$ nanorod. ..................................................................................... 69
Figure 3.6. H$_2$-TPR profiles of (a) CeO$_2$ nanorods, (b) different CuO/CeO$_2$ catalysts in same scale. ........................................................................................................................ 72
Figure 3.7. Schematic illustration of different Cu$^{2+}$ species interacting with CeO$_2$ nanorods support. (a) Highly dispersed CuO strongly interacting with CeO$_2$, (b) well-dispersed weakly-interacted CuO and (c) bulk CuO ................................................................. 73
Figure 3.8. The amount of H$_2$ consumption by the catalysts at different peaks .......... 73
Figure 3.9. (a) CO-TPD and (b) rate of desorption of different CuO/CeO$_2$ catalysts. Rate of desorption of CuO/CeO$_2$-CCP in magnified scale shown in the inset of (b). ............ 75
Figure 3.10. (a) Catalytic activity towards CO oxidation and (b) activation energy of different CuO/CeO$_2$ catalysts ........................................................................................................ 77

Figure 4.1. XRD patterns of (a) CeO$_2$ and CuO, (b) Cu-O-Ce samples, and (c) CuO/CeO$_2$ samples ........................................................................................................................................ 91

Figure 4.2 XRD patterns of CeO$_2$ (111) peak in (a) Cu-O-Ce and (b) CuO/CeO$_2$ samples. ................................................................................................................................. 93

Figure 4.3. Raman spectra of (a) CeO$_2$ and CuO, (b) Cu-O-Ce samples, and (c) CuO/CeO$_2$ samples. .................................................................................................................. 95

Figure 4.4. XPS spectra of 10-Cu-O-Ce solid solution and 10-CuO/CeO$_2$ nanorods samples ........................................................................................................................................ 98

Figure 4.5. (a) TEM and (b) HRTEM images of 10-Cu-O-Ce, and (c) TEM and (d) HRTEM images of 10-CuO/CeO$_2$. .................................................................................................................. 99

Figure 4.6. H$_2$-TPR profiles of (a) Cu-O-Ce solid solutions and (b) CuO/CeO$_2$ nanorods. ........................................................................................................................................ 101

Figure 4.7. H$_2$ consumption at each peak of (a) Cu-O-Ce solid solutions and (b) CuO/CeO$_2$ nanorods ........................................................................................................................................ 102

Figure 4.8. (a) H$_2$-TPR profiles, (b) XRD patterns, and (c) Raman spectra after each TPR-TPO cycling for the sample of 10-Cu-O-Ce. .................................................................................................................. 105

Figure 4.9. (a) H$_2$-TPR profiles, (b) XRD patterns, and (c) Raman spectra after each TPR-TPO cycling for the sample of 10-CuO/CeO$_2$. ........................................................................................................................................ 106

Figure 4.10. XRD patterns of as-synthesized, after first TPR and after first TPR-TPO cycle of both (a) 10-CuO/CeO$_2$ and (b) 10-Cu-O-Ce. .................................................................................................................. 108
Figure 4.11. (a) CO-TPD and (b) rate of desorption of 10-Cu-O-Ce solid solution and 10-CuO/CeO$_2$ nanorods samples. Rate of desorption of 10-Cu-O-Ce in magnified scale shown in the inset of (b).................................................................................................. 109

Figure 4.12. CO oxidation curves of (a) Cu-O-Ce and (b) CuO/CeO$_2$.......................... 111

Figure 4.13. Ln(rate) vs. 1000/T curves for calculating activation energies of (a) Cu-O-Ce and (b) CuO/CeO$_2$ ........................................................................................................ 112

Figure 4.14. (a) CO oxidation and (b) Ln(rate) vs. 1000/T curves of 10-Cu-O-Ce before and after redox treatment. ............................................................................................... 113

Figure 5.1. XRD patterns of (a) CuO nanopowders, SiO$_2$ nanospheres and CeO$_2$ nanorods, and (b) CuO/SiO$_2$ nanospheres and (c) CuO/CeO$_2$ nanorods oxidized at various temperatures. (d) Magnified XRD patterns of CuO/CeO$_2$ nanorods of red rectangular portion shown in (c). ..................................................................................................................... 126

Figure 5.2. Raman spectra of (a) CuO nanopowders, SiO$_2$ nanospheres and CeO$_2$ nanorods, and (b) CuO/SiO$_2$ nanospheres and (c) CuO/CeO$_2$ nanorods oxidized at various temperatures. (d) Magnified Raman spectra of CuO/SiO$_2$ nanospheres of red rectangular portion shown in (b)..................................................................................................................... 129

Figure 5.3. XPS spectra of (a) Cu 2p$_{3/2}$, (b) Ce 3d, and (c) O 1s for CuO/CeO$_2$-400. .......................... 131

Figure 5.4. XPS spectra of (a) Cu 2p$_{3/2}$, (b) Si 2p, and (c) O 1s for CuO/SiO$_2$-400........ 132

Figure 5.5. H$_2$ TPR profiles of (a) SiO$_2$ nanospheres and CeO$_2$ nanorods, and (b) CuO/SiO$_2$ and (c) CuO/CeO$_2$ oxidized at various temperatures.............................................. 134

Figure 5.6. H$_2$ consumption of (a) CuO/SiO$_2$ and (b) CuO/CeO$_2$ oxidized at various temperatures................................................................................................................................. 136
Figure 5.7. CO conversion curves of (a) CuO/SiO$_2$ and (b) CuO/CeO$_2$ oxidized at different temperatures. ................................................................. 138

Figure 5.8. (a) XRD patterns and (b) Raman spectra of CuO/SiO$_2$-400 and CuO/CeO$_2$-400 before and after reduction treatment. ................................................................. 140

Figure 5.9. (a) H$_2$-TPR profiles and (b) H$_2$ consumption of CuO/CeO$_2$-400 and CuO/SiO$_2$-400 before and after reduction treatment. ......................................................... 143

Figure 5.10. CO-TPD of CuO/CeO$_2$ and CuO/SiO$_2$ before and after reduction treatment. ........................................................................................................ 144

Figure 5.11. CO conversion of CuO/CeO$_2$-400 and CuO/SiO$_2$-400 before and after reduction treatment. ........................................................................................................ 146

Figure 5.12. TEM images of (a) CeO$_2$ nanorods, (b) SiO$_2$ nanospheres, (c) CuO/CeO$_2$-400, and (d) CuO/SiO$_2$-400. Schematical representations of (e) CuO/CeO$_2$ and (f) CuO/SiO$_2$. ........................................................................................................ 147

Figure 5.13. HRTEM images of (a) CuO/SiO$_2$-400, and (b) and (c) CuO/CeO$_2$-400. FFT of CuO/CeO$_2$-400 in the inset of (c). HRTEM images of red rectangular section I and II shown in (d) and (e) respectively. (f) Schematic representation of atomic structure of CeO$_2$ nanorods. ........................................................................................................ 149

Figure 6.1. XRD patterns of CeO$_2$-SiO$_2$ supported CuO catalysts. ....................... 163

Figure 6.2. BET surface area of CeO$_2$-SiO$_2$ supported CuO catalysts. ................. 164

Figure 6.3. Raman spectra of CeO$_2$-SiO$_2$ supported CuO catalysts. .................... 166

Figure 6.4. XPS spectra of CeO$_2$-SiO$_2$ supported CuO catalysts. ...................... 168

Figure 6.5. TEM images of (a) 100CeO$_2$, (b) 90CeO$_2$-10SiO$_2$, (c) 70CeO$_2$-30SiO$_2$, (d) 50CeO$_2$-50SiO$_2$, (e) 30CeO$_2$-70SiO$_2$, (f) 10CeO$_2$-90SiO$_2$, and (g) 100SiO$_2$. .......... 170
Figure 6.6. TEM (a-c) and HRTEM (d) images of 50CeO2-50SiO2 sample. ............... 171
Figure 6.7. H2-TPR profiles of CeO2-SiO2 supported CuO catalysts. ..................... 173
Figure 6.8. CO-TPD profiles of CeO2-SiO2 supported CuO catalysts. .................... 175
Figure 6.9. CO oxidation curves of CeO2-SiO2 supported CuO catalysts. .............. 177
Figure 6.10. Schematical representation of (a) agglomerated CeO2 nanorods, (b) SiO2 nanospheres, (c) CeO2 nanorods separated by SiO2 nanospheres, and (d) CuO nanoparticles impregnated on CeO2-SiO2................................................................. 178
Figure 7.1. XRD pattern (a) and Raman spectrum (b) of CuO/CeO2 catalyst......... 191
Figure 7.2. TEM (a) and HRTEM (b) of CuO/CeO2 catalyst .................................. 192
Figure 7.3. Light-off curves of CO oxidation (a), W/F ratio vs CO fraction (b), and Arrhenious plot (c) ........................................................................................................................................ 194
Figure 7.4. CO-TPD (a) and rate of desorption (b) of CuO/CeO2 catalyst .......... 195
Figure 7.5. TGA profile of reduction and oxidation reactions over CuO/CeO2 catalysts. ........................................................................................................................................ 199
Figure 7.6. Reduction degree profile of CuO/CeO2 catalysts using optimal kinetic results. ........................................................................................................................................ 202
Figure 7.7. Oxidation degree profile of CuO/CeO2 catalysts using optimal kinetic results. ........................................................................................................................................ 205
List of Tables

Table 1.1. Catalytic activity of various catalyst-support........................................6
Table 1.2. Methods to synthesize shape-controlled silica........................................13
Table 1.3. Synthesis methods of controlled shape and size of copper oxides..............16
Table 1.4. The catalytic activity of CuO/CeO\textsubscript{2} catalysts.............................19
Table 1.5. Kinetic models of heterogeneous catalysts for CO oxidation.......................28
Table 3.1. BET surface area of various CuO/CeO\textsubscript{2} catalysts and temperatures at which 50% and 100% CO conversion by these catalysts.................................................78
Table 4.1. Crystallite size and lattice parameter measured from CeO\textsubscript{2} (111) peak, and BET surface area of Cu-O-Ce and CuO/CeO\textsubscript{2}.........................................................92
Table 4.2. Crystallite size and lattice parameters of 10-Cu-O-Ce after each TPR-TPO cycling.........................................................................................................................107
Table 4.3. Crystallite size and lattice parameters of 10-CuO/CeO\textsubscript{2} after each TPR-TPO cycling.........................................................................................................................107
Table 4.4. The catalytic activity toward CO oxidation over Cu-O-Ce and CuO/CeO\textsubscript{2}...............................................................................................................................114
Table 4.5. The catalytic activity toward CO oxidation over 10-Cu-O-Ce before and after redox treatment, and 10-CuO/CeO\textsubscript{2}........................................................................114
Table 5.1. Average crystallite size measured using CuO (-111) and (111) peaks, BET surface area, T\textsubscript{50}, and maximum CO conversion along with temperatures of CuO/SiO\textsubscript{2} samples oxidized at different temperatures and reduced at 400 °C.....................127
Table 5.2. Crystallite size measured using CeO\textsubscript{2} (111) peak, BET surface area, T\textsubscript{50}, and maximum CO conversion along with temperatures of CuO/CeO\textsubscript{2} samples oxidized at
different temperatures and reduced at 400 °C…………………………………………..128

Table 6.1. H₂ consumptions and OSC of CeO₂-SiO₂ supported CuO catalysts……174

Table 6.2. Catalytic activity toward CO oxidation over CeO₂-SiO₂ supported CuO catalysts………………………………………………………………………………………………………………178

Table 7.1 Basic solid state kinetic models of f(X) and g(X)……………………..198

Table 7.2. Overview of fitted data (R²) for kinetic models at reduction stages……200

Table 7.3. Reaction rate at different cycles of reduction stage…………………….202

Table 7.4. Overview of fitted data (R²) for kinetic models at oxidation stages…….204

Table 7.5. Reaction rate at different cycles of oxidation stages………………….204
Chapter 1: Introduction

1.1. Background

A catalyst is affixed on a support material to maximize the surface area, as the activity of catalyst-support occurs at the surface atoms. Oxide support metal catalysts have several applications, such as catalytic converter, water gas shift reaction, SO\textsubscript{2} reduction, steam reforming of methanol/ethanol, oxidation of ammonia, solid oxide fuel cells etc.

The conversion of carbon monoxide (CO) to carbon dioxide (CO\textsubscript{2}) has made an influence on the modern world. The invention of the internal combustion engine reintroduced scientific interest in CO oxidation catalysis. Car companies required a way to convert the toxic gases into non-toxic and nonthreatening gaseous products. These activities eventually led to the improvement of the current three-way catalytic converters. A catalytic converter is a device that controls the emission of toxic gas by converting toxic gases to less toxic pollutants via catalyzing a redox reaction. Eugene Houdry invented the catalytic converter, and was awarded a US Patent in 1952. Catalytic converters with two-way catalysts were first introduced in automobile industries to use in the exhaust system. Two-way catalysts are used to oxidize unburnt hydrocarbons and CO gas efficiently. Three-way catalysts which could reduce nitrogen oxides as well were introduced in 1981. In a catalytic converter, three reactions occur as shown below:

Oxidation:

\[ C_xH_{2x+2} + [(3x+1)/2] O_2 = xCO_2 + (x+1) H_2O \]  \hspace{1cm} (1)

\[ 2CO + O_2 = 2CO_2 \]  \hspace{1cm} (2)
Reduction:

\[ 2\text{NO}_x = x\text{O}_2 + \text{N}_2 \] \hspace{1cm} (3)

The above reactions usually occur at the interface of a catalyst-support, as shown in Fig. 1.1. Noble metals, such as Pt, Rh and Pd have been used as the catalyst on various metal oxide supports, such as Al\(_2\)O\(_3\), SiO\(_2\), ZrO\(_2\) and CeO\(_2\). In Fig. 1.2, it can be seen that the catalyst can interact with the support in three ways. The catalyst can highly interact with the support, as shown in Fig. 1.2a. Small and bulk size catalysts can loosely interact with the support, as shown in Fig. 1.2b and Fig. 1.2c, respectively.

Figure 1.1. Simulated heterogeneous catalyst-support.

Figure 1.2. Various ways of interaction of the catalyst with the support.
1.2. Problem statement

The activity of a heterogeneous catalyst usually occurs at the surface [1]. Thus, a catalyst support is used to increase the surface area in order to enhance the catalytic activity. Metal oxide supports, such as Al$_2$O$_3$ and SiO$_2$, have been used as inactive support in commercial catalytic converters. The reaction rate and mechanism highly depend on the reducibility of the catalyst supports. Oxygen in an inactive support does not play any role in catalyzing the reaction rate. Therefore, non-reducible Al$_2$O$_3$ shows lower catalytic activity than the reducible and active CeO$_2$ supports [2]. Commercially prepared CeO$_2$ has octahedral shape. Although CeO$_2$ is an active support the oxygen storage and release capacity is very low in octahedral CeO$_2$ due to the presence of eight highly stable (111) planes. Researchers have been focusing on the shape-controlled catalyst support to improve the catalytic activity. In the latest advances, researchers have established several synthesis processes to control the shape and size of cerium oxide nanostructures. Controlled shape and size of ceria support can affect the catalytic activity [3]. Base metals/promoters are used to catalyze the reaction rate. Noble metals have been used as a promoter in the catalysis applications [4-6]. Various metals, such as Pt, Au, Pd, Ir, and Rh have been supported on several metal oxides for redox applications [6,7]. A mixture of Pt, Pd and Rh have been used in the catalytic converter, where Pd helps in oxidation, Rh helps in reduction, and Pt works as both [7]. The reactions (1-3) shown earlier usually occur in the range of 400-650 °C with the presence of noble metal catalysts. When a car is started, it needs time to increase the temperature of the catalytic converter. In the meantime, catalysts cannot convert toxic gases into non-toxic products. Thus, it affects the environment. Lowering the reaction temperature with 100%
conversion of toxic gases is still challenging. The high cost, the future availability, and the complicated preparation methods of noble metals forced researchers to think of different catalysts with similar performance. CuO has attracted attention as one of the most active and cheapest catalysts. CuO nanoparticles have been impregnated on controlled-shape CeO$_2$ using several methods. However, researchers have not yet investigated how to control the shape of CuO in order to use as a promoter in catalysis applications. Controlled shape and size of both catalysts and supports with the large surface area may enhance synergistic interaction at the interface, leading to higher catalytic activity. Limited investigation has been conducted on the interfacial structure to understand the mechanism of the catalytic reactions. Researchers like Burch et al. [8] and Rodriguez et al. [9] raised a question regarding whether the catalyst is activated or the support is activated or a new site formed at the interface is activated during the redox reaction. The contribution of oxygen vacancies and surface defects in the reaction is still unclear. An in-depth study of the mechanism of this catalytic reaction is challenging.

1.3. Literature review

1.3.1. Heterogeneous catalysis

Catalysts are used to speed up a reaction by arranging a reaction path with lower activation energy, but catalysts stay unchanged at the end of the reaction. There are two types of catalysts: homogeneous and heterogeneous. Homogeneous catalysts are in the same phase as the reactants and the products. Heterogeneous catalysts are the materials that are in a different phase than the reactants and the products. In this work, heterogeneous catalysts are prepared to use in catalytic converters.
Adsorption is the most important step in heterogeneous catalysis. Molecules in gas phase or in solution bind to atoms on a solid surface. The catalytic reactions occur at the surface of either the catalyst or the support. There are three mechanisms to explain the surface reaction. In the Langmuir-Hinshelwood mechanism shown in Fig. 1.3a, the two molecules A and B both are adsorbed on the surface of the catalysts. A and B meet at the surface and make A-B bonds which desorb away from the surface. In the Rideal-Eley mechanism (Fig. 1.3b), molecule A is adsorbed on the surface and molecule B meets A on the surface. Molecule B never gets adsorbed on the surface. After the reaction between A and B, they bond and desorb away from the surface. The precursor mechanism shown in Fig. 1.3c explains that one of the molecules (A) is adsorbed on the surface and the other (B) collides with the surface. Molecule B forms a mobile precursor state by colliding with the surface. Then B molecule collides with A on the surface and they react. Finally, new molecules (A-B) desorb away [10].

Figure 1.3. The Mechanisms of heterogeneous catalysts’ surface reactions: (a) Langmuir-Hinshelwood, (b) Rideal-Eley, and (c) Precursor mechanism.

Catalytic activity can be measured using different techniques, which depend on the following applications: catalytic converters [11], water gas shift [12], organic synthesis...
reactions [13] and other industrial applications. In this work, our focus is to prepare catalysts for the application of catalytic converters, where reactions (1), (2), and (3) occur as shown previously. Researchers have been trying to increase the catalytic activity by designing various catalyst-support systems. Table 1.1 shows various catalysts synthesized to increase the catalytic efficiency toward the oxidation of H\textsubscript{2} and CO. Usually, noble metals, such as Pt, Rh, Pd, and Au have been used as catalysts on supported metal oxides, such as Al\textsubscript{2}O\textsubscript{3}, ZrO\textsubscript{2}, TiO\textsubscript{2}, SiO\textsubscript{2}, and CeO\textsubscript{2}. Metal oxide supports can be two different types: reducible and non-reducible. Reducible metal oxide supports are those which can participate in the reaction by providing its oxygen. Transition metal oxides have received attention as substitutes for noble metal catalysts. Researchers have been trying to achieve similar performance by using various transition metal oxides, such as NiO, CuO, MnO, Mn\textsubscript{2}O\textsubscript{7}, FeO, and Fe\textsubscript{2}O\textsubscript{3}.

\textbf{Table 1.1. Catalytic activity of various catalyst-support}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Support</th>
<th>Catalytic activity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt</td>
<td>Al\textsubscript{2}O\textsubscript{3}</td>
<td>H\textsubscript{2} consumption at 325 °C.</td>
<td>14</td>
</tr>
<tr>
<td>Pt</td>
<td>CeO\textsubscript{2}</td>
<td>H\textsubscript{2} consumption in the range of 180-320 °C.</td>
<td>15</td>
</tr>
<tr>
<td>Pd</td>
<td>ZrO\textsubscript{2}</td>
<td>100% CO conversion at ~175 °C</td>
<td>16</td>
</tr>
<tr>
<td>Pd</td>
<td>CeO\textsubscript{2}-TiO\textsubscript{2}</td>
<td>100% CO conversion at 60 °C.</td>
<td>17</td>
</tr>
<tr>
<td>Au</td>
<td>Ce\textsubscript{0.75}Zr\textsubscript{0.25}O\textsubscript{2}</td>
<td>100% CO conversion at 65 °C.</td>
<td>18</td>
</tr>
<tr>
<td>Metal Oxide</td>
<td>Support</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>------------</td>
<td>---------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>NiO</td>
<td>γ-Al₂O₃</td>
<td>The highest amount of H₂ consumption at 430 °C for 20% Ni addition.</td>
<td>19</td>
</tr>
<tr>
<td>NiO</td>
<td>CeO₂</td>
<td>100% CO conversion at 210 °C and two peaks for H₂ consumption at 263 °C and 320 °C.</td>
<td>20</td>
</tr>
<tr>
<td>CuO</td>
<td>ZrO₂</td>
<td>H₂ consumption at 190, 210 and 270 °C for 2% Cu addition.</td>
<td>21</td>
</tr>
<tr>
<td>CuO</td>
<td>TiO₂</td>
<td>100% CO conversion at 110 °C and 140 °C for 8% Cu addition calcined at 400 and 500 °C, respectively.</td>
<td>22</td>
</tr>
<tr>
<td>Fe</td>
<td>TiO₂</td>
<td>H₂ consumption in the range of 200-350 °C and 530-850 °C.</td>
<td>23</td>
</tr>
<tr>
<td>CuO</td>
<td>SiO₂</td>
<td>H₂ consumption at 346 °C.</td>
<td>24</td>
</tr>
<tr>
<td>CuO</td>
<td>CeO₂</td>
<td>H₂ consumption at 200 °C.</td>
<td>25</td>
</tr>
</tbody>
</table>

The effect of support on catalytic activity has been documented. Researchers have been using various metal oxide supports for different catalysis applications. Supports are being used to stabilize catalyst nanoparticles along with an optimal catalytic performance. Strong metal-support interactions and/or electronic metal-support interactions are considered to be the reason of enhancing the catalytic activity due to charge transfers between metal and support, as well as the opportunity in creating highly reactive reaction sites at the interface of metal and support. As shown in Fig. 1.4, Green et al. [26] reported that CO molecules were delivered to the active sites (Au-TiO₂...
interface) through diffusion on the TiO$_2$ surface. The O-O bond from molecular oxygen was dissociated near the active sites and reacted with CO to produce CO$_2$. Kim et al. [27] used density functional theory (DFT) to study the activity of CeO$_2$ support toward the CO oxidation reaction on Au as seen in Fig. 1.5. For the Au-CeO$_2$ catalyst, they reported that CO oxidation occurs by lattice oxygen of CeO$_2$, adsorbed oxygen at Au-Ce$^{3+}$ interface, and coadsorbed CO and O$_2$ on Au nanoparticles. In this research, we have focused on reducible CeO$_2$ and non-reducible SiO$_2$ supported CuO catalysts.

Figure 1.4. CO oxidation reaction over Au-TiO$_2$ catalysts. Reprinted with permission from Science [26].
1.3.2. Cerium oxide

Cerium is a well-known, rare-earth metal, situated in the lanthanide group with an atomic number of 58. Cerium has two valence states: III and IV. Cerium (III) oxide (CeO\textsubscript{3}) is not stable and can be easily oxidized to form cerium (IV) oxide (CeO\textsubscript{2}). CeO\textsubscript{2} is also known as ceria. It has a fluorite structure with a face-centered cubic unit cell (shown in Fig. 1.6) whose lattice constant is 5.411 Å [28].

![Atomic structure of CeO\textsubscript{2} unit cell.](image)
Surface properties, which play an important role in catalysis, can be influenced by the morphology. CeO$_2$ with cubic fluorite structure shows mainly three low index planes, such as (100), (110) and (111). The stability of these planes are as follows: (111) > (110) > (100) [29,30]. Various shapes of CeO$_2$ play a key role in lowering the reduction temperature due to different exposed surface planes. Several nanostructures, such as rods, cubes, octahedron, polyhedron, and tube have been studied in recent years. Ceria octahedron usually exposes the most stable (111) planes on the surface [30,31]. According to many researchers, two planes, (110) and (100), are seen in ceria rods. However, in the previous research of our group, it was shown that (111) plane could also be found in rods [11]. Ceria cubes predominantly expose six of (100) planes [31]. Fig. 1.7 shows typical TEM images of nanorods, nanocubes, and nano-octahedral along with the corresponding simulated schematic.

Cerium oxide (CeO$_2$) is known as a three-way catalyst support because of its unique properties. It has the ability to take in and release oxygen under oxygen-rich and oxygen-lean conditions, respectively [11]. Cerium can change its valence states from Ce$^{3+}$ to Ce$^{4+}$ or from Ce$^{4+}$ to Ce$^{3+}$, depending on oxygen-rich and -lean conditions. Fluorite structure CeO$_2$ can have three different types of defects, such as Frenkel (cation) defects, anti-Frenkel (anion) defects and Schottky defects [32]. However, due to the difference in energies among the aforementioned defects, anti-Frenkel or Frenkel-type oxygen defects, which have the lowest energies, are more likely to be present in ceria. These defects play a significant role during reduction. Due to the low defects concentration, the formation of oxygen pair vacancies does not change the stoichiometry of CeO$_2$. Nevertheless, during reduction, ceria can increase the defect concentration by removing oxygen ions. High
vacancy defect concentration can affect the stoichiometry, which changes from CeO$_2$ to CeO$_{2-x}$ ($0 < x \leq 0.5$). After removing oxygen, the CeO$_2$ lattice compensates the negative charge by changing the charge of two cerium atoms from +4 to +3 [32]. Due to the oxygen vacancy defects and the interchange of valence states, Ce$^{4+}$ and Ce$^{3+}$, CeO$_2$ has a unique ability to act as an oxygen reservoir under oxygen-rich conditions and to release oxygen under oxygen-lean conditions, as shown in Fig. 1.8.

![Figure 1.7. Typical TEM images of CeO$_2$ nano-octahedra (a), nanocubes (b), and nanorods (c). Structural simulated model of a CeO$_2$ nano-octahedra (d), nanocubes (e), and nanorods (f). Reprinted with permission from Wiley [31].](image)
1.3.3. Silicon oxide

Silicon is a semiconductor with atomic number 14. It is one of the most common elements in the earth’s crust and can be found in many forms. Silicon is often bonded with oxygen and forms silicon oxide (SiO$_2$). Silicon oxide is also known as silica. As silicon is tetravalent element, each silicon atom is surrounded by four oxygens to form silica with largely interconnected network. Silica can have both crystalline and amorphous structures. Silica has a wide range of applications, such as producing glass, construction industries, optical fibers, heterogeneous catalysts support, sensor, drug delivery and biomedical applications [33,34]. Various size and shape of silica has been synthesized for last few decades. Researchers have made possible to control the size, shape, porosity and crystallinity of silica nanoparticle depending on its applications. Furthermore, various surface modifications of silica nanoparticles allow modulating precise surface chemistry. Researchers have also showed various synthesis methods to
prepare silica rods, tubes, fibers, spheres and wires. The following table shows different synthesis methods of silica nanoparticles:

**Table 1.2. Methods to synthesize shape-controlled silica**

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Shape</th>
<th>Size</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stöber method</td>
<td>Nanospheres</td>
<td>0.25 – 2.0 µm in diameter</td>
<td>35</td>
</tr>
<tr>
<td>Surfactant templated</td>
<td>Nanorods</td>
<td>~100 nm in length</td>
<td>36</td>
</tr>
<tr>
<td>Co-condensation</td>
<td>Nanorods</td>
<td>Average 10 nm in diameter</td>
<td>37</td>
</tr>
<tr>
<td>Excimer laser ablation method</td>
<td>Nanowires</td>
<td>~10 nm in diameter</td>
<td>38</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Nanotubes</td>
<td>~5 nm in diameter</td>
<td>39</td>
</tr>
</tbody>
</table>

For this work, amorphous silica nanospheres have been synthesized using modified Stöber method and this is commonly used process to synthesize silica nanosphere. Silica nanospheres can be modified using different solvent as shown in Fig. 1.9 [40]. It can be seen that tetraethoxysilane (TEOS), mixed with alcohol, ammonia and water, is used to synthesize solid silica nanospheres. By adding CTAB or polymer, mesoporous silica nanospheres can be prepared. Polyelectrolyte is used to synthesize hollow structures. Fig. 1.10 shows scanning electron microscope (SEM) images of silica nanospheres of different size synthesized using Stöber method. By changing the ratios of TEOS and methanol, size of silica nanospheres can be varied. Particle size of silica decreases from 1500 nm to 10 nm with increasing MeOH/TEOS ratios from 1125 to 6000.
Figure 1.9. Various methods to synthesized different types of silica nanospheres. Reprinted with permission from Elsevier [40].
Figure 1.10. SEM images of silica nanospheres synthesized using Stober method with variable MeOH/TEOS ratios before and after calcination. Reprinted with permission from Elsevier [40].

1.3.4. Copper oxide

Copper is a transition metal with the atomic number 29. It has high thermal and electrical conductivity. Copper can be found in two valence states (I and II) in biomolecular compounds. Thus, two different oxides of copper are copper (I) oxide
(Cu₂O) and copper (II) oxide (CuO). Cu₂O is red color solid and crystallizes in cubic structure (shown in Fig. 1.11) with the lattice constant of 4.2696 Å [41]. CuO, which is a black solid, has monoclinic structure. CuO belongs to C2/c space group where \( a = 4.6837 \) Å, \( b = 3.4226 \) Å, \( c = 5.1288 \) Å and \( \beta = 99.54^\circ \) [42].

![Atomic structure of CuO and Cu₂O](image)

Figure 1.11. Simulated atomic structure of (a) CuO and (b) Cu₂O unit cells.

While researchers have focused on controlling the shape and size of CeO₂ support to elevate the catalytic activity, similarly the shape and size of CuOₓ (0 ≤ x ≤ 1) can have an effect on the catalytic activity. Shape-controlled CuOₓ has been used for different applications. Thus, a literature review has been done on the synthesis methods to control the shape and size of CuOₓ. Various Cu phases of different shapes and sizes along with their synthesis methods are shown in Table 1.3.

**Table 1.3. Synthesis methods of controlled shape and size of copper oxides**

<table>
<thead>
<tr>
<th>Cu phase</th>
<th>Shape</th>
<th>Size</th>
<th>Synthesis method</th>
<th>Remarks</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Nanorods,</td>
<td>5-10 nm</td>
<td>Wet chemical</td>
<td>Increasing NaOH</td>
<td>43</td>
</tr>
<tr>
<td>Material</td>
<td>Shape</td>
<td>Dimension</td>
<td>Aging Method</td>
<td>Note</td>
<td></td>
</tr>
<tr>
<td>----------</td>
<td>-------------</td>
<td>-------------------</td>
<td>----------------</td>
<td>----------------------------------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Nanosphere</td>
<td>200-500 nm diameter</td>
<td>Hydrothermal</td>
<td>Poly-crystal nanospheres consist of many small nanoneedles.</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Nanocubes</td>
<td>500-700 nm edge lengths</td>
<td>Hydrothermal</td>
<td>A mixture of ethanol and water as the solvent can make the surfaces smooth.</td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Nanosphere</td>
<td>200 nm diameter</td>
<td>Hydrothermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Nanorods</td>
<td>10-20 nm breadth and several hundred nm long</td>
<td>Hydrothermal</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO, Cu₂O</td>
<td>Nanorods</td>
<td>1-3 nm diameter and 7-10 nm long</td>
<td>Solid-liquid phase arc discharge</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>Nanorods</td>
<td>12-17 nm</td>
<td>Solvothermal</td>
<td>The final product was</td>
<td></td>
</tr>
</tbody>
</table>
Controlling size and shape of CuO can be vital in the application of catalysis. Researchers have synthesized several different shapes, such as nanowires [52,53], rods [54], octahedron [55], platelets [56], spheres [57] and tubes [58] of CuO and Cu$_2$O. Derrick et al. [59] showed that CuO nanorods expose (100) and (111) faces, and nanocubes expose (100) faces. In decahedron nanoparticles, (111) faces grow faster than (100), which lead to nanorod-shaped particles. Nanocubes come from cuboctahedron nanoparticles, where (111) faces grow faster than (100). They also suggested that increasing the temperature during the hydrothermal process can increase the particle size. At 190 °C, nanorods are 700 nm in length and 100 nm in breadth. Cao et al. [48] used cetyltrimethylammonium bromide (CTAB) as a surfactant to synthesize nanorods and
nanotubes. Cu, Cu$_2$O and CuO nanorods expose (111) faces with d-spacing of 2.09, 2.47 and 2.53 Å, respectively. Chang et al. [43] showed (110) planes of CuO nanorods as their growth direction. Zhao et al. [45] synthesized Cu$_2$O nanocubes with (100) exposed planes.

1.3.5. Supported CuO catalysts

Among all of the transition metal oxides, CuO has gotten more attention because it shows similar performances as noble metal catalysts as shown in Table 1.1. Researchers have tried various ways to impregnate CuO on active support CeO$_2$. Table 1.4 shows the catalytic activity of CuO/CeO$_2$ catalysts where CeO$_2$ has different morphologies. It can be seen in the Table 1.4 that CeO$_2$ nanorods with CuO shows better catalytic activity. However, the method of impregnation of CuO on CeO$_2$ has also an effect on the catalytic reaction. Liu et al. [60] improved catalytic activity of CuO/CeO$_2$ nanorods using wet impregnation method where Cu(NO$_3$)$_2$ solution was mixed with as-prepared CeO$_2$ nanorods and the solution was stirred for 3 hrs.

<table>
<thead>
<tr>
<th>CeO$_2$ morphology</th>
<th>Impregnation method</th>
<th>Catalytic activity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Octahedral</td>
<td>Deposition-precipitation</td>
<td>H$_2$ consumption at 187 and 226 °C</td>
<td>61</td>
</tr>
<tr>
<td>Octahedral</td>
<td>Surfactant-templated</td>
<td>H$_2$ consumption at 200 and 228 °C</td>
<td>62</td>
</tr>
<tr>
<td>Octahedral</td>
<td>Urea nitrates combustion</td>
<td>H$_2$ consumption at 170 and 220 °C</td>
<td>63</td>
</tr>
<tr>
<td>------------</td>
<td>--------------------------</td>
<td>-----------------------------------</td>
<td>----</td>
</tr>
<tr>
<td>Nanorods</td>
<td>Precipitation method</td>
<td>H$_2$ consumption at 196 and 226 °C</td>
<td>64</td>
</tr>
<tr>
<td>Nanorods</td>
<td>Wet impregnation method</td>
<td>H$_2$ consumption at 157 and 179 °C</td>
<td>60</td>
</tr>
</tbody>
</table>

High-resolution transmission electron microscopy (HRTEM) can be cooperative to investigate the catalyst-support interface and the crystal defects. Lattice parameter and d-spacing can also be calculated from HRTEM images. Zabilskiy et al. [65] showed TEM and HRTEM images of CuO-CeO$_2$ catalysts with different morphologies shown in Fig. 1.12 (left). Shape-controlled CeO$_2$ exposes various lattice planes. CeO$_2$ nanocubes show the interplanar spacing of 0.27 nm which corresponds to (100) planes. CeO$_2$ nanorods expose both (100) and (110) planes with d-spacing of 0.27 and 0.19 nm, respectively. Polyhedral CeO$_2$ shows only (111) plane with d-spacing of 0.31 nm. Scanning TEM (STEM) and energy dispersive X-ray spectroscopy (EDX) were also conducted by Zabilskiy et al. [65] Fig. 1.12 (right) shows STEM images with EDX mapping of CuO-CeO$_2$ catalysts. The homogeneous Cu distribution on CeO$_2$ rods and polyhedral can be observed in EDX mapping. Liu et al. [60] found that CeO$_2$ exposed similar (100) and (110) for nanorods and (111) plane for nanopolyhedra shown in Fig. 1.13. Yao et al. [66] prepared CeO$_2$ nanorods of ~11 nm diameter shown in Fig. 1.14 (left). In the same figure, the spotlike contrast variation observed in HRSTEM image corresponds to the voids.
Chen et al. [67] investigated STEM-EDX mapping on CuO/CeO$_2$ nanorods in order to find the uniform distribution of Cu on CeO$_2$ shown in Fig. 1.14 (right).

Figure 1.12. TEM and HRTEM images (left), and STEM images with EDX mapping (right) of CuO-CeO$_2$ catalysts with various morphologies. Reprinted with permission from Zabilsky et al. [65]. Copyright (2015) American Chemical Society.
Figure 1.13. TEM and HRTEM images of CuO/CeO$_2$ nanopolyhedra, nanorods and nanocubes. Reprinted with permission from Wiley [60].

Figure 1.14. TEM, HRTEM, STEM and HRSTEM images of CuO/CeO$_2$ nanorods (left) and STEM-EDX mapping of CuO/CeO$_2$ nanorods (right). Reprinted with permission from Yao et al. [66] and Chen et al. [67]. Copyright (2014 and 2015) American Chemical Society.
Catalytic activity can be improved by the synergistic interaction between the base material and the support. [11] The base material can be highly interacted or loosely interacted with the support. The investigation of these interactions is very important to understand the mechanism of CO oxidation. Researchers, like Stephanopoulos [68], Sedmak [69], and Arias [70] proposed a mechanism for the catalytic CO oxidation of CuO/CeO$_2$ catalysts, using which they described that the catalytic process can be accomplished in several steps as shown in Fig. 1.15. Step I includes the reaction of bulk CuO with CO to reduce to Cu$^{1+}$ and a further reduction to Cu$^0$. In step II, O$_2$ reacts with reduced Cu. In step III and IV, the role of CeO$_2$ support for well-dispersed CuO can be
seen. CeO$_2$ supplies oxygen to the reduced Cu species at the interface to re-oxidize these Cu species, and Ce$^{4+}$ reduces to Ce$^{3+}$ by itself. Oxygen vacancies are formed at the CuO/CeO$_2$ interface, which can be filled by adsorbed oxygen. Redox potentials of CuO are decreased due to the electron charge transfer among Cu, O, Ce and oxygen vacancies (or other defect areas), which aid the diffusion of oxygen from bulk to surface in CeO$_2$. This diffusion, ultimately, increases the redox action of Ce$^{4+}$/Ce$^{3+}$ couples. An in-depth study of the proper mechanism is still unclear. Kinetic study and HRTEM of the interface of the catalysts can be useful to build a proper mechanism, including the effect of the shape controlled CuO$_x$.

Researchers have also impregnated CuO on SiO$_2$ nanoparticles due to its intrinsic structural characteristics. Niu et al. [71] synthesized solid SiO$_2$, and hollow SiO$_2$ nanospheres supported CuO catalysts. Hollow SiO$_2$ nanospheres were prepared using silica encapsulation via using Cu@C composite sphere hard template. The average diameter of hollow SiO$_2$ was 240 nm with 30 nm thin shell layer. CuO on hollow SiO$_2$ and solid SiO$_2$ nanospheres both showed two reduction peaks at 254 and 266 $^\circ$C, and 243 and 278 $^\circ$C, respectively. These two samples converted 100% CO into CO$_2$ at 210 and 420 $^\circ$C, respectively. Niu et al. [71] suggested that CuO on hollow SiO$_2$ can have more highly dispersed CuO nanoclusters which led to its higher catalytic activity compared to catalytic activity of CuO on solid SiO$_2$ nanospheres. Fig. 1.16 shows hollow SiO$_2$ nanosphere supported CuO catalyst where SiO$_2$ spheres were ~250 nm in diameter. In EDX mapping, it can be seen that Cu was distributed homogeneously on SiO$_2$. Song et al. [72] also synthesized hollow SiO$_2$ sphere supported CuO catalyst using carbonaceous microspheres as template. They proposed that hollow texture with porosity increased gas
diffusion into the interior of sphere and this circumstance made possible for gas to access to exterior and interior of sphere as well as active sites of CuO. SiO$_2$ spheres were about 1 µm in diameter with 100 nm thick wall as shown in Fig. 1.17. They mentioned that the wall was made of plentiful small SiO$_2$ particles (average diameter of 80 nm) linking with each other. Astudillo et al. [73] and Luo et al. [74] showed the influence of CeO$_2$ on CuO/SiO$_2$ catalyst. Astudillo et al. [73] synthesized SiO$_2$ supported CuO-CeO$_2$ catalysts where the loading amount of Cu and Ce was varied from 1 to 9 with a constant total (Cu+Ce) 10% loading amount on SiO$_2$ particles. They showed that as the Ce loading amount was increased, the reduction peak in H$_2$-TPR started shifting from ~300 ºC to 180 and 220 ºC. From the catalytic activity of CuO-CeO$_2$/SiO$_2$ catalysts, they concluded that optimum ratio of Cu/Ce was 0.43 (3Cu-7Ce) which showed the maximum reducibility to both oxides’ interface. Luo et al. [74] suggested that 8% Ce loading on CuO/SiO$_2$ showed the best catalytic activity when SiO$_2$ had large porosity.

Figure 1.16. TEM images of CuO on hollowSiO$_2$ (a-c) and EDX mapping of CuO on hollowSiO$_2$ (d-h). Reprinted with permission from Nature [71].
1.3.6. Reaction rate and mechanism for CO oxidation

Catalyst can change the reaction rate by providing a new reaction path with lower activation energy ($E_A$) of the reaction without being expended. Prior to the conversion of reactants into products, the free energy ($G$) of the system has to overcome $E_A$ for the application, as shown in Fig. 1.18. Thus, a lower $E_A$ is desired for most of the applications, and hence a faster catalytic rate is needed. For heterogeneous catalyst, each elementary step of reaction shows a local maximum which directs the speed of the step and this is called reaction determining step (rds).
Figure 1.18. Reaction coordinate diagram of an arbitrary reaction with and without the catalyst.

The most popular, LFS model for the kinetic study of the catalysts toward CO oxidation has been proposed by Liu and Flytzani-Stephanopoulos [75]. They have assumed that oxygen and CO, provided by the adsorbed amount onto metal oxide support and noble metal surface, react at the interface of noble metal and metal oxide support particle, respectively (Fig. 1.19d-f). No oxygen from the lattice is involved in this reaction. They have developed an equation of the rate of reaction as shown below. In this equation, \( k_{CO} \) and \( K_{CO} \) are the surface reaction rate constant and CO adsorption equilibrium constant, respectively. \( P_{O_2} \) and \( P_{CO} \) are the partial pressure of oxygen and CO, respectively and \( n \) is a value, which is close to zero.

\[
R_{CO} = \frac{k_{CO}K_{CO}P_{O_2}^nw}{1 + K_{CO}P_{CO}}
\]  
(Eq. 1.1)

\[
k_{CO} = A \exp\left(-\frac{E_a}{RT}\right)
\]  
(Eq. 1.2)
\[ K_{CO} = K \exp\left(\frac{Q}{RT}\right) \]  \hspace{1cm} (Eq. 1.3)

In modified Langmuir-Hinshelwood (LH) model [76], they have suggested adsorption of oxygen molecules as the rate determining step for noble metal supported on non-active supports and developed the rate of reaction as shown below.

\[ R_{CO} = \frac{k_{O_2}P_{O_2}}{1 + K_{CO}P_{CO}} \]  \hspace{1cm} (Eq. 1.4)

**Table 1.5. Kinetic models of heterogeneous catalysts for CO oxidation**

<table>
<thead>
<tr>
<th>Model</th>
<th>Description of mechanism</th>
<th>Reaction rate</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LH</td>
<td>(i) CO + #NM = CO#NM</td>
<td>[ R_{CO} = \frac{k_{O_2}}{1 + K_{CO}P_{CO}} ]</td>
<td>76</td>
</tr>
<tr>
<td></td>
<td>(ii) O_2 + 2@MOS = 2O@MOS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) O@MOS + #NM = O#NM + @MOS</td>
<td>(RDS)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iv) CO#NM + O#MOS = CO_2 + 2#NM</td>
<td></td>
<td></td>
</tr>
<tr>
<td>LFS</td>
<td>(i) CO + #NM = CO#NM</td>
<td>[ R_{CO} = \frac{k_{CO}K_{CO}P_{O_2}^n}{1 + K_{CO}P_{CO}} ]</td>
<td>75</td>
</tr>
<tr>
<td></td>
<td>(ii) O_2 + 2@MOS = 2O@MOS</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(iii) CO#NM + O@MOS = CO_2 + #NM + @MOS (RDS)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• Reaction occurs at the boundary.</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>• No lattice oxygen is involved in the reaction.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MVK</td>
<td>(i) CO + oxidized catalyst = CO₂ + reduced catalyst</td>
<td>$R_{CO}$</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>--------------------------------------------------</td>
<td>----------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ii) Reduced catalyst + O₂ = oxidized catalyst (RDS)</td>
<td>$$\frac{k_{CO}k_{O_2}P_{CO}P_{O_2}^{n}}{0.5k_{CO}P_{CO} + K_{CO}P_{CO}}$$</td>
<td></td>
</tr>
</tbody>
</table>

#NM = Noble metal site  @MOS = Metal oxide support site  RDS = Reaction determining step

![Diagram](image)

Figure 1.19. Mechanism for CO oxidation over metal oxide supported catalysts. LH model (a-c), LFS model (d-f), and MVK model (g-h).
In LH model (Fig. 1.19a-c), CO and O$_2$ molecules are adsorbed at the surface of CuO and CeO$_2$ similar to LFS model. Adsorbed oxygen moves to CuO surface from ceria surface and this part is assumed as the rate determining step. Reaction occurs at the metal surface and then CO$_2$ is desorbed away. For Mars-Van Krevelen (MVK) model (Fig. 1.19g-h), CO reacts with lattice oxygen at the surface of CuO and reduces CuO to metallic Cu. The reduced Cu gets oxidized by adsorbing oxygen molecules through the transfer of mobile oxygen from ceria lattice. Ceria can have oxygen vacancy due to transferring oxygen to metallic Cu. Thus, ceria adsorbs oxygen to fill the vacancy.

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Chapter 2: Experimental

2.1. Synthesis methods

2.1.1. Hydrothermal method

Hydrothermal synthesis method includes a technique where substances in aqueous form react under low temperature and high vapor pressure in a steel-closed vessel called autoclave (Fig. 2.1). This is one of the best synthesis methods to control the size and shape of the particles. Various parameters, such as reaction temperature, duration, and solvents, can modify the size and shape by changing the growth direction and mechanism. A temperature gradient created by heating the autoclave is maintained between the two opposite ends. Dissolved nutrient in the hotter zone at the bottom of the autoclave is transported to colder zone at the upper part of the autoclave. The solution at the upper part becomes supersaturated and then crystallization starts. The low reaction temperature is a great advantage to saving energies and to avoiding problems occurred by high temperature. This method is used to synthesize various morphologies of CeO$_2$.

2.1.2. Wet impregnation method

This is the most common method to prepare CuO$_x$-CeO$_2$ catalysts. In this method, the copper salt solution has been used as a precursor in order to make contact with the support. The precursor dissolves in the solution with same volume as the pore volume of the support. Due to the capillary action, the solution is attracted to the pores. The amount of solution in excess of pore volume of the support starts diffusing in. During the process, heat can be given into the system to create a better contact between copper oxide and the
support. Stirring of the solutions is crucial to having a homogeneous distribution of copper oxide on the support. The schematic representation of this process is shown in Fig. 2.2.

Figure 2.1. Autoclave in the furnace.

Figure 2.2. Schematic representation of wet impregnation method.
2.2. Instrumentation

In this work, various instruments, such as X-ray diffraction, Raman spectroscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, and BET surface area have been used to characterize the materials, and the catalytic activity of the materials has been tested using chemisorption instruments. Kinetic study has been conducted using thermogravimetric analyzer. To evaluate the results, it is imperative to understand how these instruments work.

2.2.1. X-ray diffraction (XRD)

XRD, which is one of the common, non-destructive characterization techniques, has been used for phase identifications and crystal structures of the materials. However, this technique can be used only for crystalline materials. X-rays are generated in a cathode ray tube where a filament is heated to produce electrons and these electrons are accelerated by applying voltage. Accelerated electrons bombard the target materials to produce characteristics X-rays. Copper is used as the target materials with CuK_α = 1.5418 Å radiation. These X-rays incident on the sample leading to produce a constructive interference which satisfies Bragg’s law (nλ = 2d Sinθ), as shown in Fig. 2.3a. A peak in intensity occurs at the constructive interference. Detectors identify the diffracted X-rays in a range of 2θ angles to reach all possible diffraction directions of the lattice (Fig. 2.3b). Diffraction peaks are converted to d-spacing to identify the phases. Each phase has a unique set of d-spacing. For our sample, we have used Rigaku Miniflex II XRD from 5 to 90° of 2θ with a scan rate of 0.5° per min. XRD pattern has been utilized to calculate the particle size using the following equation.
\[ \text{particle size} = \frac{0.94 \lambda}{\beta_{1/2} \cos \theta} \]  
(Eq. 2.1)

Here, \( \lambda \) is wavelength (1.541); \( \theta \) is diffraction angle; \( \beta_{1/2} \) is full-width-half-maximum (FWHM) of the particular peak.

2.2.2. Raman spectroscopy

Raman spectroscopy is a commonly-used, non-destructive characterization technique. The spectrometer works based on the molecular vibrations, rotational and other low-frequency modes of the materials. A laser beam illuminates the materials and excites the molecules from ground state to virtual energy state for a short period of time. As shown in Fig. 2.4a, excited molecules come back to the different ground energy states instead of returning to the original energy state and this incident is called inelastic scattering. If excited molecules come back to higher energy state than the original state (resulting low energy), then this process is called Stokes; and if excited molecules come back to lower energy state than the original state (resulting higher energy), then this process is called Anti-stokes or Raman scattering. The differences between the state energies lead to a
shift of the emitted photon’s frequency for the total energy to remain stable. After interaction of photons with the sample, the lenses collect the electromagnetic radiation and send through the monochromator. Later the notch filters or edge filters filter out the elastic scattering and send the rest of the energy to the CCD detectors. In this project, we have worked with Horiba iHR 320 Raman spectrometer (Fig. 2.4b) using a green laser beam with 532 nm of wavelength. Silicon single crystal wafer has been used to calibrate with a reference peak at 520 cm\(^{-1}\).

Figure 2.4. (a) Elastic and inelastic scattering, (b) Raman spectroscopy setup.
2.2.3. Transmission electron microscopy (TEM)

TEM has been frequently used to achieve an atomic resolution of the materials. When compared to light microscopy, in TEM, electrons are used instead of light. However, TEM works on the same principle of light microscope. With the help of high voltage (around 200 KV), electron gun produces electrons which travel through several electromagnetic lenses and are focused into a very thin beam. The electrons travel through the thin materials (around 100 nm) and the unscattered electrons produce an image on the fluorescent screen at the bottom. A CCD camera can be used to collect the image in the computer. In our facility, we have access to JEOL 2100 model of TEM along with energy dispersive spectroscopy (EDS) in our facility. This TEM can be used to magnify up to 1.5 million times and has a point resolution of 0.19 nm and informational resolution of 0.14 nm. For this research, 400 mesh copper grid (from Ted Pella) has been used to prepare TEM sample. At first, catalysts have been mixed in ethanol, and then these have been sonicated for 1 min. Samples have been taken from the solution by a small pipette, and one or two drops of sample have been poured on the copper grid.

EDS is usually attached to TEM to conduct the elemental analysis of the materials. Every element has a unique atomic structure which leads to different energies of X-ray emission. Electrons or photons with high energy hit the electron shells of the specimen and knock out an electron from the inner shell by exciting the electron creating a hole. An electron from higher-energy shell fills the hole leading to an emission of X-ray with the energy equaling to the energy difference between two shells. The X-ray is recognized by the detector and the crystal inside the detector turns the signal into a voltage signal.
electrical signals are measured by the pulse processor and then, are passed to the analyzer.

2.2.4. **X-ray photoelectron spectroscopy (XPS)**

XPS is a surface analysis technique which provides information about elemental, chemical state, and electronic properties of the surface of materials. Photoemission process has been used in this technique to collect information of the materials. Electrons from the core level adsorb x-ray energy \((h\nu)\) when x-rays incident on the surface. After overcoming the binding energy \((E_B)\), electrons are emitted out with a certain kinetic energy \((E_k)\). Einstein equation can be used to describe this process.

\[
E_k = h\nu - E_B - \Psi
\]

(Eq. 2.2)

In this equation, \(h\nu\) is the energy of x-ray, \(E_k\) is the kinetic energy of emitted electrons, \(E_B\) is the binding energy of core level electrons, and \(\Psi\) is the work function of the instrument. For our sample, Al K\(_\alpha\) x-ray source has been used and it has energy of 1486.6 eV. Kinetic energy can be measured by an analyzer. Thus, binding energy can easily be calculated using equation 2.2. We have used XPS PHI 5100 instrument which is from RBD Instruments and is housed in an Ultra High Vacuum (UHV) chamber with the base pressure of \(5\times10^{-10}\) Torr. It is equipped with a dual anode X-ray source \((h\nu (Al K\alpha) =1486.6\ eV\ and\ h\nu (Mg K\alpha) =1253.6\ eV,\ \Delta E = 0.9\ eV)\) and a hemispherical analyzer. The system is also equipped with an Ar\(^+\) ion gun which enables depth profiling. In addition, it can be operated at room temperature as well as liquid nitrogen temperature, 80 K. The instrument has been calibrated using Au 4f peaks. All of the XPS data have been collected by Dr. Balaz’s research group.
2.2.5. BET surface area

Surface area is an important physical property which affects the usefulness of solid phase. Same material with the different surface area can affect its performance characteristics. Gas adsorption technique has been frequently used to determine the surface area. In this method, gas molecules come in contact with solid surfaces under a variety of conditions in order to evaluate sample volume. Brunauer-Emmett-Teller (BET) theory is a commonly-used technique to determine the surface area of powder and porous materials. Solid surfaces are exposed to nitrogen gas which is engaged as the probe molecules at liquid nitrogen conditions. The weight of the sample, the cross-sectional area of nitrogen gas (in this case, 16.2 Å²/molecule) and the measured monolayer capacity evaluate the surface area of the sample. The equation to measure BET surface area is given below.

\[
\frac{1}{V \left( \frac{P_o}{P} - 1 \right)} = \frac{C - 1}{V_m} \left( \frac{P_o}{P} \right) + \frac{1}{V_mC}
\]  

(Eq. 2.3)

Here, \(P\) is equilibrium pressure for a specific surface coverage, \(P_o\) is the standard vapor pressure of the liquid adsorbate at the adsorption temperature, \(V\) is the volumetric uptake of gas at pressure \(P\) and \(C\) is a constant. For our project, we have used Micromeritics AutoChem™ II 2920 to measure the surface area of the sample. The sample is placed in a U-tube, and nitrogen gas is flown through it. The temperature of the sample is decreased to ~77 K. Nitrogen gas molecules get trapped at the surfaces of the sample. The temperature of the sample again is raised to a room temperature by simply putting a beaker filled with water around the U-tube. Thermal conductivity detector
(TCD) detects the amount of trapped nitrogen gas molecules at the exit of the sample container and sends the information to the computer to analyze the surface area.

2.2.6. Temperature programmed techniques

Temperature programmed methods are commonly used chemisorption techniques which produce the information about the reduction/oxidation conditions of a catalyst. We have used three different chemisorption techniques, such as temperature programmed reduction (TPR), temperature programmed oxidation (TPO), and temperature programmed desorption (TPD).

Temperature programmed reduction (TPR) is a process which determines the amount of reducible species existing in the catalyst and the temperature at which the species are reduced. In this method, usually a mixer of hydrogen and argon gas is used and argon which has low thermal conductivity (0.018 W/mK) acts as carrier gas. The thermal conductivity of reducing gas hydrogen is 0.182 W/mK. When mixed gas in a certain proportion is flown through the sample, the detector establishes the baseline based on the thermal conductivity of mixed gas. After rising the temperature, hydrogen starts to react with the catalyst and produces $\text{H}_2\text{O}$ which is removed at the cold trap. Thus, the amount of hydrogen gas decreases in the gas mixture and therefore, thermal conductivity decreases as well due to the increment of percentage of argon gas. To maintain a constant filament temperature, it requires less electricity due to the increase of low thermal conductive argon gas. The detector detects the change in electrical signal and records it uninterruptedly over a range of temperatures.
To conduct TPR, the sample catalyst is placed in a U-tube which can be connected to the instrument so that reducing gas mixture can be flown through this at a rate of 50 mL/min. In this case, 5% \( \text{H}_2 \) – 95% Ar mixture is used as the reducing gas mixture. After increasing the temperature with 10\(^\circ\)C/min rate, at a certain temperature, reduction occurs or in another way hydrogen is consumed and the composition of the gas mixture is detected by TCD at the exit of U-tube. A schematic representation of TPR process, as described, is shown in Fig. 2.5. We are using Micromeritics AutoChemTM II 2920 to conduct TPR. We used standard \( \text{Cu}_2\text{O} \) sample to calibrate this instrument and to calculate \( \text{H}_2 \) consumption amount of the catalysts.

Temperature programmed oxidation (TPO) provides information about the oxidation temperature peaks. The TPO experiments are conducted similar way as TPR; only difference is that 5% \( \text{O}_2 \) – 95% He gas mixture is used for TPO. Thermal conductivity of oxygen and helium gases is 0.027 and 0.151 W/mK. Temperature programmed desorption (TPD) technique is used for determining the strength of active sites accessible at catalyst surfaces. The temperature is increased after flowing pre-adsorbed gas through the catalyst. The pre-adsorbed gas desorbs away with increasing the temperature until the surface is unoccupied with adsorbate gas. In our experiment, the sample in U-tube has been heated from room temperature to 400 \(^\circ\)C under He gas to remove residual moisture. Then the sample has been cooled to room temperature and 5%\( \text{CO} \)– 95%He gas has been flown at 50 mL/min through the sample for 30 mins. The sample has been reheated up to 400 \(^\circ\)C under He gas and the desorption behavior of CO can be analyzed at elevated temperature.
Various masses of standard Cu$_2$O have been used in TPR where the reaction (4) occurred. From the data, H$_2$ consumption in μmol per peak area has been calculated for all of the peaks shown in Fig. 2.6. Each sample provided same result for H$_2$ consumption (22.1 μmol/peak area). Equation (2.4) can be used to calculate H$_2$ consumption for the catalysts.

\[
\text{Cu}_2\text{O} + \text{H}_2 = 2\text{Cu} + \text{H}_2\text{O} \quad (4)
\]

Figure 2.5. Schematical representation of TPR process.

Figure 2.6. Calibration curves of TPR for standard Cu$_2$O sample.
\[ \text{H}_2 \text{ consumption (mmol/g)} = \frac{22.1}{\text{peak area}} \times \frac{\text{peak area of catalyst}}{\text{mass of catalyst (mg)}} \]  
(Eq. 2.4)

Rate of desorption from CO-TPD curve can be calculated using equation (2.5) shown below.

\[ \frac{d\theta}{dt} = -\frac{k_d}{\beta} \theta^n \]  
(Eq. 2.5)

\[ k_d = A \exp\left(\frac{-E_d}{RT}\right) \]  
(Eq. 2.6)

Here, \( k_d, \beta, \theta, \) and \( n \) are rate of desorption constant, heating rate, surface coverage, and reaction order, respectively. \( k_d \) can be found using equation (3.2) where \( A, E_d, R, \) and \( T \) are rate coefficient, desorption energy, gas constant, and temperature, respectively.

2.2.7. Pulse chemisorption

Pulse chemisorption method is used to measure oxygen storage capacity (OSC) and metal dispersion percentage using Micromeritics AutoChem™ II 2920. The OSC is the measurement of the availability of reactive oxygen near the catalyst surface. It is calculated from the amount of \( \text{H}_2 \) consumption during \( \text{H}_2 \) pulse to react with the most active and available oxygen. The detector usually detects the unreacted gas and does the back calculation to determine the amount of reacted gas by using the difference between the volume of unreacted gas and the volume of injected gas. 50 mg of sample is placed in U-tube and a reducing gas (\( \text{H}_2 \)) is injected through the sample for a limited time to measure OSC of the particular catalyst. In this method, the temperature is raised up to 350 °C in an inert environment to remove any residual moisture present in the sample. Helium is used as carrier gas which is passed through the sample. 5%\( \text{H}_2 \)-95%He gas is
injected into the U-tube for 5 sec. TCD signal shows a peak for oxygen reduction. H₂ gas injection is done with 3 mins of period till the reduction peak is constant.

Metal dispersion percentage can also be measured during conducting pulse chemisorption method to calculate OSC. This value is needed to calculate turn over frequency (TOF). TOF is a measurement of catalytic activity which shows the number of cycles per unit time. Three types of TOF can be calculated as follows:

\[
\text{TOF}_1 (s^{-1}) = X_{CO} F_{CO} \frac{5 W_{Cu}}{4 m_{cat} X_{CuO} D_{CuO}}
\]  
(Eq. 2.7)

\[
\text{TOF}_2 (s^{-1}) = X_{CO} F_{CO} N \frac{m_c}{m_{cat} X_{CuO}}
\]  
(Eq. 2.8)

\[
\text{TOF}_3 (s^{-1}) = \frac{\text{TOF}_2}{\frac{4}{2} d_{Cu-O}} = X_{CO} F_{CO} N \frac{m_c}{m_{cat} X_{CuO}} \frac{2 d_{Cu-O}}{\pi d}
\]  
(Eq. 2.9)

where \(X_{CO}\) is the CO conversion at certain temperature; \(F_{CO}\) (mol.s\(^{-1}\)) is the flow rate of CO; \(N\) is the Avogadro’s constant; \(W_{Cu}\) is the molecular weight of Cu (63.545 g.mol\(^{-1}\)); \(m_{cat}\) is the weight of catalyst; \(X_{CuO}\) is the percentage of CuO loading on the catalyst support; \(D_{CuO}\) is the percentage of CuO dispersion; \(m_c\) is the weight of a single CuO crystalline and this can be calculated from the volume of assumed semi-spherical CuO and density of CuO (6.45 g.cm\(^{-3}\)); \(d\) is the crystallite size of CuO; \(d_{Cu-O}\) is distance between Cu and O atom (0.195 nm). TOF\(_1\) calculation is usually based on metal dispersion. TOF\(_2\) contributes the information about the overall activity of Cu atoms on CuO-support periphery and TOF\(_3\) refers to life cycles or turn over frequency of each Cu atom present at interface of CuO-support.
2.2.8. Catalytic activity characterization for CO oxidation

In this method, carbon monoxide (CO) is oxidized to carbon dioxide (CO$_2$) and this method gives information about the percentage of conversion of CO at a certain temperature. The sample is loaded into the glass tube and placed vertically with the instrument. A mixture of 1% CO, 20% O$_2$ and 79% He gas is flown through the glass tube at a rate of 70 mL/min. Here, helium gas acts as a carrier gas. The temperature of the sample is programmed from 30 to 350 °C. Upon exiting the gas mixture from the sample container, gas chromatography (GC) separates the components, and each component exits the column in GC at a different time. Mass spectrometer detects the amount of each component and sends the data to the computer. Fig. 2.7 shows a schematic diagram of CO oxidation process. We have used SRI multiple gas analyzer GC, 8610C chassis. The conversion of CO is calculated using equation (2.8).

\[
\text{%CO conversion} = \left[ \frac{P_{CO_2}}{P_{CO} + P_{CO_2}} \right] \times 100\% \quad \text{(Eq. 2.10)}
\]

![Figure 2.7. Schematic representation of CO oxidation process using gas chromatograph.](image)

55
Here, $P_{\text{CO}}$ and $P_{\text{CO}_2}$ are the partial pressure of CO and CO$_2$, respectively, are determined from the relative peak area of the CO and CO$_2$ peaks normalized to the He standard. Catalytic isothermal stability in function of time can also be established from CO oxidation using gas chromatograph. For this method, the sample temperature is raised up to 350 °C and then is held for 24 hrs.

2.2.9. Thermogravimetric analysis (TGA)

Thermogravimetric analysis (TGA) is a method in which the mass of any substances is monitored as a function of temperature (with constant heating rate) or as a function of time (with constant temperature). TGA usually consists with sample pan, furnace around the sample, thermocouple and microbalance. It continuously measures the sample weight and temperature. Sample weight changes for decomposition, oxidation, or loss of volatile substances. Change in weight is calculated using the following equations.

$$\text{Weight } \% = \frac{W_t}{W_i} \times 100$$  \hspace{1cm} (Eq. 2.11)  

Here, $W_i$ is the initial weight and $W_t$ is the weight at particular time/temperature. In this work, TGA has been used for kinetic study of the sample. At first, aluminum pan is tared and then sample is placed in it. The sample is heated up to 400 °C at 10 °C/min rate under inert environment. Any volatile substances or moisture can be removed during heating. Temperature is held at 400 °C during reduction/oxidation cycles. 5%CO-95%He gas is used to reduce the sample and this gas is passed through the sample at 50 ml/min rate for 30 mins at constant temperature of 400 °C. The gas is switched to oxygen to oxidize the sample. The flow rate of oxygen gas is 50 ml/min and this gas is flown for 30 mins as
well. One reduction and one oxidation process is called one redox cycle. Total 10 cycles of redox process is conducted for each sample.
Chapter 3: Effect of impregnation methods on CO oxidation over CeO$_2$ nanorods supported CuO catalysts

In this chapter, copper nitrate and copper carbonate precursors for wet impregnation method and copper nitrate for thermal decomposition method were used to impregnate CuO onto hydrothermally prepared CeO$_2$ nanorods. Several characterization techniques, such as X-ray diffraction (XRD), Raman spectroscopy, transmission electron microscopy (TEM) and hydrogen temperature programmed reduction (H$_2$-TPR) confirmed the presence of different copper species ($\alpha$, $\beta$, and $\gamma$) interacting with CeO$_2$ nanorods while forming oxygen vacancies in CeO$_2$ lattice by compensating the charges between copper and cerium. Furthermore, X-ray photoelectron spectroscopy (XPS) analysis showed a difference in the amount of Ce$^{3+}$/Ce$^{4+}$ and Cu$^{2+}$/Cu$^{+}$ couples present in the catalysts. CO oxidation and CO temperature programmed desorption (CO-TPD) were conducted on the catalysts to understand the synergistic effect in CuO/CeO$_2$ catalysts on their catalytic activity. Rate of desorption was calculated from CO-TPD curves to determine the oxygen mobility in CeO$_2$ lattice.

3.1. Introduction

Metal-based catalysts, such as Au/TiO$_2$ [1,2], Au/Fe$_2$O$_3$ [3], Au/$\gamma$-Al$_2$O$_3$ [4], Au/CeO$_2$ [5], Au/ZnO [6], Pt/CeO$_2$ [7], Pt/SnO$_2$–TiO$_2$ [8], Pd/CeO$_2$ [9], Ir/TiO$_2$ [10], and Ir/Au-Al$_2$O$_3$ [11] have been studied for long time, and these catalysts show excellent performance for automotive catalytic application. Nevertheless, these metals, as well as the preparation methods of the catalysts, are expensive which forced researchers to
consider different catalysts with comparable performance. As a consequence, CuO has attracted the attention as one of the most active and cheapest catalysts. On the other side, CeO$_2$ has fascinated as a catalyst support material due to its ability to take in and release oxygen under oxygen-rich and -lean conditions, respectively [12]. The activity of catalysts depends highly on the preparation method which ensures better contact between copper based particles and CeO$_2$ support. To prepare CuO/CeO$_2$ catalyst, researchers have reported several different methods, such as sol-gel method [13], microwave irradiation technique [14], wet chemical methods and thermal decomposition with different precursors [15], co-precipitation [16], and combustion [17]. Yet, these catalysts have been prepared on CeO$_2$ nanoparticles or octahedral shape. The shape of CeO$_2$ plays an important role in having a better contact with CuO particles [18]. Different catalyst preparation methods can alter the shape and size of the catalysts, which can have an adverse effect on the catalytic activity. In this chapter, we have compared the catalytic activity towards CO oxidation over CuO/CeO$_2$ catalysts prepared by three different methods. The presence of various copper species, such as highly-interacted CuO or Cu-Ce-O solid solutions and weakly-interacted CuO, and their influence in increasing catalytic efficiency have been described in this systematic study.

3.2. Experimental

3.2.1. Catalyst preparation

Hydrothermal method was used to prepare CeO$_2$ nanorods. The 88 mL of 0.1M Ce(NO$_3$)$_3$.6H$_2$O was transferred into a Teflon liner of 200 mL capacity, and 8 mL of 6M NaOH was added into the solution. This solution was stirred for about 15 sec, and then
the lid of Teflon liner was closed. The Teflon liner was put into a stainless steel autoclave and heated at 90 °C for 48 hrs. Finally, the product was filtered and was washed with 500 mL water and then with 50 mL ethanol. It was dried at 50 °C for 12 hrs. Later, CuO impregnation onto CeO₂ nanorods was conducted in three different methods as described below.

3.2.1.1. CuO/CeO₂ using Cu(NO₃)₃ precursor (CNP)

CeO₂ nanorods and Cu(NO₃)₃·3H₂O were mixed in stoichiometric ratio in 30 mL of water to impregnate 10% CuO on CeO₂. Ammonium hydroxide (NH₄OH) was added dropwise in the solution to get precipitation and was stopped when color of the solution turned into a light blue. After 2 hrs of stirring, it was filtered and washed with water and then ethanol. The sample was dried at 50 °C for 12 hrs. Finally, the sample was oxidized at 400 °C for 5 hrs. Then, CuO/CeO₂-CNP catalyst was collected.

3.2.1.2. CuO/CeO₂ using CuCO₃ precursor (CCP)

10% CuO was impregnated on CeO₂ using CuCO₃ precursor by mixing CeO₂ nanorods and CuCO₃ in stoichiometric ratio in 30 mL water. It was stirred for 2 hrs. After filtering the sample and washing with water and ethanol, it was dried at 50 °C for 12 hrs. The sample was oxidized at 400 °C for 5 hrs. CuO/CeO₂-CCP catalyst was collected.

3.2.1.3. CuO/CeO₂ using thermal decomposition (TD)

For this method, to impregnate 10% CuO, CeO₂ nanorods and Cu(NO₃)₃·3H₂O were mixed in stoichiometric ratio in 30 mL water. While stirring, it was heated at 120 °C until
water evaporated. Then, it was oxidized at 400 °C for 5 hrs. Finally, CuO/CeO₂-TD catalyst was collected.

3.2.2. Catalyst Characterizations

X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), BET surface area measurement, temperature programmed reduction (TPR), temperature programmed desorption (TPD), and CO oxidation were used to characterize the catalysts and their catalytic activity. The description of these techniques can be found in chapter 2.

3.3. Results and Discussions

3.3.1. XRD

The powder XRD was conducted to investigate the structure of CuO/CeO₂ catalysts. The XRD patterns of the samples were shown in Fig. 3.1. The diffraction peaks observed at 2θ of 28.85°, 33.08°, 47.48°, 56.34°, 59.09°, 69.41°, 76.70° and 79.07° can be assigned to fluorite structured CeO₂ (JCPDS 43-1002) as shown in Fig. 3.1a [14]. The diffraction peaks appeared at 2θ of 32.51°, 35.46°, 38.73°, 46.24°, 48.73°, 53.45°, 58.34°, 61.54°, 66.24°, 67.94°, 72.37° and 75.22° correspond to monoclinic CuO (JCPDS 45-0937) [14]. For the sample CuO/CeO₂-CCP, the XRD peaks corresponding to CuO nanopowders at 35.46° and 38.73° were observed. These two peaks were also observed for CuO/CeO₂-CNP shown in Fig. 3.1b after magnification. However, these two peaks were not visible for CuO/CeO₂-TD due to high homogeneity. Yang et al. [20] reported that Cu species peaks were not found in Cu₀.₁Ce₀.₉O₂ sample due to the formation of homogeneous solid
Figure 3.1. XRD patterns of (a) CeO$_2$ nanorods, various CuO/CeO$_2$ catalysts and CuO nanopowders, (b) Magnified XRD patterns of various CuO/CeO$_2$ catalysts.
solution. The presence of CuO peaks indicated that heterodisperse or aggregation of CuO nanoparticles on ceria surfaces can be found in CuO/CeO$_2$-CCP and CuO/CeO$_2$-CNP samples. However, the amount of heterodisperse or aggregation of CuO in CuO/CeO$_2$-CNP could be less than that in CuO/CeO$_2$-CCP, which can be confirmed from the intensity of CuO peaks. These CuO particles can cover a part of active surfaces of CeO$_2$, resulting in hampering the catalytic efficiency. On the other hand, XRD pattern of CuO/CeO$_2$-TD sample showed no visible CuO peaks, providing the evidence of well-dispersed CuO onto ceria surface, Cu-Ce-O solid solutions, or a blend of these two occurrences.

3.3.2. Raman spectroscopy analysis

In Fig. 3.2, Raman spectra of pure CeO$_2$, various CuO/CeO$_2$, and pure CuO have been compared. A peak with respectively high intensity observed at 456 cm$^{-1}$ was ascribed to F$_{2g}$ vibration mode of pure CeO$_2$; however this peak shifted to the lower wavenumber after loading CuO on ceria. The peak shifted from 456 cm$^{-1}$ to 447 cm$^{-1}$, 444 cm$^{-1}$ and 453 cm$^{-1}$ for CuO/CeO$_2$-CNP, -TD and -CCP, respectively. The shifting of the peak suggested that Cu$^{2+}$/Cu$^+$ ions incorporated into CeO$_2$ lattice and formed Cu-Ce-O solid solution [21]. Incorporation of Cu ions creates oxygen vacancies in CeO$_2$ lattice to compensate the ionic charge difference between Cu$^{2+}$ and Ce$^{4+}$, resulting a change in lattice parameter as the radius of Cu$^{2+}$ (0.072 nm) is smaller than that of Ce$^{4+}$ (0.101 nm). Copper ions incorporation into CeO$_2$ lattice can also tempt the lattice distortion of CeO$_2$, and this leads to the peak deviation by influencing the symmetrical stretching mode. Nevertheless, the peak shifting for CuO/CeO$_2$-CCP catalyst was very small, which concluded that it had either low amount of solid solution, or there was no solid solution in
it. Shan et al. [21] showed peak shifting toward lower wavenumber in Raman spectra of CuO/CeO$_2$ catalyst due to the presence of Cu-Ce-O solid solution. In Fig. 3.2, one small and broad peak was observed at 604 cm$^{-1}$ which corresponded to the oxygen vacancies in pure CeO$_2$. For CuO/CeO$_2$-CNP, CuO/CeO$_2$-CCP and CuO/CeO$_2$-TD, a similar broad peak found at 620 cm$^{-1}$ was a mixture of two separate peaks: one for oxygen vacancies in CeO$_2$ and another for B$_{2g}$ mode of CuO [22, 23].

![Figure 3.2. Raman spectra of CeO$_2$ nanorods, different CuO/CeO$_2$ catalysts and CuO nanopowders.](image)

**3.3.3. XPS analysis**

XPS spectra of CuO/CeO$_2$ catalysts were plotted in Fig. 3.3. Spectra for cerium can be seen in Fig. 3.3a where Ce 3d$_{3/2}$ and Ce 3d$_{5/2}$ peaks were denoted as u and v, respectively. Seven peaks can be found in this order from right to left: v (887.7), v' (890.2), v'' (894.3–893.7), v''' (903.6), u (906.1), u' (908.3–907.2), and u'' (912.7). The
assigned $u'$ and $v'$ peaks belong to Ce$^{3+}$ and the rest five peaks ($v$, $v''$, $v'''$, u, u'') correspond to Ce$^{4+}$ [23, 24]. It can easily be distinguished that the amount of Ce$^{3+}$ present in the catalysts in this order: CuO/CeO$_2$-TD > CuO/CeO$_2$-CNP > CuO/CeO$_2$-CCP. The presence of Ce$^{3+}$ produces a chance to form oxygen vacancies in CeO$_2$ ($2Ce^{4+} \leftrightarrow 2Ce^{3+} + V_{O}^{2+}$) [20]. Thus, the surface of CeO$_2$ support in CuO/CeO$_2$-TD sample was enriched with oxygen vacancies compared to other two samples. This defect has an ability to increase oxygen mobility in CeO$_2$ lattice which is beneficial in enhancing the catalytic activity. Fig. 3.3b showed XPS spectra of Cu 2p$_{3/2}$ where low-energy peak was found at 936.2 eV for CuO/CeO$_2$-CNP and at 934.4 eV for CuO/CeO$_2$-TD sample. This low-energy peak corresponds to Cu$^+$ at the surface of catalysts and this suggests a strong interaction of Cu species with CeO$_2$ [25]. It can be seen that Cu$^+$ peak was not present in CuO/CeO$_2$-CCP sample. Thus, it could be reported that CuO was weakly interacted with CeO$_2$ in CuO/CeO$_2$-CCP sample. The observation in XPS spectra of Ce and Cu was consistent with Raman analysis. Another peak can be observed in the range of 939.1 – 938.9 eV for all of the samples. This high-energy peak is attributed to Cu$^{2+}$ [24, 25]. XPS spectra of O 1s for different catalysts were shown in Fig. 3.3c. Two peaks can be observed for O 1s where low-energy and high-energy peak were found at 533.5 eV and 536.1–535.0 eV, respectively. It should be pointed out that low-energy peak corresponds to lattice oxygen being present near surface and high-energy peak is attributed to adsorbed oxygen at the surface [20,26]. Li et al. [25] explained that the intensity of adsorbed oxygen peak became stronger after doping Ni in CeO$_2$ which was a confirmation of increasing oxygen storage capacity. An attempt was made to calculate
Figure 3.3. XPS spectra of various CuO/CeO₂ catalysts.
the percentage of adsorbed oxygen in all of the samples by using the equation below.

\[
\% \text{adsorbed oxygen} = \frac{\text{high energy peak area}}{\text{Total peak area}} \times 100 \tag{Eq. 3.1}
\]

The adsorbed oxygen in CuO/CeO\(_2\)-CNP, -CCP, and -TD samples were 37, 36, and 48 \%, respectively. The adsorbed oxygen peak suggested that the catalysts could have better capability for oxygen storage [20,25]. Thus, it could be observed that CuO/CeO\(_2\)-TD sample had higher oxygen storage capacity which could improve the catalytic activity. A charging effect occurred during the experiment and this caused the peaks to shift toward higher energy compared to the literature [20,23-25].

**3.3.4. TEM analysis**

Fig. 3.4 showed TEM images of pure CeO\(_2\) and three different catalysts in 100K magnification. Pure CeO\(_2\) nanorods were shown in Fig. 3.4a. CeO\(_2\) nanorods were usually 40-100 nm in length and 5-15 nm in diameter. CeO\(_2\) nanorods with small CuO nanoparticles were agglomerated for CuO/CeO\(_2\)-CNP, shown in Fig. 3.4b. Bulk CuO (~40 nm) and cluster of small CuO were seen in CuO/CeO\(_2\)-CCP catalyst in Fig. 3.4c. Small size CuO particles were dispersed on CeO\(_2\) nanorods in both CuO/CeO\(_2\)-CNP and CuO/CeO\(_2\)-TD samples, displayed in Fig. 3.4b and 3.4d, respectively. There was no bulk CuO in CuO/CeO\(_2\)-TD sample. The TEM images were in agreement with XRD data. Additionally, rough surfaces can be observed in rods of CuO/CeO\(_2\) catalysts, whereas surfaces were smooth in pure CeO\(_2\) rods. High resolution TEM (HRTEM) images of pure CeO\(_2\) nanorods and CuO/CeO\(_2\)-CNP catalysts were shown in Fig. 3.5. CeO\(_2\) rods can be seen in Fig. 3.5a and red rectangular portion from Fig. 3.5a was shown separately in Fig. 3.5b after magnifying. CeO\(_2\) rod exposed (111) and (100) planes with d-spacing of 0.31
nm and 0.27 nm, respectively. This result was not consistent with the previously reported observations for CeO$_2$ nanorods as they reported only (100) and (110) planes [18]. However, our group earlier mentioned the presence of (111) planes in CeO$_2$ nanorods [19,23,27-28]. The inset of Fig. 3.5a displayed the calculated Fast Fourier Transform (FFT) of HRTEM image which confirmed that CeO$_2$ nanorods were single crystals. For CuO/CeO$_2$-CNP catalysts, highly interacted CuO nanoparticle (α particle) with CeO$_2$ was presented in Fig. 3.5c. No definite boundary between CuO and CeO$_2$ was seen in the inset of Fig. 3.5c. Weakly-interacted CuO (β particle) with CeO$_2$ and ~10 nm size of bulk CuO (γ particle) was noticed in Fig. 3.5d. CuO nanoparticle was shown in Fig. 3.5e after magnification. The calculate FFT image of CuO particle was shown in Fig. 3.5f and this suggested that CuO nanoparticle was single crystal. It can be seen that CuO particle can

![Figure 3.4. TEM images of (a) CeO$_2$ nanorods, (b) CuO/CeO$_2$-CNP, (c) CuO/CeO$_2$-CCP, (d) CuO/CeO$_2$-TD.](image)
Figure 3.5. HRTEM images of single CeO$_2$ nanorod (a and b), CuO/CeO$_2$-CNP (c and d), and single CuO nanoparticle (e). Calculated FFT of CuO nanoparticle (f).

Inset of (a): calculated FFT of CeO$_2$ nanorod.
have (110), (200) and (220) planes. Similar CuO nanoparticles may cover several defects in CeO$_2$ surface which is not desirable in order to improve the catalytic efficiency.

### 3.3.5. H$_2$-TPR

The H$_2$-TPR profile of pure CeO$_2$ was shown in Fig. 3.6a and H$_2$-TPR profiles of various CuO/CeO$_2$ catalysts were displayed in Fig. 3.6b. Pure CeO$_2$ showed two reduction peaks at about 474 and 763 °C. First peak was assigned to the reduction of surface oxygen of CeO$_2$, and second peak was assigned for the reduction of bulk oxygen of CeO$_2$ [29]. Conversely, various CuO/CeO$_2$ catalysts showed low-temperature reduction compared to pure CeO$_2$ due to synergistic interaction between CuO and CeO$_2$ support [30]. Preparation methods could have an effect on the TPR profiles as seen in Fig. 3.6b. CuO/CeO$_2$-CNP and CuO/CeO$_2$-CCP catalysts showed three reduction peaks, and CuO/CeO$_2$-TD catalysts showed two reduction peaks. However, position and size of the peaks were dissimilar for different CuO/CeO$_2$ catalysts. The reduction peaks were assigned as α, β and γ in order from low to high temperature. The α peaks were allocated to the reduction of strongly-interacted CuO onto CeO$_2$ surface or Cu-Ce-O solid solution [31]. The β peaks were attributed to the reduction of weakly-interacted CuO on CeO$_2$ surface [32]. The γ peaks were recognized as the reduction of larger CuO particles and agglomeration of small CuO particles [33]. Fig. 3.7 showed the schematic of CuO-CeO$_2$ synergistic interactions, where strongly-interacted CuO onto CeO$_2$ surface were shown in Fig. 3.7a, weakly-interacted CuO on CeO$_2$ surface was shown in Fig. 3.7b, and Fig. 3.7c presented how a large particle of CuO covered CeO$_2$ surface without any interaction at the interface. XRD, Raman analysis, XPS and TEM revealed the formation of Cu-Ce-O.
solid solution and weakly-interacted CuO onto CeO$_2$ surface in all catalysts, and bulk CuO in CuO/CeO$_2$-CCP and CuO/CeO$_2$-CNP catalysts. Avgouropoulos et al. [34] suggested that it is easy to reduce strongly-interacted CuO. The reducibility of highly-interacted CuO can be enriched by CeO$_2$. First peaks (α peak) of CuO/CeO$_2$-CNP, -CCP and -TD were observed at 142, 151 and 142 °C, respectively. Second peaks, which were assigned as β peak, were found at 164, 195 and 168 °C for CuO/CeO$_2$-CNP, -CCP and -TD, respectively. Third peaks (γ peaks) for CuO/CeO$_2$-CNP and CuO/CeO$_2$-CCP were seen at 176 and 213 °C, respectively. It was clear that CuO/CeO$_2$-TD catalyst showed no γ peak because this catalyst did not have any large CuO particles and this result was consistent with XRD and TEM data. Luo et al. [9] reported two reduction peaks for 10% CuO loading on CeO$_2$ nanoparticles in which α peak found near 160 °C was assigned to highly dispersed CuO particles, and β peak seen near 200 °C was attributed as bulk CuO. Shiau et al. [35] and Wang et al. [36] reported three reduction peaks which were similar to our results; however, these peaks were found at over 200 °C for their samples. For Cu-Ce-O solid solution, oxygen vacancies are already formed near the surface due to incorporation of Cu$^{2+}$ into CeO$_2$ lattice to have charge neutrality. Therefore, CeO$_2$ adsorbs oxygen to fill the vacancies near solid solution and this oxygen can be reduced at a low temperature [34,37-38]. For weakly interacted CuO, firstly CuO near the interface of CuO-CeO$_2$ reduces to Cu$^{1+}$/Cu after reacting with H$_2$. At that moment, CeO$_2$ supplies oxygen to the reduced Cu species at the interface to re-oxidize these Cu species, and Ce$^{4+}$ reduces to Ce$^{3+}$ itself. Oxygen vacancies are formed near the CuO-CeO$_2$ interface, which can be filled by adsorbed oxygen. Redox potentials of CuO are decreased due to the electron charge transfer among Cu, O, Ce and oxygen vacancies (or other defect areas).
which aids the diffusion of oxygen from bulk to surface in CeO$_2$. This ultimately increases the redox action of Ce$^{4+}$/Ce$^{3+}$ couples [34,37-38].

Figure 3.6. H$_2$-TPR profiles of (a) CeO$_2$ nanorods, (b) different CuO/CeO$_2$ catalysts in same scale.
Figure 3.7. Schematic illustration of different Cu$^{2+}$ species interacting with CeO$_2$ nanorods support. (a) Highly dispersed CuO strongly interacting with CeO$_2$, (b) well-dispersed weakly-interacted CuO and (c) bulk CuO.

Figure 3.8. The amount of H$_2$ consumption by the catalysts at different peaks.
Fig. 3.8 showed the amount of H₂ consumption by the catalysts at different peaks. The amount of H₂ consumption by three catalysts at α peak was in the following order: CuO/CeO₂-TD (1.038 mmol/g) > CuO/CeO₂-CNP (0.753 mmol/g) > CuO/CeO₂-CCP (0.393 mmol/g), which suggested that CuO/CeO₂-TD had the highest amount of Cu-Ce-O solid solution. This result was in agreement with Raman analysis. H₂ consumption at β peaks for all of the three catalysts were almost similar which confirmed that similar amount of weakly-interacted CuO nanoparticles were dispersed onto CeO₂ surface for these three samples. CuO/CeO₂-CCP catalyst displayed the lowest amount of H₂ consumption in total (2.0 mmol/g) in comparison with other two catalysts due to the presence of higher amount of bulk CuO particles, consistent with XRD data.

3.3.6. CO TPD

CO-TPD curves of CuO/CeO₂ catalysts were shown in Fig. 3.9a. For instance adsorbed CO molecules desorb away as CO₂ after reacting with lattice oxygen, CO₂ desorption peaks can be found in Fig. 3.9a. First low temperature peak can be seen when adsorbed CO reacted with surface of CeO₂ and produced CO₂. Another peak found at higher temperature is attributed to bidentate carbon species produced from CO reactive sites as mentioned in our previously reported paper [23]. First peaks for CuO/CeO₂-TD, -CNP, and -CCP were observed at 102, 102, and 98 °C, respectively. Although, low-temperature peaks were almost at similar position for all of the samples, high-temperature peaks were found at different temperature. For CuO/CeO₂-TD, -CNP, and -CCP second peaks were seen at 142, 312, and 234 °C, respectively. By comparison the peak areas, it can be said that CuO/CeO₂-TD can deliver higher quantity of lattice oxygen to react with adsorbed CO. Rate of desorption (ROD) of CO₂ for various
catalysts were shown in Fig. 3.9b. It can be observed that ROD clearly depends on sample temperature and it changes in three different steps. Firstly, ROD increased slowly with temperature up to 175 °C for both CuO/CeO$_2$-TD and CuO/CeO$_2$-CNP, and 225 °C for CuO/CeO$_2$-CCP. Then at second step, it increased linearly (but faster than previous step) up to 300 °C.

Figure 3.9. (a) CO-TPD and (b) rate of desorption of different CuO/CeO$_2$ catalysts. Rate of desorption of CuO/CeO$_2$-CCP in magnified scale shown in the inset of (b).
step) and the most part of desorption occurred at this step. Second steps for CuO/CeO$_2$-TD, -CNP, and -CCP were completed at 325, 325, and 350 °C, respectively where they reached maximum ROD ($1.3.9 \times 10^{-4}$, $5.4 \times 10^{-4}$, and $0.37 \times 10^{-4}$ mol/cm$^2$.s, respectively). In final step, ROD went down rapidly for all the samples due to the presence of low amount of adsorbed CO at this temperature. ROD of various catalysts depends on the mobility of oxygen in CeO$_2$ lattice and from Fig. 3.9b it can be said that CuO/CeO$_2$-TD catalyst can have higher oxygen mobility which eventually enhanced the catalytic efficiency. Earlier, through XPS analysis, we mentioned (Fig. 3.3) that CuO/CeO$_2$-TD sample had higher amount of Ce$^{3+}$ and oxygen vacancies at the surface which can increase oxygen mobility. Thus, CO-TPD was consistent with XPS analysis.

3.3.7. CO oxidation and BET surface area

Fig. 3.10a showed the light-off curves of CO conversion for CuO/CeO$_2$ catalysts prepared by using various precursors and methods. Table 3.1 showed that the $T_{50}$ (the temperature when the conversion was 50%) for CuO/CeO$_2$-CNP, -TD and -CCP were 84, 88 and 112 °C, respectively. Nonetheless, the total CO conversions for CuO/CeO$_2$-CNP, -TD and -CCP were achieved at 286, 220 and 278 °C, respectively. Although CuO/CeO$_2$-CNP catalyst showed lower $T_{50}$ value, there were few CuO clusters in CuO/CeO$_2$-CNP as known from TEM and XRD results, which could be the reason of 100% CO conversion at high temperature for CuO/CeO$_2$-CNP compared to CuO/CeO$_2$-TD catalyst. Zheng et al. [12] reported that $T_{50}$ and $T_{100}$ for CuO/CeO$_2$ catalysts prepared by sol-gel method were 138 and 230 °C. Full CO conversion was obtained at 225°C by Shinde et al. [39] for Sn$_{0.95}$Cu$_{0.05}$O catalyst. Activation energy ($E_A$) for CO oxidation reaction, which is shown in Fig. 3.10b, was calculated using Arrhenius equation. Calculated $E_A$ of CuO/CeO$_2$-TD,
-CNP, and –CCP were 15.0, 25.7, and 41.9 kJ/mol. CuO/CeO₂-TD sample had the lowest $E_A$ among these three catalysts probably due to the contribution of these phenomenon: (1) the presence Ce$^{3+}$ and oxygen vacancies at the surface, (2) the formation of solid solution near surface, and (3) higher oxygen mobility in CeO₂.

![Graph](image)

Figure 3.10. (a) Catalytic activity towards CO oxidation and (b) activation energy of different CuO/CeO₂ catalysts.
Table 3.1 showed BET surface area of the catalysts. BET surface area of CuO/CeO$_2$-TD, -CNP and -CCP were 39.31, 45.70 and 49.95 m$^2$/g, respectively. The surface area decreased with the increase amount of Cu-Ce-O solid solution in the sample, which was contradictory to the literature [40]. However, Luo et al. [15] showed that CuO impregnation on CeO$_2$ can decrease the surface area. Low surface area still does not affect the catalytic activity as long as the catalysts have highly synergistic interaction between CuO and CeO$_2$.

**Table 3.1. BET surface area of various CuO/CeO$_2$ catalysts and temperatures at which 50% and 100% CO conversion by these catalysts.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass (mg)</th>
<th>BET surface area (m$^2$/g)</th>
<th>T$_{50}$ (°C)</th>
<th>T$_{100}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/CeO$_2$-TD</td>
<td>25.6</td>
<td>39.31</td>
<td>93</td>
<td>211</td>
</tr>
<tr>
<td>CuO/CeO$_2$-CCP</td>
<td>25.2</td>
<td>49.95</td>
<td>112</td>
<td>278</td>
</tr>
<tr>
<td>CuO/CeO$_2$-CNP</td>
<td>24.8</td>
<td>45.70</td>
<td>84</td>
<td>286</td>
</tr>
</tbody>
</table>

**3.4. Conclusion**

In this study, a series of CuO/CeO$_2$ catalysts were successfully prepared by using three different CuO impregnation methods. The catalysts were characterized by XRD, Raman spectroscopy, XPS, TEM, and H$_2$-TPR, and their catalytic performances were characterized by CO-TPD and CO oxidation. XRD and TEM confirmed the presence of bulk and agglomerated CuO particles in CuO/CeO$_2$-CCP and CuO/CeO$_2$-CNP catalysts. Raman analysis ensured the presence of Cu-Ce-O solid solution in CuO/CeO$_2$-TD and CuO/CeO$_2$-CNP catalysts. CuO/CeO$_2$-CCP catalyst has either less amount of solid
solution or no solid solution at all. XPS spectra advised that higher amount of Ce$^{3+}$ and a strong interaction between Cu species and CeO$_2$ were present in CuO/CeO$_2$-TD sample. HRTEM images displayed different types of interactions between CuO and CeO$_2$ in the catalysts, which have a significant effect on the catalytic activity and lowering the reduction temperature. Among these three catalysts, CuO/CeO$_2$-TD consumed the highest amount of H$_2$ at low temperatures (142 and 165 °C) and converted 100% CO into CO$_2$ at low temperature (220 °C) in comparison to other two catalysts. Therefore, CuO/CeO$_2$-TD catalyst showed higher catalytic activity, which was due to the presence of strongly interacted dispersed CuO particles or Cu-Ce-O solid solution, resulting an increase in oxygen mobility in CeO$_2$ lattice.

3.5. References


39. Shinde, V. M.; Madras, G. Kinetics of carbon monoxide oxidation with Sn$_{0.95}$M$_{0.05}$O$_2$-d (M = Cu, Fe, Mn, Co) catalysts. *Catal. Sci. Technol.*, **2012**, 2, 437–446.

Chapter 4: A comparative study of CO oxidation over Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods catalysts

The distribution of copper species (on the surface or in the bulk of CeO$_2$ support) and the interfacial interactions between CuO and CeO$_2$ are critical in understanding the synergistic effect on the catalytic activity of CeO$_2$ supported CuO catalysts. In this chapter, Cu-O-Ce solid solutions and CuO impregnated on CeO$_2$ nanorods catalysts (CuO/CeO$_2$) with various compositions were prepared using thermal decomposition and hydrothermal methods, to understand the distribution effect of copper species on low temperature CO oxidation. The incorporation of copper ions into CeO$_2$ lattice in both types of catalysts was confirmed by X-ray diffraction (XRD), Raman spectroscopy, and hydrogen temperature programmed reduction (H$_2$-TPR) analysis, indicating a strong CuO-CeO$_2$ interfacial interaction and formation of oxygen vacancies which compensates the charge difference between copper (I/II) and cerium (III/IV) ions. A series of temperature programmed reduction-temperature programmed oxidation (TPR-TPO) thermal cycling studies were conducted to understand the interactions between three assigned copper species ($\alpha$, $\beta$, and $\gamma$) with CeO$_2$ support and the corresponding catalytic performance of the catalysts. In addition, an improved low temperature catalytic performance for the CuO/CeO$_2$ nanorods catalysts was observed, which was attributed to stronger interactions between copper species and CeO$_2$ nanorods enriched with surface defects (steps and voids etc.).
4.1. Introduction

Cerium oxide (CeO$_2$) supported CuO catalyst has been considered as an economically favorable material for various catalytic reactions, such as automotive three-way catalytic conversions [1,2], water gas shift reaction [3], oxidation of volatile organic compounds [4,5], and SO$_2$ reduction [6] etc. Researchers have approached various ways to investigate and improve the catalytic performance of CuO-CeO$_2$ catalysts for low-temperature reduction of nitrogen oxides and carbon monoxide oxidation. Zabilsky et al. [7] reported the effect of CeO$_2$ support shapes on the catalytic efficiency, and they concluded that CeO$_2$ nanorods presented a better catalytic performance in N$_2$O decomposition reaction due to exposing {100} and {110} high-energy surface planes. Avgouropoulos et al. [8] showed that the preparation method of CuO-CeO$_2$ catalysts can affect the catalytic activity in the selective oxidation of CO. They explored several different preparation methods, such as co-precipitation, urea-nitrates combustion, and citrate-hydrothermal method, to synthesize CuO-CeO$_2$ catalysts. The catalysts prepared by urea-nitrates combustion method showed the best catalytic activity in the selective oxidation of CO, which was contributed to the well-dispersed copper oxide species strongly interacting with CeO$_2$ surface. Zhou et al. [9] and Liu et al. [10] used deposition-precipitation method and wet impregnation method (thermal decomposition of Cu(NO$_3$)$_2$), respectively, to prepare CuO-CeO$_2$ nanorods catalysts. They investigated the support shape and crystal plane effect, and concluded that the coordination environment of copper ions is different on {111}, {110} and {100} planes of CeO$_2$ surfaces. Zheng et al. [11] demonstrated that both thermal decomposition temperature of Ce(NO$_3$)$_3$ and calcination temperature of CuO-CeO$_2$ catalysts have a significant impact on the physical
texture and catalytic activity of catalysts for low temperature CO oxidation. Avgouropoulos et al. [12] also reported that the hydrothermal treatment of citrate precursors promoted the mixing of Cu$^{2+}$ and Ce$^{4+}$ and the intimate interaction between CuO and CeO$_2$ which led to the improved structural and thermal stabilization of the catalysts.

These previous investigations pointed out the importance of mixing or interaction between CuO catalyst and CeO$_2$ support either on the CeO$_2$ surface or in the form of Cu-O-Ce solid solution phases during the catalysts preparation. CeO$_2$ nanorods have demonstrated as a highly reducible and active support for CuO catalysts compared to CeO$_2$ nanocubes and nanoctahedra. To further explore the roles of copper species distribution (on the surface or in the bulk of CeO$_2$ support), CeO$_2$ nanorods with significant surface roughness and defects were chosen as support of CuO catalyst to understand the synergistic effect in CuO-CeO$_2$ catalysts for low-temperature CO oxidation. In this chapter, Cu-O-Ce solid solutions and CuO impregnated CeO$_2$ nanorods catalysts (CuO/CeO$_2$) with various compositions were prepared and a systematic comparison study was conducted to advance our understanding of the effects of copper distribution and thermal cycling treatments on the catalytic behavior in CuO-CeO$_2$ catalysts.

4.2. Experimental

4.2.1. Catalyst preparation

To prepare the Cu-O-Ce solid solution catalyst samples with 2-12 wt% Cu addition, Ce(NO$_3$)$_3$·6H$_2$O and Cu(NO$_3$)$_2$·3H$_2$O were mixed with the stoichiometric ratios in 30 mL
deionized water. The mixture solution in a beaker was stirred and heated at 120 °C on a hot plate until water evaporated completely. The collected samples were then oxidized at 400 °C for 5 hrs in air. These samples were called as Cu-O-Ce solid solutions and were denoted as x-Cu-O-Ce, where x was the weight percentage of Cu (wt%). For example, 2-Cu-O-Ce stands for 2 wt% Cu addition in Cu-O-Ce solid solution. Reduction-oxidation (redox) thermal cycling treatments were conducted on the 10-Cu-O-Ce catalyst sample. The catalyst was reduced in a tube furnace at 400 °C for 1 hr under 5%H₂-95%Ar gas environment. After cooling down to room temperature, the sample was then oxidized in a box furnace at 400 °C for 1 hr in air. This two-step process is called one redox treatment.

Hydrothermal method is a common way to prepare CeO₂ nanorods [1], which was used in this study. 8 mL of 6 M NaOH was added into 88 mL of 0.1 M Ce(NO₃)³·6H₂O solution in Teflon liner of 200 mL capacity. After stirring the solution for about 15 sec, the lid of Teflon liner was closed. The Teflon liner along with stainless steel autoclave was heated and kept at 90 °C for 48 hrs. After cooling down to room temperature, a filtration of the suspension solution was conducted. The filtered product was washed with 500 mL water, and then with 50 mL ethanol to remove any Na⁺ ion remained in the product and most of water to avoid hard agglomeration during drying. Then the sample was dried at 50 °C for 12 hrs.

To prepare the CuO/CeO₂ catalyst samples with 6-10 wt% Cu addition (CuO impregnated CeO₂ nanorods catalysts), the as-synthesized CeO₂ nanorods powder and Cu(NO₃)₂·3H₂O solution were mixed first with the stoichiometric ratios in 30 mL of deionized water. The suspension solution was heated and kept at 120 °C until water evaporated completely. Finally, the samples were oxidized at 400 °C for 5 hrs in air. The
samples were denoted as x-CuO/CeO$_2$, where x is Cu wt%. For example, 6-CuO/CeO$_2$ stands for 6 wt% Cu loaded onto CeO$_2$ nanorods.

4.2.2. Catalyst Characterizations

X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), BET surface area measurement, temperature programmed reduction (TPR), temperature programmed oxidation (TPO), temperature programmed desorption (TPD), pulse chemisorption to calculate oxygen storage capacity (OSC), and CO oxidation were used to characterize the catalysts and their catalytic activity. The description of these techniques can be found in chapter 2.

4.3. Results and discussion

4.3.1. XRD and BET surface area

For comparison, Fig. 4.1a showed the XRD patterns of the as-synthesized CeO$_2$ nanorods and CuO powder. Typical diffraction peaks for fluorite structured CeO$_2$ were observed at 2θ of 28.8°, 33.1°, 47.5°, 56.3°, 59.1°, 69.4°, 76.7° and 79.1° (JCPDS 43-1002) [13]. Two strong and sharp diffraction peaks for monoclinic CuO were observed at 2θ of 35.6° and 38.8° which correspond to (-111) and (111) planes (JCPDS 45-0937), respectively [14,15]. Fig. 4.1b displayed the XRD patterns of the Cu-O-Ce solid solutions samples where the Cu content varied from 2 to 12 wt%. Fluorite structure CeO$_2$ phase was observed clearly in all six samples. The disappearance of the CuO diffraction peaks below 8 wt% Cu addition indicated a formation of Cu-O-Ce solid solution. There could be a possibility that amorphous or small-sized copper species could anchor onto the
surface of CeO$_2$ support, which was also invisible in XRD patterns. But a continuous CeO$_2$ (111) diffraction peak shift was observed as shown in Fig. 4.2a, indicating the incorporation of Cu$^{2+}$ into CeO$_2$ concluded that the disappearance of CuO diffraction was at least partially due to the formation of Cu-O-Ce solid solution. The characteristic (-111)/(111) CuO diffraction peaks were visible starting for 8 wt% Cu addition and more in the solid solution samples, as shown in Fig. 4.1b. The intensities of these two peaks were low in the 8-Cu-O-Ce sample and became progressively stronger with increasing the Cu content to 10 wt% and 12 wt%. The XRD patterns of the CuO/CeO$_2$ nanorods samples with 6-10 wt% Cu addition were shown in Fig. 4.1c, where the characteristic peaks of CeO$_2$ were visible for all three samples. Interestingly, no CuO diffraction peaks were detected for these three CuO/CeO$_2$ nanorods samples, which suggested a different distribution of copper species over CeO$_2$ nanorods compared to the 6-10 wt% Cu-O-Ce solid solution samples (Fig. 4.1b). Some possible reasons why CuO phase was not detected in XRD analysis were the following: poor crystallization, formation of Cu-O-Ce solid solution, and highly dispersed small copper species on CeO$_2$ nanorods, and/or a mixture of these. It was also found that when the Cu content increased, the characteristic XRD peaks of CeO$_2$ became broader for both Cu-O-Ce solid solution and CuO/CeO$_2$ nanorods samples. The peak broadening was due to decrease in crystallite size and increase in compositional heterogeneity with increasing the Cu amount. Table 4.1 showed that the crystallite size of the Cu-O-Ce samples decreased with increasing the Cu content up to 8 wt% Cu addition, and then increased with further Cu addition. For the CuO/CeO$_2$ samples, the crystallite size showed a continuous decrease from 6 wt% to 10 wt% Cu addition.
Figure 4.1. XRD patterns of (a) CeO$_2$ and CuO, (b) Cu-O-Ce samples, and (c) CuO/CeO$_2$ samples.
Table 4.1. Crystallite size and lattice parameter measured from CeO$_2$ (111) peak, and BET surface area of Cu-O-Ce and CuO/CeO$_2$.

<table>
<thead>
<tr>
<th>Cu contents (%)</th>
<th>Cu-O-Ce solid solution</th>
<th>CuO/CeO$_2$ nanorods</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Crystallite size (nm)</td>
<td>Lattice parameter (Å)</td>
</tr>
<tr>
<td>0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>6.6</td>
<td>5.4212 (±0.0005)</td>
</tr>
<tr>
<td>4</td>
<td>6.1</td>
<td>5.4274 (±0.0006)</td>
</tr>
<tr>
<td>6</td>
<td>5.5</td>
<td>5.4358 (±0.0003)</td>
</tr>
<tr>
<td>8</td>
<td>4.9</td>
<td>5.4468 (±0.0002)</td>
</tr>
<tr>
<td>10</td>
<td>5.2</td>
<td>5.4548 (±0.0002)</td>
</tr>
<tr>
<td>12</td>
<td>5.4</td>
<td>5.4324 (±0.0003)</td>
</tr>
</tbody>
</table>

Fig. 4.2a and 4.2b illustrated that the characteristic (111) peak of CeO$_2$ for both Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples shifted towards lower angle with increasing the Cu content. This peak shifting towards lower diffraction angle indicated a lattice expansion of CeO$_2$ according to the Scherrer equation ($2d \sin \theta = n\lambda$). The ionic radius of Cu$^{2+}$ and Ce$^{4+}$ were 0.072 nm and 0.103 nm, respectively [16,17]. As the radius of Cu$^{2+}$ was smaller than that of Ce$^{4+}$, the incorporation of Cu$^{2+}$ in CeO$_2$ would cause lattice contraction leading to the peak shifting towards higher diffraction angle. Most likely, the addition of Cu$^{2+}$ in CeO$_2$ created oxygen vacancies accompanied by reduction of Ce$^{4+}$ ions in their vicinity into Ce$^{3+}$ (2Ce$^{4+} + V_{O}^{2+}$) to compensate the change difference between Cu$^{2+}$ and Ce$^{4+}$. Since the ionic radius of Ce$^{3+}$ (0.111 nm) is about 7.8% larger than that of Ce$^{4+}$ (0.103 nm), the diffraction peak shifted to lower diffraction angle due to the lattice expansion observed in the samples. The change in
CeO$_2$ lattice parameter with the Cu addition was shown in Table 4.1. The lattice constant in CeO$_2$ increased with increasing the Cu content for both Cu-O-Ce solid solution and CuO/CeO$_2$ nanorods samples, except for the 12-Cu-O-Ce sample. It has been reported that Cu$^{2+}$ ions can incorporate into CeO$_2$ lattice to form CuO-CeO$_2$ solid solution [18]. As a result, oxygen vacancies are formed which leads to the formation of

![Figure 4.2. XRD patterns of CeO$_2$ (111) peak in (a) Cu-O-Ce and (b) CuO/CeO$_2$ samples.](image)

93
substoichiometric fluorite-structured CeO$_{2-y}$ (0≤y<0.5). By comparing between the Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples for 6-10 wt% Cu addition, it was found in Table 4.1 that the 10-CuO/CeO$_2$ nanorods sample showed the largest lattice constant due to possibly the presence of highest amount of Ce$^{3+}$ ions and oxygen vacancies in CeO$_2$ lattice. It also should be noted that another possible explanation for the lattice expansion is the size effect, and generally smaller particle size causes an expanded lattice due to the high concentration of defects. The particle size of these samples is in the range of 4~6 nm with evident defects shown in Fig. 4.5. Table 4.1 also showed that the BET surface area of the Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples decreased with increasing the Cu content. In principle, the surface area of the samples would increase if the crystallite size decreased. But it should be noted that the crystallite size was estimated by the CeO$_2$ (111) peak, but the BET surface areas was measured on both CeO$_2$ and copper based particles and species in the samples by N$_2$ adsorption. It was reported previously that surface area of the samples decreased due to increasing the amount of Cu ions incorporation into CeO$_2$ lattice [16].

4.3.2. Raman analysis

Raman spectra of CeO$_2$ nanorods and CuO were shown in Fig. 4.3a. The characteristic peak of CeO$_2$ observed at 456 cm$^{-1}$ corresponded to F$_{2g}$ vibrational mode [19]. Two peaks found at 258 and 605 cm$^{-1}$ were attributed to oxygen vacancies in CeO$_2$ nanorods [19]. CuO showed the typical peaks at 271, 326, 506, and 625 cm$^{-1}$, which corresponded to A$_{g}$, B$_{1g}$, B$_{2u}$, and B$_{2g}$ mode, respectively [20-22]. According to Debbichi et al., [23] the peak found at 506 cm$^{-1}$ corresponded to E$_{g}$ mode of Cu$_4$O$_3$. However, no evidence of Cu$_4$O$_3$ phase was found in the XRD patterns and thus, this peak was assumed
Figure 4.3. Raman spectra of (a) CeO$_2$ and CuO, (b) Cu-O-Ce samples, and (c) CuO/CeO$_2$ samples.
as B_{2u} mode of CuO. Fig. 4.3b showed the Raman spectra of the Cu-O-Ce solid solutions samples, where it was clear that the characteristic F_{2g} peak of CeO_2 started shifting to the left (from 456 cm\(^{-1}\) to 446 cm\(^{-1}\)) with increasing the Cu content till 8 wt%, and then the peak started shifting to the right (from 446 cm\(^{-1}\) to 451 cm\(^{-1}\)) with further increasing the Cu content. Such peak shifting to the lower wavenumber in Raman analysis occurred for two possible reasons: (i) lattice distortions in CeO_2 due to Cu addition, and (ii) decrease in crystallite size [24,25]. The incorporation of Cu ions into CeO_2 lattice led to the formation of Cu-O-Ce solid solutions. In the meantime, oxygen vacancy was created to compensate the charge discrepancy between Cu\(^{2+}\) and Ce\(^{4+}\). However, oxygen vacancy was not restricted in one single site, but instead this spread to further adjacent oxygen positions. Thus, the incorporation of Cu ions into CeO_2 lattice increased the chance of forming substoichiometric CeO_{2-y} due to the generation of many oxygen vacancies. The oxygen vacancy defect disrupted the O-Ce-O lattice, which eventually caused the Raman peak shifting. The decrease in crystallite size along with the Cu incorporation created more lattice distortion and defects. For the Cu-O-Ce solid solutions, the CeO_2 F_{2g} peak for the 10-Cu-O-Ce and 12-Cu-O-Ce samples started shifting to the right with respect to the same peak of the 8-Cu-O-Ce sample. For the 10-Cu-O-Ce sample, although the XRD pattern showed the lattice expansion due to the presence of Ce\(^{3+}\) and oxygen vacancies, CeO_2 F_{2g} peak shifted to the right due to the increment of crystallite size as shown in Table 4.1. Fig. 4.3c showed that CeO_2 F_{2g} peak for the CuO/CeO_2 nanorods samples shifted to the left (from 456 cm\(^{-1}\) to 444 cm\(^{-1}\)) with increasing the Cu content. The 10-CuO/CeO_2 nanorods sample showed the largest peak shifting to the left due to the existence of oxygen vacancies and Ce\(^{3+}\) as discussed above, which was in line with the
XRD analysis (Fig. 4.2). Shan et al. [16] reported a similar peak shift due to the formation of CuO-CeO$_2$ solid solution.

4.3.3. XPS analysis

Fig. 4.4 compared the XPS spectra of the 10-Cu-O-Ce solid solution and 10-CuO/CeO$_2$ nanorods samples. Fig. 4.4a showed spectra of Ce 3d which was used to assess the fraction of Ce$^{3+}$ state. The fitted Ce 3d spectrum was overlaid on top of the experimental data. v (882.7 eV), v’’(888.5 eV), v’’’(898.3 eV), u (901.3 eV), and u’’(907.3 eV) referred to Ce$^{4+}$ state, while v’(885.2 eV), and u’(903.4 eV) referred to Ce$^{3+}$ state [26,27]. The marked differences in v’(885.2 eV) and u’(903.4 eV) intensity indicated the higher concentration of Ce$^{3+}$ in the 10-CuO/CeO$_2$ nanorods sample, which was consistent with the XRD and Raman analysis above. XPS spectra of Cu 2p$_{3/2}$ were shown in Fig. 4.4b where one peak with high intensity can be observed at 938.9 eV for the 10-CuO/CeO$_2$ nanorods and 939.0 eV for the 10-Cu-O-Ce sample. This peak corresponded to Cu$^{2+}$ [27]. A shoulder peak can be found at low energy for both samples (at 936.0 eV for 10-CuO/CeO$_2$ and at 934.3 eV for 10-Cu-O-Ce). The shoulder peak referred to the presence of Cu$^+$ which was considered as a strong interaction of Cu types with CeO$_2$ [27,28]. As the intensity of shoulder peak in 10-CuO/CeO$_2$ was higher than that in 10-Cu-O-Ce, it suggested that 10-CuO/CeO$_2$ had larger amount of highly-interacted Cu species with CeO$_2$. Two peaks for O 1s were found in Fig. 4.4c. First peak found at 536.1 eV for 10-CuO/CeO$_2$ and 535.1 eV for 10-Cu-O-Ce was attributed to the presence of adsorbed oxygen at the surface and this adsorbed oxygen was easy to be reduced at low-temperature [29,30]. Yang et al. [29] reported that the presence of strong shoulder peak
Figure 4.4. XPS spectra of 10-Cu-O-Ce solid solution and 10-CuO/CeO$_2$ nanorods samples.
of Cu_{0.1}Ce_{0.9}O_{2} suggested an increase in oxygen storage capacity. By comparing the intensity, it could be easily concluded that the 10-CuO/CeO_{2} sample could adsorb more oxygen from the environment which eventually helped in increasing the catalytic efficiency. Another peak, which was found at 533.4 eV for both samples, corresponds to lattice oxygen of metal oxides. Charging effect during experiment caused the peak shift compared to other literatures [26-30].

4.3.4. TEM analysis

TEM analysis was performed to investigate the microstructural characteristics of the catalysts. Fig. 4.5 showed the TEM and HRTEM images of the 10-Cu-O-Ce (Fig. 4.5a

![Figure 4.5](image)

Figure 4.5. (a) TEM and (b) HRTEM images of 10-Cu-O-Ce, and (c) TEM and (d) HRTEM images of 10-CuO/CeO_{2}.  

99
and 4.5b) and 10-CuO/CeO$_2$ (Fig. 4.5c and 4.5d) samples. The TEM image of the 10-Cu-O-Ce sample, shown in Fig. 4.5a, revealed an average particle size smaller than 10 nm. In the inset of Fig. 4.5b, HRTEM image analysis of red rectangular portion indicated that the nanoparticle exposed lattice fringes with a d-spacing at 0.31 nm, which was close to CeO$_2$ (111) planes. Typical TEM image of the 10-CuO/CeO$_2$ nanorods was shown in Fig. 4.5c, confirming the thermal stability of CeO$_2$ nanorods after Cu addition and calcination at 400 °C for 5 hrs. These nanorods were 5-10 nm in width and 50-100 nm in length. The HRTEM image in Fig. 4.5d showed relatively large number of rough surfaces and defects on CeO$_2$ nanorods, which is consistent with the previous Raman and XRD analysis. The inset in Fig. 4.5d demonstrated that CeO$_2$ nanorods exposed both (100) and (110) planes.

4.3.5. H$_2$-TPR

H$_2$-TPR was conducted to determine the reduction temperature and amount of H$_2$ consumption at each peak. Fig. 4.6 showed the H$_2$-TPR profiles of the Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples, respectively. After fitting the peak profiles, it appeared the presence of two reduction peaks for 2-8 wt% Cu addition in the Cu-O-Ce solid solution samples shown in Fig. 4.6a. Whereas, there were three reduction peaks identified for the 10 and 12 wt% Cu-O-Ce solid solution samples. In literature of CuO-CeO$_2$, the first peak was designated as $\alpha$ peak, which corresponded to the reduction of solid solutions or highly interacted CuO with CeO$_2$ [31]. The second peak was assigned as $\beta$ peak, which related to the reduction of highly dispersed CuO particles on CeO$_2$ [32]. The third peak, $\gamma$ peak, was attributed to the reduction of bulk CuO [33]. However, the specific reduction temperature for these three assignments ($\alpha$, $\beta$, and $\gamma$) was quite diverse in literature. For example, Shiau et al. [34] and Wang et al. [35] reported three H$_2$
reduction peaks at over 200 °C. Luo et al. [36] stated that two reduction peaks for 10 wt% CuO loading were found near 160 and 200 °C. In our samples, for the 2-Cu-O-Ce sample, both α and β peaks were found over 200 °C and for the rest of the Cu-O-Ce samples, α peak were shown at less than 200 °C. Both α and β peaks progressively shifted to lower temperature as the Cu content increased, revealing the promoting synergistic effect of CuO addition on the low temperature reducibility in the Cu-O-Ce samples. A similar peak shifting could also be seen for the CuO/CeO$_2$ nanorods as shown in Fig. 4.6b. For the 10-CuO/CeO$_2$ sample, both α and β peaks shifted to the lowest temperature in all nine samples in this study probably because this sample had the highest lattice expansion with Ce$^{3+}$ along with a large amount of oxygen vacancies and lattice distortion in CeO$_2$ as discussed in XRD and Raman/XPS analysis. The CuO/CeO$_2$ nanorods samples did not

Figure 4.6. H$_2$-TPR profiles of (a) Cu-O-Ce solid solutions and (b) CuO/CeO$_2$ nanorods.
show γ peak due to absence of bulk CuO, which was in agreement with XRD analysis (Fig. 4.1c).

Figure 4.7. H₂ consumption at each peak of (a) Cu-O-Ce solid solutions and (b) CuO/CeO₂ nanorods.
Fig. 4.7 showed the $\text{H}_2$ consumption at each TPR peak and total $\text{H}_2$ consumption ($\alpha+\beta+\gamma$) for the Cu-O-Ce and CuO/CeO$_2$ samples. For the Cu-O-Ce catalysts, $\text{H}_2$ consumption at $\alpha$ peak increased from 2 to 8 wt% Cu addition as shown in Fig. 4.7a. $\text{H}_2$ consumption at $\alpha$ peak (0.930 mmol/g) of the 10-Cu-O-Ce sample was lower than that (2.395 mmol/g) of the 8-Cu-O-Ce sample, and this happened due to the presence of more CuO particles on CeO$_2$ surface. CuO particles could cover up CeO$_2$ surface where Cu-O-Ce solid solution was formed. The proof of having higher amount of bulk CuO in the 10-Cu-O-Ce and 12-Cu-O-Ce samples could be seen from both XRD (Fig. 4.1b) and the presence of $\gamma$ peak in $\text{H}_2$-TPR (Fig. 4.6a). For the CuO/CeO$_2$ catalysts, the $\text{H}_2$ consumption at $\beta$ peak for all three samples was very close as shown in Fig. 4.7b. $\text{H}_2$ consumption at $\alpha$ peak increased with increasing the Cu addition possibly due to the increment of oxygen vacancies in CeO$_2$ lattice as discussed in Raman analysis. The theoretical $\text{H}_2$ consumptions of 2, 4, 6, 8, 10, and 12 wt% CuO addition in CuO-CeO$_2$ are 252, 504, 756, 1008, 1260, and 1512 µmol/g, respectively. It could be seen from Fig. 4.7 that the experimental $\text{H}_2$ consumptions for both Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples were higher (3 to 6 times for Cu-O-Ce and 2 to 3 times for CuO/CeO$_2$) than the corresponding theoretical $\text{H}_2$ consumptions. Sun et al. [37] also reported that 1 wt% and 5 wt% CuO impregnated CeO$_2$ consumed ~10 times and 2.5 times respectively higher $\text{H}_2$ consumption than the theoretical values. Thus, it could be concluded that CeO$_2$ support contributed significantly to the total $\text{H}_2$ consumption. It has been reported that the interfacial structure plays a role in easy reduction of CuO-CeO$_2$ due to a synergistic effect [33,38]. Our results indicated that the interfacial structure formed in CeO$_2$ nanorods supported CuO (CuO/CeO$_2$) was more favorable for reduction compared to the formation
of Cu-O-Ce solid solution. The detailed interfacial structure and composition study of CuO/CeO\(_2\) is ongoing.

4.3.6. TPR-TPO cycling

Redox thermal cycling treatments are essential steps for the preparation and long-term applications of supported high surface area catalysts. TPR-TPO thermal cycling experiments were conducted on the 10-Cu-O-Ce solid solution and 10-CuO/CeO\(_2\) nanorods samples to investigate the correlation of redox treatments with the change in their structure and catalytic activity. Fig. 4.8 showed the TPR profiles of the pristine sample and the sample after each TPR-TPO cycle, and the XRD patterns and Raman spectra of as-synthesized and after each TPR-TPO cycle for the 10-Cu-O-Ce sample. In the TPR profiles (Fig. 4.8a), both \(\alpha\) and \(\beta\) peaks shifted to the lower temperatures after each TPR-TPO cycle with respect to the previous TPR profile. In Fig. 4.8b, the XRD patterns showed that the characteristic CeO\(_2\) (111) peak shifted to lower diffraction angle after each TPR-TPO cycle and thus, the lattice parameter of CeO\(_2\) increased after each cycle due to the increment of concentration of Ce\(^{3+}\) and oxygen vacancies in the sample. It was expected that the sample would be fully re-oxidized during the TPO treatment at 350 °C [39]. However, it appeared that the re-oxidation did not affect the lattice parameter of CeO\(_2\), confirmed from the data shown in Fig. 4.10. Table 4.2 displayed the change in crystallite size and lattice parameter determined by CeO\(_2\) (111) XRD diffraction peak and OSC of the 10-Cu-O-Ce sample with the redox treatments. The OSC of the 10-Cu-O-Ce sample increased from 1.98 to 2.27 \(\mu\)mol \(O_2/g\) after 3 TPR-TPO
cycles as shown in Table 4.2. Fig. 4.8c showed the Raman spectra of the Cu-O-Ce sample after each cycle of TPR-TPO treatment, and the CeO$_2$ $F_{2g}$ peak of the 10-Cu-O-Ce sample shifted to the right after each cycle possibly due to a combination effect of lattice distortion and crystallite size as mentioned earlier. A similar study was conducted and shown in Fig. 4.9 for the 10-CuO/CeO$_2$ nanorods sample. The TPR profiles in Fig. 4.9a displayed that $\alpha$ peaks which correspond to the solid solution copper species, remained at the same position at each cycle. No change in peak position was observed which was consistent with the XRD data. The CeO$_2$ (111) peaks in XRD presented in
Fig. 4.9b, did not change their position and thus, the lattice parameter of CeO$_2$ tabulated in Table 4.3 did not change as well. Similarly, no change in the position of CeO$_2$ (111) peak was found in Fig. 4.10 after TPR and after TPR-TPO with compared to as-synthesized sample. This explained that the concentration of Ce$^{3+}$ and oxygen vacancies in the 10-CuO/CeO$_2$ sample may have already reached its maximum during the synthesis.

On the other hand, the crystallite size increased with number of redox cycles, and this was the reason for shifting the Raman peak of CeO$_2$ to the right as shown in Fig. 4.9c. Table 4.3 showed that the OSC of the 10-CuO/CeO$_2$ sample remained constant (2.38 $\mu$molO$_2$/g) before and after redox treatments.

![Figure 4.9](image)

Figure 4.9. (a) H$_2$-TPR profiles, (b) XRD patterns, and (c) Raman spectra after each TPR-TPO cycling for the sample of 10-CuO/CeO$_2$. 
Table 4.2. Crystallite size and lattice parameters of 10-Cu-O-Ce after each TPR-TPO cycling.

<table>
<thead>
<tr>
<th>TPR-TPO cycle number</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>OSC (µmol O₂/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>5.2</td>
<td>5.4548 (±0.0002)</td>
<td>1.98</td>
</tr>
<tr>
<td>1</td>
<td>6.5</td>
<td>5.4787 (±0.0004)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>6.8</td>
<td>5.4807 (±0.0003)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>6.9</td>
<td>5.4939 (±0.0004)</td>
<td>2.27</td>
</tr>
</tbody>
</table>

Table 4.3. Crystallite size and lattice parameters of 10-CuO/CeO₂ after each TPR-TPO cycling.

<table>
<thead>
<tr>
<th>TPR-TPO cycle number</th>
<th>Crystallite size (nm)</th>
<th>Lattice parameters (Å)</th>
<th>OSC (µmol O₂/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
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<td>5.4747 (±0.0005)</td>
<td>2.38</td>
</tr>
<tr>
<td>1</td>
<td>6.0</td>
<td>5.4739 (±0.0002)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>6.3</td>
<td>5.4711 (±0.0003)</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>6.4</td>
<td>5.4742 (±0.0003)</td>
<td>2.39</td>
</tr>
</tbody>
</table>

4.3.7. CO-TPD

The CO-TPD profiles of both the 10-Cu-O-Ce and 10-CuO/CeO₂ samples were shown in Fig. 4.11a. In this experiment, CO usually adsorbs on the surface of the catalysts and desorbs away as CO₂ after reacting with surface oxygen. A large difference in the intensity of the CO-TPD curves for the two samples could be observed in Fig. 4.11a. We previously reported that two desorption peaks were seen for CuO/CeO₂ catalyst [26]. The first peak found at around 100 °C corresponded to desorption of CO₂ which was the product of reaction between adsorbed CO and CeO₂ surface. The second peak seen at 150-160 °C was attributed to desorption of CO₂ produced from the transformation of adsorbed CO into bidentate carbon species at the reactive sites. Two similar peaks (at 105 and 180 °C) with much lower intensity were found for the 10-Cu-O-
Ce sample. This data suggested that the 10-CuO/CeO sample provided higher amounts of lattice oxygen compared to the 10-Cu-O-Ce sample. Fig. 4.11b showed the rate of desorption (ROD) of CO$_2$ for both 10-Cu-O-Ce and 10-CuO/CeO$_2$ samples. The rate of desorption (ROD) for the 10-CuO/CeO$_2$ sample increased with increasing temperature and the maximum ROD ($\sim 0.0014$ mol cm$^{-2}$ s$^{-1}$) was achieved at 325 °C. After reaching the maximum, the ROD decreased rapidly because most of the adsorbed CO already desorbed away from the surface. A similar trend of the ROD can be seen for the 10-Cu-O-Ce sample.

Figure 4.10. XRD patterns of as-synthesized, after first TPR and after first TPR-TPO cycle of both (a) 10-CuO/CeO$_2$ and (b) 10-Cu-O-Ce.
Ce sample as well in the inset of Fig. 4.11b. However, the maximum ROD (∼ 6.9×10⁻⁵ mol cm⁻² s⁻¹) for the 10-Cu-O-Ce sample was found at 350 °C. The maximum ROD for the 10-CuO/ CeO₂ sample was almost 20 times larger than that for the 10-Cu-O-Ce
sample. This observation advised that more CO was absorbed on the surface in the 10-CuO/CeO$_2$ sample during the flow of 5%CO-95%He gas, which resulted in the high rate of CO$_2$ desorption. In other words, more CO adsorption sites were available on the surface of the 10-CuO/CeO$_2$ sample. Also, the 10-CuO/CeO$_2$ sample had a lower desorption energy (29.3 kJ/mol) in comparison with the 10-Cu-O-Ce sample (39.5 kJ/mol) calculated from the equation (4.2).

4.3.8. CO oxidation

Fig. 4.12 compared the light-off curves over the Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods samples toward CO oxidation. It showed that the Cu-O-Ce catalysts converted less than 90% CO up to 350 °C with the addition of 2-12 wt% Cu. It was clear that the 10-CuO/CeO$_2$ nanorods sample exhibited the highest activity with 100% CO conversion to CO$_2$ at around 220 °C. Table 4.4 displayed the T$_{50}$ temperature (the temperature at which the CO conversion reaches 50% is taken as a measurement of catalytic activity), maximum CO conversion percentage (up to 350 °C), and the T$_{max}$ temperature (the temperature at which the maximum CO conversion is achieved). The Cu-O-Ce samples achieved maximum ~88% CO conversion in the range of temperature from 220 to 270 °C. Comparing the six Cu-O-Ce catalysts studied, T$_{50}$ decreased with increasing Cu addition up to 6 wt%, and this enhancement of the catalytic activity could be attributed to the increased oxygen vacancy concentration due to the Cu ions substitutions of Ce ions in CeO$_2$ lattice as discussed earlier. The addition of higher amounts of Cu (> 6 wt%) into CeO$_2$ led to the formation of CuO as shown in Fig. 4.1b. It appeared that T$_{50}$ increased for the 8-Cu-O-Ce, 10-Cu-O-Ce, and 12-Cu-O-Ce samples.
Probably the presence of bulk CuO with large particle size covered up the active surface sites on the Cu-O-Ce solid solution particles, which was not in favor the access of the reactant to the active sites. On the other hand, the 6-CuO/CeO$_2$ and 8-CuO/CeO$_2$
nanorods converted 90 and 94% CO to CO$_2$ at 254 °C, respectively. $T_{50}$ of CuO/CeO$_2$ nanorods samples gradually decreased with increasing Cu addition from 6 to 10 wt%. As mentioned earlier, no bulk CuO was found in the CuO/CeO$_2$ nanorods samples from XRD analysis shown in Fig. 4.1c. This result suggested the addition Cu in CeO$_2$ lattice or
well-dispersed strongly-interacted small CuO favoring the low-temperature CO conversion. Zheng et al. [40] reported that $T_{50}$ and $T_{100}$ for CuO/CeO$_2$ catalysts prepared by sol-gel method were 138 and 230 °C, respectively. Zheng et al. [40] and Liu et al. [41] remarked that finely dispersed CuO on CeO$_2$ was primarily responsible for low-temperature CO oxidation and bulk CuO had no significant contributions to this

Figure 4.14. (a) CO oxidation and (b) ln(rate) vs. 1000/T curves of 10-Cu-O-Ce before and after redox treatment.
conversion. Fig. 4.13 showed activation energy of various catalysts and it can be seen that 10-CuO/CeO$_2$ which achieved an enhanced catalytic activity had the lowest activation energy (15.0 KJ/mol) among all the prepared catalysts. Fig. 4.14a compared the light-off curves of 10-Cu-O-Ce solid solutions before and after the redox treatment. It was clear that the 10-Cu-O-Ce sample after the redox treatment displayed higher catalytic activity and lower activation energy (21.3 KJ/mol shown in Fig. 4.14b), indicating a reduction activation of the sample. The $T_{50}$ of 10-Cu-O-Ce-Redox was 82 °C, and this catalyst could convert maximum 92% CO at 272 °C, as tabulated in Table 4.5.

Table 4.4. The catalytic activity toward CO oxidation over Cu-O-Ce and CuO/CeO$_2$.

<table>
<thead>
<tr>
<th>Cu contents (%)</th>
<th>Cu-O-Ce solid solution</th>
<th>CuO/CeO$_2$ nanorods</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{50}$ (°C)</td>
<td>$T_{max}$ (°C)</td>
<td>$T_{50}$ (°C)</td>
</tr>
<tr>
<td>2</td>
<td>140</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>115</td>
<td>88</td>
</tr>
<tr>
<td>6</td>
<td>100</td>
<td>88</td>
</tr>
<tr>
<td>8</td>
<td>109</td>
<td>87</td>
</tr>
<tr>
<td>10</td>
<td>124</td>
<td>87</td>
</tr>
<tr>
<td>12</td>
<td>124</td>
<td>86</td>
</tr>
</tbody>
</table>

Table 4.5. The catalytic activity toward CO oxidation over 10-Cu-O-Ce before and after redox treatment, and 10-CuO/CeO$_2$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{50}$ (°C)</th>
<th>Max conversion (%)</th>
<th>$T_{max}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10-Cu-O-Ce</td>
<td>124</td>
<td>87</td>
<td>227</td>
</tr>
<tr>
<td>10-Cu-O-Ce-Redox</td>
<td>82</td>
<td>92</td>
<td>272</td>
</tr>
<tr>
<td>10-CuO/CeO$_2$</td>
<td>88</td>
<td>100</td>
<td>220</td>
</tr>
</tbody>
</table>
4.4. Conclusion

Cu-O-Ce solid solutions (2~12 wt%) and CuO/CeO$_2$ nanorods (6~10 wt%) samples were successfully prepared using thermal decomposition method and hydrothermal methods. It could be concluded that the amount of Cu incorporation into CeO$_2$ lattice depended on the preparation methods of the catalysts and CeO$_2$ structure (shape and surface defects etc.). The different distribution and interactions of copper species with CeO$_2$ in these samples led to varied hydrogen consumption behaviors (temperature and amount). In the CuO/CeO$_2$ nanorods samples, two reduction TPR profiles were observed for the compositions from 6 wt% to 10 wt% CuO with a continuous decrease in the reduction temperature. While for the Cu-O-Ce samples, a transition from two (2~8 wt% CuO) to three (10~12 wt% CuO) reduction profiles was observed, which was explained by the formation of bulk CuO phase due to the solid solution limitation of CuO in CeO$_2$. The TPR-TPO thermal cycling treatments suggested an increase of oxygen vacancy concentration and improved low temperature reducibility over the 10-Cu-O-Ce samples after each cycle, which was further supported by the CO oxidation analysis. H$_2$ pulse chemisorption analysis showed that the OSC of the 10-Cu-O-Ce sample increased after redox treatments and 10-CuO/CeO$_2$ had the same OSC value before and after redox treatments.

4.5. References


17. Sun, S.; Zhao, X.; Lu, H.; Zhang, Z.; Wei, J.; Yang, Y. Unusual properties of nanostructured Ce$_{1-x}$Co$_x$O$_{2-y}$, Ce$_{1-x}$Ni$_x$O$_{2-y}$ and Ce$_{1-(x+y)}$Co$_x$Ni$_y$O$_{2-z}$: structural studies and catalytic activity. *CrystEngComm.*, 2013, 15, 1370-1376.


Chapter 5: Support structure effect on CO oxidation: A comparative study on SiO$_2$ nanospheres and CeO$_2$ nanorods supported CuO$_x$ catalysts

The effect of support reducibility and reduction treatment has been studied in SiO$_2$ nanospheres and CeO$_2$ nanorods supported CuO$_x$ (0≤x≤1) catalysts on CO oxidation. CuO nanoparticles were impregnated on SiO$_2$ nanospheres and CeO$_2$ nanorods using thermal decomposition method and then the samples were oxidized in air at different temperatures (400-600 °C). The sample oxidized at 400 °C was also further reduced under hydrogen atmosphere to compare the effect of reduction treatment on the catalytic activity. Detailed XRD, Raman, H$_2$-TPR, and CO oxidation analyses were carried out to understand the effect of CuO$_x$-support interaction and different CuO$_x$ species on the catalytic performance. In comparison to SiO$_2$ nanospheres supported CuO$_x$ catalysts, both CuO/CeO$_2$ and reduced CuO$_x$/CeO$_2$ catalysts exhibited superior catalytic performance in terms of CO conversion and low-temperature hydrogen consumption. The enhanced activity of CeO$_2$ nanorods supported CuO$_x$ catalysts was correlated strongly to the surface defects on CeO$_2$ nanorods and interfacial structures.

5.1. Introduction

Various oxides (SiO$_2$, TiO$_2$, ZrO$_2$, CeO$_2$, and Al$_2$O$_3$) have been extensively assessed and used as catalyst support materials in heterogeneous catalysis [1-4]. It has been widely recognized that some of these oxide supports not only can promote the dispersion and thermal stability of catalyst nanoparticles, but also benefit the catalyst activity and
selectivity via a synergistic effect or catalyst-support interaction. The oxide supports can usually be divided into two categories: reducible (CeO$_2$ and TiO$_2$) and non-reducible (SiO$_2$, ZrO$_2$, and Al$_2$O$_3$). The catalytic activity can be significantly influenced by the reducibility of oxide support and catalyst-support interaction at the interface [2-4]. For example, Wang et al. [5] presented that reducible TiO$_2$ support promoted CO oxidation over Au/TiO$_2$ catalyst by affecting the charge state of Au and the charge transfer at the interface. Non-noble metal catalyst CuO on rutile TiO$_2$ support prepared by Kang et al. [6] showed 100% CO conversion at ~200 °C due to the contribution of reduction of Ti$^{4+}$ to Ti$^{3+}$. Venezia et al. [7] reported that Au deposited on non-reducible SiO$_2$ supports converted 100% CO at over 450 °C due to the presence of weak metal-support interaction. Another reducible oxide, CeO$_2$, has also been investigated considerably as a great catalyst support candidate due to its distinctive feature as high oxygen storage and release capacity [8-10]. A possible explanation for the promotion role is reducible oxides are used as support due to charge transfer and oxygen exchange at the catalyst-support interface under reaction conditions [8, 9]. One of difficulties to study the catalyst-support interactions and the resulting catalytic activity is that preparing model catalyst systems, consisting of catalyst clusters deposited on shape well-defined support with specific crystal planes, is still challenging. In addition, catalyst preparation methods and thermal treatments also play a significant role on the catalyst-support interfacial structures [11-15]. CeO$_2$ nanorods support has been reported to present a superior low temperature surface lattice oxygen release and storage capacity compared to other CeO$_2$ shapes (octahedral and nanocube) [8]. In this chapter, a comparative study was conducted on shape-controlled non-reducible SiO$_2$ nanospheres and highly reducible CeO$_2$ nanorods
supported CuO$_x$ (0≤x≤1) catalysts to understand the effect of support reducibility and thermal treatments (oxidation and reduction treatments) on the catalytic activity of CO oxidation. The results will further improve our understanding of the interfacial interactions between catalyst and support, and possible synergistic effect for low-temperature CO conversion.

5.2. Experimental

5.2.1. Catalyst preparation

Silica (SiO$_2$) nanospheres were prepared using a hydrolysis method. First, 2 mL of Tetraethoxysilane (TEOS 99%) was dissolved in a mixture of 9 mL of deionized water and 38.2 mL of ethanol. Then, 50 mL of 28-30% NH$_4$OH was added dropwise to the solution under vigorous magnetic stirring. The reaction was kept for 4 hrs under continuous magnetic stirring. The suspension solution was centrifuged, and then washed with DI water and ethanol. The sample was dried at 60 °C overnight. CeO$_2$ nanorods were synthesized using the hydrothermal method. The 88 mL of 0.1 M Ce(NO$_3$)$_3$·6H$_2$O and 8 mL of 6 M NaOH solutions were added in a Teflon liner of 200 mL capacity. The mixture was stirred for about 15 seconds, and then the lid of Teflon liner was closed. After putting the Teflon liner into a stainless-steel autoclave, it was heated and kept at 90 °C for 48 hrs. Finally, the sample was filtered and then washed with 500 mL DI water and 50 mL ethanol. It was dried at 50 °C for 12 hrs. 10wt.% CuO was impregnated in both CeO$_2$ nanorods and SiO$_2$ nanospheres using thermal decomposition method. Cu(NO$_3$)$_2$·3H$_2$O and the oxide supports (CeO$_2$ nanorods or SiO$_2$ nanospheres) were mixed in a stoichiometric ratio in 30 mL DI water. The solution was stirred continuously
and was heated at 120 °C until the water evaporated completely. The collected samples were calcined at 400, 500 and 600 °C for 5 hrs in air. These samples were denoted as CuO/CeO$_2$-X and CuO/SiO$_2$-X, where X stands for the oxidation temperature (X=400, 500 and 600 °C). The reduction treatment was conducted on CuO/CeO$_2$-400 and CuO/SiO$_2$-400 samples at 400 °C for 5 hrs under 5%H$_2$-95%Ar environment. These samples were denoted as CuO/CeO$_2$-400R and CuO/SiO$_2$-400R.

5.2.2. Catalyst characterizations

X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), BET surface area measurement, temperature programmed reduction (TPR), temperature programmed desorption (TPD), and CO oxidation were used to characterize the catalysts and their catalytic activity. The description of these techniques can be found in chapter 2.

5.3. Results

5.3.1. The effect of oxidation temperature

The XRD patterns of CeO$_2$ nanorods, SiO$_2$ nanospheres, and CuO nanopowders were shown in Fig. 5.1a. The diffraction pattern of as-synthesized CeO$_2$ nanorods was consistent with the standard fluorite-type CeO$_2$ reported in JCPDS data (JCPDS 43-1002). A broad diffraction peak was observed in the XRD pattern of SiO$_2$ nanospheres, indicating that as-synthesized SiO$_2$ nanospheres were amorphous [16]. The XRD pattern of CuO nanopowders displayed two sharp peaks at 2θ of 35.6° and 38.8° corresponding to (-111) and (111) planes (JCPDS 45-0937) [17]. Fig. 1b displayed the XRD patterns of CuO/SiO$_2$ samples oxidized at different temperatures (400 °C-600 °C). One broad peak
for amorphous SiO$_2$ and other sharp peaks for CuO were easily visible for all three CuO/SiO$_2$ samples. For the CuO/CeO$_2$ samples, the diffraction peaks of CuO were not visible for the CuO/CeO$_2$-400 and CuO/CeO$_2$-500 samples (Fig. 5.1c and 5.1d). When the CuO/CeO$_2$ sample was oxidized at 600 °C, small (-111) and (111) diffraction peaks of CuO emerged in the XRD pattern, as shown in Fig. 5.1c, which were much evident in the magnified patterns shown in Fig. 5.1d. The presence of CuO peaks indicated that a phase separation of CuO from Cu-O-Ce solid solution occurred in these samples at elevated
oxidation temperature, and/or well-dispersed small CuO nanoparticles started to grow and sinter at a higher oxidation temperature. Table 5.1 showed the average crystallite size of CuO estimated from (-111) and (111) diffraction peaks of XRD and BET surface area of the CuO/SiO$_2$ samples. The calculated crystallite size of CuO in the CuO/SiO$_2$ samples increased with increasing the oxidation temperature from 16.2 nm (400 °C) to 20.7 nm (600 °C). The BET surface area of CuO/SiO$_2$-400 was 6.71 m$^2$/g which was very close to an average (6.92 m$^2$/g) of BET surface area of pure CuO (4.12 m$^2$/g) and SiO$_2$ nanospheres (9.72 m$^2$/g). For CuO/SiO$_2$-500 and CuO/SiO$_2$-600, the measured surface area was almost twice as that of CuO/SiO$_2$-400 possibly due to better decomposition and crystallization of copper precursor at higher oxidation temperatures [18]. In Table 5.2, the crystallite size of CeO$_2$, which was calculated using (111) peak of XRD in the CuO/CeO$_2$ samples, also increased with increasing the oxidation temperature [19, 20]. The BET surface area of the CuO/CeO$_2$ samples slightly decreased with increasing the oxidation temperatures.

**Table 5.1. Average crystallite size measured using CuO (-111) and (111) peaks, BET surface area, $T_{50}$, and maximum CO conversion along with temperatures of CuO/SiO$_2$ samples oxidized at different temperatures and reduced at 400 °C.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>BET surface area (m$^2$/g)</th>
<th>$T_{50}$ (°C)</th>
<th>Max CO conversion (%)</th>
<th>$T_{max}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/SiO$_2$-400</td>
<td>16.2</td>
<td>6.71</td>
<td>241</td>
<td>72</td>
<td>324</td>
</tr>
<tr>
<td>CuO/SiO$_2$-500</td>
<td>18.2</td>
<td>12.62</td>
<td>234</td>
<td>77</td>
<td>298</td>
</tr>
<tr>
<td>CuO/SiO$_2$-600</td>
<td>20.7</td>
<td>11.42</td>
<td>194</td>
<td>89</td>
<td>280</td>
</tr>
<tr>
<td>CuO/SiO$_2$-400R</td>
<td>18.6</td>
<td>13.24</td>
<td>246</td>
<td>68</td>
<td>298</td>
</tr>
</tbody>
</table>
Table 5.2. Crystallite size measured using CeO\(_2\) (111) peak, BET surface area, \(T_{50}\), and maximum CO conversion along with temperatures of CuO/CeO\(_2\) samples oxidized at different temperatures and reduced at 400 °C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size (nm)</th>
<th>BET surface area (m(^2)/g)</th>
<th>(T_{50}) (°C)</th>
<th>Max CO conversion (%)</th>
<th>(T_{\text{max}}) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO/CeO(_2)-400</td>
<td>5.4</td>
<td>39.42</td>
<td>88</td>
<td>100</td>
<td>220</td>
</tr>
<tr>
<td>CuO/CeO(_2)-500</td>
<td>6.4</td>
<td>39.22</td>
<td>94</td>
<td>95</td>
<td>237</td>
</tr>
<tr>
<td>CuO/CeO(_2)-600</td>
<td>7.9</td>
<td>37.33</td>
<td>117</td>
<td>92</td>
<td>263</td>
</tr>
<tr>
<td>CuO/CeO(_2)-400R</td>
<td>6.6</td>
<td>38.72</td>
<td>94</td>
<td>92</td>
<td>280</td>
</tr>
</tbody>
</table>

Fig. 5.2a showed the Raman spectra of CeO\(_2\) nanorods, SiO\(_2\) nanospheres, and CuO nanopowders. For CeO\(_2\) nanorods, typical CeO\(_2\) peak at 456 cm\(^{-1}\) corresponded to F\(_{2g}\) vibrational mode and two other peaks at 276 and 605 cm\(^{-1}\) were assigned to oxygen vacancies in CeO\(_2\) lattice [21]. A small peak of SiO\(_2\) nanospheres, observed at 504 cm\(^{-1}\), was attributed to the vibrations of four-membered ring structures called D\(_1\) vibrational mode [22, 23]. A broad peak near 440 cm\(^{-1}\) corresponded to symmetric vibrations of oxygen atoms [24]. Two other peaks at 290 and 350 cm\(^{-1}\) were attributed to D\(_3\) and D\(_4\) bands [25]. The characteristic CuO peaks were found at 276, 326 and 625 cm\(^{-1}\) which corresponded to A\(_g\), B\(_{1g}\), and B\(_{2g}\) mode, respectively [26]. Another peak found at 506 cm\(^{-1}\) in Raman spectrum of CuO sample was assigned to either E\(_g\) mode of Cu\(_4\)O\(_3\) or B\(_{2u}\) mode of CuO in literature [27-29]. In our case, this peak was assigned to CuO because there was no evidence of the presence of Cu\(_4\)O\(_3\) gathered from the XRD analysis (Fig. 5.1a).
Fig. 5.2b showed the Raman spectra of the CuO/SiO$_2$ samples oxidized at different temperatures (400 °C-600 °C). A sharp peak with large intensity observed at 506 cm$^{-1}$ for all three CuO/SiO$_2$ samples was probably a blend of two different peaks: one for D$_1$ band of SiO$_2$ (at 504 cm$^{-1}$ in Fig. 5.2a) and the other for B$_{2u}$ mode of CuO (at 506 cm$^{-1}$ in Fig. 5.2a).

Figure 5.2. Raman spectra of (a) CuO nanopowders, SiO$_2$ nanospheres and CeO$_2$ nanorods, and (b) CuO/SiO$_2$ nanospheres and (c) CuO/CeO$_2$ nanorods oxidized at various temperatures. (d) Magnified Raman spectra of CuO/SiO$_2$ nanospheres of red rectangular portion shown in (b).
5.2a). A broad peak centered near 620 cm\(^{-1}\) (in the range of 600–640 cm\(^{-1}\)) for CuO/SiO\(_2\)-400 became sharper with increasing the oxidation temperature and finally, for CuO/SiO\(_2\)-600 this peak split into two separate peaks (Fig. 5.2b: red rectangular portion). These two peaks could be assigned as one from B\(_{2g}\) mode of CuO and the other one from D\(_2\) band of SiO\(_2\). This D\(_2\) peak of SiO\(_2\) was not seen in Raman spectrum of pure SiO\(_2\), corresponding to the planar threefold [SiO\(_3\)]\(^{2-}\) rings [23, 30-32]. The formation of threefold [SiO\(_3\)]\(^{2-}\) rings was further demonstrated in magnified Raman spectra in Fig. 5.2d with increasing the oxidation temperature. In comparison, Fig. 5.2c illustrated the Raman spectra of the CuO/CeO\(_2\) samples oxidized from 400 °C to 600 °C. The characteristic CeO\(_2\) F\(_{2g}\) peak shifted from 456 cm\(^{-1}\) for CeO\(_2\) nanorods (Fig. 5.2a) to 444 cm\(^{-1}\) for CuO/CeO\(_2\)-400 (Fig. 5.2c) possibly due to the lattice distortion occurred during incorporation of Cu ions into CeO\(_2\) lattice to form solid solution [20]. With increasing oxidation temperature, this F\(_{2g}\) peak in CuO/CeO\(_2\) continuously shifted from 444 cm\(^{-1}\) in CuO/CeO\(_2\)-400 to 451 cm\(^{-1}\) in CuO/CeO\(_2\)-600. This result also supported the XRD observation in Fig. 5.1c and 5.1d that CuO emerged in CuO/CeO\(_2\)-600. This suggested a phase separation of CuO from the Cu-O-Ce solid solution, which resulted in the Raman peak shifting to close to the value of CeO\(_2\) (456 cm\(^{-1}\)) as shown in Fig. 5.2c [20]. A broad peak seen at 625 cm\(^{-1}\) was a mixture of two peaks, including oxygen vacancy peak of CeO\(_2\) at 605 cm\(^{-1}\) and B\(_{2g}\) mode of CuO at 625 cm\(^{-1}\). This peak became stronger with increasing the oxidation temperature due to the formation of CuO as discussed earlier. XPS spectra of CuO/CeO\(_2\)-400 and CuO/SiO\(_2\)-400 were shown in Fig. 5.3a-c and 5.4a-c, respectively, to study the chemical state of various elements at the catalyst surface. Cu 2p XPS spectra can be seen in Fig. 5.3a. It can be observed that Cu\(^{2+}\) component peak was present at 939.6 eV (peak shifted
Figure 5.3. XPS spectra of (a) Cu 2p$_{3/2}$, (b) Ce 3d, and (c) O 1s for CuO/CeO$_2$-400.
Figure 5.4. XPS spectra of (a) Cu $2p_{3/2}$, (b) Si $2p$, and (c) O $1s$ for CuO/SiO$_2$-400.
by +6 eV) [15, 33, 34]. Another small peak found at 935.6 eV (peak shifted by +4 eV) represented Cu$^{+}$, which implied strong interaction between CeO$_2$ and copper species [33, 34]. Fig. 5.3b showed Ce 3d XPS spectra where 3d$_{3/2}$ and 3d$_{5/2}$ peaks were labeled as u and v, respectively. There were seven peaks: u (907.1), u' (908.2), u'' (913.8), v (888.8), v' (891.1) and v'' (895.1) of Ce 3d in CuO/CeO$_2$-400. The peaks u, u'', v, v'' and v''' can be assigned to Ce$^{4+}$ and the peaks u' and v' can be assigned to Ce$^{3+}$ [33, 34]. The presence of Ce$^{3+}$ is beneficial for attaining outstanding performance in CO oxidation [33, 34]. In Fig. 5.3c, O 1s XPS spectra can be seen where two peaks were observed at 538.4 (peak shifted by +7 eV) and 535.6 eV (peak shifted by +6 eV). Higher energy peak (538.4) corresponded to adsorbed oxygen species at surface and lower energy peak (535.6) was assigned to lattice oxygen of metal oxides [33, 34]. Clearly, the intensity of lower energy peak was higher, which suggested that a large amount of lattice oxygen from CeO$_2$ was present at the surface. Cu 2p XPS spectra of CuO/SiO$_2$-400 can be seen in Fig. 5.4a where Cu$^{2+}$ peak was observed at 938.1 eV. There was no Cu$^{+}$ peak for this sample, suggesting weak interaction between SiO$_2$ and copper species. Si 2p peak was found at 106.2 eV as shown in Fig. 5.4b. In Fig. 5.4c, one strong peak for O 1s can be found at 535.8 eV (peak shifted by +4 eV) which corresponded to lattice oxygen at the surface of catalyst. All of the peaks shifted to higher energy compared to the literature [34] due to charging effect in the sample during conducting the experiments.

The H$_2$-TPR profiles of SiO$_2$ nanospheres and CeO$_2$ nanorods were shown in Fig. 5.5a. Two major reduction peaks of CeO$_2$ nanorods were visible at 470 and 824 °C, which correspond to the reduction of surface and bulk CeO$_2$, respectively. On the other hand, SiO$_2$ nanospheres did not show any reduction peak as expected. The H$_2$-TPR
Figure 5.5. H$_2$ TPR profiles of (a) SiO$_2$ nanospheres and CeO$_2$ nanorods, and (b) CuO/SiO$_2$ and (c) CuO/CeO$_2$ oxidized at various temperatures.
profiles of the CuO/SiO₂ samples were shown in Fig. 5.5b. Two well-separated reduction peaks at 207 and 288 °C can be found for CuO/SiO₂-400. According to the peak assignments of supported CuO catalysts in literature [35], the first peak at 207 °C, called β peak, corresponded to the reduction of CuO nanoparticles dispersed onto SiO₂ surface. The peak found at 288 °C, called γ peak, was attributed to the reduction of small amount of bulk CuO (larger particles). For CuO/SiO₂-500, the β peak shifted to a higher reduction temperature (254 °C) while γ peak remained at the same position. The γ peak for CuO/SiO₂-600 shifted to a higher temperature (304 °C) due to the growth and sintering of bulk CuO at higher oxidation temperature. Another peak found at 195 °C was attributed to α peak and this peak corresponded to the reduction of incorporated copper species into SiO₂ support which will be explained in details later. The H₂-TPR profiles of the CuO/CeO₂ samples were presented in Fig. 5.5c. It should be noted that the same TCD signal scales and similar sample weight (~90 mg) in all six supported CuO samples in Fig. 5.5b and 5.5c were used to make the hydrogen consumption calculation comparable. The TPR profiles of the CuO/CeO₂-400 sample showed two reduction peaks. The first peak (called α peak) found at 142 °C was assigned to Cu-O-Ce solid solution or strongly interacting copper species [36-38]. The β peak at 165 °C was attributed to the reduction of well-dispersed CuO onto CeO₂ surface. For the CuO/CeO₂-500 sample, both α and β peaks shifted a little to higher reduction temperatures at 146 and 170 °C, respectively. The α and β reduction peaks in the CuO/CeO₂-600 sample showed a continuous shift to a higher temperature (150 and 175 °C) due to the increased crystallite size (Table 5.2). Meanwhile, another peak (γ peak) was found at 210 °C which corresponded to bulk CuO reduction. Fig. 5.6 illustrated the H₂ consumption of the CuO/SiO₂ and CuO/CeO₂
Figure 5.6. H₂ consumption of (a) CuO/SiO₂ and (b) CuO/CeO₂ oxidized at various temperatures.
samples. In the temperature range of 150 to 400 °C, the H₂ consumptions in the CuO/CeO₂ samples were all higher than the counterpart in the CuO/SiO₂ samples. This confirmed the advantage of reducible CeO₂ support compared to the non-reducible SiO₂ support for H₂ consumption. The calculated H₂ consumption for the γ peak increased with increasing the oxidation temperature in the CuO/SiO₂ samples as shown in Fig. 5.6a. The CuO/SiO₂-500 and CuO/SiO₂-600 samples demonstrated a similar total amount of H₂ consumption in the range of 150 to 400 °C. The H₂ consumption of the CuO/CeO₂ samples decreased with increasing the oxidation temperature as shown in Fig. 5.6b. The H₂ consumption for both the α and β peaks clearly decreased with increasing the oxidation temperature, which is probably due to the CuO and CeO₂ phase separation at higher oxidation temperature as discussed earlier. These results support the hypothesis that the reducible CeO₂ support favors the low-temperature reduction and H₂ consumption in CeO₂ nanorods supported CuO catalysts [39].

The light-off curves for CO oxidation conversion of the CuO/SiO₂ and CuO/CeO₂ samples were plotted in Fig. 5.7. The T₅₀ temperatures where 50% CO conversion occurred for CuO/SiO₂-400, CuO/SiO₂-500, and CuO/SiO₂-600 were 241, 234 and 194 °C, respectively, as shown in Table 5.1. These samples did not achieve 100% CO conversion up to 350 °C. The CuO/SiO₂-400, CuO/SiO₂-500, and CuO/SiO₂-600 samples converted maximum 72, 77, and 89 % CO at 324, 298, and 280 °C, respectively, indicating that the catalytic efficiency of CuO/SiO₂ increased with increasing the oxidation temperatures. The CuO/CeO₂ samples presented an opposite trend toward CO conversion. The T₅₀ of the CuO/CeO₂-400, CuO/CeO₂-500, and CuO/CeO₂-600 samples were found at 88, 94, and 117 °C, respectively, as displayed in Table 5.2. The CuO/CeO₂-
Figure 5.7. CO conversion curves of (a) CuO/SiO$_2$ and (b) CuO/CeO$_2$ oxidized at different temperatures.
400 sample was the only sample which achieved 100% CO conversion at 220 °C among all of the prepared samples. The CuO/CeO₂-500 and CuO/CeO₂-600 samples attained maximum 95 and 92 % CO conversion at 237 and 263 °C, respectively.

5.3.2. Reduction treatment effect

Fig. 5.8a illustrated the XRD patterns of the CuO/CeO₂-400 and CuO/SiO₂-400 catalysts before and after reduction treatment at 400 °C in 5% H₂-95% Ar. The XRD patterns of CuO/CeO₂-400 and CuO/CeO₂-400R only showed the presence of fluorite-structured CeO₂, but no copper-containing phases were detected in both samples. The possible reasons that no copper-containing phases (CuOₓ, 0≤x≤1) were found from XRD analysis were due to the presence of small well dispersed CuOₓ on CeO₂ nanorods, Cu-O-Ce solid solutions or a mixture of both cases. The presence of small well-dispersed CuOₓ on CeO₂ was supported by XRD and Raman analysis as shown in Fig. 5.1c/5.1d and 5.2c, respectively. CuOₓ was clearly visible from XRD patterns and Raman spectra in the CuO/CeO₂-600 sample with a higher thermal treatment temperature (at 600 °C). The formation of Cu-O-Ce solid solution was supported by the peak shifting in Raman spectra for the samples heat-treated from 400 °C to 600 °C, as shown in Fig. 5.2c [39]. After the reduction treatment, the crystallite size of CeO₂ in CuO/CeO₂-400R increased from 5.4 nm to 6.6 nm.

The XRD patterns of CuO/SiO₂-400 and CuO/SiO₂-400R exhibited the presence of a monoclinic CuO phase (JCPDS 45-0937) and metallic Cu (JCPDS 04-0836), respectively, as shown in Fig. 5.8a. Thus, after the reduction treatment, CuO existed in CuO/SiO₂-400 was reduced to metallic Cu in CuO/SiO₂-400R. Except for the peak
Figure 5.8. (a) XRD patterns and (b) Raman spectra of CuO/SiO$_2$-400 and CuO/CeO$_2$-400 before and after reduction treatment.
broadness, no evident change was observed for amorphous SiO$_2$ support. Although negligible changes were found for both CeO$_2$ and SiO$_2$ supports from the XRD profiles before and after the reduction treatment, the visibility and reduction behavior of copper species were completely different on them, suggesting that support kind/structure had a critical impact on the structure, texture, and distribution of CuO$_x$ catalyst.

Raman spectra of the CuO/CeO$_2$-400 and CuO/SiO$_2$-400 samples before and after the reduction treatment were shown in Fig. 5.8b. For the CuO/CeO$_2$-400 sample, the characteristic CeO$_2$ F$_{2g}^2$ peak shifted to 444 cm$^{-1}$ from 456 cm$^{-1}$ in CeO$_2$ due to incorporation of Cu ions into CeO$_2$ to form solid solution as discussed earlier. After the reduction treatment, this peak shifted to 448 cm$^{-1}$ due to either a phase separation of CuO from Cu-O-Ce solid solution or increment of crystallite size of CeO$_2$ [20]. For both CuO/CeO$_2$-400 and CuO/CeO$_2$-400R samples showed two peaks at 270 and 624 cm$^{-1}$. These two peaks were assigned to the combination of oxygen vacancies in CeO$_2$ and CuO B$_{2g}^2$ mode.

For the CuO/SiO$_2$-400 sample, the peak corresponded to D$_1$ vibrational mode of SiO$_2$ (at 504 cm$^{-1}$ in Fig. 5.2a) and the B$_{2u}$ mode peak of CuO (at 506 cm$^{-1}$ in Fig. 5.2a) were overlapped, and then they became one sharp peak at around 506 cm$^{-1}$[22-23, 27]. After the reduction treatment, a similar peak at 506 cm$^{-1}$ in CuO/SiO$_2$-400R became much weaker. Since CuO was reduced to metallic Cu after the reduction treatment (Fig. 5.8a), the remaining peak at around 506 cm$^{-1}$ was assigned to D$_1$ mode of SiO$_2$.

Fig. 5.9a showed the H$_2$-TPR profiles of both CuO/CeO$_2$ and CuO/SiO$_2$ samples before and after the reduction treatment. The CuO/CeO$_2$-400 sample displayed two
reduction peaks at 142 and 164 °C which corresponded to α and β peak, respectively, as discussed earlier. For the CuO/CeO$_2$-400R sample, the α and β peaks were found at 137 and 157 °C. Two reduction peaks at 208 and 291 °C were found for the CuO/SiO$_2$-400 sample. For this case, the first peak was assigned to the β peak which was attributed to the reduction of dispersed CuO, and the second peak was the γ peak which corresponded to bulk CuO reduction. There was no α peak for this case, indicating no strong interaction between CuO and SiO$_2$ during the oxidation treatment at 400 °C. However, one α peak was found at 165 °C for CuO/SiO$_2$-400R. This α peak probably corresponded to the copper species diffused and incorporated into threefold SiO$_3$ rings during the reduction treatment. There was no β or γ peak for the CuO/SiO$_2$-400R sample, indicating the dispersed and bulk CuO particles were reduced to metallic Cu. The most remarkable fact was that surprisingly H$_2$ consumption peaks were still found for both CuO/CeO$_2$-400R and CuO/SiO$_2$-400R samples. This may have happened due to the presence of Cu-O-Ce solid solution and CuO$_x$ (1≥x>0) at the interface for the CuO/CeO$_2$-400R sample, and the presence of copper species in threefold SiO$_3$ rings for the CuO/SiO$_2$-400R sample. Fig. 5.9b displayed that the H$_2$ consumption in the CuO/CeO$_2$-400 and CuO/CeO$_2$-400R samples are 2.692 and 1.487 mmol/g, respectively. On the other hand, the CuO/SiO$_2$-400 and CuO/SiO$_2$-400R samples consumed 1.102 and 0.342 mmol/g of H$_2$, respectively. The H$_2$ consumption at β peak for CuO/CeO$_2$-400R decreased abruptly after the reduction treatment due to the reduction of dispersed CuO to metallic Cu. However, the H$_2$ consumption at α peak remained constant. BET surface areas of both CuO/SiO$_2$-400 and CuO/CeO$_2$-400 samples before and after reduction treatment were tabulated in Table 5.1 and 5.2, respectively. It was found that surface area of CuO/SiO$_2$-400R increased
Figure 5.9. (a) H₂-TPR profiles and (b) H₂ consumption of CuO/CeO₂-400 and CuO/SiO₂-400 before and after reduction treatment.
significantly after the reduction treatment and surface area of CuO/CeO$_2$-400R decreased after the reduction treatment.

![Figure 5.10. CO-TPD of CuO/CeO$_2$ and CuO/SiO$_2$ before and after reduction treatment.](image)

Typical CO-TPD profiles of CuO/CeO$_2$-400 and CuO/SiO$_2$-400 before and after reduction were shown in Fig. 5.10. Generally, CO desorbs as CO$_2$ during the heating process produced by the reaction of adsorbed CO with lattice oxygen. CuO/CeO$_2$-400 showed two desorption peaks; one peak at 100 °C and another peak at 150-160 °C. The first peak was attributed to desorption of CO$_2$ produced from the reaction of adsorbed CO with CeO$_2$ surface [33, 34]. The second peak was assigned to desorption of CO$_2$, which was formed by adsorbed CO developing into bidentate carbonate species on the reactive sites [33, 34]. CuO/SiO$_2$-400 also showed two desorption peaks at 95 and 192 °C;
however, the intensity of these two peaks was very low in comparison to the peaks of 
CuO/CeO$_2$-400. After the reduction of CuO/CeO$_2$-400, only one peak at 104 °C was 
observed for CuO/CeO$_2$-400R because only CeO$_2$ lattice could be available for CO 
reaction after CuO being reduced to metallic Cu. Surprisingly, CuO/SiO$_2$-400R still 
showed one peak at 106 °C with higher intensity compared to that of CuO/SiO$_2$-400, 
implying that more CO$_2$ could desorb at a lower temperature. A possible explanation is 
that after the reduction treatment, the presence of [SiO$_3$]$^{2-}$-rings increased suggesting that 
there was more active oxygen formed in SiO$_3$ rings [23].

For the CuO/CeO$_2$-400 and CuO/SiO$_2$-400 catalysts before and after reduction, the 
light-off curves of CO conversion as a function of temperature were shown in Fig. 5.11. 
The temperatures ($T_{50}$) where 50% CO conversion occurred for the CuO/CeO$_2$-400 and 
CuO/CeO$_2$-400R samples were at 88 and 94 °C respectively as shown in Table 5.2. The 
CuO/CeO$_2$-400 sample converted 100% CO at 220 °C, and the CuO/CeO$_2$-400R sample 
converted maximum 92% CO at 280 °C. On the other hand, 50% CO conversion for both 
CuO/SiO$_2$-400 and CuO/SiO$_2$-400R samples were found at ~240 °C. The maximum CO 
conversions for the CuO/SiO$_2$-400 and CuO/SiO$_2$-400R samples were 72% at 324 °C and 
68% at 298 °C, respectively. Clearly, the CuO/CeO$_2$-400 sample showed the best 
performance of CO oxidation conversion, indicating the effect of reducible CeO$_2$ support 
on the catalytic efficiency. Again, an unexpected result could be seen that both of the 
reduced catalysts could still convert CO into CO$_2$ due to the reducibility of CeO$_2$ support 
($2\text{CeO}_2 + \text{CO} \rightarrow \text{Ce}_2\text{O}_3 + \text{CO}_2$) and the presence of Cu-O-Ce solid solution at the 
interface for the CuO/CeO$_2$-400R sample, and the presence of copper species in threefold 
SiO$_3$ rings for the CuO/SiO$_2$-400R sample.
5.3.3. TEM analysis

Fig. 5.12 exhibited typical TEM images of CeO$_2$ nanorods and SiO$_2$ nanospheres samples before and after CuO loading. In Fig. 5.12a, as-synthesized CeO$_2$ nanorods were 50-150 nm long and 5-20 nm in width. Fig. 5.12b showed that SiO$_2$ nanospheres were ~300 nm in diameter. After CuO loading, no visible size/shape change was observed for
Figure 5.12. TEM images of (a) CeO$_2$ nanorods, (b) SiO$_2$ nanospheres, (c) CuO/CeO$_2$-400, and (d) CuO/SiO$_2$-400. Schematical representations of (e) CuO/CeO$_2$ and (f) CuO/SiO$_2$.

SiO$_2$ nanospheres. These results are consistent with XRD and BET surface area analysis about the particle size. Fig. 5.12 c and d revealed TEM images of the CuO/CeO$_2$-400 and CuO/SiO$_2$-400 samples after CuO loading. A uniform dispersion of CuO on SiO$_2$ was
clearly shown, while no apparent CuO was found on CeO$_2$ nanorods consistent with the XRD analysis (Fig. 5.1c). Fig. 5.12e and 5.12f schematically showed how CuO particles were attached onto CeO$_2$ nanorods and SiO$_2$ nanoshperes, respectively.

In high resolution TEM (HRTEM) image of the CuO/SiO$_2$-400 sample, it appears that some small CuO nanoparticles were attached with SiO$_2$ nanosphere with a partially embedded CuO as shown in Fig. 5.13a. In the inset of Fig. 5.13a, HRTEM image of SiO$_2$ provided an evidence for their amorphous structure. The boundary of CuO particle can easily be separated from SiO$_2$, indicating that CuO and SiO$_2$ did not make very strong bond or interaction and this was the main reason of β peak observed in H$_2$-TPR. Fig. 5.13b showed HRTEM image of CuO/CeO$_2$-400 where CuO particle interacted with CeO$_2$ nanorod can be seen. In the inset of Fig. 5.13b, the interface between CuO and CeO$_2$ showed non-distinguishable boundary of CuO and CeO$_2$, leading to the conclusion of strong CuO-CeO$_2$ interaction. This type of strong interaction caused α peak in H$_2$-TPR. Fig. 5.13c showed HRTEM image of CuO/CeO$_2$-400 where a CeO$_2$ nanorod was presented and oriented along [011] projection. In the inset of Fig. 5.13c, the calculated Fast Fourier Transform (FFT) pattern from HRTEM image of CeO$_2$ nanorod was shown, which indicated that CeO$_2$ nanorod was a single crystal with [011] growth direction and [001] surface termination along this projection. Fig. 5.13d and 5.13e showed that CeO$_2$ nanorods exposed (111), (110), and (100) planes with d-spacing of 3.1 Å, 1.9 Å, and 2.7 Å, respectively. Zhou et al. [40] and Pan et al. [41] reported that CeO$_2$ nanorods prepared by a similar hydrothermal method have dominantly (100) and (110) planes. Our group previously reported the presence of (111) planes in CeO$_2$ nanorods [42]. Fig. 5.13f
illustrated a schematic representation of CeO$_2$ nanorod exposing (111), (110) and (100) planes from [10-1] projection.

Figure 5.13. HRTEM images of (a) CuO/SiO$_2$-400, and (b) and (c) CuO/CeO$_2$-400. FFT of CuO/CeO$_2$-400 in the inset of (c). HRTEM images of red rectangular section I and II shown in (d) and (e) respectively. (f) Schematic representation of atomic structure of CeO$_2$ nanorods.
5.4. Discussion

The results discussed above demonstrated that the CuO/CeO$_2$-400 nanorods sample showed the best catalytic performance toward both H$_2$ consumption and CO oxidation. It also showed that the catalytic efficiency of CuO/CeO$_2$ nanorods decreased with increasing the oxidation temperatures, which was ascribed to the phase separation of CuO and CeO$_2$ at elevated temperature. The presence of CuO in CuO/CeO$_2$-600 was exhibited in Fig. 5.1c and 5.1d. The XRD result agreed with the H$_2$-TPR analysis because the γ peak corresponded to bulk CuO can be found in CuO/CeO$_2$-600 (Fig. 5.5c). The bulk CuO had higher reduction temperature and also could cover up the surfaces of CeO$_2$ where Cu-O-Ce solid solution was formed, which has a negative effect on the catalytic activity. In the Cu-O-Ce solid solution, Cu$^{2+}$ or Cu$^{+}$ ions replace Ce$^{4+}$, resulting in oxygen vacancies in CeO$_2$ structure to reach the charge neutrality [39]. The catalysts with oxygen vacancies can adsorb oxygen from the environment near the solid solution surface. The adsorbed oxygen, which is loosely bonded with the catalysts, can be easily accessible to H$_2$ or CO for conversion reaction at low temperature. Fig. 5.2c illustrated that the characteristic CeO$_2$ peak shifted to a lower wavenumber at 444 cm$^{-1}$ for the CuO/CeO$_2$-400 sample due to the incorporation of Cu ions into CeO$_2$ to form solid solution. This peak continuously shifted to the right with increasing the oxidation temperature in the CuO/CeO$_2$ samples. This Raman peak shifting attests a lower concentration of Cu ions incorporated into CeO$_2$ lattice for the samples treated at higher oxidation temperature. For further verification, the amount of H$_2$ consumption at α peak (shown in Fig. 5.5b) decreased with increasing the oxidation temperature in the CuO/CeO$_2$ catalysts, and this result was in agreement with Raman and XRD analysis as discussed above.
The CuO/SiO$_2$ samples showed an opposite catalytic activity trend in comparison with the CuO/CeO$_2$ samples as the catalytic efficiency of the CuO/SiO$_2$ samples increased with increasing the oxidation temperature. A probable mechanism was suggested based on the presence of threefold [SiO$_3$]$^{2-}$ rings as Raman spectra showed a gradual increase of D$_2$ peak with increasing the oxidation temperature of the CuO/SiO$_2$ samples as shown in Fig. 5.2d.

5.5. Conclusion

The reducibility and surface structure of oxide supports showed a significant effect on the catalytic activity toward CO oxidation and hydrogen consumption in supported CuO$_x$ catalysts. The CuO/CeO$_2$ nanorods exhibited a great enhancement in catalytic efficiency than the CuO/SiO$_2$ nanospheres. Incorporation of Cu ions in CeO$_2$ lattice promoted the lower reduction temperature and enhanced the catalytic efficiency by increasing oxygen mobility via redox reaction at the catalyst-support interface. Increasing the oxidation temperature of CuO/CeO$_2$ decreased the catalytic activity by lowering the amount of incorporation of Cu in CeO$_2$ lattice. Conversely, increasing oxidation temperature of CuO/SiO$_2$ increased the presence of threefold SiO$_3$ rings, and incorporating Cu into these rings enhanced the catalytic efficiency. Both CuO/CeO$_2$-400R and CuO/SiO$_2$-400R samples after reduction treatment still displayed H$_2$ consumption and CO conversion even although CuO was not detected in XRD analysis. The activity of the CuO/CeO$_2$ and CuO/SiO$_2$ catalysts highly depends on the catalyst-support interaction in which reducible oxide support acts a significant role through redox reaction.
5.6. References


Chapter 6: CeO$_2$ nanorods and SiO$_2$ nanospheres composite supported CuO catalysts for the application of CO oxidation

In this chapter, synthesized CeO$_2$ nanorods and SiO$_2$ nanospheres were mixed in various ratios and 10 wt% CuO nanoparticles were impregnated onto CeO$_2$-SiO$_2$ composite using thermal decomposition method. X-ray diffraction and Raman spectroscopy were used to confirm the presence of CeO$_2$, SiO$_2$, and CuO. Agglomeration of CeO$_2$ nanorods were stopped by introducing SiO$_2$ nanospheres in the catalyst system and this phenomenon increased the chance to expose CeO$_2$ surface to CuO nanoparticles in order to form higher amount of surface defects (incorporation of Cu ions and oxygen vacancies) and to have higher synergistic interaction between CuO and CeO$_2$. H$_2$ temperature programmed reduction (TPR) and CO oxidation experiments suggested an enhanced low-temperature catalytic performance for 1:1 ratio mixture of CeO$_2$ and SiO$_2$ due to a strong interfacial interaction among SiO$_2$-CeO$_2$-CuO.

6.1. Introduction

Cerium oxide (CeO$_2$) and silica (SiO$_2$) have been widely used as substrates in supported-metal catalysts for many industrial applications, such as catalytic converter [1, 2], water-gas shift reactions [3], SO$_2$ reduction [4], ethanol reforming [5, 6], and photosynthesis [7], etc. Compared to the unsupported catalysts, both CeO$_2$ and SiO$_2$ supports can significantly increase the dispersion and thermal stability of catalyst nanoclusters; however, CeO$_2$ is also considered as an active support due to oxygen storage capacity and strong interactions in supported-metal catalysts. For example, Huang
et al. [8] reported that CeO$_2$ supported Au catalyst achieved 100% CO conversion at 170 °C due to the presence of reactive oxygen at the surface of CeO$_2$ and a synergistic strong interaction between support Au and CeO$_2$. On the other hand, Venezia et al. [9] showed that SiO$_2$ supported Au catalyst attained 100% CO conversion over 450 °C, indicating a weak metal-support interaction. A mix of these oxide supports can act differently as there can be a synergistic interaction between the oxide supports due to the formation of Si-O-Ce bond at the interface [10]. Xi et al. [11] mixed CeO$_2$, Fe$_2$O$_3$, and MnO$_2$ with SiO$_2$ support for better catalytic activity. They reported that SiO$_2$ supported CuO catalyst achieved 100% CO at 280 °C, and after introducing Fe$_2$O$_3$, MnO$_2$, and CeO$_2$ separately in the catalyst system a complete CO conversion occurred at 240, 200, and 160 °C respectively, which were 40, 80, and 120 °C correspondingly lower than CuO/SiO$_2$. They suggested that these added metal oxides increased the oxygen mobility of catalyst by promoting Cu$^+$ species in copper oxides. CeO$_2$-SiO$_2$ composite supported gold catalyst was reported by Huili et al. [12], and they mentioned that CeO$_2$ enriched oxygen mobility to exhibit high CO conversion activity and SiO$_2$ promoted the thermal stability of gold catalysts. Controlling the shape and size of oxide supports can affect the catalytic activity due to different exposed surfaces [13]. CeO$_2$ nanorods exposed highly reactive {110} and {100} planes and CeO$_2$ nanoparticles have stable {111} planes [13, 14]. Wang et al. [13] presented that CeO$_2$ nanorods supported CuO catalysts can obtain higher catalytic efficiency than CeO$_2$ nanoparticles or nanospheres supported CuO catalysts due to the presence of highly reactive planes in CeO$_2$ nanorods. In this chapter, we synthesized CeO$_2$ nanorods and SiO$_2$ nanospheres composite with varied compositions and impregnated 10 wt% CuO in shape-controlled oxide composites. A systematic study was
conducted to understand the synergistic interaction among CeO$_2$, SiO$_2$, and CuO and to investigate the effect of various composition of oxide composite support on low-temperature CO oxidation.

6.2. Experimental

6.2.1. Catalyst preparation

A hydrolysis method (modified Stober method) was used to synthesize silica (SiO$_2$) nanospheres. First, a mixture of 9 mL of deionized water and 38.2 mL of ethanol was prepared in which 2 mL of Tetraethoxysilane (TEOS 99%) was added. Then, 50 mL of 28-30% NH$_4$OH was added dropwise to the solution while it was stirred vigorously. After adding NH$_4$OH, it was held under continuous magnetic stirring for 4 hrs to complete the reaction. The suspension solution was centrifuged to collect the solid silica. It was then washed with DI water and ethanol. The sample was dried at 60 $^\circ$C overnight. Hydrothermal method was used to synthesize CeO$_2$ nanorods as reported previously [15]. 0.1 M Ce(NO$_3$)$_3$·6H$_2$O and 6 M NaOH solutions were added in 11:1 ratio in a Teflon liner of 200 mL capacity. Before closing the lid of Teflon liner, the mixture was stirred for about 15 seconds. A stainless-steel autoclave along with Teflon liner was heated and kept at 90 $^\circ$C for 48 hrs. When the autoclave cooled down to room temperature, the precipitates were collected via filtration. After filtration, the sample was washed with 500 mL DI water and 50 mL ethanol. It was then dried at 50 $^\circ$C for 12 hrs.

Thermal decomposition method was used to impregnate 10 wt% CuO on CeO$_2$-SiO$_2$ composite. The as-synthesized CeO$_2$ nanorods and SiO$_2$ nanospheres were mixed in various compositions (0-100 wt%) in 30 mL DI water. It was stirred for 30 mins. Then,
Cu(NO$_3$)$_2$:3H$_2$O was added in a stoichiometric ratio in the solution. The composite mixtures were stirred continuously and were heated at 120 °C until the water evaporated completely. The collected samples were calcined at 500 °C for 5 hrs in air.

6.2.2. Catalyst characterization

X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), BET surface area measurement, temperature programmed reduction (TPR), temperature programmed desorption (TPD), pulse chemisorption to calculate oxygen storage capacity (OSC), and CO oxidation were used to characterize the catalysts and their catalytic activity. The description of these techniques can be found in chapter 2.

6.3. Results and discussions

6.3.1. XRD and BET surface area

The XRD patterns of CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts were shown in Fig. 6.1. A broad peak with a center at 2θ of 21.7° confirmed the presence of amorphous SiO$_2$ in the SiO$_2$ supported 10 wt% CuO catalysts (100SiO$_2$) [16]. Except for the broad peak at around 21.7° for amorphous SiO$_2$ support, all other diffraction peaks can be assigned to monoclinic CuO phase (JCPDS 45-0937) in 100SiO$_2$ [17]. Two very sharp peaks at 2θ of 35.6° and 38.8° found in 100SiO$_2$ sample corresponded to (-111) and (111) planes of CuO. Although the amount of CuO addition was kept constant at 10wt% in all of the eleven catalyst samples, the intensity of CuO peaks became smaller with increasing CeO$_2$ amount; and finally, these peaks completely disappeared for the CeO$_2$
supported 10 wt% CuO catalysts (100CeO₂). The intensity of SiO₂ peak found at 21.7° in 100SiO₂ decreased with increasing the amount of CeO₂ in the samples. For the rest of the samples from 10CeO₂-90SiO₂ (xCeO₂-(100-x)SiO₂ referred to xCeO₂-(100-x)SiO₂ supported 10 wt% CuO catalyst) to 100CeO₂, the observed CeO₂ diffraction peaks were consistent with fluorite-structured CeO₂ reported in JCPDS data (JCPDS 43-1002). The intensity of those peaks increased with increasing the amount of CeO₂ in the composite samples. This occurrence happened, as reported previously [18], because CuO nanoclusters can form strong interactions with CeO₂ support or even Cu-O-Ce solid solution. Due to the strong CuO-CeO₂ interactions (α, β, γ phases), tiny CuO cluster can be well dispersed on CeO₂ nanorods [2]. Both the high dispersion and formation of Cu-

Figure 6.1. XRD patterns of CeO₂-SiO₂ supported CuO catalysts.
O-Ce solid solutions could lead to the decreased intensity of CuO phase or even disappearance in the diffraction patterns of CeO$_2$-SiO$_2$ composites samples.

Fig. 6.2 showed that BET surface area of the synthesized composite catalysts increased in a fine trend from 12.6 to 39.2 m$^2$/g with increasing the weight percentage of CeO$_2$. BET surface area of pure SiO$_2$ nanospheres, CeO$_2$ nanorods and CuO nanopowders were 9.72, 64.65 and 4.12 m$^2$/g, respectively. Thus, the increased surface area of the composite catalysts was due to the addition of CeO$_2$ in the composite samples.

**Figure 6.2.** BET surface area of CeO$_2$-SiO$_2$ supported CuO catalysts.
6.3.2. Raman analysis

Fig. 6.3 showed Raman spectra of CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts. One sharp peak observed at 508.6 cm$^{-1}$ for 100SiO$_2$ sample which was a mixture of D$_1$ mode of SiO$_2$ and B$_{2u}$ mode of CuO [19, 20]. D$_1$ vibrational mode is due to vibrations of four-membered ring structures of SiO$_2$. This mixed peak started decreasing with increasing the amount of CeO$_2$ in the composite catalysts and finally for 100CeO$_2$ sample, only B$_{2u}$ mode of CuO peak was observed at 505.5 cm$^{-1}$. Other Raman peaks found at 288, 379, and 436 cm$^{-1}$ were attributed to D$_3$, D$_4$ and symmetric vibrations of oxygen atoms in SiO$_2$, respectively [21]. Another CuO peak could be seen at 623 cm$^{-1}$ which corresponded to B$_{2g}$ mode [22]. After addition of CeO$_2$ in the composite catalysts, a peak appeared at 459 cm$^{-1}$ corresponded to F$_{2g}$ vibrational mode of CeO$_2$ [23]. This peak gradually shifted to the lower frequency with increasing the amount of CeO$_2$ in the composite catalysts. At first, this F$_{2g}$ peak for 10CeO$_2$-90SiO$_2$ sample shifted from 459 cm$^{-1}$ to 452 cm$^{-1}$ for 50CeO$_2$-50SiO$_2$. Then this F$_{2g}$ peak of CeO$_2$ was found at 455 cm$^{-1}$ for 60CeO$_2$-40SiO$_2$. This peak again started gradually shifting to the lower frequency from 455 cm$^{-1}$ for 60CeO$_2$-40SiO$_2$ to 447 cm$^{-1}$ for 100CeO$_2$. The peak shifting was also observed in CeO$_2$ supported CuO catalysts by several other groups, which was attributed to the strong interactions between CuO and CeO$_2$ [24, 25]. For example, Shan et al. [26] reported previously that a peak shifting happened due to the presence of oxygen vacancies, leading to the formation of substoichiometric structured CeO$_2$$_y$ (0≤y<0.5), which was associated with the formation of solid solution in the presence of copper species. Incorporation of Cu species into CeO$_2$ lattice can disrupt the Ce-O bond due to the charge and coordination number difference between Cu$^{2+}$ and Ce$^{4+}$. With the
increased CeO$_2$ content in the composite samples, the amount of highly interacted CuO or Cu-O-Ce solid solution increases, resulting in a continuous F$_{2g}$ peak shift to the lower frequency. The incorporation of Cu into CeO$_2$ lattice is also verified by both the decreased intensity of CuO B$_{2u}$ and the broadening of F$_{2g}$ of CeO$_2$ with the increased CeO$_2$ content in the composite catalysts. As shown in Fig. 6.3, among all of the composite (xCeO$_2$-(100-x)SiO$_2$) samples, 50CeO$_2$-50SiO$_2$ possessed the lowest frequency of F$_{2g}$ peak of CeO$_2$ found at 452 cm$^{-1}$, indicating a highest Cu substitution and lattice disruption.

![Figure 6.3. Raman spectra of CeO$_2$-SiO$_2$ supported CuO catalysts.](image)

Figure 6.3. Raman spectra of CeO$_2$-SiO$_2$ supported CuO catalysts.
6.3.3. XPS analysis

XPS spectra of 10CeO$_2$-90SiO$_2$, 50CeO$_2$-50SiO$_2$ and 90CeO$_2$-10SiO$_2$ were shown in Fig. 6.4. In Fig. 6.4a, 90CeO$_2$-10SiO$_2$ sample displayed 7 peaks for Ce 3d at 889.0, 891.5, 895.1, 904.6, 907.4, 910.1, and 913.6 eV, which were called as v, v', v'', v''', u, u', and u'', respectively. Among these peaks, u' and v' were attributed to Ce$^{3+}$ and rest of the 5 peaks were recognized as Ce$^{4+}$ [27, 28]. The peaks (u' and v'), which belong to Ce$^{3+}$, were not visible for 10CeO$_2$-90SiO$_2$ sample, and one peak (u') was not visible for 50CeO$_2$-SiO$_2$ sample. Visibility of only v' peak suggested a low amount of Ce$^{3+}$ present in 50CeO$_2$-50SiO$_2$, and non-visibility of these two peaks (u' and v') advised that there was no Ce$^{3+}$ in 10CeO$_2$-90SiO$_2$. The intensity of Ce 3d peaks became smaller, and this suggested that the amount of Ce at the surface decreased with decreasing the amount of CeO$_2$ in the sample. Fig. 6.4b presented spectra of Cu 2p$_{3/2}$ where one peak for 10CeO$_2$-90SiO$_2$ found at 938 eV corresponded to Cu$^{2+}$ [27]. This peak can also be seen for 50CeO$_2$-50SiO$_2$ and 90CeO$_2$-10SiO$_2$ samples. Another shoulder peak was observed at 935 – 933 eV for 50CeO$_2$-50SiO$_2$ and 90CeO$_2$-10SiO$_2$ samples, and this peak was attributed to Cu$^+$ [27, 28]. It can be observed that the amount of Cu$^+$ was higher in 50CeO$_2$-50SiO$_2$ than in 90CeO$_2$-10SiO$_2$, and this can happen due to a strong synergistic interaction among Ce, Si, and Cu. Spectra of O 1s were shown in Fig. 6.4c. Only one peak was found at 536 eV for 10CeO$_2$-90SiO$_2$; whereas two peaks were seen at 538 – 536 eV and 535 – 534 eV for 50CeO$_2$-50SiO$_2$ and 90CeO$_2$-10SiO$_2$ samples. Higher energy peak was attributed to adsorbed oxygen, and lower energy peak corresponded to lattice oxygen [29]. Clearly, SiO$_2$ did not provide any lattice oxygen because there was no low energy peak for 10CeO$_2$-90SiO$_2$. In this case, the adsorbed oxygen peak may also come
from –OH present on the surface of SiO$_2$. Spectra of Si 2p were seen in Fig. 6.4d and one broad peak can be observed for all of the samples. This peak was found at 109.0, 108.4, and 107.8 eV for 90CeO$_2$-10SiO$_2$, 50CeO$_2$-50SiO$_2$ and 10CeO$_2$-90SiO$_2$, respectively. These peaks corresponded to Si$^{4+}$ [30]. All of the peaks in Fig. 6.4 may shift to higher energy compared to the literatures due to the charging effect during the execution of the experiment [27-30].

![XPS spectra of CeO$_2$-SiO$_2$ supported CuO catalysts.](image)

**Figure 6.4.** XPS spectra of CeO$_2$-SiO$_2$ supported CuO catalysts.
6.3.4. TEM analysis

TEM images of CuO on CeO$_2$-SiO$_2$ composites were shown in Fig. 6.5. It can be seen in Fig. 6.5a that CeO$_2$ nanorods were agglomerated in 100CeO$_2$ samples and agglomeration of CeO$_2$ can be harmful to the catalytic efficiency due to lowering the chance of exposing of active surface. After introducing 10 wt % of SiO$_2$ nanospheres, a part of CeO$_2$ nanorods was separated by SiO$_2$ as seen in Fig. 6.5b. Similar agglomerated CeO$_2$ nanorods could still be found near SiO$_2$ nanospheres in 70CeO$_2$-30SiO$_2$ shown in Fig. 6.5c. CeO$_2$ nanorods spread out well onto SiO$_2$ nanospheres in 50CeO$_2$-50SiO$_2$ sample observed in Fig. 6.5d, and this increased CeO$_2$ active surfaces to be exposed. For 30CeO$_2$-70SiO$_2$ and 10CeO$_2$-90SiO$_2$, a very few CeO$_2$ nanorods were observed onto SiO$_2$ nanospheres as shown in Fig. 6.5e and 6.5f, respectively. Fig. 6.5g showed SiO$_2$ nanospheres, which were 200 – 250 nm in diameter for 100SiO$_2$ samples. Although 100SiO$_2$ had CuO particles, it cannot be visible because CuO particles were usually almost 5 – 15 nm, which were very small compared to SiO$_2$ nanospheres. Thus, they were hard to observe at this magnification. CeO$_2$ nanorods were usually 5 – 15 nm in width and 100 – 150 nm in length and SiO$_2$ nanospheres had 200 – 250 nm diameter for all of the samples. Fig. 6.6 presented TEM and HRTEM images of 50CeO$_2$-50SiO$_2$. In Fig. 6.6a, the surface of SiO$_2$ nanospheres were not smooth, and few SiO$_2$ nanospheres were broken. These defects may help in improving the catalytic activity. Fig. 6.6b showed that a single CeO$_2$ nanorod stayed in between two SiO$_2$ nanospheres, and Fig. 6.6c showed one CeO$_2$ nanorod onto SiO$_2$ nanosphere. As CuO nanoparticles were placed near the interface of SiO$_2$ and CeO$_2$, there can be a charge transfer among Ce, O, Cu, and Si due to synergistic interaction among SiO$_2$, CuO, and CeO$_2$. HRTEM image shown in
Figure 6.5. TEM images of (a) 100CeO$_2$, (b) 90CeO$_2$-10SiO$_2$, (c) 70CeO$_2$-30SiO$_2$, (d) 50CeO$_2$-50SiO$_2$, (e) 30CeO$_2$-70SiO$_2$, (f) 10CeO$_2$-90SiO$_2$, and (g) 100SiO$_2$. 
Fig. 6.6d presented a clear distinguishable boundary between CeO$_2$ and SiO$_2$. It can also be seen that CeO$_2$ nanorods were single crystal and SiO$_2$ nanospheres were amorphous.

![Figure 6.6. TEM (a-c) and HRTEM (d) images of 50CeO$_2$-50SiO$_2$ sample.](image)

6.3.5. $\text{H}_2$-TPR

$\text{H}_2$-TPR of CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts were observed in Fig. 6.7. Two reduction peaks were found at 250 and 285 °C for 100SiO$_2$. First peak seen at 250 °C was called $\beta$ peak, which corresponded to reduction of weakly interacted small CuO particles with SiO$_2$ [31]. The peak ($\gamma$ peak) found at higher temperature was attributed to reduction of bulk CuO [31]. After introducing 10 wt% CeO$_2$ in the catalyst system, these peaks shifted to lower temperature (180 and 228 °C). This clearly suggested
that there was an effect of CeO$_2$ on reduction behavior. In this case, β peak corresponded to reduction of small CuO particles, which may have interacted weakly with either SiO$_2$ nanospheres or CeO$_2$ nanorods or at the interface of SiO$_2$-CeO$_2$. Further addition of CeO$_2$ caused an appearance of another low-temperature reduction peak (α peak). This peak could be found at 151 °C for 20CeO$_2$-80SiO$_2$. The α peak corresponded to reduction of strongly interacted small CuO particles with CeO$_2$ [32]. We previously reported that CuO/SiO$_2$ nanospheres oxidized at 500 °C did not show any α reduction peak [33]. The α and β peak intensity started increasing and γ peak started decreasing with increasing the amount of CeO$_2$ up to 50 wt%. Increasing of the peak intensity can be associated with the surface oxygen availability. For 50CeO$_2$-50SiO$_2$, the α, β, and γ peak were observed at 150, 179, and 227 °C, respectively. A large amount of highly-interacted CuO with CeO$_2$ were present in 50CeO$_2$-50SiO$_2$ sample as described in Raman analysis (Fig. 6.3) and many CeO$_2$ nanorods were not agglomerated (seen in Fig. 6.5d), which increased the chances of exposing active surface of CeO$_2$. Thus, H$_2$-TPR was clearly in agreement with Raman and TEM analysis. Table 6.1 represented that the OSC of catalysts increased with increasing CeO$_2$ until 50 wt% addition and then decreased for further addition of CeO$_2$. Here, 50-CeO$_2$-50SiO$_2$ catalyst achieved maximum OSC of 1.56 μmol[O$_2$]/g. Trovarelli et al. [34] reported that mixing of CeO$_2$ and SiO$_2$ at 500-700 °C produced a mixture of crystalline CeO$_2$, amorphous SiO$_2$ and residual Ce$_{9.33}$(SiO$_4$)$_6$O$_2$. After reoxidation, this complex compound decomposed into amorphous SiO$_2$ and small CeO$_2$ crystallites, which increased OSC of the catalyst. With further addition of CeO$_2$ in our samples, all of the reduction peaks progressively shifted to higher temperature up to 70 wt% CeO$_2$ additions and then again gradually shifted to the lower temperature up to 100CeO$_2$. For 70CeO$_2$-
30SiO$_2$ sample, a large part of CeO$_2$ nanorods were still agglomerated as seen in Fig. 6.5c and thus, the peaks shifted to higher temperatures. The $\alpha$, $\beta$, and $\gamma$ peak were found at 179, 204, and 249 °C respectively for 70CeO$_2$-30SiO$_2$. With further increasing the amount of CeO$_2$ nanorods, the percentage of agglomeration increased (Fig. 6.5a and 6.5b). However, the presence of Cu-O-Ce solid solutions of highly interacted CuO increased in 80CeO$_2$-20SiO$_2$, 90CeO$_2$-10SiO$_2$ and 100CeO$_2$ as reported in Raman analysis (Fig. 6.3), and this surpassed the effect of CeO$_2$ agglomeration, causing the peaks shifting back to the lower temperature. The $\gamma$ peak intensity decreased for 80 wt% CeO$_2$ addition in the catalyst system, and this peak completely disappeared for 90CeO$_2$-10SiO$_2$ due to the absence of bulk CuO as in agreement with XRD analysis (Fig. 6.1).
The α and β peak could be observed at 147 and 179 °C for 100CeO\textsubscript{2}. Table 6.1 showed the H\textsubscript{2} consumption of the catalysts at different peaks, and it could be seen that it did not follow any particular trend. That happened because H\textsubscript{2} consumptions usually depended on the total amount of available various oxygen species, such as adsorbed oxygen, lattice oxygen of CeO\textsubscript{2}, and lattice oxygen of CuO. On the other hand, reduction peaks could be seen at different temperature due to different activation energies of various oxygen species.

<table>
<thead>
<tr>
<th>Samples</th>
<th>α peak (mmol/g)</th>
<th>β peak (mmol/g)</th>
<th>γ peak (mmol/g)</th>
<th>Total (mmol/g)</th>
<th>OSC (μmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100CeO\textsubscript{2}</td>
<td>0.763</td>
<td>1.036</td>
<td>0</td>
<td>1.799</td>
<td>0.86</td>
</tr>
<tr>
<td>90CeO\textsubscript{2} - 10SiO\textsubscript{2}</td>
<td>0.602</td>
<td>1.826</td>
<td>0</td>
<td>2.428</td>
<td>1.07</td>
</tr>
<tr>
<td>80CeO\textsubscript{2} - 20SiO\textsubscript{2}</td>
<td>0.359</td>
<td>1.435</td>
<td>0.083</td>
<td>1.878</td>
<td>-</td>
</tr>
<tr>
<td>70CeO\textsubscript{2} - 30SiO\textsubscript{2}</td>
<td>0.672</td>
<td>1.220</td>
<td>0.621</td>
<td>2.513</td>
<td>1.18</td>
</tr>
<tr>
<td>60CeO\textsubscript{2} - 40SiO\textsubscript{2}</td>
<td>0.903</td>
<td>0.504</td>
<td>0.715</td>
<td>2.123</td>
<td>-</td>
</tr>
<tr>
<td>50CeO\textsubscript{2} - 50SiO\textsubscript{2}</td>
<td>0.338</td>
<td>0.661</td>
<td>0.679</td>
<td>1.677</td>
<td>1.56</td>
</tr>
<tr>
<td>40CeO\textsubscript{2} - 60SiO\textsubscript{2}</td>
<td>0.248</td>
<td>0.686</td>
<td>0.650</td>
<td>1.584</td>
<td>-</td>
</tr>
<tr>
<td>30CeO\textsubscript{2} - 70SiO\textsubscript{2}</td>
<td>0.223</td>
<td>0.478</td>
<td>0.717</td>
<td>1.418</td>
<td>0.72</td>
</tr>
<tr>
<td>20CeO\textsubscript{2} - 80SiO\textsubscript{2}</td>
<td>0.169</td>
<td>0.447</td>
<td>1.050</td>
<td>1.667</td>
<td>-</td>
</tr>
<tr>
<td>10CeO\textsubscript{2} - 90SiO\textsubscript{2}</td>
<td>0.000</td>
<td>0.530</td>
<td>0.771</td>
<td>1.300</td>
<td>0.48</td>
</tr>
<tr>
<td>100SiO\textsubscript{2}</td>
<td>0</td>
<td>1.407</td>
<td>0.233</td>
<td>1.64</td>
<td>0.29</td>
</tr>
</tbody>
</table>
In this method, after CO molecules are being adsorbed, they react with lattice oxygen of metal oxides during heating and desorb away as CO$_2$. Fig. 6.8 presented CO$_2$ desorption peaks of various CeO$_2$-SiO$_2$ composite supported CuO catalysts. 100SiO$_2$ showed a broad desorption peak centered at 180 °C. This peak may have corresponded to CO$_2$ produced by the reaction between adsorbed CO and surface oxygen of SiO$_2$ and/or CuO [27, 28, 33]. As SiO$_2$ support was inactive, the intensity of desorption peak was very low. As the amount of CeO$_2$ was increased, desorption peak intensity increased and the

**Figure 6.8. CO-TPD profiles of CeO$_2$-SiO$_2$ supported CuO catalysts.**

**6.3.6. CO-TPD**

In this method, after CO molecules are being adsorbed, they react with lattice oxygen of metal oxides during heating and desorb away as CO$_2$. Fig. 6.8 presented CO$_2$ desorption peaks of various CeO$_2$-SiO$_2$ composite supported CuO catalysts. 100SiO$_2$ showed a broad desorption peak centered at 180 °C. This peak may have corresponded to CO$_2$ produced by the reaction between adsorbed CO and surface oxygen of SiO$_2$ and/or CuO [27, 28, 33]. As SiO$_2$ support was inactive, the intensity of desorption peak was very low. As the amount of CeO$_2$ was increased, desorption peak intensity increased and the
peak shifted to lower temperature due to the presence of surface oxygen of CeO$_2$. The support CeO$_2$ takes part in the reaction by providing oxygen and reducing itself (4CeO$_2$ = 2Ce$_2$O$_3$ + O$_2$). Oxygen vacancies in CeO$_2$ lattice help in increasing the oxygen mobility to reach at the surface, and this surface oxygen reacts with adsorbed CO easily.

6.3.7. CO oxidation

The light-off curves of CO oxidation for CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts were shown in Fig. 6.9. It can be seen that only two catalysts (40CeO$_2$-60SiO$_2$ and 50CeO$_2$-50SiO$_2$) achieved 100% CO conversion to CO$_2$ at 306 and 263 $^\circ$C, respectively. Table 6.2 displayed $T_{50}$, $T_{max}$ and maximum CO conversion up to 350 $^\circ$C. $T_{50}$ is the temperature at which 50% CO conversion is achieved and $T_{max}$ is the temperature at which maximum CO conversion is achieved. As displayed in Table 6.2, $T_{50}$ of 100SiO$_2$ was at 234 $^\circ$C and it gradually decreased with increasing CeO$_2$ amount in the CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts. 100SiO$_2$ sample only achieved a maximum 77% CO conversion at 350 $^\circ$C, and this conversion value rapidly increased to over 90% by introducing CeO$_2$ in CeO$_2$-SiO$_2$ composite supported 10 wt% CuO catalysts. In the CeO$_2$-SiO$_2$ composite supported 10wt% CuO catalysts, SiO$_2$ nanospheres not only offer support to increase the dispersion of CuO, but also can separate CeO$_2$ nanorods so that CeO$_2$ nanorods do not agglomerate. Fig. 6.10a showed a schematic of agglomerated CeO$_2$ supported CuO and SiO$_2$ nanospheres schematic was seen in Fig. 6.10b. After mixing CeO$_2$ nanorods and SiO$_2$ nanospheres, CeO$_2$ nanorods spread out and lie on SiO$_2$ surface as shown in Fig. 6.10c and CuO nanoparticles lie on the interface of CeO$_2$-SiO$_2$ (shown in Fig. 6.10d). It was confirmed earlier in TEM images as shown in Fig. 6.5. This effect usually helped to expose maximum surface area
of CeO$_2$ nanorods and created more chances to form Cu-O-Ce solid solutions and/or CuO onto the interface of SiO$_2$-CeO$_2$. 100CeO$_2$ can convert maximum 95% CO up to 350 °C due to the presence of agglomeration of CeO$_2$ nanorods. We previously reported that CuO impregnated CeO$_2$ nanorods oxidized at 400 °C showed 100% CO conversion at 220 °C [33]. Small CuO particles became larger at high temperature calcination (500 °C), and this affected the catalytic efficiency for 100CeO$_2$ sample. Qian et al. [35] and Dekkers et al. [36] reported that CeO$_2$-SiO$_2$ supported Au catalysts achieved 50% CO conversion at 110 and 115 °C, respectively. On the other hand, $T_{50}$ for our 50CeO$_2$-50SiO$_2$ sample was 100 °C, which confirmed an enhanced catalytic activity without using noble metal catalyst.

![Figure 6.9. CO oxidation curves of CeO$_2$-SiO$_2$ supported CuO catalysts.](image-url)
Table 6.2. Catalytic activity toward CO oxidation over CeO$_2$-SiO$_2$ supported CuO catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>T$_{50}$ (°C)</th>
<th>T$_{Max}$ (°C)</th>
<th>Max CO conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 CeO$_2$</td>
<td>94</td>
<td>237</td>
<td>95</td>
</tr>
<tr>
<td>90CeO$_2$-10SiO$_2$</td>
<td>95</td>
<td>263</td>
<td>93</td>
</tr>
<tr>
<td>80CeO$_2$-20SiO$_2$</td>
<td>100</td>
<td>220</td>
<td>92</td>
</tr>
<tr>
<td>70CeO$_2$-30SiO$_2$</td>
<td>102</td>
<td>220</td>
<td>90</td>
</tr>
<tr>
<td>60CeO$_2$-40SiO$_2$</td>
<td>98</td>
<td>263</td>
<td>93</td>
</tr>
<tr>
<td>50CeO$_2$-50SiO$_2$</td>
<td>100</td>
<td>263</td>
<td>100</td>
</tr>
<tr>
<td>40CeO$_2$-60SiO$_2$</td>
<td>114</td>
<td>306</td>
<td>100</td>
</tr>
<tr>
<td>30CeO$_2$-70SiO$_2$</td>
<td>127</td>
<td>263</td>
<td>97</td>
</tr>
<tr>
<td>20CeO$_2$-80SiO$_2$</td>
<td>127</td>
<td>280</td>
<td>93</td>
</tr>
<tr>
<td>10CeO$_2$-90SiO$_2$</td>
<td>168</td>
<td>289</td>
<td>91</td>
</tr>
<tr>
<td>100SiO$_2$</td>
<td>234</td>
<td>298</td>
<td>77</td>
</tr>
</tbody>
</table>
6.4. Conclusion

The composite of shape-controlled CeO$_2$-SiO$_2$ supported 10 wt% CuO catalysts were successfully synthesized for low-temperature CO oxidation applications. Both 100SiO$_2$ and 100CeO$_2$ samples did not achieve 100% CO conversion. However, a mixture of CeO$_2$ nanorods and SiO$_2$ nanospheres changed the catalytic activity depending on the percentage of CeO$_2$ or SiO$_2$ in the catalyst mixture. 50CeO$_2$-50SiO$_2$ showed low-temperature (150, 179, and 227 °C) H$_2$ reduction peaks with total of 1.677 mmol H$_2$ consumption. This sample also converted 100% CO at 263 °C. When comparing with rest of the prepared catalysts, it can be concluded that 50CeO$_2$-50SiO$_2$ achieved higher catalytic activity, and this happened because 50% SiO$_2$ reduced agglomeration of CeO$_2$ nanorods, leading to an increase of oxygen availability by increasing CuO dispersion on both CeO$_2$ nanorods and the interface of SiO$_2$-CeO$_2$.

6.5. References


179


Chapter 7: Kinetic study of CeO\textsubscript{2} supported CuO catalyst toward CO oxidation reaction

This chapter investigates the redox kinetics of CeO\textsubscript{2} nanorods supported CuO catalyst prepared by thermal decomposition method. 5\%CO-95\%He and O\textsubscript{2} gases were used to reduce and oxidize CuO/CeO\textsubscript{2} catalyst respectively at a constant temperature of 400 °C (isothermal process). Mathematical formulas for power law, diffusion, nucleation and contraction models have been used to compare with the experimental data collected during the reduction and oxidation process of the catalyst to determine the best fitted reaction mechanism.

7.1. Introduction

CO oxidation reaction is one of the most studied catalytic reactions and has gotten more attention due to industrial concern for treatment of automotive exhaust and in the preferential oxidation of CO in the excess H\textsubscript{2} (PROX reaction) for hydrogen fuel cells [1]. Researchers have been trying to synthesize various metal oxide supported catalysts for low-temperature CO oxidation. Metal oxides, such as Al\textsubscript{2}O\textsubscript{3}, SiO\textsubscript{2}, CeO\textsubscript{2}, TiO\textsubscript{2}, SnO\textsubscript{2}, and ZrO\textsubscript{2} have been used as support for noble metals (i.e. Pt, Au, Pd, and Rh) and/or transition metal oxides (i.e. NiO, CuO, ZnO, and MnO\textsubscript{2}) catalysts [1-12]. Among various catalyst systems, CeO\textsubscript{2} supported CuO is one of the most active transition metal catalysts for low-temperature CO oxidation application; and thus, this catalyst system has been studied extensively. However, the reaction mechanism of CO oxidation over CuO/CeO\textsubscript{2} catalyst is still unclear. Compared to vast majority of publications on synthesis and
catalytic activity of CuO/CeO₂, there is relatively small number of publications on kinetic study of CO oxidation reaction over CuO/CeO₂ catalyst, even though the kinetic study can aid important information on the reaction mechanism. In literature, several kinetic models, including Langmuir-Hinshelwood (L-H) [13], Mars-Van Krevelen (MVK) [14], and Liu and Flytzani-Stephanopoulos (LFS) [15] mechanisms, are often used to understand CO oxidation over CuO/CeO₂ catalysts. L-H model predicted that the reaction occurs at noble metal catalyst, where adsorbed oxygen and CO react and lattice oxygen does not take part in the reaction. On the other hand, MVK model has been explained based on involving lattice oxygen of CeO₂ in the reaction. LFS model exhibited a different view because they reported that the reaction occurs at the interface of CuO and CeO₂. In this chapter, we have attempted a distinct way for kinetic study of CO oxidation over CuO/CeO₂ and various solid state kinetic models, such as contraction, power, nucleation and diffusion models, have been used to determine reaction mechanism and activation energy for CO oxidation.

7.2. Experimental

7.2.1. Catalyst preparation

Hydrothermal method was used to prepare CeO₂ nanorods. The 88 mL of 0.1 M Ce(NO₃)₂.6H₂O was transferred into Teflon liner of 200 mL capacity, and 8 mL of 6 M NaOH was added into the solution. This solution was stirred for about 15 sec, and then the lid of Teflon liner was closed. The Teflon liner was put into a stainless steel autoclave and heated at 90 °C for 48 hrs. Finally, the product was filtered and was washed with 500 mL water and then with 50 mL ethanol. It was dried at 50 °C for 12 hrs. To impregnate
10% CuO, CeO$_2$ nanorods and Cu(NO$_3$)$_3$·3H$_2$O were mixed in stoichiometric ratio in 30 mL water. While stirring, it was heated at 120 °C until water evaporated. Then, it was oxidized at 400 °C for 5 hrs. Finally, CuO/CeO$_2$ catalyst was collected.

7.2.2. Catalyst characterizations

The X-ray diffraction of powder samples were carried out on Mini-Flex II diffractometer. The diffraction patterns were recorded with Cu Kα source (λ = 0.154 nm) in the range of 2θ between 5° and 90°. Raman spectroscopy analysis on the samples was done using the Horiba iHR-320 Raman spectrometer with a laser at an excitation wavelength of 532 nm. Exposure time of 5 sec and accumulation number of 10 were used for all of the samples. The Raman spectrometer was calibrated before testing the catalyst samples. Silicon single crystal wafer was used to calibrate with a reference peak at 520 cm$^{-1}$. TEM was performed on the samples to analyze the morphology and size of the catalysts using JEOL 2100 TEM. 400 mesh copper grid (from Ted Pella) was used to prepare TEM sample. At first, the catalysts powder sample was mixed with ethanol in a beaker, and the suspension was sonicated for 1 min. Samples were taken from the solution by a small pipette, and one or two drops of sample were poured on the hydrocarbon copper grid. Oxygen storage capacity (OSC) of the catalysts and metal dispersion percentage were measured by H$_2$ pulse chemisorption using Micromeritics Autochem$^\text{TM}$ II 2920. Prior to the measurement, the sample loaded in U-tube was pre-treated at 350 °C in 5%O$_2$-95%He for 30 mins. After cooling down to room temperature, He gas was flown for 30 mins to take excess oxygen out of the system. Then the sample was again heated to 350 °C and 5%H$_2$-95%Ar gas was injected into the sample U-tube every 3 mins until the intensity of the hydrogen consumption peaks was nearly equal. The
OSC was expressed as µmol of O$_2$ per gram catalyst sample. For CO temperature programmed desorption (TPD), the sample was heated up to 400 °C under inert environment (He gas) with a flow rate of 50 mL/min to remove residual moisture. After cooling down to room temperature, 5% CO – 95% He gas with 50 mL/min rate was flown through the sample for 30 mins. Helium gas was flown again for 30 mins. Then the sample was reheated up to 400 °C under inert environment. Rate of desorption was calculated using equation (7.1) shown below.

\[
\frac{d\theta}{dt} = - \frac{k_d}{\beta} \theta^n \quad \text{(Eq. 7.1)}
\]

\[
k_d = A \exp \left( - \frac{E_d}{RT} \right) \quad \text{(Eq. 7.2)}
\]

Here, $k_d$, $\beta$, $\theta$, and $n$ are rate of desorption constant, heating rate, surface coverage, and reaction order, respectively. $k_d$ can be found using equation (7.2) where $A$, $E_d$, $R$, and $T$ are rate coefficient, desorption energy, gas constant, and temperature, respectively. The CO oxidation was performed in a quartz reactor inserted in a vertical furnace. The mixture gases consisted with 1% CO, 20% O$_2$ and the rest He. The flow rate of the mixture gas was 70 mL/min. The reaction was done between room temperature and 350°C. The CO conversion was calculated using the following equation:

\[
\% \text{CO conversion} = \left[ \frac{P_{CO_2}}{P_{CO} + P_{CO_2}} \right] \times 100\%, \quad \text{(Eq. 7.3)}
\]

Here, $P_{CO}$ and $P_{CO_2}$ are the partial pressure of CO and CO$_2$, respectively, are determined from the relative peak area of the CO and CO$_2$ peaks normalized to the He standard. Turnover frequency (TOF) is a measurement of catalytic activity which shows the number of cycles per unit time. Three types of TOF can be calculated as follows [16, 17]:

188
TOF\(_1\) (s\(^{-1}\)) = X\(_{CO}\) \(\frac{5 \, W_{Cu}}{4 \, m_{cat} \, X_{CuO} \, D_{CuO}}\) \hspace{1cm} (Eq. 7.4)

TOF\(_2\) (s\(^{-1}\)) = X\(_{CO}\) \(\frac{F_{CO}}{N \, \frac{m_c}{m_{cat} \, X_{CuO}}}\) \hspace{1cm} (Eq. 7.5)

TOF\(_3\) (s\(^{-1}\)) = \frac{\frac{\text{TOF}_2}{\pi \, d_{Cu-O}}}{2 \, d_{Cu-O}} = X\(_{CO}\) \(\frac{F_{CO}}{N \, \frac{m_c}{m_{cat} \, X_{CuO}} \, \frac{2d_{Cu-O}}{\pi^2 \, d}}\) \hspace{1cm} (Eq. 7.6)

Here, \(X_{CO}\) is the CO conversion percentage (%) at certain temperature; \(F_{CO}\) (mol·s\(^{-1}\)) is the flow rate of CO; \(N\) is the Avogadro’s constant; \(W_{Cu}\) is the molecular weight of Cu (63.545 g·mol\(^{-1}\)); \(m_{cat}\) is the weight of catalyst; \(X_{CuO}\) is the percentage of CuO loading on the catalyst support; \(D_{CuO}\) is the percentage of CuO dispersion; \(m_c\) is the weight of a single CuO crystalline and this can be calculated from the volume of assumed semi-spherical CuO and density of CuO (6.45 g·cm\(^{-3}\)); \(d\) is the crystallite size of CuO; \(d_{Cu-O}\) is distance between Cu and O atom (0.195 nm). TOF\(_1\) calculation is usually based on metal dispersion. TOF\(_2\) contributes the information about the overall activity of Cu atoms on CuO-support periphery and TOF\(_3\) refers to life cycles or turn over frequency of each Cu atom present at interface of CuO-support. Thermogravimetric analyzer (TGA) under different atmosphere was used for kinetic study of the catalyst in this study. At first, an aluminum pan was tared and then sample was placed in it. The sample was heated up to 400 °C at 10 °C/min rate under inert environment (He gas). Any volatile substances or moisture can be removed during heating. Temperature was held at 400 °C during reduction/oxidation cycles. 5%CO-95%He gas was used to reduce the sample and this mixture gas was passed through the sample at 50 mL/min rate for 30 mins at a constant temperature of 400 °C. The gas was switched to pure oxygen to oxidize the sample. The flow rate of oxygen gas was 50 mL/min and this gas was flown for 30 mins as well. The
pair of one reduction and one oxidation processes is mutually called one redox cycle. In total, 10 cycles of redox process was conducted for the catalyst. Sample weight changed for decomposition, oxidation, or loss of volatile substances.

7.3. Results and Discussion

7.3.1. Structural analysis

XRD and Raman analysis were conducted to determine the presence of CeO$_2$ and CuO in the catalyst. Fig. 7.1a showed XRD pattern of CuO/CeO$_2$ catalyst. The peaks for fluorite structured CeO$_2$ were observed, and these peaks matched with JCPDS data (JCPDS 43-1002) [18]. CuO peak was not present in the XRD pattern due to the presence of small CuO nanoparticles or Cu-O-Ce solid solutions [19]. We previously showed that increasing the oxidation temperature causes to increase the particle size of CuO as well as the possibility of CuO phase separation from solid solutions [20]. Thus, CuO peaks can be visible in XRD profiles for higher oxidation temperature. Raman analysis in Fig. 7.1b confirmed the presence of CuO in the catalyst. The peaks found at 271 and 625 cm$^{-1}$ corresponded to $A_g$ and $B_{2g}$ mode of CuO [18]. One peak with large intensity can be seen at 444 cm$^{-1}$, and this peak was associated with $F_{2g}$ mode of CeO$_2$. According to the literature, this peak was usually found at 456 cm$^{-1}$ [20]. For this catalyst, CeO$_2$ peak shifted to lower wavenumber due to the presence of oxygen vacancies in CeO$_2$ lattice. TEM and HRTEM images of CuO/CeO$_2$ were presented in Fig. 7.2. CeO$_2$ nanorods of 50-100 nm long and 10-20 nm width can be observed in Fig. 7.2a. CuO nanoparticle was attached onto the surface of CeO$_2$ nanorods as shown in Fig. 7.2b.
Figure 7.1. XRD pattern (a) and Raman spectrum (b) of CuO/CeO₂ catalyst.
Figure 7.2. TEM (a) and HRTEM (b) of CuO/CeO₂ catalyst.
7.3.2. CO oxidation and pulse chemisorption

The light-off curves of CO oxidation over CuO/CeO$_2$ catalysts were shown in Fig. 7.3a. The weight of the catalysts was varied from 23.7 to 124.3 mg for this experiment, and it can be seen that rate of reaction changed with increasing the weight of the sample. The $T_{50}$ (the temperature when 50% CO was converted) of the samples were 119, 101, 97, 93, and 87 °C for 23.7, 49.0, 73.7, 100.0, and 124.3 mg of sample, respectively. An attempt was conducted to calculate activation energy of prepared CuO/CeO$_2$ catalyst. We considered that $W$ is weight of the sample and $F_{CO}$ is fraction of CO conversion. Fig. 7.3b showed the changes of $W/F_{CO}$ ratio with fraction of CO conversion at different temperatures. As the temperature increased, the conversion ratio lost the linearity with $W/F_{CO}$. The reaction rate was calculated, using the slope of curves up to 0.40 fraction of CO conversion from Fig. 7.3b. Arrhenius plot for CO oxidation was shown in Fig. 7.3c. Activation energy of CuO/CeO$_2$ for CO conversion reaction was calculated and the value was 20.2 KJ/mol. Using CO oxidation light-off curves shown in Fig. 7.3a, three different TOFs were calculated at 50% CO conversion. Calculated TOF$_1$, TOF$_2$ and TOF$_3$ were 0.8605, 0.136, and $11.94 \times 10^{-4}$ s$^{-1}$, respectively. Lu et al. [16] presented TOF$_1 = 0.00852$ s$^{-1}$, TOF$_2 = 5.22$ s$^{-1}$, and TOF$_3 = 30.02 \times 10^{-4}$ s$^{-1}$ for CuO/CeO$_2$. Our calculated TOF$_1$ was 100 times higher than the reported data due to well dispersed CuO nanoparticles onto CeO$_2$ surface. However, our calculated TOF$_2$ and TOF$_3$ were lower than the reported data and Lu et al. [16] explained that smaller CuO particles could give low TOF$_2$ and TOF$_3$ values and this was consistent with our XRD data.
Figure 7.3. Light-off curves of CO oxidation (a), W/F ratio vs CO fraction (b), and Arrhenious plot (c).
Figure 7.4. CO-TPD (a) and rate of desorption (b) of CuO/CeO$_2$ catalyst.
7.3.3. CO TPD

CO-TPD profile of CuO/CeO$_2$ was shown in Fig. 7.4a. Two desorption peaks were found at 100 and 150 °C. These peaks are fundamentally for CO$_2$ produced from the reaction between adsorbed CO and the surface of CeO$_2$. Lattice oxygens at the interface of CuO-CeO$_2$ may take part in the reaction. Rate of desorption (ROD) of CO$_2$ was measured from CO-TPD curve and was shown in Fig. 7.4b. It can be observed that the temperature affected ROD. At first, desorption increased with temperature up to 175 °C. Then at latter step, it still increased linearly, however quicker than the former step; and this step was completed at 325 °C where it showed maximum ROD (13.9 \times 10^{-4} \text{ mol/cm}^2.s). In final step, ROD started going down rapidly probably due to the presence of low amount of adsorbed CO at this temperature.

7.3.4. Kinetic model

As mentioned earlier, TGA was used to conduct kinetic study on CO oxidation reaction over CuO/CeO$_2$ catalyst. Reduction degree and oxidation degree were calculated using the change in weight from TGA measurements. The equations were used as follows.

\[
\text{Reduction degree (RD)} \% = \frac{W_i-W_t}{W_i-W_f} \times 100 \quad \text{(Eq. 7.7)}
\]

\[
\text{Oxidation degree (OD)} \% = \frac{W_t-W_i}{W_f-W_i} \times 100 \quad \text{(Eq. 7.8)}
\]

Here, $W_i$, $W_f$, and $W_t$ are initial weight before reduction or oxidation reaction, final weight after reduction or oxidation reaction and weight at time $t$, respectively. For solid-state kinetics, a series of mathematical models was compared with experimental data collected
during redox reaction in order to find an appropriate one. Statistical parameters were used for ideal selection. Now, gas-solid reaction rate can be expressed as follows [21].

\[
\frac{dx}{dt} = k(T). f(X) \tag{Eq. 7.9}
\]

Here, \(X\) is the reduction/oxidation degree, \(k\) is reaction rate or Arrhenius parameter, \(T\) is reaction temperature, \(t\) is time and \(f(X)\) is the empirical function for solid-state kinetics.

Now, equation 7.9 can be rewritten which is shown in equation 7.10 and 7.11.

\[
g(X) = \int_0^x \frac{dx}{f(X)} = k(T) \int dt \tag{Eq. 7.10}
\]

\[
g(X) = \int_0^x \frac{dx}{f(X)} = kt \tag{Eq. 7.11}
\]

The Arrhenius parameter \(k\) can vary with temperature \(T\) and this can be shown in equation 7.12.

\[
k = k_o \exp \left(-\frac{E_a}{RT}\right) \tag{Eq. 7.12}
\]

Here, \(k_o\) pre-exponential factor, \(E_a\) is activation energy, and \(R\) is universal gas constant.

Ipsakis et al. mentioned that \(f(X)\) usually depends on the reaction mechanism and it can be expressed as follows [20]:

\[
f(X) = X^m. (1 - X)^n. [-\ln(1 - X)]^p \tag{Eq. 7.13}
\]

where \(m\), \(n\), and \(p\) are empirical dependence parameters.

Various empirical models for gas-solid kinetics were shown in Table 7.1 [21, 22]. The experimental data were compared with the simulated data calculated using these kinetic models. The error between experimental and simulated data was minimized using equation 7.14 and then \(R^2\) values were calculated to determine the fitting result.

\[
Minimized \ error = (Y_{Sim} - Y_{Exp})^2 \tag{Eq. 7.14}
\]
where $Y_{Sim}$ and $Y_{Exp}$ were simulated and experimental data of reduction or oxidation degree respectively at normalized range of 0-1.

**Table 7.1 Basic solid state kinetic models of f(X) and g(X).**

<table>
<thead>
<tr>
<th>Model</th>
<th>$f(X)$</th>
<th>$g(X)$</th>
<th>Model name</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>$3(1-X)^{\frac{2}{3}}$</td>
<td>$1-(1-X)^{\frac{1}{3}}$</td>
<td>Contraction</td>
</tr>
<tr>
<td>M2</td>
<td>$(1-X)$</td>
<td>$-ln(1-X)$</td>
<td>Kinetic order</td>
</tr>
<tr>
<td>M3</td>
<td>$2(1-X)^{\frac{1}{2}}$</td>
<td>$1-(1-X)^{\frac{1}{2}}$</td>
<td>Contraction</td>
</tr>
<tr>
<td>M4</td>
<td>$\frac{3}{2}(1-X)^{\frac{1}{3}}$</td>
<td>$1-(1-X)^{\frac{2}{3}}$</td>
<td>Contraction</td>
</tr>
<tr>
<td>M5</td>
<td>$4(1-X)^{\frac{3}{4}}$</td>
<td>$1-(1-X)^{\frac{4}{4}}$</td>
<td>Contraction</td>
</tr>
<tr>
<td>M6</td>
<td>$\frac{2}{3}X^{\frac{1}{2}}$</td>
<td>$(X)^{\frac{3}{2}}$</td>
<td>Power law</td>
</tr>
<tr>
<td>M7</td>
<td>$X(1-X)$</td>
<td>$ln\left(\frac{X}{1-X}\right)$</td>
<td>Power law</td>
</tr>
<tr>
<td>M8</td>
<td>$n(1-X).(-ln(1-X))^\left(1-\frac{1}{n}\right)$</td>
<td>$(-ln(1-X))^{\frac{1}{n}}$</td>
<td>Nucleation /Avramai-Erofeev</td>
</tr>
<tr>
<td>M9</td>
<td>$\frac{3(1-X)^{\frac{1}{3}}}{2(1-X)^{-\frac{1}{3}}-1}$</td>
<td>$\frac{1}{2}[(1-X)^{\frac{2}{3}}-4(1-X)^{\frac{1}{3}}+3]$</td>
<td>Diffusion</td>
</tr>
<tr>
<td>M10</td>
<td>$\frac{3}{2}(1-X)^{-\frac{1}{3}}-1$</td>
<td>$\frac{1}{2}-\frac{1}{2}(1-X)^{\frac{4}{3}}-\frac{1}{3}X$</td>
<td>Diffusion</td>
</tr>
</tbody>
</table>
Fig. 7.5 showed TGA profile of reduction and oxidation reaction over CuO/CeO$_2$ catalyst. First 40 mins, moisture in catalysts evaporated as the temperature was increased from room temperature to 400 °C. Then, weight of the catalyst decreased again rapidly in almost 1 min due to reduction reaction under CO environment. Weight of the catalyst stopped changing after completing the reduction reaction with all available oxygen in the catalyst. When oxygen gas was started flowing, the catalyst restored oxygen and gained weight. As it fully restored all of the available sites with oxygen, weight of the catalyst became constant. The redox reaction was conducted for total 10 cycles.

Figure 7.5. TGA profile of reduction and oxidation reactions over CuO/CeO$_2$ catalysts.
For kinetic analysis of CuO/CeO$_2$ catalyst, cycle 1, 2, 3, 5, and 10 for reduction and oxidation stages were selected. The mathematical models mentioned earlier in Table 7.1 were used to find out the best fitted model with the experimental data. Table 7.2 showed an overview of fitting results for reduction reaction kinetic models. Here, $R^2$ values varied from 0.24 to 0.99 for most of the kinetic models. It can also be seen that some of the kinetic models totally rejected this reaction and thus there was no $R^2$ values for them.

**Table 7.2. Overview of fitted data ($R^2$) for kinetic models at reduction stages.**

<table>
<thead>
<tr>
<th>Model</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 5</th>
<th>Cycle 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.9904</td>
<td>0.8138</td>
<td>0.5103</td>
<td>0.4730</td>
<td>0.4058</td>
</tr>
<tr>
<td>M2</td>
<td>0.9746</td>
<td>0.6861</td>
<td>0.3827</td>
<td>0.3441</td>
<td>0.2746</td>
</tr>
<tr>
<td>M3</td>
<td>0.9827</td>
<td>0.8653</td>
<td>0.5779</td>
<td>0.5418</td>
<td>0.4765</td>
</tr>
<tr>
<td>M4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M5</td>
<td>0.9897</td>
<td>0.7841</td>
<td>0.4733</td>
<td>0.4396</td>
<td>0.3717</td>
</tr>
<tr>
<td>M6</td>
<td>0.9752</td>
<td>0.1999</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M8  n = 1.5</td>
<td>0.9903</td>
<td>0.9908</td>
<td>0.9928</td>
<td>0.9922</td>
<td>0.9924</td>
</tr>
<tr>
<td>n = 2</td>
<td>0.8226</td>
<td>0.9380</td>
<td>0.9904</td>
<td>0.9935</td>
<td>0.9941</td>
</tr>
<tr>
<td>n = 3</td>
<td>0.6465</td>
<td>0.8432</td>
<td>0.9007</td>
<td>0.9081</td>
<td>0.9203</td>
</tr>
<tr>
<td>n = 4</td>
<td>0.5308</td>
<td>0.7861</td>
<td>0.8351</td>
<td>0.8435</td>
<td>0.8575</td>
</tr>
<tr>
<td>M9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
From the comparison among all the kinetic models, it can be visible that M8 model or Avrami-Erofeev model for \( n = 1.5 \) fitted the best for this reduction reaction. Fig. 7.6 represented the reduction profile of CuO/CeO\(_2\) catalyst using the optimal fitting result which was 1.5\(^{\text{th}}\) order of Avrami-Erofeev or nucleation model; and here the change in reduction degree as function of time was shown for 5 different cycles (1, 2, 3, 5, and 10). Cycle 1 took relatively longer reduction time (0.8 min) to stabilize RD value at 90%. Higher cycles (2 to 10) took 0.66 – 0.63 min to stabilize at 90% RD. Constant stabilized RD value (90%) for all cycles suggested that the amount of available oxygen in the catalyst did not change with increasing redox cycles. However, after cycle 1 the reduction time decreased due to the increment in oxygen mobility in CeO\(_2\) lattice. We earlier showed in Chapter 4 that oxygen storage capacity (OSC) of CuO/CeO\(_2\) was 2.39 \( \mu \text{mol/g} \) and this value did not vary after 3 redox cycles. In Fig. 7.6, the reaction initially started with faster and constant reduction rate up to 67% reduction for cycle 1 and 78% reduction for cycle 2-10. In this stage, CO gas reacted with the most easily-reducible oxygen species, which possibly originated from adsorbed oxygen near Cu-O-Ce solid solution and/or oxygen at the interface of CuO and CeO\(_2\). At the next stage, the reaction rate slowly decreased. In this case, we assumed that oxygen needs to travel within CeO\(_2\) lattice to reach near the surface or at the interface of CuO and CeO\(_2\). Depending on the mobility of oxygen in CeO\(_2\) lattice, the reaction rate may vary at different cycles. This reduction profile was the best fitted with 1.5\(^{\text{th}}\) order of Avrami-Erofeev model or nucleation model where both point defects (oxygen vacancy) and nucleation need to be considered. In this case, random nucleation and significant growth of Cu\(^0\) possibly occurred during reduction. However, this model failed to show exact reduction pathways.
and/or timeline of reduction reaction, Cu\(^0\) nucleation and Cu\(^0\) growth. Table 7.3 represented that reaction rate increased from 2.33 to 2.72 with increasing the redox cycle from 1 to 10. This data was retrieved using 1.5\(^{\text{th}}\) order of Avrami-Erofeev kinetic model.

![Graph showing reduction degree profile of CuO/CeO\(_2\) catalysts using optimal kinetic results.](image)

**Figure 7.6.** Reduction degree profile of CuO/CeO\(_2\) catalysts using optimal kinetic results.

**Table 7.3.** Reaction rate at different cycles of reduction stages.

<table>
<thead>
<tr>
<th></th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 5</th>
<th>Cycle 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>(R^2)</td>
<td>0.9903</td>
<td>0.9908</td>
<td>0.9928</td>
<td>0.9922</td>
<td>0.9924</td>
</tr>
<tr>
<td>(k)</td>
<td>2.33</td>
<td>2.55</td>
<td>2.59</td>
<td>2.67</td>
<td>2.72</td>
</tr>
</tbody>
</table>
The oxidation analysis was conducted with same principle as the reduction stage. The mathematical models used for the reduction stage were also used for the oxidation stage. In this case, $R^2$ values varied from 0.5452 to 0.9948 at different cycles as shown in Table 7.4. After comparison, it can be concluded that 4$^{th}$ order of Avrami-Erofeev model fitted the oxidation reactions. Oxidation degree (OD) as a function of time was represented in Fig. 7.7. The stabilized experimental OD value was found at 96% for all of the cycles. However, the reaction rate was different at different cycles. It can be seen that oxidation reaction at first cycle occurred faster than rest of the cycles. At first cycle, 88% OD was achieved in 0.13 min, and then the reaction rate continuously decreased up to stabilized 96% OD at 0.24 min. For other cycles, it took 0.16 min to achieve 88% OD before stabilizing at 96% OD in 0.24 min. The mathematical reaction rate $k$ values retrieved from 4$^{th}$ order of Avrami-Erofeev or nucleation model were listed in Table 7.5. This model employed that during oxidation, Cu$^{2+}$ nucleation perhaps occurred on specific sites, such as grain boundaries or impurities and saturated rapidly. Due to unhindered growth of the nuclei, 3-dimensional growth can be assumed. A part of CeO$_{2-x}$ can also be oxidized to transform into CeO$_2$ during oxidation process. With compared to the reduction profile, it can be seen that reaction rates of oxidation reaction were much higher (~2.75 times) than those of reduction reaction, and this can happen due to unhindered 3-D growth Cu$^{2+}$ during oxidation reaction. However, this model failed to predict the timeline for oxidation of Cu$^0$ and CeO$_{2-x}$. 

203
Table 7.4. Overview of fitted data ($R^2$) for kinetic models at oxidation stages.

<table>
<thead>
<tr>
<th>Model</th>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 5</th>
<th>Cycle 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>M1</td>
<td>0.9442</td>
<td>0.8675</td>
<td>0.8755</td>
<td>0.8752</td>
<td>0.8734</td>
</tr>
<tr>
<td>M2</td>
<td>0.9169</td>
<td>0.8352</td>
<td>0.8341</td>
<td>0.8333</td>
<td>0.8312</td>
</tr>
<tr>
<td>M3</td>
<td>0.9538</td>
<td>0.8938</td>
<td>0.8928</td>
<td>0.9456</td>
<td>0.9466</td>
</tr>
<tr>
<td>M4</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M5</td>
<td>0.9386</td>
<td>0.8668</td>
<td>0.9318</td>
<td>0.9316</td>
<td>0.9306</td>
</tr>
<tr>
<td>M6</td>
<td>0.8581</td>
<td>0.8501</td>
<td>0.9233</td>
<td>0.9236</td>
<td>0.9225</td>
</tr>
<tr>
<td>M7</td>
<td>0.5452</td>
<td>0.6958</td>
<td>0.6949</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M8</td>
<td>n = 1.5</td>
<td>0.9758</td>
<td>0.9297</td>
<td>0.9273</td>
<td>0.9283</td>
</tr>
<tr>
<td></td>
<td>n = 2</td>
<td>0.9926</td>
<td>0.9700</td>
<td>0.9694</td>
<td>0.9693</td>
</tr>
<tr>
<td></td>
<td>n = 3</td>
<td>0.9705</td>
<td>0.9836</td>
<td>0.9734</td>
<td>0.9541</td>
</tr>
<tr>
<td></td>
<td>n = 4</td>
<td>0.9895</td>
<td>0.9932</td>
<td>0.9934</td>
<td>0.9943</td>
</tr>
<tr>
<td>M9</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>M10</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 7.5. Reaction rate at different cycles of oxidation stages.

<table>
<thead>
<tr>
<th>Cycle 1</th>
<th>Cycle 2</th>
<th>Cycle 3</th>
<th>Cycle 5</th>
<th>Cycle 10</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^2$</td>
<td>0.9895</td>
<td>0.9932</td>
<td>0.9934</td>
<td>0.9943</td>
</tr>
<tr>
<td>$k$</td>
<td>11.25</td>
<td>8.08</td>
<td>8.07</td>
<td>8.12</td>
</tr>
</tbody>
</table>
CeO$_2$ nanorods were successfully synthesized using hydrothermal method, and then CuO nanoparticles were incorporated on CeO$_2$ using thermal decomposition method. Solid state kinetic study of CuO/CeO$_2$ presented the effect of increasing the cycle number of reduction and oxidation reactions. Both reactions followed Avrami-Erofeev or nucleation model. Reduction reactions proceeded via $1.5^{th}$ order nucleation model in which possible random Cu$^0$ nucleation and growth occurred. On the other hand, oxidation reactions progressed likely via 3-dimensional growth of Cu$^{2+}$.

Figure 7.8. Oxidation degree profile of CuO/CeO$_2$ catalysts using optimal kinetic results.

7.4. Conclusion

CeO$_2$ nanorods were successfully synthesized using hydrothermal method, and then CuO nanoparticles were incorporated on CeO$_2$ using thermal decomposition method. Solid state kinetic study of CuO/CeO$_2$ presented the effect of increasing the cycle number of reduction and oxidation reactions. Both reactions followed Avrami-Erofeev or nucleation model. Reduction reactions proceeded via $1.5^{th}$ order nucleation model in which possible random Cu$^0$ nucleation and growth occurred. On the other hand, oxidation reactions progressed likely via 3-dimensional growth of Cu$^{2+}$.
7.5. References


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Chapter 8: Summary

This dissertation presented the information of CeO$_2$ nanorods and SiO$_2$ nanospheres supported CuO catalysts including their synthesis, structural characterization, and catalytic characterization. Reaction mechanism was also discussed in order to design catalysts with enhanced performance in future.

Chapter 3 described how synthesis of catalyst can have an effect on the catalytic activity of CeO$_2$ nanorods supported CuO catalysts. A series of CuO/CeO$_2$ catalysts were successfully prepared by using three different CuO impregnation methods. It illustrated that CuO/CeO$_2$ synthesized by using thermal decomposition method consumed the highest amount of H$_2$ at low temperatures (142 and 165 °C) and converted 100% CO into CO$_2$ at low temperature (220 °C) in comparison to other two catalysts and this happened due to the presence of strongly interacted dispersed CuO particles or Cu-Ce-O solid solution, resulting an increase in oxygen mobility in CeO$_2$ lattice.

Chapter 4 presented the effect of Cu amount on the catalytic activity of Cu-O-Ce solid solutions and CuO/CeO$_2$ nanorods catalysts. It concluded that the amount of Cu incorporation into CeO$_2$ lattice depends on the preparation methods of the catalysts and CeO$_2$ structure (shape and surface defects etc.). The different distribution and interactions of copper species with CeO$_2$ in these samples led to varied hydrogen consumption behaviors (temperature and amount). The TPR-TPO thermal cycling treatments suggested an increase of oxygen vacancy concentration and improved low temperature reducibility over the 10 wt% Cu impregnated in Cu-O-Ce samples after each cycle, which was further supported by the CO oxidation analysis.
Chapter 5 and chapter 6 discussed a comparison between reducible CeO$_2$ and non-reducible SiO$_2$ support for the application of CO oxidation and the effect of CeO$_2$-SiO$_2$ co-support on the catalytic activity. The CuO/CeO$_2$ nanorods exhibited a great enhancement in catalytic efficiency than the CuO/SiO$_2$ nanospheres. Incorporation of Cu ions in CeO$_2$ lattice promoted the lower reduction temperature as well as increasing the catalytic efficiency by increasing oxygen mobility via redox reaction at the catalyst-support interface. Increasing the oxidation temperature (from 400 to 600 °C) of CuO/CeO$_2$ decreased the catalytic activity by decreasing the amount of incorporation of Cu in CeO$_2$ lattice. Conversely, increasing oxidation temperature of CuO/SiO$_2$ increased the presence of threefold SiO$_3$ rings, and incorporation of Cu into these rings increased the catalytic efficiency. Mixing of these two oxide supports in 1:1 ratio and impregnation of 10 wt% CuO on CeO$_2$-SiO$_2$ composite eventually increased the catalytic efficiency because the presence of SiO$_2$ reduced the agglomeration of CeO$_2$ nanorods leading to an increase of oxygen availability by increasing CuO dispersion on both CeO$_2$ nanorods and the interface of SiO$_2$-CeO$_2$.

Chapter 7 illustrated solid state kinetic study of CuO/CeO$_2$ by increasing the cycle number of reduction and oxidation reactions in isothermal process. Both reactions followed Avrami-Erofeev or nucleation model. Reduction reactions proceeded via 1.5$^{th}$ order nucleation model in which possible random Cu$^0$ nucleation and growth occurred. On the other hand, oxidation reactions progressed likely via 3-dimensional growth of Cu$^{2+}$.

This work suggested that the preparation method of the catalysts could have an effect on the catalytic activity by changing the structure of catalyst and support, varying
dispersion amount of catalyst on the support, varying the interfacial structure, and varying the amount of defects in the support. For CeO$_2$ supported CuO catalysts, the formation of Cu-O-Ce solid solutions aided in lowering the reduction temperature by increasing the amount of oxygen vacancy in CeO$_2$ lattice. The oxygen vacancy in CeO$_2$ could also be increased by increasing the redox reaction cycles. For SiO$_2$ supported CuO catalysts, incorporation of Cu into SiO$_3$ rings of SiO$_2$ helped in lowering the reduction temperature. CeO$_2$ nanorods supported 10 wt% CuO catalysts, which was synthesized using thermal decomposition method and then oxidized at 400 °C, showed the best catalytic activity among all of the prepared catalysts for this project.

Although this dissertation enhances our understanding in CeO$_2$ and SiO$_2$ supported catalyst systems, an in-situ characterization of catalysts may give a better understanding in the structure effect of CeO$_2$ and SiO$_2$ on the catalytic activity. In the future, we will investigate the structural change in CeO$_2$ during CO oxidation in an in-situ technique (Raman spectroscopy or TEM). A model catalyst in which shape-controlled CuO impregnated on shape-controlled CeO$_2$ will be synthesized and characterized to conduct an in-depth analysis of reaction mechanism at CeO$_2$-CuO interface. The presence of threefold SiO$_3$ rings in SiO$_2$ supported catalysts and its effect on the catalytic activity will need more attention in future as this may turn non-active SiO$_2$ support into an active support like CeO$_2$. 