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I, Jiann-Horng Lin, hereby submit this original work as part of the requirements for the degree of Doctor of Philosophy in Chemical Engineering.

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Supported Copper, Nickel and Copper-Nickel Nanoparticle Catalysts for Low Temperature Water-Gas-Shift Reaction

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Supported Copper, Nickel and Copper-Nickel Nanoparticle

Catalysts for Low Temperature Water-Gas-Shift Reaction

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by

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ABSTRACT

Hydrogen is being considered worldwide as a future replacement for gasoline, diesel fuel, natural gas in both the transportation and non-transportation sectors. Hydrogen is a versatile energy carrier that can be produced from a variety of widely available primary energy sources, including coal, natural gas, biomass, solar, wind, and nuclear power. Coal, the most abundant fossil fuel on the planet, is being looked at as the possible future major source of H₂, due to the development of the integrated gasification combined cycle (IGCC) and integrated gasification fuel cell technologies (IGFC). The gasification of coal produces syngas consisting of predominately carbon monoxide and hydrogen with some remaining hydrocarbons, carbon dioxide and water. Then, the water-gas shift reaction is used to convert CO to CO₂ and additional hydrogen.

The present work describes the synthesis of model Cu, Ni and Cu-Ni catalysts prepared from metal colloids, and compares their behavior in the WGS reaction to that of traditional impregnation catalysts.

Initially, we systematically explored the performance of traditional Cu, Ni and Cu-Ni WGS catalysts made by impregnation methods. Various bimetallic Cu-Ni catalysts were prepared by supported impregnation and compared to monometallic Cu and Ni catalysts. The presence of Cu in bimetallic catalysts suppressed undesirable methanation side reaction,
while the Ni component was important for high WGS activity.

Colloidal Cu, Ni and Cu-Ni alloy nanoparticles obtained by chemical reduction were deposited onto alumina to prepare supported catalysts. The resulting Cu and Ni nanoparticle catalysts were found to be 2.5 times more active in the WGS reaction per unit mass of active metal as compared to catalysts prepared by the conventional impregnation technique. The powder XRD and HAADF-STEM provided evidence supporting the formation of Cu-Ni particles containing the Cu core and Cu-Ni alloy shell. The XPS data indicated surface segregation of Cu in the bimetallic Cu-Ni catalysts after reduction. The colloidal Cu5Ni5 alloy catalyst exhibited the WGS reaction rate that was higher than that observed over colloidal Cu and Ni catalysts indicating for the very first time a favorable bimetallic effect for the Cu-Ni system. The presence of Cu in these bimetallic catalysts induced favorable structural and electronic effects not only for enhancing the WGS activity, but also for suppressing methane yield.

Bimetallic Cu-Ni catalysts possessing a core-shell structure were synthesized that provided important insights into their structure-activity relationships in the WGS reaction. We employed a successive reduction route to synthesize Cu@Ni and Ni@Cu core-shell nanoparticles and deposited them onto alumina support to obtain supported bimetallic catalysts. The powder XRD patterns, CO chemisorption data, and UV-vis spectra indicated the formation of core-shell structures in the bimetallic Cu-Ni nanoparticles. Cu@Ni catalysts
showed similar WGS activities to supported Ni catalysts but lower methanation activity. Suppressed methanation activity observed for Cu@Ni nanoparticles may be due to Cu segregation to the surface. Supported Ni@Cu catalysts displayed WGS activity comparable to supported Cu catalysts.

Therefore, these findings strongly suggested that supported Cu, Ni and Cu-Ni alloy nanoparticle catalysts prepared from metal colloids are very promising as highly active WGS catalysts.
DEDICATION

With all my love, respect and admiration to my parents and parents in law:

HUI-HUA LIN
HSUEH-HUA HSU
TSANN-YU NI
PI-CHU TSENG

With love and thanks to my uncle and aunt:

MAOJUNG CHEN
CHUNTAO LIN

With sincere love to my wife and daughter:

SHU-TING NI
PATTIE LIN
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CHAPTER I

Introduction

1.1 Motivation

The fuel cell is becoming an increasingly attractive alternative to the rechargeable battery. When combined with the oxygen in the air, hydrogen produces an electric current which is able to power a vehicle engine. Instead of the exhaust gases from the internal combustion engine, the byproducts are heat and water. Fuel cells also have a high energy output and no noise pollution. For these reasons, hydrogen, like biofuels, can be considered as an energy vector, and thus, the core of an energy economy on its own.\(^1\)

Producing hydrogen directly from coal by gasification is much more efficient than burning coal to make electricity which is then used to make hydrogen. Low-cost hydrogen from coal will allow the United States 250-year supply of domestic coal to replace imported oil. The benefit of producing enough hydrogen in efficient coal-to-hydrogen technologies to power 100 million fuel cell vehicles will be a reduction of 3 million barrels per day of imported oil.\(^2\) Even without carbon sequestration, carbon dioxide emissions will be reduced by over 275 million tons per year, and nearly 540 million tons per year with sequestration. Coal gasification produces synthesis gas with a composition\(^3\) ranging from 30-45% H\(_2\), 35-55% CO, and 5-20% CO\(_2\) (on dry basis). If the H\(_2\)-to-CO ratio of the syngas from the gasifier is not appropriate for the synthesis of fuels or chemicals, the ratio can be adjusted
using the water gas shift (WGS) reaction which converts CO and H₂O to CO₂ and H₂. The reaction is also used to increase the concentration of hydrogen in the syngas, and, when combined with an appropriate separation technology, can produce high-purity hydrogen in high yields.

The design of WGS catalysts has been based on exploratory approaches yielding a very large number of compositions to be screened. Recently, much attention has been paid to developing theoretical models for the WGS reaction. A deeper understanding of the sequence of molecular events on the surface of the catalyst might eventually provide a more systematic and efficient theory-guided catalyst design.¹⁻⁶ For example, Schumacher et al.⁶ used a microkinetic model based on a redox mechanism to investigate the low-temperature WGS reactivity trends on transition metals, and suggested that Cu and Ni may be promising as superior catalytic components for WGS catalysts. Zeigarnik et al.⁵ proposed a theoretical approach, which included the generation of a complete set of elementary steps, the calculation of the activation energy using unity-bond index-quadratic exponential potential (UBI-QEP) method and the preexponential factor using transition state theory, along with kinetic simulations, for predicting comparative catalytic activities. Their approach also indicated that Cu and Ni may possess optimal activity in the WGS reaction. Callaghan et al.,⁴ using a systematic theoretical approach, namely Reaction Route Graph Analysis, also proposed that Cu and Ni are the most promising metal catalysts for the WGS reaction as
compared to other transition metals. Moreover, transition metal alloys often possess superior properties as compared to pure transition metals as the active components of heterogeneous catalysts.\[^7\] Through the combination of different metals their geometries and electronic structures can be varied over wide ranges that allow tuning their catalytic reactivities. Alloys of nickel with copper are receiving increased attention because these two metals form a solid solution.\[^8\] Ni-based catalysts containing Cu have already been found to have significantly different catalytic activity and selectivity as compared to monometallic Ni catalysts in many reactions, such as CO\(_2\) hydrogenation, hydrodechlorination of 1,1,2-trichloroethane, steam reforming reaction, and so on.\[^9\text{-}^{13}\] However, despite their promise, CuNi alloy catalysts have not been sufficiently investigated as low-temperature WGS catalysts.

The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal, the size of particles, the preparation method, and the support composition.\[^{14}\] Traditionally, supported nanoparticle catalysts for industrial applications are prepared by impregnation of metal salt solutions onto oxide support, followed by high temperature oxidation and reduction. Because such methods are inexpensive, they are widely used for various metals and supports. However, they provide limited control over particle size distribution, bimetallic composition in final catalysts, which represents a considerable drawback to achieving fundamental understanding of catalytic phenomena for these catalysts. Hence, an alternative method to obtain supported catalysts with well-defined metal particles
is the preparation of supported catalysts from metal colloids. This promising approach also permits facile control over different parameters of supported metal nanoparticle catalysts, such as the particle size distribution and loading.\textsuperscript{[15]} The influence of oxide supports on nanoparticle size is minimized because the nanoparticles are synthesized before they are immobilized on the oxide surface. Supported nanoparticles prepared by metal colloids already showed superior catalytic activities in many reactions as compared to those obtained via conventional impregnation methods.\textsuperscript{[16, 17]} Therefore, the development of well-defined supported Cu, Ni and bimetallic Cu-Ni catalysts made by metal colloidal routes and displaying desirable morphological, compositional and structural characteristics for the WGS reaction is the focus of this Ph.D. thesis.

1.2 Objectives

According to this research focus, the following specific research thrusts are pursued:

**Objective 1:** *Demonstrate the proof of concept for supported Cu-Ni alloys as superior catalysts for low temperature water gas shift reaction*

**Objective 2:** *Elucidate the role of nanoscale structure and composition of Cu, Ni, and Cu-Ni alloys on their activity and selectivity in water gas shift reaction*

Accordingly, the dissertation is divided into another five interrelated chapters focused on the synthesis and characterization of supported Cu, Ni and bimetallic Cu-Ni catalysts made by deposition of metal colloids.
In Chapter II, we provide a comprehensive literature review of previous studies of the WGS catalysts. Then, we discuss novel synthesis methods leading to well-defined, monodisperse nanoparticles with tunable structures, which provide fundamental understanding of catalyst structure – WGS reactivity relationships.

In Chapter III, we report the Cu, Ni and Cu-Ni catalysts supported on partially reducible ceria oxide support prepared by traditional impregnation methods and examine the effect of Cu/Ni ratio on the physicochemical characteristics and catalytic performance of these traditional catalysts.

In Chapter IV, we report the preparation of Cu, Ni and Cu-Ni alloy nanoparticles and their deposition on the alumina support. The comparison of catalytic activity for catalysts prepared from metal colloids and by conventional impregnation is also conducted in this chapter.

The fabrication of core-shell nanoparticles has developed in recent years into an increasingly important research area at the frontier of advanced materials chemistry. In Chapter V, the colloidal methods are applied to synthesize novel bimetallic CuNi catalysts possessing core-shell structure.

Finally, in Chapter VI, we summarize major findings of this Ph.D. thesis and on their basis provide suggestions for future research directions to develop the next generation of highly active and chemically resistant WGS catalysts.
1.3 References


CHAPTER II

Background and Objectives of Proposed Research

2.1 Hydrogen Economy

Hydrogen is being considered worldwide as a future replacement for gasoline, diesel fuel, natural gas in both the transportation and non-transportation sectors. Hydrogen is a versatile energy carrier that can be produced from a variety of widely available primary energy sources, including coal, natural gas, biomass, solar, wind, and nuclear power.\[^1\]

Hydrogen can be subsequently utilized at high conversion efficiency with essentially zero emissions. Many technologies are currently being developed for the production of hydrogen based on: (1) thermochemical reforming of hydrocarbons; (2) partial oxidation of fossil fuels; (3) gasification with hot coal-derived or petroleum derived coke to generate synthesis gas; (4) distillation of coal; (5) thermal cracking, pyrolysis or decomposition of hydrocarbons; (6) electrolysis of conductive water.\[^1\]\ Gasification-based systems are capable of utilizing all carbon-based feedstocks, including coal, petroleum coke, biomass. Gasification-based systems are the most efficient and environmentally friendly technologies for the production of low-cost electricity. Gasification-based process options are schematically shown in Figure 2.1.\[^1\]\ In these processes, carbon-based feedstocks are converted in the gasifier in the presence of steam and oxygen at high temperature and moderate pressure to synthesis gas, a mixture of carbon monoxide and hydrogen. Then, the water-gas shift reaction is used to
convert CO to CO\(_2\) and additional hydrogen.

![Gasification-based energy conversion options](image)

**Figure 2.1** Gasification-based energy conversion options\(^1\)

### 2.2 Water Gas Shift (WGS) Reaction and Its Applications

The WGS reaction is an important reaction for H\(_2\) production from syngas. In this heterogeneously catalyzed reaction, steam and CO react to produce H\(_2\) and CO\(_2\):

\[
\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H = -40.6 \text{kJ/mol} \tag{2.1}
\]

Traditional applications of the WGS reaction include H\(_2\) production for ammonia synthesis, hydrotreating of petroleum feedstocks, and coal processing.\(^2\) Recently, the WGS reaction has been incorporated in fuel processors for fuel cell application.\(^3\) The historical
background of the WGS reaction is described in a recent review article.\textsuperscript{[4]} The WGS reaction was for the first time reported in the literature at the end of the 19\textsuperscript{th} century. In 1913, the WGS reaction found industrial application in the production of synthesis gas, as a part of the Haber-Bosch process of ammonia manufacture.\textsuperscript{[4]} Industrially, the process of integration of the WGS reaction is dependent upon the origin of the syngas. By the beginning of 20\textsuperscript{th} century, the most common design was to carry out the reaction in a single stage employing Fe oxide based catalysts at 450-600°C. The next step in the evolution of the process was the introduction of a second-stage converter operating at 320-360°C using the same Fe catalyst. The two-stage converter system reduced the CO level to 3000-4000 ppm.\textsuperscript{[5]} With the discovery in the 1960s of Cu-based low-temperature shift (LTS) catalysts and improvements in high-temperature shift (HTS) Fe based shift catalysts, a CO content $< 0.5\%$ in the reformate stream was achieved.

The WGS process facilities are economically dependent on the feedstock used for syngas generation, both in terms of equipment and catalysts. Coal, the most abundant fossil fuel on the planet, is being looked at as the possible future major source of H\textsubscript{2}, due to the development of the integrated gasification combined cycle (IGCC) and integrated gasification fuel cell technologies (IGFC).\textsuperscript{[6]} The gasification of coal produces syngas consisting of predominately carbon monoxide and hydrogen with some remaining hydrocarbons, carbon dioxide and water. The syngas then can be used directly to produce electricity, or further
processed and purified to give pure hydrogen product for such end uses, as ammonia production, hydrocracking of petroleum, or as a fuel for fuel cells to power vehicles and for stationary electricity production. Typically, the raw gasifier syngas undergoes preliminary purification and is either utilized directly in a fuel cell or gas turbine or put through a WGS reactor to increase the hydrogen content. Following the WGS, H\textsubscript{2} can be purified and acid gases disposed by sequestration.

The concept of the fuel cell is that it directly produces electricity from chemical energy of fuels instead of combustion followed by raising steam, which drives a turbine to produce electricity. In the case of the proton exchange membrane (PEM) fuel cell, hydrogen is dissociated over a Pt catalyst at the anode into protons and electrons. The electrons proceed through an external circuit where the energy can be in the form of electricity and applied to a load. The protons diffuse through the PEM and arrive at the cathode where they combine with oxygen to form water. Thus, we find that only environmentally friendly byproducts, water and heat, are produced. However, the hydrogen from a reformer contains residual CO which acts as a poison for the Pt catalyst in fuel cells. The performance of the fuel cells depends on the quality of reformate stream that feeds to the fuel cell. Therefore, the two-stage water gas shift converter was applied to convert residual CO and water into CO\textsubscript{2} and additional usable hydrogen for the fuel cell.
2.3 Thermodynamic Considerations and WGS Reaction Mechanisms

The WGS reaction is an equilibrium-limited reaction, and CO conversion is favored at low temperatures due to its exothermicity. Equation 2.2 is widely reported in the literature to describe the WGS equilibrium constants as a function of temperature.\[^7\]

\[
K_p = \exp[(4577.8/T)-4.33] \tag{2.2}
\]

where T is in K. As the temperature increases, the equilibrium constant and the equilibrium CO conversion decrease. Hence, H\(_2\) production and CO consumption are favored at low reaction temperatures. However, the WGS reaction is controlled by the kinetics at low temperatures, which requires the use of highly active and stable WGS catalysts. The WGS reaction is traditionally conducted in two stage catalytic converters. The first stage is characterized by working at higher temperatures, favoring fast CO consumption and minimizing catalyst bed volume. In the second stage, the reaction takes place at a lower temperature in order to obtain higher conversions.

Because of the industrial significance of the WGS reaction, many researchers\[^8, 9\] have investigated the reaction mechanism and developed models to reflect the behavior of the reaction over common industrial catalysts (Cu- or Fe-based). Two main reaction mechanism have been proposed:\[^10, 11\] (1) the redox mechanism,\[^9, 10, 12-14\] (2) the associative mechanism.\[^8, 10, 15, 16\]

In the redox mechanism, CO adsorbs on the active metal surface which then diffuses at the metal-support interface and reacts with lattice oxygen of support to form CO\(_2\)(g). Water adsorbes and dissociates mainly on the support sites, thus re-oxidizing them and subsequently
producing H₂(g). In the associative mechanism, CO and H₂O were proposed to adsorb on catalytically active sites to form a carbon-containing intermediate, e.g., formate, carbonate, or bicarbonate, which further reacts or decomposes to form H₂ and CO₂. These two mechanisms are described in more detail below.

**Redox Mechanism**

Ovesen et al. has analyzed the microkinetics of the WGS reaction over three different Cu-based catalysts, Cu-ZnO-Al₂O₃, Cu-Al₂O₃, and Cu-SiO₂, under industrial conditions.⁹ Their model is based on the following surface redox mechanism:

S₁. H₂O + * ⇌ H₂O*

S₂. H₂O* + * → H* + OH*

S₃. 2OH* ⇌ H₂O* + O*

S₄. OH* + * → O* + H*

S₅. 2H* ⇌ H₂(g) + 2*

S₆. CO(g) + * ⇌ CO*

S₇. CO* + O* → CO₂* + *

S₈. CO₂* ⇌ CO₂(g) + *

where * represents a surface site and X* is an adsorbed species X. When this model was tested at 1 atm, a good agreement was found. The nature of the rate-limiting step was dependent on the composition of the feed gas mixture. It was found that reaction step S₂
above is rate-limiting in a gas with low \( \text{H}_2\text{O}/\text{CO} \) ratio, whereas reaction step S7 is rate-limiting in a gas with a high \( \text{H}_2\text{O}/\text{CO} \) ratio. Reaction step S4 was significant in a \( \text{CO}_2 + \text{H}_2 \) mixture. However, when this model was tested against the high pressure data, a deviation between calculated and experimental rates was found. Thus, it was necessary to include the synthesis and hydrogenation of formate to describe the kinetics of WGS reaction at high temperatures (S9 to S11 below):

\[
\begin{align*}
S9. \text{H}^\ast + \text{CO}_2^\ast & \rightleftharpoons \text{HCOO}^\ast + \ast \\
S10. \text{HCOO}^\ast + \text{H} & \rightleftharpoons \text{H}_2\text{COO}^\ast+ \ast \\
S11.\text{H}_2\text{COO}^\ast + 4\text{H}^\ast & \rightleftharpoons \text{CH}_3\text{OH}(g) + \text{H}_2\text{O}(g) + 5\ast
\end{align*}
\]

Kalamaras et al.\textsuperscript{[10]} investigated the kinetic and mechanistic aspects of the WGS reaction over a series of ceria-supported Pt catalysts. A combination of steady-state isotopic transient kinetic analysis (SSITKA), DRIFTS, and mass spectrometry experiments has been performed to probe the chemical structure of reaction intermediates. They found evidence that the WGS reaction over \( \text{Pt}/\text{CeO}_2 \) catalysts (\( d_{\text{Pt}} = 1.3-8.0 \) nm) at 300\(^\circ\)C occurs mainly through a redox mechanism.

**Associative Mechanism**

Campbell et al.\textsuperscript{[8]} explored the WGS reaction in terms of a formate mechanism:

\[
\begin{align*}
S6. \text{CO}(g) + \ast & \rightleftharpoons \text{CO}^\ast \\
S1. \text{H}_2\text{O} + \ast & \rightleftharpoons \text{H}_2\text{O}^\ast
\end{align*}
\]
S2. $\text{H}_2\text{O}^* + \ast \rightleftharpoons \text{H}^* + \text{OH}^*$

S12. $\text{CO}^* + \text{OH}^* \rightleftharpoons \text{HCOO}^* + \ast$

S13. $\text{HCOO}^* \rightleftharpoons \text{CO}_2 + \text{H}^*$

S5. $2\text{H}^* \rightleftharpoons \text{H}_2(\text{g}) + 2\ast$

Experimental investigation of the Cu surface suggested that CO and $\text{H}_2\text{O}$ coverages are very low under reaction conditions resulting in a rate that is nearly independent of the partial pressure of CO and a strong increase with the partial pressure of $\text{H}_2\text{O}$. This was explained by the inclusion of a hydroxyl intermediate formed from the surface dissociation of adsorbed water.

Chenu et al. investigated WGS reaction mechanism over Pt/MgO and Pt/ZrO$_2$ using \textit{in-situ} DRIFTS measurements and proposed surface formate as a WGS intermediate, which decomposes in the rate-limiting step.$^{[15]}$ Shido and Iwasawa also reported that surface formate was produced from CO and surface OH groups over a Rh/CeO$_2$ WGS catalyst.$^{[16]}$

2.4 Rational Design of WGS Catalysts

The catalyst design has been traditionally exploratory and more recently based on combinatorial screening of single, binary, and tertiary catalysts of varying compositions. A deeper understanding of the sequence of molecular events on the surface of the catalyst might eventually provide a more systematic and efficient theory-guided catalyst design. Because of the broad range of applications and the importance of the WGS reaction, a number of
theoretical studies\textsuperscript{[17-23]} have been conducted. Trends of the WGS activity for various transition metals have been studied by the estimation of the reaction rate with the use of a microkinetic model based on the redox mechanism where only two descriptors, binding energy of atomic oxygen and of CO, have been used to describe surface reactivity.\textsuperscript{[23]} The redox mechanism taken from Ovesen et al.\textsuperscript{[9]} was used as the basis of the kinetic model over all metal catalysts according to reaction steps S1-S9 shown above. The elementary reaction steps 2, 4, and 7 are assumed to be rate-limiting steps. The adsorption energies for the adsorbed species are calculated by the periodic, self-consistent density function theory (DFT) methods, whereas the activation energies are estimated from the Brønsted-Evans-Polanyi (BEP) relations. From the chemisorption energies on terraces published by Mavrikakis et al., the order of activity is predicted to be Cu > Ni > Pt > Rh > Ru > Au > Ir > Pd.

Zeigarnik et al.\textsuperscript{[22]} proposed a method for predicting catalytic activity and illustrated its use for the WGS reaction on a series of single crystalline surfaces. The method is mainly composed of three stages. In the first stage, a computer program generates complete lists of elementary steps and intermediate species. In the second stage, the activation energies and binding energies should be calculated for each elementary step by using the unity bond index-quadratic exponential potential (UBI-QEP) and the preexponential factor of the Arrhenius equation should be chosen or calculated. The activation energies of steps in the forward and reverse directions in WGS reaction are shown in Table 2.1. In the third stage, the
reaction kinetics should be simulated for any given condition. The following series of the catalytic activity is obtained for the crystal (111) face: Cu > Ni > Fe > Pt > Pd > Ag > Au.

Table 2.1 The activation energies (kcal/mol) of steps in the forward and reverse directions in WGS reaction

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<tbody>
<tr>
<td>$\text{H}_2\text{O}_g = \text{H}<em>2\text{O}</em>{\text{ads}}$</td>
<td>(XV)</td>
<td>13.5</td>
<td>0</td>
<td>9.6</td>
<td>0</td>
<td>19.0</td>
<td>0</td>
<td>15.3</td>
<td>0</td>
<td>14.9</td>
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<td>17.1</td>
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<td>19.0</td>
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<tr>
<td>$\text{CO}<em>g = \text{CO}</em>{\text{ads}}$</td>
<td>(XVI)</td>
<td>12.0</td>
<td>0</td>
<td>9.6</td>
<td>0</td>
<td>36.0</td>
<td>0</td>
<td>32.0</td>
<td>0</td>
<td>36.0</td>
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<td>0</td>
<td>36.0</td>
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<tr>
<td>$\text{CO}<em>2,</em>{\text{ads}} = \text{CO}<em>{2,</em>{\text{ads}}}$</td>
<td>(XVII)</td>
<td>5.3</td>
<td>0</td>
<td>3.2</td>
<td>0</td>
<td>6.5</td>
<td>0</td>
<td>3.6</td>
<td>0</td>
<td>7.7</td>
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<td>$\text{H}<em>2,</em>{\text{ads}} + \text{H}_{\text{ads}}$</td>
<td>(I)</td>
<td>15.3</td>
<td>15.4</td>
<td>11.0</td>
<td>19.4</td>
<td>3.6</td>
<td>8.2</td>
<td>23.3</td>
<td>8.8</td>
<td>22.2</td>
<td>9.5</td>
<td>21.0</td>
<td>6.2</td>
<td>26.8</td>
<td></td>
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<tr>
<td>$\text{H}<em>2,</em>{\text{ads}}$</td>
<td>(XVIII)</td>
<td>5.4</td>
<td>0</td>
<td>4.7</td>
<td>0</td>
<td>6.8</td>
<td>0</td>
<td>6.6</td>
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<td>0</td>
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</tbody>
</table>

Callaghan et al.\cite{21} recently developed a new theoretical tool, namely Reaction Route (RR) Graph analysis, to gain unprecedented insights into molecular mechanisms and reaction pathways on a catalytic surface by rigorously analyzing network chemistry. The RR analysis
was subsequently simplified and reduced to a network involving only 3 dominant RRs. The schematic of the RRs of the WGS reaction are shown in Figure 2.2. The associative formate route is dominant at temperatures < 550K, while the modified redox mechanism dominates at higher temperatures. The modified redox mechanism differs only by one elementary reaction from the conventional redox mechanism (step S1-S8). In the conventional redox mechanism, the dissociation of OH* and the production of H2* occurs in separate steps, namely

\[ S4. \quad \text{OH}^* + * \rightleftharpoons \text{O}^* + \text{H}^* \]
\[ S5. \quad 2\text{H}^* \rightleftharpoons \text{H}_2(\text{g}) + 2* \]

On the other hand, in the modified redox mechanism, the production of both takes place in a single step

\[ S14. \quad \text{OH}^* + \text{H}^* \rightleftharpoons \text{O}^* + \text{H}_2^* \]

Callaghan et al. compared the energetics of these elementary reactions and found that the pathway involving S14 was more favorable. The rate-limiting step for the associative formate mechanism is the formation of adsorbed HCOO species from adsorbed CO and OH species. The rate-limiting step for the modified redox pathway is formation of adsorbed CO2 from adsorbed CO and O species. The activity trend observed from simulations suggested that Cu > Ni > Fe > Ru > Rh > Pd > Pt > Ag, Au as shown in Figure 2.3. The above theoretical studies confirmed Cu, Ni, Fe, Pt, and Au to be highly promising catalytic metals for the WGS catalysts. Therefore, a brief description of these catalytic systems is provided below.
Figure 2.3 Schematic of the RRs of the WGS reaction.\textsuperscript{[21]}

Figure 2.3 Trends in the transition metal catalysts tested for a given set of input conditions, i.e catalyst properties and feed conditions: catalyst loading 0.14 g/cm$^3$; total flow rate of 236 (STP) min$^{-1}$; residence time $\tau = 1.8$ s; feed composition of H$_2$O (10%), CO (10%) and N$_2$ (balance).\textsuperscript{[21]}
2.5 Current WGS Catalysts

2.5.1 Cu-based catalysts

Cu-based catalysts, especially Cu/ZnO-based catalysts, have been widely used in many industrial chemical processes, such as the WGS reaction, methanol steam reforming and so on.[7, 24] Saito et al. considered the effect of pretreatment, such as calcination and reduction temperatures, to optimize the WGS activity of Cu/ZnO-based catalysts.[25] They found that progressive crystallization of constituents in Cu/ZnO-based catalysts with calcination temperature led to a decrease in surface area. The activity of the Cu/ZnO/ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst for the WGS reaction was less affected by heat treatments. Accordingly, the Cu/ZnO/ZrO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} catalyst is considered to be more suitable for a practical use in the WGS reaction.

Other researchers also investigated various kinds of metal dopants in the Cu-based catalysts.[26, 27] Kam et al. demonstrated that the La addition to Cu/ZnO-based catalysts decreased the apparent activation energy and improved the WGS activity.[26] Nishida et al. studied the catalytic behavior of Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} doped by noble metals, i.e., Pt, Rh or Ru. Among the noble metals tested, Pt was the most effective for improving both the activity and stability. They concluded that trace amounts of Pt enhanced both the intrinsic activity and stability of these catalysts by accelerating the Cu\textsuperscript{0}/Cu\textsuperscript{+} redox kinetics as well as suppressing the oxidative sintering of active Cu metal species by hydrogen spillover from Pt metal to Cu metal particles.[27] Various solution-based techniques have been used for the preparation of
supported Cu catalysts. Shishido et al.\textsuperscript{[28]} synthesized Cu/ZnO-based catalysts by homogeneous precipitation (hp) and coprecipitation (cp). The Cu-based catalysts prepared by homogeneous precipitation were characterized by highly dispersed Cu metal particles as well as strong metal-support interactions resulting in high and stable activity. Chen et al. used atomic layer epitaxy (ALE) to prepare Cu nanoparticles with a 2.4 nm average diameter on a silica support. They demonstrated that ALE-Cu catalysts showed significantly higher WGS activity as compared to those prepared by traditional impregnation methods. Therefore, if properly developed, nanoscale Cu catalysts could be much more economical and may even be able to replace conventional Cu-based WGS catalysts.\textsuperscript{[29]}

Cerium oxide has been identified as a potentially important catalytic support for the hydrogen production from syngas due to its ability to undergo rapid reduction/oxidation cycles.\textsuperscript{[14, 30-32]} The high activity of ceria in redox reactions can be related to its ability to exist in different oxidation states (+3 and +4). Cu-ceria WGS catalysts have been developed as potentially better alternatives to the pyrophoric Cu/ZnO-based catalysts. Li et al.\textsuperscript{[14]} reported that Cu on Ce(La)Ox catalysts prepared by urea precipitation-gelation displayed good WGS activity at high space velocity when tested under low CO concentration. Pradhan et al. investigated three Cu catalysts supported on ceria, ceria-zirconia, and ceria-titania.\textsuperscript{[33]} They found that CuO-CeO$_2$-ZrO$_2$ showed highest activity among these three catalysts, stressing the importance of oxide support. Furthermore, Yahiro et al. studied Cu/ZnO catalysts supported
on several high surface area oxides (Al₂O₃, MgO, SiO₂-Al₂O₃, SiO₂-MgO, β-zeolite, and CeO₂) in the WGS reaction. Among these supports, Cu/ZnO catalysts supported on Al₂O₃, MgO, and CeO₂ were found to be more active than on other supports. They suggested the support reducibility is one of the important factors controlling the catalytic activity in the WGS reaction.

2.5.2 Iron-based catalysts

Fe-Cr oxide catalysts have been used industrially in the WGS reaction at high temperatures (320-480°C). These catalysts demonstrated high WGS activity and excellent thermal stability, probably because the Cr component functions as a structural stabilizer and promoter. To further improve the catalytic performance of Fe oxide catalysts, researchers have examined other promoters including Rh, Pt, Pd, Ag, Zn, Cu, Ni, Co, Pb, and Ba. Andreev et al. investigated the effect of CuO, CoO and ZnO on the WGS activities. They demonstrated that the CuO-doped Fe₃O₄/Cr₂O₃ catalysts had the highest activity. Lei et al. compared several Fe₃O₄/Cr₂O₃ catalysts promoted with precious metals (Pt, Pd, Rh) and transition metals (Cu, Ni) and found that Rh was the most active promoter for the Fe-Cr oxide catalysts (Figure 2.4).
The commonly used Fe-Cr catalysts contain ca. 2 wt. % of highly toxic Cr\textsuperscript{6+} during its manufacture and deposition.\cite{35} Thus, there have been efforts to replace Cr in these catalysts with other less toxic components while maintaining the activity, selectivity and stability of the Fe-based WGS catalysts.\cite{42-46} Cr-free HTS catalysts containing Ca, Ce, Zr were first claimed by Chinchen.\cite{46} However, they suffered from low catalytic activities. Ladebeck et al. studied the combinations of Al\textsubscript{2}O\textsubscript{3}/ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}/MnO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}/La\textsubscript{2}O\textsubscript{3}, and Al\textsubscript{2}O\textsubscript{3}/CeO\textsubscript{2} to replace Cr\textsubscript{2}O\textsubscript{3}. The highest activity and sufficient thermal resistance were found for the Fe catalyst containing Al\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}.\cite{42} de Araújo et al. investigated the WGS activity of the catalyst where Cr was replaced by aluminum and a small amount of copper.\cite{44} The catalyst had similar catalytic activities as compared to the commercial Cr-containing catalyst. Additionally, promotional effects of Al and Cu were also examined.\cite{36} Al was found to help
prevent sintering, minimize surface area loss and suppress over-reduction of hematite. Cu contributes significantly to the activity enhancement as a structural promoter. The extent of Cu promotional effect is largely dependent on preparation method, i.e., on the manner in which Cu dopes the iron oxide structure. Thus, Zhang et al. investigated the influence of preparation methods on catalytic activity.\cite{36} Catalysts prepared by a sol-gel technique were found to be more active as compared to those prepared by one-step precipitation and two-step precipitation-impregnation techniques. Cu was distributed more uniformly in the iron oxide structure using a sol-gel method, which not only prevented Cu sintering at high temperature, but also ensured efficient electron transfer properties of Cu.

2.5.3 Nickel-based catalysts

Ni-based catalysts have been recognized as alternative catalysts for the WGS reaction.\cite{14, 30, 47} Kim et al. used Ni catalysts in a one-stage instead of the usual two-stage WGS process.\cite{48} Chu et al. observed that the Ni/CeO\textsubscript{2} catalysts had a higher activity in the WGS reaction than the Fe/CeO\textsubscript{2} catalysts.\cite{47} Ni catalysts appear to be more suitable for the HTS than LTS WGS process. Li et al. investigated the use of ceria-lanthanum supported catalysts in the WGS reaction. They found that the Ni-Ce(La)O\textsubscript{x} catalysts were greatly superior to Ni supported on binary oxide supports. It was also observed that, at around 350°C, the activity of the Ni catalyst surpassed the activity of the Cu catalyst.\cite{14} Haryanto et al. investigated Ni supported on different supports, such as Al\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}, CeO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3}, CeZrO\textsubscript{4},
and CeO$_2$-Gd. They concluded that CeO$_2$-Al$_2$O$_3$ supported Ni catalysts demonstrated the best performance.$^{[47]}$ However, the methanation side reaction observed over the Ni catalysts which consumes hydrogen is a serious drawback for a WGS catalyst. Hwang et al. developed effective medium-temperature shift Ni catalysts modified by potassium to suppress the methanation side reaction. The potassium-modified Ni was both more active and selective in the WGS reaction. The suppression of methanation side reaction over the K-modified Ni is attributed to the effect of K on increasing the density of the active hydroxyl groups that take part in the WGS reaction.$^{[49]}$  

### 2.5.4 Platinum-based catalysts

Conventional Cu- and Fe-based catalysts used in large-scale WGS reactors are unsuitable for mobile fuel processors due to their relatively low reactivity (based on total volume).$^{[50]}$ Furthermore, conventional Cu and Fe WGS catalysts require activation by $in-situ$ reduction and can lose activity upon exposure to air. Finally, they suffer from transportation issues related to their pyrophoric nature ultimately leading to decomposition. Precious catalysts have been proposed as alternatives to increase tolerance to temperature excursions and reduce the size of shift reactors.

Several research groups have reported that ceria-supported Pt catalysts are more active than the alumina-supported ones.$^{[51, 52]}$ Recently, Panagiotopoulou and Kondarides have investigated the effect of support on the catalytic performance of noble metal catalysts
in the WGS reaction. They concluded that for all metal-support combinations investigated, Pt was much more active than Rh, Ru and Pd. The turnover frequency (TOF) of CO conversion did not depend on metal loading, dispersion or crystallite size but depends strongly on the nature of the metal oxide support. The WGS activity of Pt and Ru catalysts was 1-2 orders of magnitude higher when supported on reducible (TiO$_2$, CeO$_2$, La$_2$O$_3$ and YSZ) rather than on irreducible (Al$_2$O$_3$, MgO and SiO$_2$) supports.$^{[53]}$ Furthermore, they also investigated the WGS activity of Pt supported on Me-doped ceria catalysts (Me = Ca, La, Mg, Zn, Zr, Yb, Y, Gd) prepared by urea-nitrate combustion method. They found that the WGS activity of Pt/Ce-MeO catalysts depended on the nature of the dopant employed, varying in the order of Yb > Gd > Zr > Mg > La > CeO$_2$ (undoped) > Ca > Y > Zn. Dopant cations incorporated into the ceria lattice affected the reducibility and oxygen ion mobility of the CeO$_2$ support, and thus, the WGS activity.

Jacobs et al. investigated the mechanism of WGS reaction on Pt-ceria catalysts. The partial reduction of ceria by Pt is necessary for the generation of bridging OH groups on the surface of ceria. In addition, Pt is involved in accelerating the decomposition of surface formates, the proposed rate-limitation step of the reaction mechanism.$^{[54]}$

Liu et al. investigated deactivation of Pt/CeO$_2$ under WGS shutdown and re-startup process conditions. They showed that carbonates form on the catalyst surface during shutdown in reformate stream leading to deactivation. The carbonates originating from both
CO and CO₂ covered the surface of CeO₂ and Pt and affected their electronic properties. Pt metal sintering was not found to be a factor contributing to the catalyst deactivation under shutdown and re-startup conditions (at low temperature in reformate). Hilaire et al. investigated precious metal supported on ceria and claimed that the over-reduction of ceria and surface carbonate species may be responsible for the low WGS rate. Zalc et al. provided evidence that first-order deactivation of the Pt/CeO₂ catalyst is due to over-reduction of ceria. Therefore, alternatives to Pt are desirable in order to overcome these challenges and reduce high cost associated with Pt-based catalysts.

2.5.5 Gold-based catalysts

Gold-based catalysts have received great attention since Haruta et al. discovered that gold exhibits surprisingly high catalytic activity for CO oxidation at temperatures as low as 200K when it is deposited as nanoparticles on metal oxides. The literature on the fine gold particles supported on reducible oxides has focused on the gold particle size and oxidation states. Bulk gold is chemically inert and known to possess poor catalytic activity. However, when gold nanoparticle size is below 10 nm, it is surprisingly active in a number of reactions, such as CO oxidation and propylene epoxidation. The average size of gold nanoparticles and their interactions with the metal oxide support depend critically on the choice of the synthesis technique used. Haruta et al. have shown that incipient wetness impregnation is unsuitable to produce highly dispersed gold catalysts due to weak
interactions between gold and metal oxide support.\textsuperscript{[57, 61]} They have developed four techniques, i.e., co-precipitation, co-sputtering, deposition-precipitation and gas-phase grafting, that allow to deposit gold nanoparticles on certain metal oxides. The preparation technique strongly influenced the catalytic activity due to large differences in gold particles size and to the availability of active gold sites. The small gold nanoparticles (~1 nm) were more active in the WGS reaction than large gold particles (~15 nm).\textsuperscript{[60]}

Sakurai et al. investigated the Au/CeO\(_2\) catalysts prepared by the deposition-precipitation method and compared their WGS activity with that of Pt/CeO\(_2\), Au/TiO\(_2\), and Cu/ZnO/Al\(_2\)O\(_3\). Au/CeO\(_2\) was found to be the most active at 373 and 523 K. Based on the transient experiments consisting of injecting CO and H\(_2\)O pulse into H\(_2\) and He streams, the interface between small Au particles and a reduced cerium oxide have been identified as important for the WGS reaction.\textsuperscript{[58]}

Andreeva et al. investigated Au catalysts prepared by co-precipitation (CP) and mechanochemical activation (MA) and supported on ceria modified by rare earth metals (La, Sm, Gd, Yb, Y).\textsuperscript{[62]} They found that the WGS activity of the catalysts made by MA was higher than that of CP catalysts. The Au catalysts based on ceria doped by Yb and Sm exhibited the highest activity.\textsuperscript{[62]}

Fu et al. investigated the effect of gold-ceria interaction on WGS activity.\textsuperscript{[59, 63]} Metallic Au nanoparticles as well as ionic Au were found in gold-ceria catalysts. The leached
catalysts prepared by leaching of original gold-ceria catalysts were free of metallic gold and contained Au in the oxidized form. Thus, the leached catalysts contained only a small fraction of the original amount of Au in the form of cations, bound in the ceria lattice as Au-O-Ce species. The leached and original gold-ceria catalysts were found to possess similar rates of CO₂ production. This indicated that nonmetallic Au-O-Ce species appear to be responsible for the WGS activity. Furthermore, the number of active sites was found to correlate with the properties of the support oxide, namely the ceria surface area and crystallite size. For the Au-ceria catalysts prepared by deposition-precipitation, the smaller the crystallite size of ceria, the larger the amount of gold retained after leaching. Because Au cations are stabilized in the ceria matrix through strong interaction with the Ce-O species, gold-ceria catalysts are stable under low-temperature WGS reaction conditions for at least 12 h. However, a stability problem due to cerium oxide-hydroxycarbonate formation has been identified in the shutdown operation.

Metal oxide-supported Au and Pt catalysts have been reviewed by Burch. An attempt was made by Burch to compare the intrinsic activity of Pt and Au catalysts under a wide range of experimental conditions used to determine the WGS reaction kinetics. Table 2.2 shows a considerable variation in the reported activity of Au and Pt catalysts. Clearly, it is premature to make definitive statements about the relative activities of gold and platinum catalysts for the water-gas shift reaction. However, in parallel experiments employing a series
of Au and Pt catalysts on the optimal ceria support, it was established that Au catalysts are significantly more active than corresponding Pt catalysts. Overall, the differences in preparation methods may be the critical factor and it seems that a well-prepared Au catalyst can be significantly more active than a well-prepared Pt catalyst.

Burch also considered the stability of Au catalysts by reviewing the results of several reported studies and suggested that deactivation may take place according to several mechanisms operating simultaneously.\cite{56, 59, 65-67} At higher temperatures, sintering of the support and Au could be important to cause the irreversible loss of the required intimate contact between the small Au clusters and the ceria surface. At intermediate temperatures, the strong adsorption of CO$_2$ results in surface carbonates that may block the active sites and lead to deactivation. At low temperatures in a wet CO$_2$-containing atmosphere, some irreversible loss of surface area of the support could account for the irreversible loss of activity observed in shutdown simulation experiments.

**Table 2.2 Kinetics of the water-gas-shift reaction on supported Au and Pt catalysts**\cite{64}

<table>
<thead>
<tr>
<th>Catalyst composition</th>
<th>Method of preparation</th>
<th>Pre-treatment</th>
<th>Gas mixture</th>
<th>T $^\circ$C</th>
<th>Rate cm$^3$ g$^{-1}$ h$^{-1}$</th>
<th>Rate at 200$^\circ$C cm$^3$ g$^{-1}$ h$^{-1}$</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.75Au/CeO$_2$</td>
<td>Deposition precipitation</td>
<td>Calcined 400$^\circ$C</td>
<td>2%CO; 10.7%H$_2$O</td>
<td>200</td>
<td>296</td>
<td>296</td>
<td>\cite{68}</td>
</tr>
<tr>
<td>2Au/CeO$_2$</td>
<td>Deposition precipitation (HAuCl$_4$)</td>
<td>105$^\circ$C for 16h</td>
<td>2%CO; 2.5%CO$_2$; 7.5%H$_2$O; 8.1%H$_2$</td>
<td>250</td>
<td>48</td>
<td>15</td>
<td>\cite{69}</td>
</tr>
<tr>
<td>2Au/CeZrO$_4$</td>
<td>Deposition precipitation (HAuCl$_4$)</td>
<td>105$^\circ$C for 16h</td>
<td>2%CO; 2.5%CO$_2$; 7.5%H$_2$O; 8.1%H$_2$</td>
<td>175</td>
<td>720</td>
<td>1402</td>
<td>\cite{69}</td>
</tr>
<tr>
<td>2Pt/CeO$_2$</td>
<td>Impregnation</td>
<td></td>
<td>2%CO; 2.5%CO$_2$;</td>
<td>250</td>
<td>80</td>
<td>10</td>
<td>\cite{69}</td>
</tr>
<tr>
<td>Catalyst</td>
<td>Method</td>
<td>Description</td>
<td>Reaction Conditions</td>
<td>Results</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>---------------------------</td>
<td>------------------------------------------------------------------------------</td>
<td>--------------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Au/CeO₂</td>
<td>Vapor phase grafting</td>
<td>(dimethyl acetylacetone) Au(III)</td>
<td>Calcined 250°C in O₂; reduced in H₂ at 175°C</td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Au/CeO₂</td>
<td>Vapor phase grafting</td>
<td>(dimethyl acetylacetone) Au(III)</td>
<td>Calcined 250°C in O₂; reduced in H₂ at 175°C</td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Pt/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Pt/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Au/CeO₂</td>
<td>Deposition precipitation</td>
<td></td>
<td>Vacuum dried for 6h; 4% H₂ for 4h</td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.7Au/CeO₂</td>
<td>Various precipitation</td>
<td>(modified)</td>
<td>Calcined 400°C</td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Au/CeO₂</td>
<td>Vapor phase grafting</td>
<td>(dimethyl acetylacetone) Au(III)</td>
<td>Calcined 250°C in O₂; reduced in H₂ at 175°C</td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5Au/CeO₂</td>
<td>Deposition precipitation</td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4Au/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Pt/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4Au/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.5Pt/CeO₂</td>
<td></td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Au/Fe₂O₃</td>
<td>Deposition precipitation</td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3Au/Fe₂O₃</td>
<td>Co-precipitation</td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Au/CeO₂</td>
<td>Co-precipitation</td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1Au/CeO₂</td>
<td>Co-precipitation</td>
<td></td>
<td></td>
<td>1.57%CO; 52.4%H₂O; 41.9%H₂; 7.5%H₂O; 8.1%H₂</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^70]: [70]
[^71]: [71]
[^72]: [72]
[^73]: [73]
[^74]: [74]
[^75]: [75]
[^76]: [76]
<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Method</th>
<th>Calcination Temp (°C)</th>
<th>Calcination Time</th>
<th>CO (%)</th>
<th>H₂O (%)</th>
<th>Rate of CO (mL/min)</th>
<th>Rate of H₂O (mL/min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1Pt/CeO₂</td>
<td>Co-precipitation</td>
<td>500 for 5 h</td>
<td></td>
<td>4%</td>
<td>2.6%</td>
<td>250</td>
<td>72</td>
<td>9 [76]</td>
</tr>
<tr>
<td>2.5Au/ZrO₂</td>
<td>Deposition precipitation</td>
<td>400 for 2 h</td>
<td></td>
<td>4.49%</td>
<td>30.8%</td>
<td>200</td>
<td>6</td>
<td>6 [77]</td>
</tr>
<tr>
<td>5Au/ZrO₂</td>
<td>Deposition precipitation</td>
<td>400 for 2 h</td>
<td></td>
<td>4.49%</td>
<td>30.8%</td>
<td>200</td>
<td>16</td>
<td>16 [77]</td>
</tr>
<tr>
<td>2Au/ThO₂</td>
<td>Deposition precipitation</td>
<td>400 for 2 h</td>
<td></td>
<td>4.42%</td>
<td>30.8%</td>
<td>200</td>
<td>18</td>
<td>18 [78]</td>
</tr>
<tr>
<td>4.4Au/CeO₂ (leached)</td>
<td>Deposition precipitation</td>
<td>400 for 10 h</td>
<td></td>
<td>11%</td>
<td>7%</td>
<td>250</td>
<td>386</td>
<td>123 [32]</td>
</tr>
<tr>
<td>Standard Cu catalyst</td>
<td>Deposition precipitation</td>
<td>400</td>
<td></td>
<td>11%</td>
<td>7%</td>
<td>250</td>
<td>4000</td>
<td>[32]</td>
</tr>
<tr>
<td>4.5Au/CeO₂</td>
<td>Various precipitation</td>
<td>400 °C</td>
<td></td>
<td>2%</td>
<td>11%</td>
<td>200</td>
<td>832</td>
<td>832 [66]</td>
</tr>
<tr>
<td>Au/TiO₂</td>
<td>Deposition precipitation</td>
<td>400 °C</td>
<td></td>
<td>4.4%</td>
<td>30%</td>
<td>200</td>
<td>117</td>
<td>117 [75]</td>
</tr>
<tr>
<td>5Au/TiO₂</td>
<td>Deposition precipitation</td>
<td>Not specified</td>
<td></td>
<td>4.5%</td>
<td>31%</td>
<td>200</td>
<td>94</td>
<td>94 [65]</td>
</tr>
<tr>
<td>1Au/TiO₂</td>
<td></td>
<td></td>
<td></td>
<td>4.5%</td>
<td>31%</td>
<td>200</td>
<td>86</td>
<td>86 [65]</td>
</tr>
<tr>
<td>3Au/TiO₂</td>
<td></td>
<td></td>
<td></td>
<td>4.5%</td>
<td>31%</td>
<td>200</td>
<td>45</td>
<td>45 [65]</td>
</tr>
<tr>
<td>Au/Fe₂O₃</td>
<td>Various precipitation</td>
<td>400 °C for 2h</td>
<td></td>
<td>5.68%</td>
<td>33%</td>
<td>200</td>
<td>125</td>
<td>125 [79]</td>
</tr>
<tr>
<td>5Au/TiO₂</td>
<td>Deposition precipitation</td>
<td>400 °C</td>
<td></td>
<td>1%</td>
<td>2%</td>
<td>100</td>
<td>11.3</td>
<td>244 [80]</td>
</tr>
<tr>
<td>2Au/Fe₂O₃</td>
<td>Co-precipitation</td>
<td>400 °C for 2h</td>
<td></td>
<td>4.88%</td>
<td>33%</td>
<td>200</td>
<td>160</td>
<td>160 [81]</td>
</tr>
</tbody>
</table>

Note: The rate calculated at 200°C assumes activation energies of 47 kJ mol⁻¹ for all the supported gold catalysts (after 24) and 86 kJ mol⁻¹ for all the supported Pt catalysts (after 64).

### 2.6 Metal Nanoparticles as Water-Gas-Shift Catalysts

The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal, the size of metallic particles, the preparation method, and the support composition. Recent advances in nanoparticle preparation techniques [82-85] offer new opportunities for the preparation of well-defined and well-dispersed supported catalysts. In this process, surface-protected mono- or bimetallic nanoparticles are prepared in solution,
deposited onto a support, and the colloid stabilizers are removed yielding well-dispersed supported nanoparticles. Recent studies also showed that supported catalysts prepared by this colloid method were more active in several reactions than those made by conventional impregnation methods.\(^{86-89}\) Although nanoscale nature of WGS catalysts is of great importance according to previous studies, it has not been explored systematically and is poorly understood at present time. Therefore, the topic of nanoparticle synthesis is reviewed next due to its importance to the focus of this Ph.D. thesis.

### 2.6.1 Metal nanoparticles

Metal nanoparticles have a large surface area-to-volume ratio as compared to bulk phases, making them attractive candidates for catalytic applications. Their main features also include a unique transition between molecular to metallic states (density of states), a short-range ordering and increased number of kinks, corners, and edges.\(^{83, 90}\) Thus, it is not surprising that the number of publications dealing with metal nanoparticles has increased almost exponentially over the last decade (Figure 2.5). A significant amount of research with the expressed aim of inhibiting aggregation and producing highly active nanoparticles of uniform size has been published.\(^{82, 84, 85, 91}\) The control of size, shape and dispersity of nanoparticles is key to enhanced selectivity and activity. Recent advances\(^{83, 85, 90, 91}\) in controlling the particle size and shape have opened possibility to optimize the geometry of nanoparticles for enhanced activity, providing the optimum size and surface properties for
specific reactions. Changes in properties at the nano level occur by different mechanisms for
different materials. As bulk metal transitions in size to decreasingly small metal nanoparticles,
the energy continuum of the bulk metal changes to produce increasingly more discrete energy
level structure (Figure 2.6). Furthermore, these features may be enhanced, modified or
suppressed in the case of bimetallic and multi-metallic nanoparticles, because of
inter-metallic interactions arising from their constitutional and morphological combinations.
Totally new functions may be created by overcoming disadvantages of single component
nanoparticles. Unique features expected for multi-metallic nanoparticles may include: (1)
physical and chemical interactions among different atoms and phases that lead to novel
functions; (2) altered miscibility and interactions unique to nanometer dimensions; and (3)
morphological variations that are related to new properties.\textsuperscript{92} The possible morphologies of
bimetallic nanoparticles are summarized in Figure 2.7.\textsuperscript{92} In turn, the unique properties of
supported metal nanoparticles are directly related to specific particle morphology (size and
shape), metal dispersion, concentration and the electronic properties of the metal within their
host environment.\textsuperscript{83} Supported metal nanoparticles play an important role in catalysis, as
they have been extensively employed in many industrial processes.\textsuperscript{93}
Figure 2.5 The growth in the number of publications dealing with metal nanoparticles (1997-2010). Source: SciFinder Scholar.

Figure 2.6 Relationships between nanoparticle size, energy, and the principle of energy states. Stabilization and control of nanoparticle size can be achieved by selecting a nanoporous support potentially leading to enhanced catalytic activity.\textsuperscript{[90]}
2.6.2 Nanoparticle synthesis:

Dispersions of metallic nanoparticles can be obtained by two main methods (Figure 2.8): (1) mechanic subdivision of metallic aggregates (physical or top-down method) or (2) nucleation and growth of metallic atoms (chemical or bottom-up method).\cite{84}

2.6.2.1 Physical methods

Physical methods yield dispersions where the particle size distribution is very broad. Traditional colloids are typically larger (> 10 nm) and not reproducibly prepared giving irreproducible catalytic activity.\cite{94}

2.6.2.2 Chemical reduction

The chemical reduction of transition metal salts in the presence of stabilizing agents to generate zero-valent metal colloids in aqueous or organic media was first published in 1857 by Faraday.\cite{85, 95} His approach has become one of the most common and powerful
The reduction of oxidized metallic species leading to neutral atoms, the building blocks of metal particles, is the result of redox reactions in which electrons from a reducing agent are transferred to the metal according to the following schematic chemical equation:

$$mMe^{n+} + n\text{Red} \rightarrow mMe^0 + n\text{Ox}$$  \hspace{1cm} (2.3)

The driving force of the reaction is the difference between the redox potentials of the two half-cell reactions, $\Delta E$. The magnitude of $\Delta E$ determines the value of the equilibrium constant of the reaction, $K_e$, according to the relationship:

$$\ln K_e = nF \frac{\Delta E}{RT}$$  \hspace{1cm} (2.4)

where $F$, $R$ and $T$ have the usual meanings.

The reduction reaction is thermodynamically possible only if $\Delta E$ is positive, which implies that the redox potential of the reducing agent must have more negative value than that of the metallic species. This difference should be larger than 0.3-0.4 V. Thus, strongly electropositive metals like Au, Pt, Pd, Ag, Rh ($E_0 > 0.7$ V) will react even with mild reducing agents, while more electronegative metals ($E_0 < -0.2$ V) require strong reducing agents and extreme conditions of temperature and pressure. Table 2.3 gives a list of reducing agents most widely used to prepare metallic nanoparticles. For example, Hirai\textsuperscript{[97]} or more recently Delmas\textsuperscript{[98]} have extensively used alcohols as reducing agents in the synthesis of colloidal transition metals, such as Rh, Pt, Pd or Ir. These colloids were stabilized by organic polymer
or oligomers, such as polyvinyl alcohol (PVA), poly(N-vinyl-2-pyrrolidone (PVP) or polyvinyl ether (PVE).\textsuperscript{[84]} Another method that should be mentioned is to prepare metal nanoparticles in microemulsions, a micellar nanoreactor (Scheme 2.1). A microemulsion is defined as a system of water, oil, and amphiphile (surfactant). This system is optically isotropic and thermodynamically stable solution. At high concentration of water, the internal structure of microemulsion consists of small oil droplets in a continuous water phase (micelles). With increased oil concentration, a bicontinuous phase without any clearly defined shape is formed. At high oil concentration, the bicontinuous phase is transformed into a structure of small water droplets in a continuous oil phase (reverse micelles), also known as a w/o (water/oil) microemulsion.\textsuperscript{[99, 100]} The size of the final metallic particle will greatly depend on the size of the droplets in the microemulsion. The droplet size will be influenced by the water-to-surfactant ratio. The reverse micelle methods have been used to produce some metal and semiconductor nanoparticles, such as Fe,\textsuperscript{[101]} Ni,\textsuperscript{[102]} Au,\textsuperscript{[103]} ZnS,\textsuperscript{[104]} CdS,\textsuperscript{[104]} Fe-Ni and Cu-Ni alloy nanoparticles.\textsuperscript{[105, 106]}

2.6.2.3 Thermal, photochemical and sonochemical decomposition of metal precursors

Many organometallic compounds are thermally decomposed to their respective zero-valent element. For example, the synthesis of Pd and Pt organosols by thermolysis of precursors, such as Pd acetate, Pd acetylacetonate, or Pd halides have been reported in the literature.\textsuperscript{[107-109]} The solvents used had high boiling points, such as methyl-iso-butylketone.
These syntheses were performed without stabilizing agents, and as a result, broad size distributions and large particles are observed.\textsuperscript{[107-109]} Photochemical synthesis of metal nanoparticles can be accomplished either by (i) transition metal salt reduction by radiolytically produced reducing agents or (ii) degradation of an organometallic complex by radiolysis. A wide range of transition metal nanoparticles, such as Ag, Au, Ir, Pt, Pd or Cu colloids were prepared by this method.\textsuperscript{[84, 110-113]} The sonochemical reduction of transition metal salts occurs in three steps: the generation of the active species, the reduction of the metal and the growth of the colloids. These three-steps occur in different compartments: (i) in gaseous phase into the cavitation bubbles where high temperature and pressure allow water pyrolysis to form H\textsuperscript{+} and OH\textsuperscript{−}, (ii) at the interface between the cavitation bubbles and the solution, and finally (iii) in the solution. This method has been applied to colloidal synthesis of transition metal nanoparticles, such as Au, Ag, Pt, and Pd.\textsuperscript{[114-121]}
Figure 2.8 Schematic illustration of preparative methods of metal nanoparticles\textsuperscript{[122]}

Table 2.3 Guidelines for the choice of reducing agents and reaction conditions in the precipitation of metal particles\textsuperscript{[123]}

<table>
<thead>
<tr>
<th>Metal species</th>
<th>$E^{0}/V$</th>
<th>Reducing Agent</th>
<th>Conditions</th>
<th>Rates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au$^{3+}$, Pt$^{4+}$, Pd$^{2+}$, Ag$^{+}$, Rh$^{3+}$, $\geq +0.7$</td>
<td>Organic acids, alcohols, polyols $\geq +0.7$</td>
<td>$\geq 70^\circ\text{C}$</td>
<td>Slow</td>
<td></td>
</tr>
<tr>
<td>Hg$^{2+}$, Ir$^{3+}$</td>
<td>Aldehydes, sugars</td>
<td>$&lt; 50^\circ\text{C}$</td>
<td>Moderate</td>
<td></td>
</tr>
<tr>
<td>Hydrazine, H$_2$SO$_3$, H$_3$PO$_2$</td>
<td>Ambient</td>
<td>Fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$, boranes, hydrated e$^-$</td>
<td>Ambient</td>
<td>Very fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$, Re$^{3+}$, Ru$^{3+}$</td>
<td>$&lt; +0.7$ and $\geq 0$</td>
<td>Polyols</td>
<td>$&gt; 120^\circ\text{C}$</td>
<td>Slow</td>
</tr>
<tr>
<td>Aldehydes, sugars</td>
<td>$&gt; 120^\circ\text{C}$</td>
<td>Slow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrazine, hydrogen</td>
<td>$&lt; 70^\circ\text{C}$</td>
<td>Moderate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$</td>
<td>Ambient</td>
<td>Fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cd$^{2+}$, Co$^{2+}$, Ni$^{2+}$, Fe$^{2+}$, In$^{3+}$, $&lt; 0$ and $\geq -0.5$</td>
<td>Polyols</td>
<td>$&gt; 180^\circ\text{C}$</td>
<td>Slow</td>
<td></td>
</tr>
<tr>
<td>Hydrazine, hydroxylamine</td>
<td>70-100$^\circ\text{C}$</td>
<td>Slow</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$, boranes</td>
<td>Ambient</td>
<td>Moderate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrated e$^-$, radicals</td>
<td>Ambient</td>
<td>Fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn$^{2+}$, Mo$^{3+}$, W$^{6+}$</td>
<td>Hydrazine, hydroxylamine</td>
<td>70-100$^\circ\text{C}$</td>
<td>Slow</td>
<td></td>
</tr>
<tr>
<td>NaBH$_4$, boranes</td>
<td>Ambient</td>
<td>Moderate</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrated e$^-$, radicals</td>
<td>Ambient</td>
<td>Fast</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mn$^{2+}$, Ta$^{5+}$, V$^{2+}$</td>
<td>$&lt; -0.6$</td>
<td>NaBH$_4$, boranes</td>
<td>$T, P &gt; \text{Ambient}$</td>
<td>Slow</td>
</tr>
<tr>
<td>Hydrated e$^-$, radicals</td>
<td>Ambient</td>
<td>Fast</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Scheme 2.1 Proposed mechanism for the formation of metal particles by microemulsion approach\textsuperscript{[100]}

2.6.3 Stabilization of metal nanoparticles

Protective agents are necessary to stabilize nanostructured colloidal metals and to prevent agglomeration. Two basic modes of stabilization have been distinguished: (1) electrostatic stabilization based on the Coulombic repulsion between the particles caused by the electrical double layer formed by ions adsorbed at the particle surface and the corresponding counterions; and (2) steric stabilization achieved by the coordination of sterically demanding organic molecules that act as protective shields on the metallic surface. The electrostatic and steric stabilization can be combined to maintain stable metallic nanoparticle suspensions. This kind of stabilization is generally provided by means of ionic surfactants. These compounds bear a polar headgroup able to generate an electric double
layer and a lipophilic side chain able to provide steric repulsion. In this way, nanometallic cores are separated from each other and aggregation is prevented. The main classes of protective groups reported from the literature are as follows:

### 2.6.3.1 Linear polymer as a stabilizer

Polymer provides stabilization of metal nanoparticles through the steric bulk of their framework. Poly(N-vinyl-2-pyrrolidone (PVP) is the most widely used polymer for nanoparticle stabilization and catalysis, because it fulfills both steric and ligand requirements. For example, Cu nanoparticles were prepared by chemical reduction using PVP as a stabilizer.\(^\text{124}\) The size of Cu nanoparticles depended strongly on the solution concentration of PVP.

### 2.6.3.2 Surfactants

Surfactants have been utilized as surface stabilizers and/or templates in the synthesis of nanoparticles. These molecules, by their binding to the nanoparticle surface, decrease the surface energy, control growth and shape of the particles\(^\text{125}\) and act as stabilizers against coagulation. Neutral surfactants, such as alkanethiols, alkylphosphines, and amines, are used as stabilizers in the synthesis of different nanoparticles.\(^\text{126, 127}\) Charged surfactants have also been used as stabilizers and templates for the growth of a variety of semiconductor and/or metallic quantum dots.\(^\text{128, 129}\) Mixtures of cationic surfactants have also been used as templates and stabilizers to prepare rod-shaped metallic and semiconductors
nanoparticles.\textsuperscript{[130,131]}

\section*{2.6.3.3 Dendrimer stabilizers}

Dendrimers, like polymers, are macromolecules, but unlike polymers, they are perfectly defined on the molecular level with a polydispersity of 1.0.\textsuperscript{[82, 132]} Having shapes that resemble molecular trees or cauliflowers, they become globular after a few generations, and behave as molecular boxed that can entrap and stabilize metal nanoparticles. The formation of nanoparticles stabilized by dendrimers for catalysis has been proposed in 1998 by research groups of Crooks, Tamalia, and Esumi.\textsuperscript{[82]} Metal nanoparticles were introduced inside the dendrimers or at the dendrimer periphery. Crooks et al. complexed metal ions (Cu$^{2+}$, Au$^{3+}$, Pt$^{2+}$, Pd$^{2+}$, Fe$^{3+}$, Ru$^{3+}$) to the inner nitrogen atoms of the tertiary amines of poly(amidoamine) (PAMAM) dendrimers. The reduction of the metal ions to M$^0$ by NaBH$_4$ led to the aggregation of metal atoms to form nanoparticles inside the dendrimer (Scheme 2.2).\textsuperscript{[86, 133-137]}

\section*{2.6.3.4 Stabilizing ligands}

The term of ligand stabilization has been chosen to describe the use of traditional ligands to stabilize transition metal colloids. The stabilization occurs by the coordination of metallic nanoparticles with ligands, such as phosphines,\textsuperscript{[138]} thiols,\textsuperscript{[139]} amines,\textsuperscript{[140]} or carbon monoxide.\textsuperscript{[141]} For example, Amiens et al. synthesized Pt and Pd colloids stabilized by phosphines.\textsuperscript{[138]}
2.6.4 Bimetallic nanoparticle synthesis

Alloy catalysts are typically prepared using traditional approaches which involve impregnation of metal precursors and post-treatment at high temperatures. However, bimetallic nanoparticles made by this method are typically large with wide size distributions also lacking uniform compositions. In addition, bimetallic nanoparticles with core-shell structure cannot be made by this conventional method. Therefore, the preparation of these bimetallic nanoparticles can be conducted either by simultaneous or successive reduction of two metallic precursors. The co-reduction is the most widely reported method since this method is easy to implement. Most of the synthetic procedures used to prepare monometallic

Scheme 2.2 Dendrimer-encapsulated metal nanoparticles\[137\]
particles can be applied to bimetallic particles.

2.6.4.1 Co-reduction of metal precursors

The principles of this synthetic procedure are the same as those applied for monometallic nanoparticles. The metallic precursors are reduced in the presence of stabilizing agents to prevent aggregation of the formed particles. For example, 3 nm Pd-Cu alloy nanoparticles were prepared by co-reduction using oleylamine as a reduction agent and oleic acid as a stabilizer.[142]

2.6.4.2 Successive reduction

A successive reduction of transition metal salts is the most suitable method to synthesize core/shell bimetallic colloids. Fu et al. obtained Pt coated Ni nanoparticles by successive reduction of NiCl₂ and H₂PtCl₆ in ethylene glycol solution (Scheme 2.3).[143] Tsuji et al. synthesized Cu@Ag core@shell nanoparticles by successive polyol reduction.[144] Ni@Ag nanoparticles were also prepared by Chen et al. via successive hydrazine reduction.[145]

2.6.4.3 Redox-transmetalation

The main concept for redox-transmetalation is the reduction and deposition of metal (M₂) on another metal M₁ through sacrificial oxidation of the M₁ surface atoms via a redox-transmetalation process (Scheme 2.4).[146] Because the redox reaction can spontaneously proceed under favorable redox conditions, i.e., at positive electrochemical
potential of the redox reaction ($\Delta E$), this method has been regarded as an efficient route only for some selective metals. The transmetalation process has several advantages for the fabrication of core-shell structured nanoparticles: (1) no additional reducing agent is needed; (2) spontaneous formation of the shells deposited on the surface of the initial cores; (3) self-nucleation of secondarily added metals can be avoided; (4) inhomogeneous growth of the shells on the surface of the initial cores can be prevented.\[147\] Various Co@Au, Co@Pd, Co@Pt, and Co@Cu nanoparticles have been synthesized by Lee et al. through transmetalation reaction.\[146\]

\[\text{Scheme 2.3} \text{ Formation of process of core-shell structure Pt layer coated Ni nanoparticles}^{[143]}\]

\[\text{Scheme 2.4} \text{ Schematic of core-shell nanoparticle formation via Redox Transmetalation process}^{[146]}\]
2.6.5 Synthesis of Cu, Ni and Cu-Ni nanoparticles

The development of synthesis routes in order to obtain nonaggregated Cu, Ni and Cu-Ni nanoparticles with a well-controlled average size and narrow size distribution is critical for the synthesis of superior low temperature WGS catalysts. A number of methods have been used for the production of Cu, Ni and Cu-Ni nanoparticles and their results are summarized in Table 2.4.

<table>
<thead>
<tr>
<th>Nanoparticles</th>
<th>Synthesis route</th>
<th>Particle size</th>
<th>Reference:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Microemulsion</td>
<td>5 nm</td>
<td>Chen et al. [148]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>50 nm</td>
<td>Bai et al. [149]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>30-40 nm</td>
<td>Duan et al. [150]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>50 nm</td>
<td>Gao et al. [151]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>40-60 nm</td>
<td>Hald et al. [152]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>4 nm</td>
<td>Couto et al. [153]</td>
</tr>
<tr>
<td>Ni</td>
<td>Chemical reduction</td>
<td>90-340 nm</td>
<td>Ying et al. [154]</td>
</tr>
<tr>
<td>Ni</td>
<td>Electroless plating</td>
<td>40-100 nm</td>
<td>Wu et al. [155]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical reduction</td>
<td>5-25 nm</td>
<td>Mott et al. [156]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical reduction</td>
<td>10 nm</td>
<td>Sailova et al. [157]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical reduction</td>
<td>4-25 nm</td>
<td>Yu et al. [124]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical reduction</td>
<td>2-30 nm</td>
<td>Zhang et al. [158]</td>
</tr>
<tr>
<td>Cu</td>
<td>Chemical reduction</td>
<td>100 nm</td>
<td>Wang et al. [159]</td>
</tr>
<tr>
<td>Cu</td>
<td>Photolysis</td>
<td>4-30 nm</td>
<td>Ensign et al. [160]</td>
</tr>
</tbody>
</table>

Table 2.4 Synthesis routes for Cu, Ni, and Cu-Ni nanoparticles
<table>
<thead>
<tr>
<th>Method</th>
<th>Nanoparticle Size</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microemulsion</td>
<td>9-30 nm</td>
<td>Giuffrida et al. [161]</td>
</tr>
<tr>
<td></td>
<td>12 nm</td>
<td>Kitchens et al. [162]</td>
</tr>
<tr>
<td></td>
<td>10-20 nm</td>
<td>Salzemann et al. [163]</td>
</tr>
<tr>
<td></td>
<td>10-40 nm</td>
<td>Qiu et al. [164]</td>
</tr>
<tr>
<td>Supercritical water</td>
<td>10-35 nm</td>
<td>Ziegler et al. [165]</td>
</tr>
<tr>
<td>Microwave irradiation</td>
<td>10-60 nm</td>
<td>Zhu et al. [166]</td>
</tr>
<tr>
<td>Successive reduction</td>
<td>200 nm</td>
<td>Carroll et al. [167]</td>
</tr>
<tr>
<td>Arc-plasma evaporation</td>
<td>50 nm</td>
<td>Song et al. [168]</td>
</tr>
<tr>
<td>Physical method</td>
<td>300-400 nm</td>
<td>Chatterjee et al. [169]</td>
</tr>
<tr>
<td>Microwave irradiation</td>
<td>12-22 nm</td>
<td>Yamauchi et al. [170]</td>
</tr>
<tr>
<td>Microemulsions</td>
<td>5-12 nm</td>
<td>Feng et al. [106]</td>
</tr>
<tr>
<td>Chemical reduction</td>
<td>7-30 nm</td>
<td>Ahmed et al. [171]</td>
</tr>
<tr>
<td></td>
<td>19-30 nm</td>
<td>Zhang et al. [172]</td>
</tr>
<tr>
<td></td>
<td>0.3-1 μm</td>
<td>Bonet et al. [173]</td>
</tr>
<tr>
<td></td>
<td>50-80 nm</td>
<td>Chatterjee et al. [169]</td>
</tr>
</tbody>
</table>

### 2.6.6 Immobilization of nanoparticles on solid supports

Direct application of liquid suspensions of metal nanoparticles in catalysis is limited by several drawbacks, mostly due to the challenge of separating the products from the nanoparticulate catalyst and the recycling of the catalyst. The immobilization of such nanoparticles on a solid support is a straightforward approach to solving this challenge since the catalyst can be recycled by simple filtration. However, the catalytic performance of supported nanoparticles is often adversely affected by the presence of salts and other
stabilizers adsorbed on their surface.\textsuperscript{[174]} Therefore, a proper choice of immobilization methods to make supported catalysts containing well-dispersed nanoparticles is key to the preparation highly active and selective heterogeneous catalysts. Several immobilization methods have been investigated in the literature for the immobilization of metal colloids. Adsorption on inorganic supports or chemical bonding to polymeric supports was found to be particularly promising for the preparation of supported transition metal nanoparticles.\textsuperscript{[84]}

2.6.6.1 Nanoparticle adsorption on supports

Charcoal, silica, alumina, TiO$_2$ or MgO are among the most widely used inorganic supports to immobilize colloidal nanoparticles.\textsuperscript{[84]} In this simple method, (1) metallic nanoparticles are first made by reduction, (2) then impregnated onto the support, (3) followed by washing the obtained supported catalyst. The main advantage of this process is that the size of the colloidal nanoparticles is largely fixed during their preparation in solution. Zheng et al. used approaches based on the general concept of utilizing relatively weak interaction between metal nanoparticles and the support in aprotic solvents to achieve homogeneous loading of the particles. After deposition, the nanoparticles are then locked in place by calcination. Zheng et al. have successfully deposited gold nanoparticles on different supports, such as $\alpha$-Fe$_2$O$_3$, TiO$_2$, hydroxyapatite, Al$_2$O$_3$, ZnO, and fumed SiO$_2$.\textsuperscript{[175]} Wang et al. reported the immobilization of Pd, Pt or Rh colloids stabilized by PVP or PVA on silica.\textsuperscript{[176]} The authors claimed that the immobilization of the metal nanoparticles occurred by adsorption of
the protective polymers/metal complex on silica due to hydrogen bonds formed between polymers and silica hydroxyls.

2.6.6.2 Grafting of colloids onto supports

A wide range of chemical bonds have been explored to immobilize nanoparticles on supports.\[^{84, 97, 177, 178}\] Liu developed an immobilization procedure based on the coordination of a metal by a thiol-modified silica.\[^{178}\] Hiraï and Toshima grafted Pt and Rh colloids onto polyacrylamide gel having aminoethyl groups.\[^{97, 177}\] The immobilization is generated by formation of amide bonds by reaction of ester functions of the protecting PVP/methyl polyacrylate copolymer with amine functions of the gel.

2.7 Limitations of Current WGS Catalysts

As the review of current WGS catalysts conducted above indicated, conventional Cu-and Fe-based catalysts used in the WGS reaction are unsuitable for mobile fuel processors due to their low reactivity. The Au-ceria catalysts were reported to undergo fast deactivation, which was attributed to the blockage of active sites by carbonates and/or formates formed during the WGS reaction.\[^{67}\] In addition, besides high cost of Au, catalytic properties of nanosized Au are particularly sensitive to the choice of preparation method and post-treatment conditions, which are difficult to control accurately during their large-scale synthesis. Highly active Pt-ceria catalysts also experienced deactivation. Zalc et al. claimed that over-reduction of ceria in these catalysts cannot be avoided, thus rendering
ceria-supported catalysts impractical for the use in the WGS reaction in fuel cell systems.\textsuperscript{[56]}

Therefore, high costs associated with precious metals and extreme sensitivity of precious metal catalysts to the presence of sulfur and other impurities in coal syngas effectively precluded their use as WGS catalysts. Moreover, conventional synthesis methods of current WGS catalysts offered poor control over nanoparticle size, bimetallic structure and composition since they are largely influenced by the nature of oxide support. Accordingly, these methods were unable to provide novel well-defined bimetallic catalysts in order to explore the bimetallic effect in the WGS catalysis.

\textbf{2.8 Novel Approaches to WGS Catalysts}

As discussed above, recent theoretical studies indicated that Cu and Ni are highly promising as superior catalytic components of the WGS catalysts. Moreover, Cu/Ni alloys are currently receiving increased attention as catalysts because these two metals form solid solution over a wide range of compositions. In addition, their electronic properties are very different. Copper has a completely filled 3d-band and therefore no d states at the Fermi level; in contrast, nickel has a partially filled 3d-band and a high density of states at the Fermi level. Therefore, bimetallic Cu-Ni catalysts are potential candidates as superior WGS catalysts. Ni-based catalysts containing Cu have already been found to display significantly different catalytic activity and selectivity as compared to monometallic Ni catalysts in many reactions. These studies suggested that changes in the catalytic properties induced by the presence of Cu
may be caused by changes in the electronic and/or geometric properties of bimetallic Cu/Ni particles. Besides homogeneous alloys, near-surface alloys possessing a core-shell structure and presenting surfaces with novel catalytic properties have also received significant attention of the catalysis community.\textsuperscript{[179]} Nanoscale regime is also expected to play an important role through increased surface area and novel electronic and structural effects encountered in (bi)metallic nanoparticles. However, these effects have not been investigated yet for the CuNi system in the WGS catalysis due to lack of studies employing well-defined model Cu, Ni and CuNi catalysts.

As described above, controlled reduction of Cu and Ni sources gives rise to mono- and bimetallic nanoparticles that possess narrow size distributions as well as homogeneous alloy and core-shell structures. These nanoparticle systems are highly promising as well-defined model WGS catalysts for establishing the fundamental structure-reactivity relationships that will aid in the rational design of improved WGS catalysts to produce hydrogen for fuel cell applications. Therefore, the preparation and characterization of these well-defined WGS catalysts is the focus of this Ph.D. research.

2.9 Objectives

Accordingly, this PhD research explored the following two major objectives related to supported Cu-Ni WGS catalysts:
Objective 1: Demonstrate the proof of concept for supported Cu-Ni alloys as superior catalysts for low temperature water gas shift reaction

Objective 2: Elucidate the role of nanoscale structure and composition of Cu, Ni, and Cu-Ni alloys on their activity and selectivity in water gas shift reaction

In Chapter III, we explored traditional Cu, Ni and Cu-Ni WGS catalysts made by impregnation methods. Various bimetallic Cu-Ni catalysts were prepared by support impregnation and compared to monometallic Cu and Ni catalysts. The effect of Cu/Ni ratio on the physicochemical properties and catalytic performance were examined. In Chapter IV, we reported Cu, Ni and Cu-Ni catalysts containing well-defined metallic nanoparticles prepared from metal colloids and supported on alumina, and compared their behavior in the WGS reaction to that of traditional impregnation catalysts. In Chapter V, we described bimetallic Cu-Ni catalysts possessing a core-shell structure and discussed our insights into their structure-activity relationships in the WGS reaction. Finally, in Chapter VI, we summarized our findings and outlined how insights obtained in this work could guide future efforts to design highly active and chemically stable catalysts for low-temperature WGS reaction.
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CHAPTER III

Hydrogen Production by Water-Gas Shift Reaction over Bimetallic Cu-Ni Catalysts Supported on La-Doped Mesoporous Ceria

3.1 Introduction

The water-gas shift reaction (CO + H₂O ⇌ CO₂ + H₂, ΔH = -40.6 kJ/mol) has recently attracted renewed attention because of its potential use in connection with fuel cell power generation. WGS reaction is the critical step in maximizing H₂ yield from syngas, produced by steam reforming or partial oxidation of hydrocarbons.[1] Since the WGS reaction is an exothermic reaction, it is favored at low temperatures. On the other hand, the current WGS catalysts are kinetically limited at low temperature since they are not active enough to attain equilibrium. Current commercial large-scale industrial plants often use a two-step process employing high-temperature shift (Fe₂O₃/Cr₂O₃) and low-temperature shift catalysts (Cu/ZnO/Al₂O₃). However, such a two-step process is not a viable solution for small-scale applications, because of its technical complexity and multiple stages involved.[2] Therefore, it is very important to develop new WGS catalysts with higher activity at lower temperatures than the present Cu-based WGS catalysts.

WGS catalysts based on nanocrystalline cerium oxide have been investigated in recent years for fuel cell applications. Cerium oxide is a highly promising support for WGS catalysts because of its ability to undergo rapid reduction and oxidation cycles.[3, 4] Ceria can
also serve as a stabilizer for alumina and other metal oxide supports, maintaining a high
dispersion of the catalytic components.\textsuperscript{[5]} However, ceria is prone to sintering under reaction
conditions. The incorporation of other rare-earth elements (i.e., La and Zr) into ceria is
reported to improve the structural stability of ceria toward sintering and thus, enhance WGS
activity.\textsuperscript{[6]} Noble metals supported on ceria, such as Pt, were demonstrated to have excellent
WGS activities. However, the deactivation of Pt/CeO\textsubscript{2} catalysts used on real WGS streams\textsuperscript{[7]}
and in start-stop operation has also been reported. In addition, high cost associated with
Pt-based catalysts is also considered a serious drawback.

Schumacher et al.\textsuperscript{[8]} used a microkinetic model based on a redox mechanism to
investigate the low-temperature WGS reactivity trends on transition metals, and suggested
that Cu and Ni may be promising as superior catalytic components for WGS catalysts.
Zeigarnik et al.\textsuperscript{[9]} also proposed a theoretical approach, which included the generation of a
complete set of elementary steps, the calculation of the activation energy using unity-bond
index-quadratic exponential potential (UBI-QEP) method and the preexponential factor using
transition state theory, along with kinetic simulations, for predicting comparative catalytic
activities. Their approach indicated that Cu and Ni may possess optimal activity in the WGS
reaction. Callaghan et al.,\textsuperscript{[10]} using a systematic theoretical approach, namely Reaction Route
Graph Analysis, also proposed that Cu and Ni are the most promising metal catalysts for the
WGS reaction as compared to other transition metals.
Transition metal alloys often possess superior properties as compared to pure
transition metals as the active components of heterogeneous catalysts.[11] Their geometries
and electronic structures can be varied over wide ranges through the combination of different
metals that allow tuning their catalytic reactivities. Alloys of nickel with copper are currently
receiving increased attention because these two metals form a solid solution.[12] Ni-based
catalysts containing Cu have already been found to have significantly different catalytic
activity and selectivity as compared to monometallic Ni catalysts in many reactions.[13-17] For
example, the addition of Cu to Ni enhanced the catalytic effect in dimethyl carbonate
synthesis.[13] In CO₂ hydrogenation, the addition of Cu favored CO production.[14] It is also
reported that adding Cu to Ni in ethanol steam reforming reaction not only reduced CO
generation, but also improved resistance to coke formation on Ni catalysts.[15] The addition of
Cu to Ni/SiO₂ also led to a low conversion in the hydrodechlorination of
1,1,2-trichloroethane and a high selectivity to vinyl chloride monomer.[16] It is suggested that
changes in the catalytic properties induced by Cu addition to Ni can be caused by changes in
the electronic and/or geometric properties of the homogeneous bimetallic particles.[16, 18]

However, despite their promise, CuNi alloy catalysts supported on ceria have not been
sufficiently investigated as low-temperature WGS catalysts. Huang et al. studied the WGS
reaction during steam reforming of methane over supported CuNi catalysts and showed the
addition Cu to Ni catalysts enhanced the WGS activity.[19] The presence of Cu in Ni catalysts
may suppress methane steam reforming activity and thus, enhance the extent of WGS reaction in methane steam reforming. In addition, Li et al.\textsuperscript{[20]} also reported that the Cu- and Ni-loaded ceria catalyst retained highly activity in the WGS reaction. However, the bimetallic CuNi catalysts have not been systematically investigated. Therefore, in our study, a number of bimetallic Cu\textsubscript{2}Ni\textsubscript{20-y}/CeLaO\textsubscript{x} catalysts have been prepared and compared as the WGS catalysts to monometallic Cu and Ni catalysts supported on La-doped ceria. The effect of Cu/Ni ratio on the physicochemical properties and catalytic performance of these model WGS catalysts were specifically examined. A detailed characterization of the CuNi catalysts by XRD, TPR and TEM was conducted to elucidate the alloy structure and catalytic performance, which shed new light on the bimetallic effect in the WGS reaction.

3.2 Experimental

3.2.1 Catalyst preparation and characterization

\textit{Materials.} The starting metal sources were Ce(NO\textsubscript{3})\textsubscript{3} \cdot 6H\textsubscript{2}O (Sigma-Aldrich, 99.99%), La(NO\textsubscript{3})\textsubscript{3} \cdot 6H\textsubscript{2}O (Sigma-Aldrich, 99.99%), Ni(NO\textsubscript{3})\textsubscript{2} \cdot 6H\textsubscript{2}O (Sigma-Aldrich, 99.99%) and Cu(NO\textsubscript{3})\textsubscript{2} \cdot 2.5H\textsubscript{2}O (Sigma-Aldrich, 99.99%). Aqueous ammonia 28\% (Pharmco, ACS reagent grade) was used as a precipitation agent.

\textit{Support preparation.} Ceria supports (doped with 10 at. \% La) were prepared by coprecipitating nitrate salts using aqueous ammonia at 100°C\textsuperscript{[21]} La-doped ceria is denoted as CeLaO\textsubscript{x} throughout this paper. Aqueous ammonia was added dropwise at room temperature
to an aqueous solution containing 5.7 mmol of Ce(NO₃)₃·6H₂O and a desired amount of
doping element source, La(NO₃)₃·6H₂O, under rapid stirring with a careful control of the pH
at 11. After precipitation, the slurry was stirred for another 30 min and then refluxed at 100°C
for 24 h under continuous stirring. The mixture was cooled to room temperature, filtered, and
washed. The final product was dried at 80°C overnight and calcined in air at 400°C for 5 h.

**Catalyst preparation.** Supported Cu, Ni and bimetallic Cu-Ni catalysts were prepared by
incipient-wetness impregnation of the ceria support with a mixed solution of corresponding
metal sources. After impregnation with aqueous solutions of metal nitrates, the support was
dried at 80°C overnight and then calcined in air at 400°C for 3 h. The catalysts thus prepared
were denoted as CuₓNi₂₀₋ₓ/CeLaOₓ, where y corresponds to a nominal Cu loading (wt. %).

### 3.2.2 Catalysts Characterization

**BET surface areas.** The N₂ adsorption-desorption isotherms were measured at 77K using
Micromeritics ASAP 2020 porosimeter. The pore size distributions and surface areas were
determined by the Barrett-Joyner-Halenda (BJH)\(^{[22]}\) and Brunauer-Emmett-Teller (BET)\(^{[23]}\)
methods, respectively.

**XRD measurements.** The crystal structures were determined by powder X-ray diffraction
(XRD) using a Siemens D-500 diffractometer equipped with a Cu Kα radiation source. The
XRD data were collected in a step-scan mode at 2θ = 20-70° and a step size of 0.02°/s. The
full-profile structure refinement was performed according to the Rietveld method using
The average size of particles was determined from the XRD peak broadening by the Scherrer’s equation, \( t = \frac{K\lambda}{\beta \cos \theta} \), where \( t \) is the average dimension of crystallites along the \([hkl]\) direction; \( \lambda \) is the wavelength of X-ray irradiation (1.5418 Å); \( \theta \) is the position of the \((hkl)\) diffraction peak; \( K \) is the Scherrer constant usually taken as 0.9; and \( \beta \) is the line width at half-maximum height which was calculated by the CMPR software. X-ray diffraction measurements were also recorded using a custom high-temperature X-ray diffractometer employing a position-sensitive detector and Co Kα radiation. Heating and cooling rates were 30 K/min, and the detector scan rate was 2°/min over a range of 15 to 115° 2θ. Powdered samples were mounted onto Pt-coated polycrystalline alumina sample holders as a layer of ~500 μm in thickness. The diffraction furnace temperature was calibrated using common phase transformation standards.

**TPR measurements.** The H₂-TPR studies were performed using an automated catalyst characterization system (Micromeritics model AutoChem II 2920) equipped with a thermal conductivity detector (TCD). The reactive gas composition was H₂ (10 vol. %) in argon and the flow rate was fixed at 20 ml/min (STP), at a heating rate of 5°C/min from 50 to 800°C. The total reactive gas consumption during TPR analysis was measured.

**Transmission electron microscopy (TEM).** The samples for TEM were prepared by first dispersing powdered catalysts in ethanol and then allowing a drop of the suspension to evaporate onto a carbon film supported by a gold grid. TEM was performed employing a
Phillips CM20 electron microscope at a 200-kV accelerating voltage and a high brightness LaB$_6$ gun for high coherence and small probes.

**ICP-MS elemental analysis.** Determination of total Ni and Cu was accomplished via microwave digestion followed by ICP-MS analysis. The sample digestion was accomplished with a CEM Discover/Explorer microwave system. Approximately 5 mg of samples and 0.500 ml of *aqua regia* (0.125 ml nitric acid and 0.375 ml hydrochloric acid) were placed into a CEM standard 10 ml glass digestion microwave vial fitted with a Teflon lined snap cap. Each sample was digested at 140°C for 2 min, followed by dilution with doubly deionized water to 100 ml before ICP-MS analysis. Fresh 1000 ng/ml Ni and Cu standard solution was prepared daily from stock solutions in 2% nitric acid. An Agilent ICP-MS 7500ce was used for the element specific detection of $^{60}$Ni and $^{63}$Cu. The ICP-MS was equipped with a micro-concentric nebulizer supplied by Glass Expansion, a Scott type double channel spray chamber (cooled to 2°C), a shield torch, an octopole collision/reaction cell with pressurized helium gas (purity of 99.999%), a quadrupole mass analyzer and an electron multiplier. Instrumental parameters: RF forward power 1500 W; plasma Ar gas flow rate, 15.0 l/min; carrier Ar gas flow rate, 1.05 l/min; He collision gas, 3.7 ml/min. The resulting data were analyzed using Agilent Mass Hunter ICP-MS software.

**3.2.3 Catalytic activity**

Catalytic activities were determined employing a continuous fixed-bed tubular quartz
microreactor (0.55cm ID) operated at atmospheric pressure using 0.1 g catalyst diluted with 0.2 g of quartz powder. The feed gas mixture typically contained 10 mol. % CO and 20 mol. % H₂O in helium. The total feed flow rate was 100 ml/min. All catalysts were reduced under 20 mol. % H₂ in He at 400°C before catalytic tests at 150-400°C. Water was injected into a flowing gas stream by a syringe pump and vaporized in the heated gas feed line before entering the reactor. A condenser filled with ice was installed at the reactor exit to collect water. The gas mixture was analyzed by a gas chromatograph, HP-5580A, equipped with a thermal conductivity detector. The carbon balance agreed within ±5 mol. %.

3.3 Results and Discussion

3.3.1 Textural and structural properties

The surface areas, chemical compositions and textural properties of the CeLaOₓ supported catalysts of the present study are summarized in Table 3.1. The BET surface areas before and after impregnation were in the range of 70-90 m²/g. The size and morphology of supported catalyst particles were analyzed by TEM. The TEM images of the CeLaOₓ support and Cu₁₀Ni₁₀/CeLaOₓ catalyst (Figure 3.1) show the absence of particles greater than 50 nm in diameter. From the TEM image of supported bimetallic catalysts, it is clear that the particle size and morphology of Cu₁₀Ni₁₀/CeLaOₓ is similar to that of ceria.
3.3.2 XRD patterns of bimetallic CuNi catalysts

XRD patterns of the calcined samples are shown in Figure 3.2(A). The distinct fluorite-type oxide structure of CeO$_2$ (PDF 00-004-0593) is evident in all samples. La was in the solid solution with ceria and no separate XRD reflections from a La oxide were observed.$^{[20]}$ Figure 3.2(A) shows three diffraction peaks at $\theta = 37.3^\circ$, $44.3^\circ$, and $62.9^\circ$, which correspond well to NiO (PDF 00-004-0835), and $\theta = 35.7^\circ$, $39^\circ$, $49.2^\circ$ which correspond to CuO (PDF 00-001-1117). The metal oxide reflections were seen to increase in intensity with the metal content. The XRD patterns of the reduced catalysts are shown in Figure 3.2(B). The reduced Ni$_{20}$/CeLaO$_x$ catalysts exhibited Ni metal reflections at $\theta = 44.6^\circ$, $51.9^\circ$ (PDF 00-001-1260), and reduced Cu$_{20}$/CeLaO$_x$ catalysts displayed Cu metal reflections at $\theta = 43.4^\circ$, $50.6^\circ$ (PDF 00-001-1242).

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Composition (ICP)</th>
<th>Cu/Ni</th>
<th>$S_{\text{BET}}$</th>
<th>H$_2$ uptake ($\mu$mol)</th>
<th>H$_2$ predicted ($\mu$mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni$_{10}$/CeLaO$_x$</td>
<td>10.2</td>
<td>--</td>
<td>90</td>
<td>140</td>
<td>139</td>
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<tr>
<td>Ni$_{20}$/CeLaO$_x$</td>
<td>19.2</td>
<td>--</td>
<td>91</td>
<td>296</td>
<td>248</td>
</tr>
<tr>
<td>Cu$<em>4$Ni$</em>{16}$/CeLaO$_x$</td>
<td>18.8</td>
<td>4/16</td>
<td>71</td>
<td>347</td>
<td>177</td>
</tr>
<tr>
<td>Cu$<em>{10}$Ni$</em>{10}$/CeLaO$_x$</td>
<td>15.2</td>
<td>10/10</td>
<td>76</td>
<td>351</td>
<td>209</td>
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<tr>
<td>Cu$_{16}$Ni$_4$/CeLaO$_x$</td>
<td>16.6</td>
<td>16/4</td>
<td>75</td>
<td>417</td>
<td>215</td>
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<tr>
<td>Cu$_{20}$/CeLaO$_x$</td>
<td>14.1</td>
<td>--</td>
<td>65</td>
<td>347</td>
<td>177</td>
</tr>
<tr>
<td>CeLaOx</td>
<td>--</td>
<td>--</td>
<td>95</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Figure 3.1 TEM images of (A) CeLaO₅ and (B) Cu₁₀Ni₁₀/CeLaO₅ catalysts.

Figure 3.2(B) also shows corresponding peaks of Cu and Ni in reduced catalysts with different Cu/Ni ratios. In the case of bimetallic catalysts, a progressive shift of metallic phase peaks is observed in Fig 3.2(C). Their XRD patterns showed diffraction peaks at intermediate
positions, i.e., located between those for pure Cu and Ni, indicating the formation of Cu-Ni alloys.\textsuperscript{[29-32]} The reduced Cu\textsubscript{10}Ni\textsubscript{10} catalyst displayed two alloy phases, which were Cu- and Ni-rich, respectively. Similar results were also reported previously for the supported CuNi catalysts.\textsuperscript{[29, 31-33]} On the contrary, the bulk Cu-Ni binary phase diagram shows a continuous solid alloy solution for all compositions above the critical temperature of 354\degree C.\textsuperscript{[12]} It is unknown, however, whether this solid solution would also be generated for finely dispersed CuNi catalysts stabilized on ceria. For the Cu\textsubscript{10}Ni\textsubscript{10} composition, the XRD data were collected at room temperature after the 400\degree C reduction in H\textsubscript{2} (Figure 3.2(B)). Since the alloy particles had nanoscale dimensions, it should be possible for the phase separation to occur rapidly at temperatures below 354\degree C. The phase composition of the Cu\textsubscript{10}Ni\textsubscript{10}/CeLaO\textsubscript{x} catalyst was further investigated by an \textit{in situ} XRD technique during reduction in 4 vol.% H\textsubscript{2} in N\textsubscript{2}. As seen in Figure 3.3(A), as-prepared catalysts showed the corresponding CuO and NiO peaks at room temperature. The Cu-rich and Ni-rich phases were visible from 300 to 550\degree C during reduction. After being heated to 550\degree C for 18 h, the supported Cu\textsubscript{10}Ni\textsubscript{10} catalyst still exhibited two separate Cu-rich and Ni-rich phases (Figure 3.3(B)). Therefore, the XRD patterns revealed that supported Cu\textsubscript{10}Ni\textsubscript{10} catalyst showed the lack of complete solubility above the critical temperature, probably due to strong metal-support interactions preventing the interdiffusion of Cu and Ni atoms. In order to verify this hypothesis, the bulk CuNi system was characterized by XRD under conditions similar to those used for supported CuNi
catalysts. As seen in Figure 3.4, as-synthesized bulk CuNi system showed the presence of separate CuO and NiO phases. A single CuNi alloy phase was visible after reduction at 550°C for 2 h indicating that strong metal-support interactions were responsible for the formation of the Cu-rich and Ni-rich phases in the supported Cu$_{10}$Ni$_{10}$ catalyst.
The structural analysis of reduced catalysts was performed by full-profile Rietveld refinement of their XRD patterns to obtain lattice parameters, crystallite sizes, and metal-metal bond lengths. These structural characteristics are shown in Table 3.2 indicating a continuous increase in the lattice parameter as the Cu content of the alloy phase increases mostly likely due to the incorporation of larger Cu atoms into the Ni lattice.\[30] The crystallite size in reduced catalysts decreased upon alloying as compared to both pure Cu and Ni. It is possible that strong interactions between the Cu and Ni atoms prevent sintering of the bimetallic catalysts.
Figure 3.3 In situ XRD patterns (Co Kα radiation) of (A) Cu_{10}Ni_{10}/CeLaO_{x} catalyst collected at 20-550°C in 4% H_{2}/N_{2} and (B) after holding it at 550°C in 4% H_{2}/N_{2} for 18 h.
Figure 3.4 XRD patterns of bulk CuO-NiO sample (A) after calcination in air at 400°C for 3 h and (B) after reduction in 20% H2/He at 550°C for 2 h.

Table 3.2 Structural parameters of the Cu-Ni alloys

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu20Ni20-x wt%</th>
<th>Particle size (nm)</th>
<th>Lattice Parameter (Å)</th>
<th>M-M distance (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni20/CeLaOx</td>
<td>19.2</td>
<td>23</td>
<td>3.5079</td>
<td>0.2480</td>
</tr>
<tr>
<td>Cu4Ni16/CeLaOx</td>
<td>18.8</td>
<td>21</td>
<td>3.5188</td>
<td>0.2488</td>
</tr>
<tr>
<td>Cu10Ni10/CeLaOx</td>
<td>15.2</td>
<td>14</td>
<td>3.5411</td>
<td>0.2504</td>
</tr>
<tr>
<td>Cu16Ni4/CeLaOx</td>
<td>16.6</td>
<td>32</td>
<td>3.5981</td>
<td>0.2544</td>
</tr>
<tr>
<td>Cu20/CeLaOx</td>
<td>14.1</td>
<td>37</td>
<td>3.6096</td>
<td>0.2545</td>
</tr>
</tbody>
</table>

*a Determined from ICP 
*b Calculated from XRD measurements of reduced catalysts
3.3.3 TPR measurements

The reducibility of as-synthesized supported catalysts was investigated by TPR in H₂. The TPR plots of supported catalysts are shown in Figure 3.5. The reduction profile of the CuO/CeLaOₓ sample was characterized by two reduction peaks at 228 and 263°C. It is widely accepted that the peak at lower temperature represents the reduction of CuO nanoparticles highly dispersed on CeO₂, while the peak at high temperature represents the reduction of bulk CuO particles. Similar H₂ reduction profiles were obtained for the supported NiO, which displayed a broad multipeak reduction profile at 200-400°C. The TPR patterns of the CuNi alloy catalysts were somewhat different from those of supported pure CuO and NiO catalysts. Supported CuNi bimetallic catalysts exhibited five TPR peaks, indicating that the reduction process for the bimetallic oxide system was more complicated than for the constituent binary oxides. Figure 3.5 shows that the presence of a second metal lowered the reduction temperature of Cu or Ni catalysts as was previously demonstrated for the Cu-Ni/SiO₂ catalysts. This is also consistent with in situ EELS nanoprobe chemical analysis of the reduced Cu-Ni/TiO₂ where it was suggested that the presence of metallic Cu enhanced or catalyzed the reduction of a Ni precursor. The improvement of reducibility of NiO or CuO when a second metal is present may be due to both a synergistic interaction between the metal oxide phases and a decrease of their crystallite size, which were also confirmed by the XRD data. The lowest reduction temperature was observed for the Cu₁₀Ni₁₀ composition suggesting a much stronger interaction between CuO and NiO. Quantitative analysis of
supported Cu and Ni catalysts showed that the actual hydrogen consumption was higher than the one predicted from the reduction stoichiometry \((\text{MO} + \text{H}_2 \rightarrow \text{M}^0 + \text{H}_2\text{O})\) probably due to the promotion of surface reduction of ceria at these temperatures.\(^{[37]}\)

**Figure 3.5** H\(_2\)-TPR profile of supported Cu, Ni and CuNi catalysts.

### 3.3.4 WGS reaction over CuNi/CeLaO\(_x\) catalysts

The catalytic activity of the Cu-Ni/CeLaO\(_x\) catalysts was determined at 150-400\(^\circ\)C. The CO conversion in the WGS reaction over the CuNi/CeLaO\(_x\) catalysts as a function of temperature is shown in Figure 3.6 (A). Supported Cu catalysts showed a light-off temperature of 200\(^\circ\)C, while the Ni and CuNi catalysts displayed a higher light-off temperature of 250\(^\circ\)C. Supported Ni and bimetallic Cu-Ni catalysts were highly active, showing CO conversions of up to 90 mol. % above 350\(^\circ\)C. At 300\(^\circ\)C, the Ni\(_{20}\) catalyst still
showed high activity (ca. 90 mol. % CO conversion), while the Cu$_4$Ni$_{16}$ catalyst displayed ca. 80 mol. % CO conversion. In the case of supported bimetallic catalysts, the presence of Cu led to a marked decrease of CO conversion below 300°C as compared to the Ni$_{20}$ catalyst (Figure 3.7 (A)).

When carrying out the WGS reaction, methane can be formed (Figure 3.6 (B)) by CO/CO$_2$ hydrogenation in a methanation reaction.\[^{[38]}\] Reactions leading to CH$_4$ formation during WGS reaction are shown below:\[^{[39]}\]

\[
\begin{align*}
\text{CO} + 3\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{H}_2\text{O} \quad \Delta H = -205.8 \text{ kJ/mol} \\
\text{CO}_2 + 4\text{H}_2 & \leftrightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad \Delta H = -165 \text{ kJ/mol} \\
2\text{CO} + 2\text{H}_2 & \leftrightarrow \text{CH}_4 + \text{CO}_2 \quad \Delta H = -170.8 \text{ kJ/mol}
\end{align*}
\]

It has been reported that Ni is an effective catalyst for the methanation reaction.\[^{[40]}\] Since methanation consumes H$_2$, the higher the CH$_4$ yield, the lower the H$_2$ yield in the WGS reaction. Figure 3.6 (B) shows methane yield during the WGS reaction for all bimetallic catalysts as a function of reaction temperature. Significant methane formation was observed above 275°C for the Ni$_{20}$ catalyst. Figures 3.7 (A) and (B) also show that supported monometallic Ni catalyst was more active but produced the highest amount of CH$_4$. This is an indication of the potential drawbacks of Ni as a WGS catalyst. For supported bimetallic catalysts, CO conversion progressively decreased with Cu content (Figure 3.7 (A)). However, supported CuNi alloy catalysts were still highly active, displaying the CO conversion of up to
90 mol. % at 350-400°C. At 300°C, the Cu₄Ni₁₆ catalyst showed the CO conversion of up to 80 mol. %, which was somewhat lower than for supported Ni catalysts. The addition of only 4 wt. % Cu, however, was sufficient to reduce methane yield from 12 to 3 mol. %. The methanation reaction was further suppressed as the Cu content increased in the alloy catalysts. The yield of methane was almost negligible over the entire temperature range for the Cu₂₀ and Cu₁₆Ni₄ catalysts. On the other hand, the introduction of 4 wt. % Ni in the Cu₁₆Ni₄ catalysts enhanced the WGS activity which is attributed to suppression of Cu sintering in the presence of Ni. These results revealed important modifications of the surface properties of bimetallic catalysts, which were consistent with the formation of Cu-Ni, Cu-rich, or Ni-rich alloy phases indicated by XRD and TPR. The Cu₄Ni₁₆ catalyst showed the best WGS performance among all catalysts of this study at 300-400°C. The presence of Cu produced favorable structural and electronic effects for enhancing the WGS activity and suppressed undesirable methanation side-reaction which resulted in greater H₂ yield in the WGS reaction.
Figure 3.6 (A) CO conversion and (B) methane yield during WGS reaction over Cu, Ni, Cu-Ni/CeLaOₓ catalysts. Feed composition: 10% CO-20% H₂O in He
Figure 3.7 (A) CO conversion and (B) methane yield over CuNi/CeLaO$_x$ catalysts as a function of Cu loading at different WGS reaction temperatures. Feed composition: 10% CO-20% H$_2$O in He
A number of different WGS catalysts were reported in the literature.\textsuperscript{[20, 41-44]} These catalyst formulations typically contained a precious (Ru, Pt, Au)\textsuperscript{[42, 44]} or base metal (Cu, Ni, Fe)\textsuperscript{[20, 41, 43]} supported on a partially reducible metal oxide (e.g., CeO\textsubscript{2}, TiO\textsubscript{2}, ZrO\textsubscript{2}). However, a direct comparison of these catalysts is complicated since they have been tested under very different WGS reaction conditions. The product species (CO\textsubscript{2} and H\textsubscript{2}) usually inhibit the WGS reaction rate.\textsuperscript{[42]} Moreover, the catalyst synthesis method also has a large impact on the resulting performance. The WGS reaction rates for the CuNi catalysts of this study were compared with WGS activities of the representative published catalysts estimated from literature data for similar reaction conditions in Table 3.3.\textsuperscript{[20, 42-45]} On the basis of unit mass of a catalyst, the Ni\textsubscript{20} catalyst is the most active. However, the undesired methane yields of up to 12 mol. \% were observed during the WGS reaction. For the bimetallic Cu\textsubscript{4}Ni\textsubscript{16} catalysts, the reaction rate was 31 \mu mol g\textsuperscript{-1} s\textsuperscript{-1} at 300\degree C which is comparable to that of the Ni\textsubscript{20} (35 \mu mol g\textsuperscript{-1} s\textsuperscript{-1}), while undesired methane yield was suppressed to 3 mol. \%. On the basis of total mass of active metal, the Pt/TiO\textsubscript{2} system is the most active catalyst. However, as discussed above, the deactivation behavior of this catalyst and high cost of Pt are considered to be serious drawbacks for their practical application as the WGS catalysts. The specific WGS reaction rates on the basis of total active metal present in the CuNi/CeLaO\textsubscript{x} catalysts as a function of temperature are shown in Figure 3.8. The supported bimetallic CuNi catalysts of this study showed superior WGS performance at 300-400\degree C relative to pure Cu and Ni
catalysts.

**Table 3.3** WGS reaction rates for representative supported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate</th>
<th>Reaction rate</th>
<th>Reaction temperature</th>
<th>Reaction gas mixture</th>
<th>Reference</th>
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<tbody>
<tr>
<td>Ni&lt;sub&gt;10&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>14.8</td>
<td>145</td>
<td>275</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Ni&lt;sub&gt;20&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>27.4</td>
<td>143</td>
<td>275</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;4&lt;/sub&gt;Ni&lt;sub&gt;16&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>15.6</td>
<td>83</td>
<td>275</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu&lt;sub&gt;10&lt;/sub&gt;Ni&lt;sub&gt;10&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
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<td>275</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
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<tr>
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<td>9.6</td>
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<td>275</td>
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<td>This study</td>
</tr>
<tr>
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<td>CuO&lt;sub&gt;42&lt;/sub&gt;-ZnO-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; (commercial)</td>
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<td>275</td>
<td>1.8%CO, 1.8%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
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<td>[43]</td>
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<tr>
<td>Ni&lt;sub&gt;20&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>35.2</td>
<td>183</td>
<td>300</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
</tr>
<tr>
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<td>31.1</td>
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<td>This study</td>
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<tr>
<td>Cu&lt;sub&gt;20&lt;/sub&gt;/CeLaO&lt;sub&gt;x&lt;/sub&gt;</td>
<td>13</td>
<td>92</td>
<td>300</td>
<td>10%CO, 20%H&lt;sub&gt;2&lt;/sub&gt;O, balance He</td>
<td>This study</td>
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3.4 Conclusions

The WGS reaction activities were investigated for supported Cu, Ni and bimetallic Cu-Ni catalysts at 150-400°C. The WGS activity of supported catalysts was largely influenced by the chemical composition, i.e., the Cu and Ni loadings in the catalysts. We have shown that the Cu₄Ni₁₆/CeLaOₓ catalyst is highly active and H₂-selective in the WGS reaction. The Cu addition to Ni/CeLaOₓ catalysts suppressed the formation of methane during the WGS reaction, while the addition of Ni to Cu/CeLaOₓ catalysts enhanced the WGS activity. Moreover, the addition of a second element prevented both Cu and Ni from sintering due to the stronger metal-metal interactions in the CuNi system. The H₂-TPR results for
as-synthesized supported CuNi catalysts indicated lower reduction temperature than for monometallic catalysts and suggested an interaction between CuO and NiO. The Cu$_4$Ni$_{16}$ catalyst showed high WGS activity and strong inhibition of methane formation. These changes in WGS activity are consistent with the formation of alloys in the CuNi catalysts confirmed by XRD.
3.5 References


CHAPTER IV

Hydrogen Production by Water-Gas Shift Reaction over

Supported Cu, Ni and Cu-Ni Nanoparticle Catalysts Prepared

From Metal Colloids

4.1 Introduction

The water-gas-shift (WGS) reaction (CO + H₂O \rightarrow CO₂ + H₂, ΔH = -40.6 kJ/mol) has received renewed interest because of its potential use in connection with fuel cell power generation and small-scale hydrogen production for mobile and on-site stationary applications.\[^{[1]}\] The current WGS catalysts are kinetically limited at low temperature since they are not active enough to attain equilibrium. Current large-scale industrial plants often use a two-step process employing high-temperature shift (Fe₂O₃/Cr₂O₃) and low-temperature shift catalysts (Cu/ZnO/Al₂O₃). However, such a two-step process is not a viable solution for small-scale applications, because of its technical complexity and multiple stages involved.\[^{[2]}\] Therefore, it is very important to develop new WGS catalysts with higher activity at lower temperatures than the present Cu-based WGS catalysts. The activity and selectivity of supported metal catalysts are strongly influenced by the amount of metal, the size of metallic particles, the preparation method, and the support composition.\[^{[3]}\] Traditionally, supported nanoparticle catalysts for industrial applications are prepared by impregnation of metal salt solutions onto oxide support, followed by high temperature oxidation and reduction. Because
such methods are inexpensive, they are widely used for various metals and supports. However, conventional impregnation methods provide limited control over particle size distribution in final catalysts, which represents a considerable drawback for achieving fundamental understanding of catalytic phenomena for these catalysts. Hence, it is highly attractive to obtain supported catalysts with well-defined metal particle size from metal colloids. In a previous study,\[4\] we systematically investigated and compared WGS activity of alumina-supported Cu catalysts prepared from colloidal Cu and synthesized by conventional impregnation. We have shown that the reaction rate per unit mass of active metal at 200°C for supported Cu catalysts prepared from colloidal Cu was 2.5 times higher than for traditionally impregnated catalysts. Other recent studies\[5, 6\] also suggested that supported nanoparticles prepared from metal colloids possess superior catalytic activities in the WGS reaction as well as toluene hydrogenation and CO oxidation as compared to those obtained via conventional impregnation methods. The synthesis procedures to obtain well-defined colloidal nanoparticles have already been established for several systems, and some recent reviews in this area have recently appeared.\[7-9\]

Schumacher et al.\[10\] investigated the trends in low-temperature WGS reactivity on transition metals using a microkinetic model based on a redox mechanism, and suggested that Cu and Ni may be promising as superior catalytic components for WGS catalysts. Zeigarnik et al.\[11\] also proposed a theoretical approach, which included the generation of a complete set
of elementary steps, the calculation of the activation energy and the preexponential factor, along with kinetic simulations, for predicting comparative catalytic activities. They indicated that Cu and Ni may possess optimal activity in the WGS reaction. Callaghan et al.\textsuperscript{[12]} used a Reaction Route Graph Analysis, that indicated Cu and Ni as the most promising metal catalysts for the WGS reaction as compared to other transition metals.

We have previously reported ceria-supported Cu, Ni and Cu-Ni WGS catalysts prepared by conventional impregnation approaches. We have shown that the Cu addition to Ni/CeLaO\textsubscript{x} catalysts suppressed the formation of methane during the WGS reaction, while the addition of Ni to Cu/CeLaO\textsubscript{x} catalysts enhanced the WGS activity.\textsuperscript{[13]} In the present study we report the preparation, characterization and water-gas-shift activity of Al\textsubscript{2}O\textsubscript{3}-supported Cu, Ni and Cu-Ni nanoparticles synthesized as metal colloids. Systematic studies reporting the use of colloidal Cu and Ni nanoparticles in the preparation of heterogeneous catalysts are very few.\textsuperscript{[14-20]} The majority of supported catalysts reported in these studies were not made by the deposition of pre-formed metallic nanoparticles. The metal colloidal particle size and shape, thus, were significantly influenced by the support. In addition, the WGS activity of supported Cu, Ni and Cu-Ni catalysts prepared from metal colloids has not been reported by other research groups. Therefore, the main goal of the present study is to synthesize stabilized and well-defined Cu, Ni and bimetallic nanoparticles by chemical reduction and investigate their behavior in the WGS reaction employing alumina as a catalytic support. A detailed
characterization of supported Cu-Ni nanoparticles by XRD, XPS, \( \text{N}_2 \) adsorption-desorption, TEM, STEM equipped with HAADF detector, and thermogravimetric analysis (TGA) was conducted to elucidate the nanoparticle structure and catalytic performance. For comparison, traditional catalysts prepared by incipient wetness impregnation were also investigated.

### 4.2 Experimental

#### 4.2.1 Preparation of Cu, Ni and Cu-Ni/Al\(_2\)O\(_3\) catalysts

**Materials.** The starting materials were Ni(NO\(_3\))\(_2\)\(\cdot\)6H\(_2\)O (Sigma-Aldrich, 99.99%) and Cu(NO\(_3\))\(_2\)\(\cdot\)2.5H\(_2\)O (Sigma-Aldrich, 99.99%) as metal precursors, hydrazine monohydrate (Alfa Aesar, 99%+) as reducing agent, cetyltrimethylammonium bromide (CTAB) (Alfa Aesar, 98%) as a protecting surfactant, and \( \gamma \)-alumina (Sumitomo, AKP-G015, BET: 185 m\(^2\)/g) as a support. Sodium hydroxide was supplied by Fisher Scientific.

**Catalyst preparation.** A series of Cu, Ni, and Cu-Ni (total 10 wt. %)/\( \gamma \)-alumina catalysts were prepared from metal colloids. Cu, Ni and Cu-Ni nanoparticles were synthesized using a modified version of the wet chemical solution route reported by Wu et al.\(^{[21, 22]}\) Typically, the preparation of metallic Cu nanoparticles was carried out in a sealed bottle by mixing equal volumes of two 0.1M aqueous CTAB solutions, one containing hydrazine (3M) and the other containing Cu(II) nitrate (45 mM) and NaOH (90 \( \mu \)l of 1M NaOH/ml aqueous solution of Cu(II) nitrate. At 25\(^\circ\)C, Cu nanoparticles were obtained after 2h. \( \gamma \)-Al\(_2\)O\(_3\) was subsequently added and resulting slurry was sonicated for 1h. The slurry was filtered and water evaporated
slowly overnight at room temperature. The dried catalyst was washed with ethanol and water to remove excess CTAB surfactant instead of calcination to avoid particle aggregation. Finally, supported catalysts were dried again overnight under vacuum at 80°C. In order to investigate the role of CTAB in the synthesis of supported Cu catalysts, two more supported Cu catalysts were prepared. One of them was prepared by the same procedure without using CTAB and denoted as Cu10WC. The second catalyst was synthesized as follows. Cu nanoparticles were first prepared in the absence of the surfactant, followed by adding 0.1 M CTAB, NaOH (90 μl 1 M NaOH/ml aqueous solution of Cu(II) nitrate) and γ-Al₂O₃, and sonicating the resulting slurry for 1 h. The catalyst thus obtained was referred to as Cu10C. For comparison, a traditional impregnated catalyst, referred to as Cu10I, was also synthesized. The catalysts synthesized in this study are listed in Table 4.1 and Table 4.3.

To obtain Ni nanoparticles, Ni nitrate was dissolved directly in alcohol (47 mM). Then, excess 0.9 M hydrazine and 1 M NaOH solution (80 μl/ml) were added sequentially. Ni nanoparticles were formed at 80°C after 2h which was followed by the addition of γ-Al₂O₃ and sonication of the resulting slurry for 1h. The slurry was then dried overnight under vacuum at 80°C.

Bimetallic Cu-Ni nanoparticles were synthesized following the same procedure as for the Cu nanoparticles, but obtained at 60°C instead of 25°C. For comparison, two traditional impregnated catalysts, referred to as Cu10I and Ni10I, were also synthesized. All catalysts
were reduced in flowing 20 mol. % H₂ in He at 300°C before catalytic tests at 125-400°C.

4.2.2 Catalysts Characterization

**BET surface areas.** The N₂ adsorption-desorption isotherms were measured at -196°C using Micromeritics ASAP 2020 porosimeter. The pore size distributions and surface areas were determined by the Barrett-Joyner-Halenda (BJH)[23] and Brunauer-Emmett-Teller (BET)[24] methods, respectively.

**Powder XRD measurements.** The XRD patterns were collected using a PANalytical X’pert diffractometer equipped with a Cu Kα radiation source. The XRD data were collected in a step-scan mode at 2θ = 30-70° and a step size of 0.05°/s.

**Scanning transmission electron microscopy (STEM).** Samples for examination by scanning transmission electron microscopy (STEM) were prepared by dispersing the powdered catalysts in ethanol and then allowing a drop of the suspension to evaporate on a carbon film supported by a gold grid. STEM images were collected on a Tecnai F20 and JEOL 2010F equipped with a high-angle annular dark field (HAADF) detector. TEM imaging was performed employing a Phillips CM20 electron microscope at a 200-kV accelerating voltage and a high brightness LaB₆ gun for high coherence and small probes.

**ICP-MS elemental analysis.** Determination of total Ni and Cu content was accomplished via microwave digestion followed by the ICP-MS analysis. The sample digestion was accomplished using a CEM Discover/Explorer microwave system. Approximately 5 mg of a
catalyst and 0.500 ml of *aqua regia* (0.125 ml nitric acid and 0.375 ml hydrochloric acid) were placed in a standard CEM 10 ml glass digestion microwave vial fitted with a Teflon lined snap cap. Each sample was digested at 140°C for 2 min, followed by dilution with doubly deionized water to 100 ml before the ICP-MS analysis. Fresh 1,000 ng/ml Ni and Cu standard solution was prepared daily from stock Ni and Cu solutions in 2% nitric acid. Agilent ICP-MS model 7500ce was used for the element specific detection of $^{60}$Ni and $^{63}$Cu. The ICP-MS was equipped with a micro-concentric nebulizer supplied by Glass Expansion, a Scott type double channel spray chamber (cooled to 2°C), a shield torch, an octopole collision/reaction cell with pressurized helium gas (purity of 99.999%), a quadrupole mass analyzer and an electron multiplier. Instrumental parameters were as follows: RF forward power 1500 W; plasma Ar gas flow rate, 15.0 l/min; carrier Ar gas flow rate, 1.05 l/min; He collision gas, 3.7 ml/min. The resulting data were analyzed using Agilent MassHunter ICP-MS software.

**TGA.** Thermogravimetric analysis was performed using a TA Instruments SDT-Q600. In order to dry samples for the study of the oxidation behavior of as-prepared nanoparticles, the temperature was raised from 30°C to 110°C at a rate of 20°C/min and kept at 110°C for 0.5 h under N$_2$ flow. Then, the temperature was increased at a rate of 7°C/min from 80 to 700 °C under air flow of 100 ml/min.

**XPS.** X-ray photoelectron spectroscopy (XPS) was used to analyze the atomic surface
concentration on each catalyst. All samples were analyzed in a Kratos Axis Ultra XPS. A monochromatic Al Kα X-ray source was used, along with pressures in the analysis chamber of $10^{-6}$-$10^{-7}$ torr. The spectra were recorded in the fixed analyzer transmission mode with pass energies of 80 and 20 eV for recording survey and high resolution spectra, respectively. The resolution function of the instrument has been found to have a width of 0.2 eV. Peak shift due to any apparent charging were normalized with the C 1s peak set to 284.6 eV. Quantification was accomplished by determining the elemental peak areas following a Shirley background subtraction.

4.2.3 Catalytic activity

The WGS activities were determined employing a continuous fixed-bed tubular quartz microreactor (0.55 cm ID) operated at atmospheric pressure and using 0.1 g of each catalyst diluted with 0.2 g of quartz powder. The feed gas typically contained 10 mol. % CO and 20 mol. % H₂O in helium. The total feed flow rate was 100 ml/min. All catalysts were reduced in flowing 20 mol. % H₂ in He at 300°C before catalytic tests at 125-400°C. Liquid water was injected into flowing gas stream by a syringe pump and vaporized in the heated gas feed line before entering the reactor. A condenser filled with ice was installed at the reactor exit to collect water. The gas mixture was analyzed by a gas chromatograph (Hewlett-Packard HP-5580A) equipped with a thermal conductivity detector. Intrinsic reaction rate is the rate of CO conversion, and was determined in separate experiments where the conversions of
reactants were kept below 10 mol. %. These results were used to determine the turnover frequencies (TOFs) of CO consumption, defined as the number of CO molecules converted per surface Cu metal atom per second[^25].

4.3 Results and Discussion

4.3.1 Structural properties of Cu catalyst

A typical TEM image and the size distribution of Cu nanoparticles are shown in Figures 4.1(a) and (b). The particle size distribution was obtained by measuring a sample of ~100 particles. The particles were very fine and roughly monodisperse with a mean diameter of 4.6 nm which is comparable to that in Cu nanoparticles (5.1 nm) reported in a previous study.[^21] The next preparation step consisted of the deposition of the CTAB-capped Cu particles on the 𝛾-alumina support. Figures 4.1 (c) and (d) showed STEM images and particle size distribution of Cu nanoparticles supported on 𝛾-alumina after activation in hydrogen at 300°C. The nanoparticles with an average size of 5.2 nm were well dispersed over the oxide support. The removal of a protective polymer or surfactant while maintaining the nanoparticle dispersion and size represents a great challenge for utilizing pre-formed nanoparticles to form supported heterogeneous catalysts. These protective agents are typically removed during thermal activation in air or inert atmosphere followed by catalyst reduction.[^26-28] In this study, the CTAB surfactant was easily removed by simple washing supported catalysts with ethanol. Therefore, these catalysts can be activated directly by reducing them at 300°C without further
thermal treatment. As can be seen from Figure 4.1, the particle size increased only slightly from 4.6 nm to 5.2 nm for supported Cu nanoparticles after reduction at 300°C in hydrogen. These results demonstrated that the colloidal deposition method employed in this study is well suited for the preparation of well-dispersed supported metal nanoparticles.

Table 4.1 Physicochemical characteristics of supported Cu catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Copper content (wt.%)</th>
<th>$S_{BET}$ (m$^2$g$^{-1}$)</th>
<th>Dispersion (%)</th>
<th>Cu surface atoms ($\mu$mol/g$_{cat}$)</th>
<th>Cu surface area ($m^2/g_{cat}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu10</td>
<td>7.5</td>
<td>147</td>
<td>44</td>
<td>520</td>
<td>21</td>
</tr>
<tr>
<td>Cu10I</td>
<td>9.5</td>
<td>143</td>
<td>26</td>
<td>383</td>
<td>16</td>
</tr>
<tr>
<td>Cu10C</td>
<td>8.4</td>
<td>145</td>
<td>40</td>
<td>526</td>
<td>22</td>
</tr>
<tr>
<td>Cu10WC</td>
<td>8.4</td>
<td>146</td>
<td>34</td>
<td>450</td>
<td>18</td>
</tr>
</tbody>
</table>

Table 4.2 Catalytic activity of supported Cu catalysts in WGS reaction at 200°C

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate ($\mu$molg$^{-1}$s$^{-1}$)</th>
<th>Reaction rate ($\mu$molg$_M^{-1}$s$^{-1}$)</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu10</td>
<td>15.3±0.7</td>
<td>204±10</td>
<td>0.029±0.001</td>
</tr>
<tr>
<td>Cu10I</td>
<td>8.0±0.4</td>
<td>84±4</td>
<td>0.021±0.001</td>
</tr>
<tr>
<td>Cu10C</td>
<td>14.7±0.7</td>
<td>164±8</td>
<td>0.028±0.001</td>
</tr>
<tr>
<td>Cu10WC</td>
<td>9.3±0.4</td>
<td>111±5</td>
<td>0.021±0.001</td>
</tr>
</tbody>
</table>
Figure 4.1 (a) TEM images and (b) size distribution of Cu nanoparticles. (c) STEM images and (d) size distribution of supported Cu nanoparticles after activation at 300°C.
4.3.2 WGS reaction over supported Cu catalysts

The catalytic activity of the supported Cu catalysts prepared from colloidal Cu and by conventional impregnation method was determined at 125-400°C. The CO conversion in the WGS reaction over Cu10 and Cu10I catalysts as a function of temperature is shown in Figure 4.2. The onset temperatures of catalytic activity for the supported Cu catalysts showed that the catalyst prepared from colloidal nanoparticles was more active than the conventional catalyst. The CO conversion over supported Cu catalysts prepared from colloidal Cu was higher by ca. 60% at 275°C as compared to the supported catalysts prepared by the conventional impregnation method. The intrinsic reaction rate (μmol/per gram of active metal) is a good indicator of the influence of the active metal content on the reaction kinetics. The results obtained at 200°C showed that the reaction rate for the catalysts prepared from metal colloids was 2.5 times higher (204 μmol/gCu) than for the impregnated catalysts (84 μmol/gCu) (Table 4.2). Although the colloidal method can provide metal nanoparticles displaying a narrow size distribution, a major drawback is the presence of a protecting agent, e.g., a polymer or surfactant, which may be detrimental to their catalytic function. Recently, Rinaldi et al.\cite{15} investigated heterogeneous Ni catalysts made from colloidal nanoparticles, and demonstrated that well-dispersed Ni nanoparticles can be successfully deposited on silica and activated carbon support. However, despite the well-dispersed nature and uniform size of supported Ni nanoparticles, this synthetic route did not result in active Ni catalysts for the
hydrogenation of cyclohexene and steam reforming of ethanol due to the presence of protecting agents at the Ni surface in working catalysts. By contrast, we successfully prepared a new class of well-dispersed supported Cu catalysts employing CTAB surfactant that was easily removed by washing with ethanol.

**Figure 4.2** CO conversion over Cu/Al$_2$O$_3$ catalysts prepared from Cu colloids and conventional impregnation. Feed composition: 10% CO-20% H$_2$O in He.
4.3.3 The role of CTAB in supported Cu nanoparticles

An important challenge in the area of nanoscale materials is the ability to characterize the structure of protecting agents on the surface of inorganic nanoparticles. TGA was used in this study to quantify the CTAB content and suggest its structural motif on the nanoparticle surface. The bottom part of Figure 4.3 shows the weight loss curves for the free CTAB surfactant and surfactant-capped Cu nanoparticles. The upper part of Figure 4.3 shows the corresponding derivative weight loss curves. For the free surfactant, the major weight loss range is from 223 to 275°C. The range for CTAB-capped Cu nanoparticles spans from 150 to 770°C. In the case of CTAB-capped Cu nanoparticles, the first weight loss occurs below 270°C (relative to the free surfactant) which may be due to the presence of weakly bound surfactant similar to earlier observations by Nikoo bakht et al.\(^{[29]}\) Above 270°C, the second and third peaks are observed centered at 397 and 610°C, respectively. These observations may suggest the formation of a bilayer structure for CTAB capping the Cu surface. The inner layer is bound to the Cu nanoparticle surface through the charged alkylammonium headgroups and is connected to the outer layer by hydrophobic interactions of hydrocarbon tails. Thus, the first peak might be assigned to the free surfactant weakly bound to the outer layer surfactant. The second and the third peak are assigned to CTAB molecules that are weakly coordinated and strongly bound to the Cu surface, respectively. Similar conclusions were advanced by Nikootbakht and Wu in the studies of assembly of cationic surfactants on
the surface of Au nanorods and synthesis of Cu nanoparticles in aqueous CTAB solutions, respectively.\cite{21, 29} However, a conclusive evidence of the surfactant bilayer structure in the capped nanoparticles was not obtained in our TGA study of CTAB-capped Cu nanoparticles. Our estimates based on TEM images indicated the surface area of 66.5 nm\(^2\) for an average Cu nanoparticle in our catalysts. Assuming the surfactant bilayer packing area of \(21\,\text{Å}^2\),\cite{30-32} each nanoparticle would on average have \(~630\) CTAB molecules on its surface in a bilayer structure. The removal of a CTAB bilayer completely covering these Cu nanoparticles would result in 45 wt. % loss during TGA. However, our TGA data indicated only 18 wt. % loss strongly suggesting a less ordered structure of the surfactant layer covering the Cu nanoparticles. The interactions between Cu nanoparticles and CTAB led to improvement of nanoparticle dispersion on the support and thus enhanced WGS activity. Two model catalysts, Cu10C and Cu10WC, were synthesized in order to investigate the effect of CTAB surfactant on the WGS activity. The XRD patterns of the Cu10, Cu10WC, and Cu10C after activation at 300°C are shown in Figure 4.4. The XRD patterns of Cu10 (CTAB added before Cu nanoparticle formation) and Cu10C (CTAB added after Cu nanoparticle formation, but before their deposition onto support) showed a weak peak of Cu at \(2\theta =43.4^\circ\), suggesting the presence of smaller Cu nanoparticles. In addition, the mean Cu particle sizes in Cu10, Cu10C and Cu10WC after activation determined by STEM were 5.2, 4.9 and 9.8 nm, respectively (Figure 4.5). These results indicated that CTAB-capped Cu nanoparticles were well dispersed
on the alumina support. The strong bonds between the γ-alumina surface and Cu particles effectively anchored Cu at the particle-support interface during deposition. Afterwards, the supported Cu catalysts were washed with ethanol to remove the CTAB without further aggregation. After activation at 300°C, Cu nanoparticles still appeared to be well-dispersed on the alumina surface (Fig 4.1 and Fig 4.4). On the other hand, Cu nanoparticles in the absence of CTAB were aggregated on the alumina support (Cu10WC). After activation at 300°C, the small particles underwent sintering into bigger particles that resulted in reduced active surface area (Scheme 4.1). The dispersion of Cu catalysts determined by N₂O oxidation (Table 4.1) showed the following order: Cu10 = Cu10C > Cu10WC > Cu10I, which also agreed with this observation. It should be noted that the supported Cu nanocatalysts that were not washed with ethanol but instead directly activated at 300°C, showed no WGS activity. Therefore, the surfactant covering the Cu surface even after heat treatment at 300°C blocked the active surface sites. This result is also in agreement with the TGA observation that CTAB was completely removed only after calcination of the supported Cu catalysts at 800°C. Accordingly, ethanol washing used in this study was highly effective in removing CTAB. The WGS activity of the Cu10, Cu10C and Cu10WC catalysts is shown in Figure 4.6. Cu10 and Cu10C showed comparable activity, while Cu10WC showed significantly lower CO conversion (by ca. 20%) than Cu10. Cu10 and Cu10C showed higher WGS activity than Cu10WC, which is consistent with higher dispersion of Cu nanoparticles.
synthesized in the presence of CTAB. Therefore, these promising results strongly indicated that CTAB-capped Cu nanoparticles are very promising for preparing highly active supported WGS catalysts.

**Figure 4.3** TGA and derivative curves shown in the bottom and top part of the graph, respectively. a) CTAB; and b) CTAB-capped Cu nanoparticles.
Figure 4.4 XRD patterns of supported Cu catalysts after activation at 300°С
Figure 4.5 STEM image and size distribution of (a and b) Cu10C, (c and d) Cu10WC, and (e and f) Cu 10I
Scheme 4.1 Synthesis of supported Cu catalysts prepared from CTAB-capped and CTAB-free Cu nanoparticles.

Figure 4.6 CO conversion over model Cu/γ-Al₂O₃ catalysts: (●)Cu10WC, (■)Cu10, (▲)Cu10C. Feed composition: 10% CO-20% H₂O in He.
The activity and structure-(in)sensitivity of the WGS reaction over Cu-Zn-Al mixed oxide catalysts were studied by Ginés et al.\textsuperscript{[33]} They observed that the turnover frequency was essentially constant over a wide range of metallic Cu dispersions. Thus, the WGS reaction was apparently structure-insensitive over the Cu/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts. From the previous discussion of catalyst characterization and activity studies, it can be inferred that the dispersion of the active Cu in supported catalysts had a significant effect on the CO conversion (Table 4.1 and Table 4.2). Although WGS reaction rates were different for the four types of catalysts, their TOFs were similar (0.020-0.030 s\textsuperscript{-1} at 200\textdegree C), consistent with structure insensitivity of this reaction.

4.3.4 Morphological and structural characterization of Cu, Ni and Cu-Ni nanoparticles

The typical XRD patterns of as-synthesized Cu and Ni nanoparticles obtained by chemical reduction are shown in Figure 4.7. Two main characteristic peaks of Cu at 43.3\textdegree and 50.4\textdegree and one minor characteristic peak of Cu\textsubscript{2}O at 36.4\textdegree are observed in Figure 4.7 (a). The XRD pattern of the Ni nanoparticles showed the presence of the mixture of hexagonal Ni(OH)\textsubscript{2} (PDF 00-003-0177) and cubic Ni phase (PDF 00-001-1260) (Fig 4.7 (b)). The XRD pattern of as-synthesized Cu\textsubscript{5}Ni\textsubscript{5} nanoparticles is shown in Figure 4.7 (c). The broad diffraction peaks at 2\theta = 42-46\textdegree and 48-52\textdegree can be resolved into two peaks which corresponded to a Cu phase and Cu-Ni alloy phase. The Cu phase is characterized by two
main peaks of Cu at 43.3° and 50.4° (PDF 00-001-1241). The Cu-Ni alloy phase is identified by two well-defined reflections whose positions are slightly shifted from those of pure Ni (PDF 00-001-1260) towards the Cu reflections (Figure 4.7 (d)). Its unit cell parameter was calculated to have a value of 3.559 Å, which is different from that of pure nickel (3.524 Å) and pure copper (3.615 Å) indicating an alloy phase. The copper-nickel alloy phase composition in the Cu5Ni5 catalyst calculated by Vegard’s law is Cu/Ni = 0.61. In this synthesis by chemical reduction, the formation of Cu and Ni nanoparticles depends on the following redox reactions:[34]

\[
2\text{Cu}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Cu} + \text{N}_2 + 4\text{H}_2\text{O} \quad (1)
\]
\[
2\text{Ni}^{2+} + \text{N}_2\text{H}_4 + 4\text{OH}^- \rightarrow 2\text{Ni} + \text{N}_2 + 4\text{H}_2\text{O} \quad (2)
\]

The standard reduction potential of copper (0.337V) is higher than that of nickel (-0.25V).[35] Therefore, Cu is easier to reduce when both Cu and Ni ions are present during reduction. Cu-Ni nanoparticles are more likely to be produced through the following heterogeneous nucleation process due to the difference in their redox potentials. Cu nanoparticles are produced first and then act as nucleation sites inducing the reduction of Ni and formation of a copper-nickel alloy phase. As reduction proceeds, the unreacted nickel undergoes reduction, resulting in a shell of copper-nickel alloy. No nickel reduction was observed in the aqueous solution without the Cu precursor. This suggests that available Cu surface assists in the Ni reduction and helps nucleate the Cu-Ni shell. As the synthesis
proceeds, the solution color first changes from light green to reddish corresponding to the formation of Cu nanoparticles, and then to black indicating a Cu-Ni alloy shell. These observations are also consistent with the XRD patterns. Similar results have been reported by Bonet et al.\textsuperscript{[36]} and Yamauchi et al.\textsuperscript{[37]} The XRD patterns of as-synthesized Cu2Ni8 and Cu8Ni2 nanoparticles are shown in Figure 4.8. The XRD pattern of Cu8Ni2 nanoparticles showed a typical Cu peak with a shoulder corresponding to a Cu-Ni alloy, while the Cu2Ni8 nanoparticles displayed characteristic peaks of Ni(OH)\textsubscript{2} in addition to the Cu and Cu-Ni alloy phases. Low content of surface Cu in the Cu2Ni8 nanoparticles resulted in only partial reduction of Ni\textsuperscript{2+} and consequently Ni(OH)\textsubscript{2} was also present in this system in addition to Ni and/or Cu-Ni alloy phases.

A typical TEM image and size distribution of Ni nanoparticles are shown in Figure 4.9 (a)(e). The particles were very fine and relatively monodisperse with a mean diameter of 4.7 nm which is similar in size to the Cu nanoparticles (4.6 nm)(Figure 4.1) Figures 4.9 (b)(f) shows HAADF-STEM images and particle size distribution of Ni nanoparticles supported on γ-alumina after reduction in hydrogen at 300°C. The STEM data indicated that the nanoparticles were well dispersed over the alumina support and suggested a slight size increase from 4.7 to 5.5 nm. A slight size increase for supported Cu nanoparticles from 4.6 to 5.2 nm was also observed in Figure 4.1.
Figure 4.7 XRD patterns of as-synthesized (a) Cu, (b) Ni, and (c) Cu$_5$Ni$_5$ nanoparticles. (○)Ni(OH)$_2$, (△)Cu, (□)Ni, (◇)Cu$_2$O, (ε)CuNi alloy, (d) details of the range of $2\theta = 39-56^\circ$ of Figure 4.7(c).
The Cu and Ni nanoparticles supported on metal oxides are traditionally imaged by S/TEM with respect to their particle size. However, the analysis of metal nanoparticles by S/TEM on supports is often complicated because of low contrast difference between the support and metallic nanoparticles. In such cases the use of alternative methods, such as selective chemisorption, to determine the average size of metallic particles can provide independent measurements in support of S/TEM characterization. Other analytical methods to determine particle sizes and corresponding active surface site concentrations have been also employed depending on the system being studied. Electrochemists and electrochemical engineers often use cyclic voltammetry (CV) to determine active site concentrations, while inorganic chemists and materials scientists may prefer X-ray line broadening and transmission electron microscopy methods to infer active particle sizes and corresponding
active site concentrations.\[^{38}\] On the other hand, researchers in heterogeneous catalysis typically prefer selective chemisorption methods and S/TEM to determine particle sizes and active surface area. Very often, different results are obtained depending on the underlying assumptions and limitations of each method. Reliable determination of average particle size by S/TEM depends on (1) the availability of an accurate, high resolution transmission electron microscope that can image all metallic particles with high contrast, since they have very high surface/volume atomic ratios, (2) imaging a statistically relevant number of particles, and (3) reliable assignment of particle geometry.\[^{38, 39}\] In the present case, our results indicated the average Ni particle size of 9.5±0.4 nm (from CO chemisorption) and 5.5±1.5 nm (from STEM imaging). CO chemisorption does not probe those surface Ni atoms that are in contact with support and inaccessible for chemisorption, and thus leads to larger particle size estimates.\[^{40}\] Therefore, the results of both techniques are reasonably matched.

Figures 4.9 (c) and (d) show the S/TEM images for Cu5Ni5 nanoparticles and supported Cu5Ni5 nanoparticles after reduction at 300°C, respectively. Large particles (ca. 50 nm) were observed in the case of bimetallic Cu5Ni5 nanoparticles prepared in aqueous solution (Fig. 2(g)(h)). Ahmed et al.\[^{41}\] reported bimetallic nanoparticles prepared in water-in-oil microemulsions ranging in size from 7 to 50 nm depending on the synthesis Cu/Ni ratio. Similar morphology and smaller particle sizes were observed in supported Cu8Ni2 and Cu2Ni8 nanoparticles (not shown here). The particle sizes of supported
nanoparticles after reduction at $300^\circ\text{C}$ are summarized in Table 4.3.
Figure 4.9 TEM images and particle size distributions of as-synthesized (a and e) Ni and (c and g) Cu5Ni5 nanoparticles. HAADF-STEM images and size distribution of supported Ni nanoparticles (b and f) and supported Cu5Ni5 nanoparticles (d and h) after reduction at 300°C in hydrogen.
A representative HAADF-STEM image of as-synthesized Cu-Ni nanoparticles is shown in Figure 4.10 (a) for Cu5Ni5 nanoparticles. The particle sizes determined from this image agree with those from the TEM image shown in Figure 4.9 (c). The X-ray line scan profile along the line in a single particle shown in the HAADF-STEM image further suggested that as-synthesized Cu5Ni5 nanoparticles have a Cu-rich core and Ni-rich shell (Figure 4.10 (b)).

The TGA curves of as-prepared Cu, Ni, and Cu5Ni5 nanoparticles in air are shown in Figure 4.11. The as-synthesized Ni nanoparticles showed a weight loss of ca. 18% from 275 to 300°C due to Ni(OH)2 dehydration to NiO and weight gain of ca. 5% from 350 to 450°C due to the Ni oxidation to NiO. The TGA curves of as-synthesized Cu nanoparticles showed a weight gain of ca. 22% at 173-332°C due to Cu oxidation. The XRD patterns of as-prepared Cu nanoparticles indicated the presence of metallic Cu⁰ and some Cu₂O phase (Figure 4.7). Therefore, the total weight gain observed in the TGA curves corresponded to Cu⁰ and Cu₂O oxidation. The lack of weight loss features at low temperatures suggested that the surfactant was removed completely after washing with ethanol. The weight gain observed due to Cu⁰ and Cu₂O oxidation allowed estimation of the Cu⁰/Cu₂O ratio in as-synthesized nanoparticles, which was ~3.5.
Figure 4.10 (a) HAADF-STEM image of as-synthesized Cu5Ni5 nanoparticles; the line scan profiles along the cross-section of a single (b) as-synthesized Cu5Ni5 particle and (c) supported Cu5Ni5 nanoparticle after reduction at 300°C in hydrogen; (d) Cu/Ni atomic ratios in the surface region of (I) as-synthesized and (II) supported Cu5Ni5 nanoparticles after reduction at 300°C in hydrogen.

The Cu5Ni5 nanoparticles showed the onset of oxidation at 227°C. As compared to pure Cu nanoparticles, the Cu5Ni5 nanoparticles exhibited improved stability under oxidation conditions reflected in higher temperatures required for their oxidation under TGA conditions. The as-prepared Cu5Ni5 nanoparticles showed a small weight loss due to Ni(OH)2 dehydration to NiO and a weight gain due to Cu or Cu-Ni alloy oxidation. The TGA curve of as-synthesized Cu2Ni8 (not shown here) showed greater weight loss due to Ni(OH)2 dehydration as compared to TGA curves of Cu5Ni5 and Cu8Ni2, which were in agreement with our XRD data.
Figure 4.11 TGA curves of as-synthesized Cu, Ni and Cu5Ni5 nanoparticles heated in air at 7°C/min.

4.3.5 Characterization of supported WGS catalysts

Table 4.3 reports the physicochemical characteristics of WGS catalysts investigated in this work. Supported Cu, Ni and Cu-Ni nanoparticle catalysts prepared from metal colloids and by conventional impregnation methods (Cu10I and Ni10I) are shown in Table 4.3 for comparison.

Protective agents, such as CTAB, employed in nanoparticle synthesis and covering the surface of as-synthesized Cu nanoparticles are detrimental to their catalytic activity. These protective agents are typically removed by thermal activation in air or inert atmosphere followed by the catalyst reduction. As we discussed above, CTAB-capped Cu nanoparticles were well dispersed on the alumina support. The interactions between the γ-alumina surface and Cu particles effectively anchored Cu at the particle-support interface
during deposition. It was subsequently demonstrated that CTAB can be removed from the Cu surface in supported catalysts by washing with ethanol without causing particle aggregation. Therefore, these catalysts can be directly reduced in hydrogen at 300°C. It should be noted that supported Cu nanocatalysts that were not washed with ethanol and were instead directly activated at 300°C, showed no WGS activity. Therefore, the surfactant decomposition products covering the Cu surface after the heat treatment at 300°C blocked the surface active sites.

Table 4.3 Physicochemical characteristics of as-synthesized supported Cu-Ni catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Active metal content (wt.% by ICP)</th>
<th>$S_{\text{BET}}$ (m$^2$ g$^{-1}$)</th>
<th>Mean particle size (nm)$^{a}$</th>
<th>Metal surface area (m$^2$/gM)$^{b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu10</td>
<td>7.5</td>
<td>147</td>
<td>5.2±1.8</td>
<td>129±44</td>
</tr>
<tr>
<td>Cu10I</td>
<td>9.5</td>
<td>143</td>
<td>8.8±2.9</td>
<td>77±25</td>
</tr>
<tr>
<td>Ni10</td>
<td>--</td>
<td>135</td>
<td>5.5±1.5</td>
<td>123±33</td>
</tr>
<tr>
<td>Ni10I</td>
<td>--</td>
<td>144</td>
<td>7.2±2.6</td>
<td>94±33</td>
</tr>
<tr>
<td>Cu2Ni8</td>
<td>0.9</td>
<td>150</td>
<td>19±5</td>
<td>35±9</td>
</tr>
<tr>
<td>Cu5Ni5</td>
<td>3</td>
<td>152</td>
<td>54±8</td>
<td>12±2</td>
</tr>
<tr>
<td>Cu8Ni2</td>
<td>5.3</td>
<td>150</td>
<td>18±5</td>
<td>37±10</td>
</tr>
</tbody>
</table>

$^{a}$determined from HAADF-STEM images

$^{b}$metal surface area was calculated by the following equation: $\frac{6 \times 10^3}{\rho d}$
On the other hand, Ni nanoparticles tend to aggregate more easily due to van der Waals forces and additional attractive magnetic forces. In order to prevent aggregation, surfactants and/or polymers have to be added to nanoparticle suspensions. However, these protective agents covering the particle surface are detrimental to catalytic activity. Rinaldi et al. demonstrated that well-dispersed Ni nanoparticles prepared from metal colloids can be successfully deposited on silica and activated carbon supports.\textsuperscript{[15]} Despite the well-dispersed nature and uniform size of supported Ni nanoparticles, this synthesis route did not result in active catalysts for the hydrogenation of cyclohexene and steam reforming of ethanol due to the presence of protective agents at the Ni surface in working catalysts. Mayer et al. reported that Ni(OH)\textsubscript{2} nanoparticle suspensions could be stabilized due to the negative charge of the surface OH\textsuperscript{-} groups, which causes mutual repulsions between the nanoparticles preventing their aggregation.\textsuperscript{[42]} Besides, Wang et al. demonstrated that Ni/Ni(OH)\textsubscript{2} mixed phase nanoparticles possess a reduced magnetic dipole strength as compared to that of the pure Ni phase due to the presence of nonmagnetic Ni(OH)\textsubscript{2}.\textsuperscript{[43]} Thus, the Ni\textsuperscript{0}/Ni(OH)\textsubscript{2} mixed phase nanoparticles (Figure 4.7 and 4.11) obtained in this study are important for the preparation of well-dispersed nanocatalysts. To further demonstrate this effect, we synthesized a pure fcc Ni phase by hydrazine reduction in ethylene glycol (EG) instead of absolute ethanol. Figure 4.12 (a) shows the XRD pattern of as-synthesized Ni nanoparticles prepared in EG. Three characteristic Ni peaks at $\theta = 44.6$, 51.9 and 76.8\textdegree{} were observed indicating a pure fcc Ni
phase. The TEM images suggested that spherical aggregates of primary Ni nanoparticles can be regarded as a secondary nanostructure (Figure 4.12 (b)). The formation of aggregated secondary structure may be explained by mutual attractions of Ni magnetic dipoles.\[44, 45\] Furthermore, the WGS reaction studies have revealed that the CO conversion rate of as-prepared supported Ni nanoparticles containing a pure Ni fcc phase with aggregated structure was significantly lower (0.4 \(\mu\)mol•gcat\(^{-1}\)s\(^{-1}\) at 230°C) than that of the Ni/Ni(OH)\(_2\) mixed phase containing well-dispersed nanoparticles (9.8 \(\mu\)mol•gcat\(^{-1}\)s\(^{-1}\) at 230°C). These results demonstrated that the colloidal deposition method employed in this study is well suited for the preparation of well-dispersed supported metal nanoparticles.
Figure 4.12 (a) XRD pattern and (b) TEM image of as-synthesized Ni nanoparticles prepared in ethylene glycol.
4.3.6 Surface composition of Cu-Ni system: alloying and segregation

Surface structures, composition and segregation properties of bimetallic catalysts are of great interest since they are important for the catalytic activity. The XPS data provide information about the composition and chemical state of active metals in the near-surface region. Binding energies of selected photoemission lines of supported Cu2Ni8, Cu5Ni5 and Cu8Ni2 catalysts are summarized in Table 4.4. The XPS spectra of Cu 2p and Ni 2p for as-prepared, reduced at 300°C, and used Cu5Ni5 catalysts are shown in Figure 4.13. In the Cu core level XPS spectra, the Cu2p\textsubscript{3/2} signal of as-prepared catalyst is composed of two overlapping peaks at 932.8 and 935.3 eV (Figure 4.13 (a)). In addition to these peaks, a shakeup satellite peak is observed in the region of 941-946 eV. The intense peak at 932.8 eV could be assigned to Cu or Cu\textsubscript{2}O and the peak with higher binding energy of 935.3 eV could be attributed to the CuO moiety.\cite{46-49} The deconvolution of the Cu\textsuperscript{0} and Cu\textsubscript{2}O peaks could not be accomplished due to close proximity of the binding energies.\cite{48, 49} Since the XRD analysis showed the presence of metallic Cu and minor Cu\textsubscript{2}O phase, the peak at 932.8 eV represents a Cu\textsuperscript{0} and Cu\textsuperscript{+} mixture. Moreover, the minor satellite peak located about 10 eV higher than 2p\textsubscript{3/2} was observed and indicated the presence of some Cu(II) species in the Cu5Ni5 catalysts.\cite{46-47} The presence of Cu(II) in the as-synthesized catalysts suggests a thin layer of CuO on the nanoparticle surface. The low intensity satellite peak was also observed.
in reduced and used catalysts indicating that Cu was easily oxidized even at room
temperature during the transfer of the catalysts to the XPS instrument.

In the Ni core level XPS, the deconvoluted Ni2p3/2 spectra of as-prepared catalyst
displayed two peaks (Figure 4.13 (b)). The lower binding energy peak at 852.1 eV is
attributed to Ni0 and higher binding energy peak at 856.1 eV is due to Ni(OH)2.\textsuperscript{[50,51]} Figure
4.13 (b) also indicated a higher surface concentration of Ni(OH)2 in Cu5Ni5 catalyst as
compared to that of Ni0. In the case of as-synthesized supported Cu2Ni8 catalysts, the XPS
data indicated the absence of Ni0 and showed the presence of Ni(OH)2 (Table 4.4). The XPS
data are in agreement with the results of XRD and TGA characterization of this catalyst
(Figure 4.7 and 4.11). The chemical state of as-synthesized supported Cu8Ni2 was similar to
that in supported Cu5Ni5 catalysts.

The Ni surface concentration in reduced and used Cu5Ni5 catalysts was quite low as
compared to that in the as-prepared catalyst (Figure 4.13 (b)). The Cu/Ni atomic surface
ratios ranged from 1.0 for the as-prepared catalyst to 1.7 and 1.8 for reduced and used
catalysts, respectively. Thus, Cu appears to be mostly segregated to the surface after heat
treatment. The chemical composition of the alloy surface may differ from the bulk
composition resulting in surface enrichment by one component. The surface segregation of
Cu was reported in the literature for the Cu-Ni system.\textsuperscript{[51-53]} On the basis of thermodynamics,
the lower surface free energy or surface segregation energy of Cu in the Cu-Ni system leads
to Cu occupying the surface sites of the bimetallic particles.\(^{52, \ 53}\) In our system, as-synthesized Cu5Ni5 nanoparticles possessed a Cu core and Cu-Ni alloy shell structure (Figure 4.7 and 4.10). This result indicated that the structure of Cu5Ni5 particles is controlled by kinetics related to the formation process and not by thermodynamics because the nanoparticles were synthesized at a relatively low temperature. The bimetallic particles with the Cu core are unstable and are expected to become surface-enriched in Cu at high temperatures. In agreement with these expectations, the Cu/Ni atomic ratios in the surface region increased from 1 for the as-synthesized Cu5Ni5 catalyst to 1.7 and 1.8 for the reduced and used catalysts, respectively, indicating surface segregation of Cu in the Cu5Ni5 catalyst. In the case of Cu2Ni8 catalysts, the Cu/Ni atomic ratios determined by XPS also increased from 0.3 for the as-synthesized catalyst to 0.6 and 0.7 for the reduced and used catalysts (Table 4.4). Similar results for surface segregation of Cu were also observed in supported bimetallic Cu8Ni2 nanoparticles after reduction (Table 4.4). In addition, the X-ray line scan profile along the line in a single supported Cu5Ni5 particle after reduction at 300°C shown in Figure 4.10 (c) also suggested that Cu migrated to the surface region as compared to the profile of the as-synthesized catalyst shown in Figure 4.10 (b). The Cu/Ni atomic ratios of as-synthesized Cu5Ni5 nanoparticles and supported Cu5Ni5 nanoparticles after reduction at 300°C determined from the line scan data at 7-12 nm are shown in Figure 4.10 (d). This distance range was selected as representative of the surface region, since the distance range
from 0 to 6 nm in Figures 4.10 (a) and (b) is outside the nanoparticles. The higher Cu/Ni atomic ratios observed in the surface region of the reduced Cu5Ni5 catalyst as compared to as-synthesized Cu5Ni5 catalyst also indicated Cu segregation to the surface region after reduction.

Table 4.4 Binding energies and Cu/Ni atomic ratios of bimetallix CuNi catalysts determined by XPS

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Type</th>
<th>BE of Cu 2p3/2 (eV)</th>
<th>BE of Ni 2p3/2 (eV)</th>
<th>(Cu/Ni)$_{XPS}$</th>
<th>(Cu/Ni)$_{ICP}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu2Ni8/Al$_2$O$_3$ as-synthesized</td>
<td>932.8</td>
<td>--</td>
<td>855.4</td>
<td>0.3</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu2Ni8/Al$_2$O$_3$ reduced at 300°C</td>
<td>932.8</td>
<td>852.3</td>
<td>855.7</td>
<td>0.6</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu2Ni8/Al$_2$O$_3$ used</td>
<td>932.5</td>
<td>852.2</td>
<td>855.5</td>
<td>0.7</td>
<td>0.13</td>
</tr>
<tr>
<td>Cu5Ni5/Al$_2$O$_3$ as-synthesized</td>
<td>932.8</td>
<td>852.1</td>
<td>856.1</td>
<td>1.0</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu5Ni5/Al$_2$O$_3$ reduced at 300°C</td>
<td>932.7</td>
<td>852.2</td>
<td>856.0</td>
<td>1.7</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu5Ni5/Al$_2$O$_3$ used</td>
<td>932.5</td>
<td>852.4</td>
<td>856.0</td>
<td>1.8</td>
<td>1.3</td>
</tr>
<tr>
<td>Cu8Ni2/Al$_2$O$_3$ as-synthesized</td>
<td>933.1</td>
<td>852.1</td>
<td>856.1</td>
<td>6.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Cu8Ni2/Al$_2$O$_3$ reduced at 300°C</td>
<td>932.9</td>
<td>852.2</td>
<td>856.0</td>
<td>6.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Cu8Ni2/Al$_2$O$_3$ used</td>
<td>932.6</td>
<td>852.4</td>
<td>856</td>
<td>7.6</td>
<td>3.5</td>
</tr>
</tbody>
</table>
Figure 4.13 (a) Cu 2p and (b) Ni 2p XPS spectra of as-synthesized, reduced in hydrogen at 300°C and used Cu5Ni5 catalysts.
4.3.7 WGS reaction over supported Cu, Ni and Cu-Ni catalysts

The catalytic activity of the supported Cu, Ni and Cu-Ni catalysts was determined at 125°C-400°C. The CO conversion in the WGS reaction over a series of Cu and Ni/Al₂O₃ catalysts as a function of temperature is shown in Figure 4.14. Supported Cu nanoparticles showed a light-off temperature of 125°C, which is lower than that of the supported Ni nanoparticles (200°C), and promising WGS activity at low temperatures (125-250°C). Supported Ni nanoparticle catalysts were more active than the Cu catalysts above 275°C. However, up to 12 mol. % CH₄ yield was observed during WGS reaction over supported Ni catalysts due to methanation side reaction (Figure 4.15). It has been reported that Ni is an effective catalyst for the methanation reaction.¹³,⁵⁴ Since the methanation reaction consumes H₂, the higher the CH₄ yield, the lower the H₂ yield in the WGS reaction, which indicates a potential drawback of using Ni as a WGS catalyst. The CO conversion over traditional supported catalysts prepared by impregnation and those prepared from metal colloids is also shown in Figure 4.14. The onset temperatures of catalytic activity for two kinds of supported Cu and Ni catalysts demonstrated that the catalysts prepared from colloidal nanoparticles are significantly more active than the traditional catalysts. The CO conversion over supported Cu and Ni catalysts prepared from metal colloids was ca. 50-60% higher at 275°C as compared to those prepared by the impregnation method. The CO conversion and methane yield in the WGS reaction at 350°C and 400°C over Cu, Ni and Cu-Ni catalysts is shown in Figure 4.15.
Methane byproduct was observed in the case of pure Ni catalysts due to CO/CO$_2$ hydrogenation in a methanation reaction.$^{[55]}$ The methanation reaction was suppressed as the Cu content increased in the bimetallic catalysts (Figure 4.15). The addition of only 2 wt. % Cu was sufficient to reduce methane yield from 12 to 6 mol. % at 350°C. The yield of methane was almost negligible for Cu$_5$Ni$_5$ and Cu$_8$Ni$_2$ catalysts. The Cu component in supported bimetallic catalysts was segregated to the surface after activation at 300°C, and thus, suppressed the methanation reaction. In addition, supported bimetallic catalysts still showed high WGS activity at 350-400°C without methane formation. These results were consistent with those reported in our previous study$^{[13]}$ indicating that this bimetallic system is promising for WGS catalysis at 350-400°C.

Figure 4.14 CO conversion over supported Cu and Ni nanoparticles prepared by conventional impregnation and colloidal deposition methods. Feed composition: 10% CO-20% H$_2$O in He.
Figure 4.15 CO conversion and methane yield during WGS reaction over supported Cu, Ni and bimetallic Cu-Ni catalysts as a function of Cu atomic fraction determined by XPS. Feed composition: 10%CO-20%H₂O in He.

The intrinsic reaction rate is a good indicator of the influence of the active metal content on the reaction kinetics. Table 4.5 summarizes the intrinsic reaction rates observed for the Cu, Ni and Cu-Ni catalysts of this study where they are compared with those for the representative reported WGS catalysts under similar reaction conditions. The results (per gram of catalyst) obtained at 230°C showed a much higher reaction rate for the catalysts prepared from metal colloids than for the impregnated catalysts: Cu10 > Cu10I > Ni10 > Ni10I (Table 4.5). Thus, supported Cu catalysts prepared from CTAB-capped Cu nanoparticles are highly active WGS catalysts. The high WGS activity could be explained by the presence of well-dispersed nanoparticles on the alumina support. The apparent activation energies (Eₐ) of the WGS reaction calculated from the slopes of the Arrhenius plots of
reaction rates shown in Figure 4.16 are summarized in Table 4.5. The activation energies observed for Cu and Ni catalysts prepared by impregnation and colloidal deposition were very similar resulting in values of ca. 10 and 20 kcal/mol for Cu and Ni, respectively. This implies that the nature of the surface active sites and the rate-limiting step are not affected by the preparation methods employed in this study. The calculated values of the activation energy are in good agreement with those reported previously for ZnO- and Al₂O₃-supported Cu and Al₂O₃-supported Ni catalysts. The Eₐ of bimetallic Cu-Ni catalysts is in the range between those for pure Cu and Ni catalysts (ca. 10-13 kcal/mol). The surfaces of bimetallic catalysts appear to be more Cu-like since their Eₐ is similar to that for pure Cu, which is also in agreement with both our XPS and line scan profile data for the reduced catalysts.

A number of different WGS catalysts were reported in the literature. The main challenge in comparing intrinsic activities of various WGS catalysts is due to significant differences in reaction conditions employed in these previous studies. In some studies only CO and water were employed in the feed, while others used feeds containing also the reaction products. The product species (CO₂ and H₂) usually inhibit the WGS reaction rate. Moreover, the catalyst synthesis method also has a large impact on the resulting performance. The WGS reaction rates for the Cu, Ni and Cu-Ni catalysts of this study were compared with WGS activities of representative catalysts reported in the literature under similar reaction
conditions in Table 4.5.\textsuperscript{[13, 25, 56, 59-61]} On the basis of unit mass of a catalyst, the Cu10 catalyst prepared from colloidal Cu is the most active at 230°C. On the basis of total mass of an active metal, the precious catalysts, Pt/TiO\textsubscript{2} and Au/CeO\textsubscript{2}, are the most active catalysts at 230°C. However, the deactivation behavior of these catalysts and high cost of Pt and Au are considered to be serious drawbacks for their practical application as the WGS catalysts. Therefore, these promising results strongly indicated that supported catalysts prepared by deposition of pre-formed Cu nanoparticles are highly active. It should be noted that the similar values of the WGS reaction rate normalized to the Cu surface area for the Cu10 and Cu10I in Table 4.5 (2.1-2.9 \(\mu\text{mol}\cdot\text{m}_{\text{Cu}}^{-2}\cdot\text{s}^{-1}\)) also indicated that the nature of the surface active sites was not significantly affected by the synthesis methods employed in this study. A comparison of WGS reaction rates reported in the literature for various supported Cu catalysts also indicated similar values (per Cu surface area) under different experimental conditions shown in Table 4.5. In a previous study, Koryabkina et al. reported the WGS reaction rates for the CuO\textsubscript{8}-Al\textsubscript{2}O\textsubscript{3}, CuO\textsubscript{12}-Al\textsubscript{2}O\textsubscript{3} and commercial CuO\textsubscript{40}-ZnO-Al\textsubscript{2}O\textsubscript{3} catalysts that were essentially the same (2-2.6 \(\mu\text{mol}\cdot\text{m}_{\text{Cu}}^{-2}\cdot\text{s}^{-1}\)).\textsuperscript{[61]} Our results are also in agreement with those of Kam et al., that reported essentially identical WGS reaction rates for the Cu37/ZnO and commercial Cu37/ZnO/Al\textsubscript{2}O\textsubscript{3} catalysts.\textsuperscript{[56]} Overall, it can be concluded that the surface area of active Cu in supported catalysts has a significant impact on CO conversion.
One of the main goals of this study was to explore the bimetallic effect on the WGS activity. The reaction rate normalized to the surface area of an active metal as a function of Cu atomic fraction at the surface (from XPS) is presented in Figure 4.17 and Table 4.5. As these data indicated, the WGS reaction rate initially increased upon the Cu addition to Ni. The highest WGS reaction rate was observed at the Cu atomic fraction of 0.63 for the Cu5Ni5 catalyst. In addition, this catalyst showed no methanation activity and possessed comparable WGS reaction rate to that observed for precious catalysts. Therefore, the presence of Cu in these bimetallic catalysts induced favorable structural and electronic effects not only for enhancing the WGS activity, but also for suppressing methane yield. Although the Cu5Ni5 nanoparticles were much bigger than pure Cu and Ni nanoparticles (ca. 50 nm vs. 4-5 nm), the WGS reaction rate over the Cu5Ni5 catalyst normalized to its active metal surface area was higher than that for smaller Cu and Ni particles.
Table 4.5 WGS reaction rates of representative catalysts at 230°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Reaction rate&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Reaction rate&lt;sup&gt;c&lt;/sup&gt;</th>
<th>$E_a$</th>
<th>Feed composition</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni10/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.8±0.5</td>
<td>151±8</td>
<td>1.23±0.30</td>
<td>20.4±1.0</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu10/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>28.4±1.4</td>
<td>378±19</td>
<td>2.93±0.45</td>
<td>9.9±0.5</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Ni10I/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>5.4±0.3</td>
<td>57±3</td>
<td>0.61±0.20</td>
<td>19.7±1.0</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu10I/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>15.4±0.8</td>
<td>163±8</td>
<td>2.13±0.50</td>
<td>9.8±0.5</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu2Ni8/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4.5±0.2</td>
<td>59±3</td>
<td>1.68±0.40</td>
<td>12.9±0.7</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu5Ni5/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.5±0.2</td>
<td>56±3</td>
<td>4.27±0.50</td>
<td>10.1±0.5</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Cu8Ni2/Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>9.0±0.5</td>
<td>134±6.7</td>
<td>3.59±0.45</td>
<td>11.8±0.6</td>
<td>10%CO, 20%H₂O, balance He</td>
<td>This study</td>
</tr>
<tr>
<td>Pt0.5-TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>5.7&lt;sup&gt;d&lt;/sup&gt;</td>
<td>1140&lt;sup&gt;d&lt;/sup&gt;</td>
<td>4.89&lt;sup&gt;d&lt;/sup&gt;</td>
<td>15.7</td>
<td>3%CO, 10%H₂O, balance He</td>
<td>[25]</td>
</tr>
<tr>
<td>Au0.76/CeO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>14.7&lt;sup&gt;e&lt;/sup&gt;</td>
<td>1934&lt;sup*e&lt;/sup&gt;</td>
<td>3.11&lt;sup&gt;e&lt;/sup&gt;</td>
<td>10.2</td>
<td>43%H₂, 6%CO₂, balance N₂</td>
<td>[60]</td>
</tr>
<tr>
<td>CuO8-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6&lt;sup&gt;f&lt;/sup&gt;</td>
<td>75&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2.03&lt;sup&gt;f&lt;/sup&gt;</td>
<td>14.8</td>
<td>7%CO, 22%H₂O, 37%H₂, 8.5%CO₂, balance Ar</td>
<td>[61]</td>
</tr>
<tr>
<td>CuO12-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>10.2&lt;sup&gt;f&lt;/sup&gt;</td>
<td>85&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2&lt;sup&gt;f&lt;/sup&gt;</td>
<td>14.8</td>
<td>7%CO, 22%H₂O, 37%H₂, 8.5%CO₂, balance Ar</td>
<td>[61]</td>
</tr>
<tr>
<td>CuO40-ZnO-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>25&lt;sup&gt;f&lt;/sup&gt;</td>
<td>63&lt;sup&gt;f&lt;/sup&gt;</td>
<td>2.6&lt;sup&gt;f&lt;/sup&gt;</td>
<td>14.8</td>
<td>7%CO, 22%H₂O, 37%H₂, 8.5%CO₂, balance Ar</td>
<td>[61]</td>
</tr>
</tbody>
</table>
Cu37/ZnO  5.8  16  0.67  10.2  37.5%H₂, 8.5%CO₂, \(^\text{[56]}\) balance N₂

Cu37/ZnO/Al₂O₃  14.3  39  0.52  14.6  37.5%H₂, 8.5%CO₂, \(^\text{[56]}\) balance N₂

\(^a\) rate per gram of catalyst \(^b\) rate per gram of active metal \(^c\) rate per surface area of active metal \(^d\) extrapolated from the data in\(^{[25]}\) to 230°C using \(E_a\) of 15.7 kcal/mol \(^e\) extrapolated from the data in\(^{[57]}\) to 230°C using \(E_a\) of 10.2 kcal/mol. \(^f\) extrapolated from the data in\(^{[58]}\) to 230°C using \(E_a\) of 14.8 kcal/mol.

**Figure 4.16** Arrhenius plots of CO conversion rate in WGS reaction observed over supported Cu, Ni and CuNi catalysts.
The energetics and kinetics of adsorption, desorption and dissociation of molecules on a surface strongly depend on the local bond formation between single surface atoms and the adsorbate as well as on the short range geometrical arrangement of surface atoms near the adsorption sites. The bond formation between single atoms and molecules is governed by the binding energy, orientation, and occupation of the valence orbitals and the surface band structure.\cite{53} For bimetallic surfaces, the occupation of the valence orbitals and surface band structure are determined by the coupling between the electronic states of the two metals involved.\cite{62,63} Since the arrangement of surface atoms influences the electronic structure of the surface and vice versa, it is often impossible to discriminate between geometric and electronic effects.
CO adsorption is an important mechanistic step in the chemical reaction pathway of many heterogeneous catalytic reactions. WGS reaction is an important example of CO oxidation to CO$_2$. Hence theoretical studies of the trends of CO adsorption on transition metal clusters are of significant importance towards the screening of relevant surface reactions energetics on supported metal catalysts. One of the interesting points of this combination is that Ni and Cu have similar geometric but very different electronic properties. Since Cu and Ni do alloy above 900K, the absolute amount of Cu or Ni deposited on the substrate surface cannot be determined directly by temperature programmed desorption (TPD) of the adlayer. However, the adlayer coverage can be determined by TPD and XPS. Held explored a Cu-Ni model which contained a Cu monolayer (ML) on Ni(111) by CO-TPD and XPS.$^{[53]}$ We briefly summarize their studies as follows. Figure 4.18 shows a series of CO TPD spectra recorded from 1ML Cu on Ni(111) after different annealing treatments with increasing temperature.$^{[64]}$ Cu deposition at a sample temperature at 350K with a CO adsorption at 90K, leads to a CO desorption peak at T < 220K which is attributed to Cu-terminated and, above 220K, to Ni-terminated surface areas. Annealing to 700K (Figure 4.18 b) causes this high temperature peak to vanish almost completely, while the desorption signal from Cu areas (T < 220K) increases by about the same amount. Very similar TPD spectra are also obtained after annealing to 600 and 800K. Annealing to 900K, however, leads to the re-occurrence of the high-temperature CO desorption peak from uncovered Ni areas. This observation is an
indication for alloying of copper and nickel, which leads to the replacement of Cu atoms by Ni atoms in the topmost layer. This creates a large number of CO adsorption sites influenced by both Ni and Cu atoms. Such mixed Cu-Ni adsorption sites for CO have also been postulated by Garfunkel et al.\[65\] according to their high resolution electron energy loss spectroscopy (HREELS) measurements. One reason for this observation may be the fact that the d-band of copper and nickel partly overlap each other and are spread over a relatively large energy interval.\[66\] Hsieh et al., investigated charge redistribution in a series of Ni-Cu alloys using XPS, XANES, and suggest that both Ni and Cu gain a small but measurable amount of d charge in alloy formation through rehybridization (loss of non-d conduction charge).\[67\] Figure 4.19 shows the XPS spectra of Ni, and Cu 3d valence bands in the Ni\textsubscript{1-x}Cu\textsubscript{x} collected by Hsieh et al.\[67\] The Cu d band in the Cu-Ni alloys clearly moves to lower binding energy as the concentration of Cu increases. Hsieh et al. attributed this behavior to the effect of charge redistribution at the Ni and Cu atomic sites.

In our case, the irreversible CO (CO-irr) uptake also indicated that Cu covered the Ni surface after reduction at 450°C. This sample for CO chemisorption was first reduced in H\textsubscript{2} at 450°C for 120 min, followed by evacuation at 450°C for 180 min. The sample was then cooled to 50°C under vacuum for 30 min. A change in the adsorption sites of CO (higher CO-irr uptake) were observed in the Cu5Ni5 catalysts which is explained by the surface
alloying responsible for high reaction rate as compared to pure Cu and Ni catalysts (Figure 4.17 and Table 5.1).

**Figure 4.18** CO TPD spectra for 1 ML Cu/Ni(111) after different consecutive annealing procedures: (a) after deposition at 350 K; (b) annealed at 700 K followed by immediate cooling; (c) annealed at 900K followed by immediate cooling; (d) after 30 s at 900 K; (e) after 120 s at 900 K; (f) after 120 s at 950 K; (g) after 120 s at 1000 K. All spectra are recorded from the same layer in the order (a) to (g). CO was adsorbed at 90 K; heating rate for TPD: 5 K/s[^53]
Figure 4.19 (a) Representative Ni 3d valence-band spectra of Cu-Ni alloys. The inset shows the Cu 3d valence-band spectra. The intensities have been normalized to the maximum height of the bands. (b) A plot of Ni and Cu 3d binding energy position vs. Cu concentration \((x)\) in alloys.\(^{67}\)

4.4 Conclusions

In this study, we successfully developed highly active supported Cu, Ni and CuNi catalysts by a simple soft chemical route from pre-formed colloidal metal nanoparticles. The S/TEM studies showed the average sizes of 4.6–4.7 nm for the Cu and Ni nanoparticles, which increased slightly after their reduction in hydrogen at 300°C. The combination of XRD and HAADF-STEM indicated that Cu5Ni5 nanoparticles consisted of a Cu core and Cu-Ni
alloy shell. Supported Cu and Ni nanoparticles prepared from metal colloids were 2.5 times more active per unit mass of active metal in the WGS reaction at 230°C as compared to traditional impregnated catalysts. The important result of this study is the improvement of the dispersion and catalytic activity of supported Cu catalysts in the presence of CTAB. In the case of Ni catalysts, well-dispersed Ni/Ni(OH)₂ nanoparticles were obtained due to electrostatic stabilization effect of the surface OH⁻ groups and reduced mutual attractions of magnetic dipoles of the Ni/Ni(OH)₂ particles.

Another significant finding of this study was the demonstration of the bimetallic effect on the WGS activity. Bimetallic catalysts showed strong inhibition of methane yield and high activity in the medium to high temperature range (above 350°C). Moreover, the Cu₅Ni₅ catalyst exhibited the WGS reaction rate that was higher than that observed over colloidal Cu and Ni catalysts. Therefore, the presence of Cu in these bimetallic catalysts induced favorable structural and electronic effects not only for enhancing the WGS activity, but also for suppressing methane yield.
4.5 References


CHAPTER V

Alumina-Supported Cu@Ni and Ni@Cu Core-Shell Nanoparticles: Synthesis, Characterization, and Catalytic Activity in Water-Gas Shift Reaction

5.1 Introduction

Metallic nanoparticles are known to display unique properties, such as plasmon absorption, improved magnetic properties, specific selectivity and enhanced catalytic activity, due to electronic effects related to their small size and extremely large surface areas.\textsuperscript{[1-4]} These properties may be further tailored in the case of bimetallic and multi-metallic nanoparticles, because of unique inter-metallic interactions. In recent years, the preparation and exploration of core-shell nanoparticles have developed into an increasingly important research area at the frontier of advanced materials chemistry.\textsuperscript{[5]} Some research thrusts have been focused on improving the utilization of expensive and highly active noble metals by depositing them as thin shells on base metal core nanoparticles.\textsuperscript{[1, 6, 7]} Other studies aimed to take advantage of the unique structure of core-shell nanoparticles to improve their catalytic activity and selectivity.\textsuperscript{[2, 6]} For example, Alatoglu et al. reported that distinct catalytic properties in PROX were displayed by Ru-Pt core-shell nanoparticles as compared to both nanoalloy and monometallic Ru and Pt catalysts.\textsuperscript{[2]}

Bimetallic Cu-Ni nanoparticles have been recently shown to be efficient
heterogeneous catalysts for some industrially important reactions, such as methane decomposition,\textsuperscript{[8]} ethanol steam reforming,\textsuperscript{[9]} water gas shift reaction,\textsuperscript{[10]} and electrocatalytic oxidation of methanol.\textsuperscript{[11]} Recently, several research groups\textsuperscript{[12-15]} reported the preparation of Cu-Ni nanoparticles possessing a core-shell structure. Simultaneous reduction procedures have been used to prepare bimetallic Cu-Ni nanoparticles with a core-shell structure protected by surfactants or polymers.\textsuperscript{[13]} The redox potentials for Cu\textsuperscript{2+} and Ni\textsuperscript{2+} reduction are 0.337V and -0.257V, respectively.\textsuperscript{[13]} Therefore, Cu-Ni nanoparticles are more likely to be produced via heterogeneous nucleation due to the difference in the redox potentials. First, Cu nanoparticles are produced at a lower reduction temperature followed by heterogeneous nucleation of Ni on the surface of Cu. For instance, CuNi nanowires displaying a Cu core and Ni shell have been prepared by the co-reduction of Cu\textsuperscript{2+} and Ni\textsuperscript{2+} with N\textsubscript{2}H\textsubscript{4} under strongly basic conditions.\textsuperscript{[14]} The Cu core and Cu-Ni alloy shell nanoparticles were also synthesized by a simultaneous reduction of Cu and Ni precursors. Yamauchi et al. used microwave irradiation synthesis to produce Cu-rich core and Ni-rich shell nanoparticles.\textsuperscript{[13]} However, nanoparticles with a Ni core and Cu shell structure cannot be prepared by such one-step reaction. Furthermore, these methods are limited to synthesis of unsupported nanoparticles, which must then be impregnated onto a desired support in order to be used as heterogeneous catalysts. Subsequent anchoring of nanoparticles onto the support is the main concern to prepare well-dispersed supported catalysts. In addition, Cu-Ni nanoparticles with a core-shell
structure have not been explored previously as heterogeneous catalysts. Recently, we have reported supported catalysts prepared by deposition of colloidal Cu and Ni particles that showed promising WGS activity as compared to traditional catalysts prepared by impregnation methods. Bimetallic CuNi catalysts were also highly active in the WGS reaction at moderately high temperatures (350-400°C). Moreover, fabrication of colloidal metals can yield desirable nanostructures that cannot be otherwise prepared by direct impregnation methods. In this paper, we report the results of applying this fabrication method for the first time to the preparation of supported core-shell Cu@Ni and Ni@Cu nanoparticles as WGS catalysts. These novel catalysts were made by successive reduction of Cu and Ni sources in solution, i.e., deposition of the shell on the surface of a pre-formed seed, followed by the deposition of core-shell nanoparticles on alumina support.

5.2 Experimental

5.2.1 Preparation of alumina-supported Cu@Ni and Ni@Cu catalysts

Materials. Ni(NO₃)₂·6H₂O (Sigma-Aldrich, 99.99%) and Cu(NO₃)₂·2.5H₂O (Sigma-Aldrich, 99.99%) were used as metal precursors, hydrazine monohydrate (Alfa Aesar, 99%+) as a reducing agent, cetyltrimethylammonium bromide (CTAB) (Alfa Aesar, 98%) as a protecting surfactant, ethanol (Sigma-Aldrich, 99.5%) and ethylene glycol (Sigma-Aldrich, 99%) as solvents, and γ-alumina (Sumitomo, AKP-G015, BET: 185 m²/g, pore volume: 1.95 cm³/g, pore size: 35 nm) as a support. Sodium hydroxide was supplied by Fisher Scientific.
**Synthesis of Cu@Ni nanoparticles.** Cu core-Ni shell nanoparticles denoted as Cu@Ni were prepared by successive reduction as shown in Scheme 5.1. First, Cu nanoparticles were synthesized as seeds. Appropriate amounts of copper nitrate were dissolved in the alcohol (47mM). Then, excess 0.9M hydrazine and 1M NaOH solution (80μl NaOH solution/ml-EtOH) were added sequentially. Nanosized Cu particles formed after 2h at 80°C. Then, a Ni precursor solution containing nickel nitrate, 0.9M hydrazine and 1M NaOH solution (80μl NaOH solution/ml-EtOH) was added to the Cu seed solution at 70°C 2h resulting in the formation of Cu@Ni nanoparticles.

**Synthesis of Ni@Cu nanoparticles.** The successive two-step chemical reduction that produced the Cu@Ni nanoparticles does not allow the formation of Ni@Cu nanoparticles since Cu nanoparticles are easily reduced at room temperature by mild chemical reduction agents. Accordingly, Ni core-Cu shell nanoparticles denoted as Ni@Cu were synthesized by a successive three-step chemical reduction shown in Scheme 5.2. Ni nitrate was dissolved in ethylene glycol (EG) to yield a 47 mM solution. Then, excess 0.9 M hydrazine and 1 M NaOH solution (80μl/ml) were added sequentially to the Ni nitrate solution resulting in Ni nanoparticles at 60°C after 1h that were separated from the EG solution by centrifugation. The obtained Ni nanoparticles were re-dispersed in fresh ethanol. Then, Cu nitrate (Cu/Ni = 1.5 wt. ratio), and 80μl of 1M NaOH per 1 ml of reaction solution were added to deposit a CuO layer on the surface of Ni nanoparticles at 80°C for 2 h. Finally, the Ni@CuO
nanoparticles thus obtained were re-dispersed in 0.1M aqueous CTAB solution containing 1.5M hydrazine. The pH of the solution was adjusted to 13 using NaOH and the Ni@CuO nanoparticles were reduced for 1 h to form Ni@Cu core-shell nanoparticles.

**Synthesis of supported Ni@Cu and Cu@Ni core shell nanoparticles.** To deposit the Cu@Ni nanoparticles onto γ-Al₂O₃ support, γ-Al₂O₃ was added to the Cu@Ni nanoparticle suspensions, followed by sonication for 1h and then drying overnight under vacuum at 80°C. In the case of supported Ni@Cu core-shell nanoparticles, γ-Al₂O₃ was added to the Ni@Cu core-shell nanoparticle suspensions, after which they were sonicated for 1 h, filtered and dried overnight at room temperature. The dried Ni@Cu catalysts were washed with ethanol and water to remove excess CTAB and dried again overnight under vacuum at 80°C. The catalysts thus obtained were labeled as Cux@Niy and Niy@Cux, where x and y represent Ni and Cu content (wt.%) relative to γ-Al₂O₃.

### 5.2.2 Catalyst Characterization

The N₂ adsorption-desorption isotherms were measured at -196°C using Micromeritics ASAP 2020 porosimeter. The XRD patterns were collected using a PANalytical X’pert diffractometer equipped with a Cu Kα radiation source. The XRD data were collected in a step-scan mode at 2θ = 30-70° and a step size of 0.05°/s. Samples for examination by transmission electron microscopy (TEM) were prepared by dispersing powdered catalysts in ethanol and then allowing a drop of the suspension to evaporate on a
carbon film supported by a gold grid. TEM imaging was performed employing a Phillips CM20 electron microscope at a 200-kV accelerating voltage and a high brightness LaB$_6$ gun for high coherence and small probes. Determination of total Ni and Cu content was accomplished via microwave digestion followed by the ICP-MS analysis using an Agilent ICP-MS model 7500ce. Thermogravimetric analysis (TGA) was performed using a TA Instruments SDT-Q600. In order to dry samples for the study of the oxidation behavior of as-prepared nanoparticles, the temperature was raised from 30°C to 110°C at a rate of 20°C/min and kept at 110°C for 0.5 h under N$_2$ flow. Then, the temperature was increased at a rate of 7°C/min from 80 to 700 °C under air flow of 100 ml/min. UV-vis absorption spectra were measured over a range of 250-800 nm with a Varian Carry 50 recording spectrophotometer using a quartz cell. CO chemisorption was performed on a Micromeritics ASAP2020 instrument. The sample was first reduced by H$_2$ at 300°C for 120 min, followed by evacuation at 500°C for 180 min. The sample was then cooled to 35°C under vacuum for 30 min.

5.2.3 WGS activity

The WGS activities were determined employing a continuous fixed-bed tubular quartz microreactor (0.55 cm ID) operated at atmospheric pressure and using 0.1 g of each catalyst diluted with 0.2 g of quartz powder. The feed gas typically contained 10 mol. % CO and 20 mol. % H$_2$O in helium. The total feed flow rate was 100 ml/min. All catalysts were reduced
under 20 mol. % H₂ in He at 300°C before catalytic tests at 125-400°C. Water was injected into flowing gas stream by a syringe pump and vaporized in the heated gas feed line before entering the reactor. A condenser filled with ice was installed at the reactor exit to condense moisture. The reactant and product mixtures were analyzed by a gas chromatograph (Hewlett-Packard HP-5580A) equipped with a thermal conductivity detector. Intrinsic reaction rates were determined in separate experiments where the conversions of reactants were kept below 10 mol. %.

5.3 Results and Discussion

5.3.1 Formation of Cu@Ni and Ni@Cu core-shell nanoparticles

A series of Cu@Ni and Ni@Cu bimetallic nanoparticles were prepared by successive two-step and three-step reduction procedures, respectively. Our previous study[16] indicated that the presence of both Ni and Ni(OH)₂ in pre-formed Ni nanoparticles was important for the preparation of well-dispersed supported Ni catalysts. Similarly, the presence of the Ni/Ni(OH)₂ shell in Cu@Ni nanoparticles was expected to be important for their dispersion on the alumina support. The successive two-step reduction that produced Cu@Ni core shell nanoparticles with the Ni/Ni(OH)₂ shell are described below: Cu core nanoparticles were obtained, then a Ni/Ni(OH)₂ layer was deposited on the Cu core particle. The color change of particles from reddish Cu (core particles) to black (Ni/Ni(OH)₂ layer), shown in Scheme 5.1, is indicative of the successful synthesis of core-shell nanoparticles.
The successive two-step chemical reduction process described above does not allow the formation of Ni@Cu nanoparticles since Cu nanoparticles are easily reduced at room temperature by mild chemical reduction agents. To the best our knowledge, there has only been one previous report of a two-step polyol method used to synthesize Ni@Cu core shell nanoparticles.\cite{18} First, Ni nanoparticles were formed after heating to 175°C followed by addition of a Cu precursor solution and cooling to 165°C that led to the formation of Cu shells on the Ni nanoparticles. However, large particle size (ca. 200 nm) observed in this two-step reduction using a weak reducing agent (ethylene glycol) at high temperatures indicated that this procedure is not promising for Ni@Cu nanoparticle synthesis. Therefore, a modified procedure shown in Scheme 5.2 was employed.

Scheme 5.1 Synthesis of Cu@Ni core-shell nanoparticles.
Scheme 5.2 Synthesis of Ni@Cu core-shell nanoparticles

TEM images of Cu5@Ni5 and Ni5@Cu6.5 nanoparticles are shown in Figure 5.1. The particles were very fine and monodisperse with a mean diameter of 4.7 and 5.4 nm for Cu@Ni and Ni@Cu core shell nanoparticles, respectively. A series of UV-visible absorption spectra of Cu@Ni, Ni@Cu, Cu and Ni nanoparticles are shown in Figure 5.2. Cu nanoparticles exhibited a distinct absorption band at 580 nm whereas a sharp continuous tail band was observed above 300 nm for Ni/Ni(OH)2 particles (Figure 5.2 (a)).[19] The UV-vis absorption spectra of Cu@Ni/Ni(OH)2 did not show a Cu absorption band, and thus, indicated that the nanoparticles had a Cu core and a Ni/Ni(OH)2 shell structure. The UV-vis absorption spectra of Ni, Cu, Ni@CuO, and Ni@Cu nanoparticles are shown in Figure 5.2 (b). Ni nanoparticles showed a monotonic decrease in absorbance with decreasing wavelength. The absorption peaks of Ni@CuO and Ni@Cu occurred around 300 nm and 580...
nm corresponding to the CuO and Cu absorption bands, respectively.\textsuperscript{[20, 21]} The observation of distinct Cu and CuO absorption bands in the Ni@Cu and Ni@CuO nanoparticle absorption spectra also suggested formation of Cu shells on the surface of Ni particles.

TGA curves of Cu, Ni and Ni@Cu nanoparticles in air are shown in Figure 5.3. The oxidation of Cu nanoparticles occurred at 150-325\textdegree C, while that of Ni nanoparticles was observed at 250-475\textdegree C. The oxidation of Ni@Cu nanoparticles occurred over the temperature range from 150 to 525\textdegree C. The corresponding derivative weight loss curves are shown in Figure 5.3 (b). The Cu nanoparticles showed two oxidation peaks centered at 190 and 315\textdegree C. For the Ni nanoparticles, a single peak centered at 428\textdegree C resulted from Ni oxidation. In the case of the Ni@Cu nanoparticles, the first two weight gain peaks were observed at ca. 190 and 315\textdegree C which corresponding to Cu oxidation, and the third peak centered at 482\textdegree C corresponded to Ni oxidation. As compared to pure Ni nanoparticles, the Ni@Cu nanoparticles exhibited improved stability under oxidation conditions reflected in higher temperatures required for the Ni core oxidation observed in TGA and derivative weight loss curves. These observations agree with the Ni core and Cu shell nanostructure in the Ni@Cu nanoparticles. The as-synthesized Cu@Ni/Ni(OH)\textsubscript{2} system showed more complicated behavior in TGA in air, i.e., Cu oxidation to CuO, Ni to NiO, and Ni(OH)\textsubscript{2} dehydration to NiO, which didn’t provide further insights into its structure. Thus, the investigation of Cu@Ni core shell nanoparticles was not conducted in this study.
Figure 5.1 TEM images and particle size distribution of (a and c) Cu5@Ni5 and (b and d) Ni5@Cu6.5 nanoparticles.
**Figure 5.2** UV/vis spectra of (a) Cu@Ni and (b) Ni@Cu core-shell nanoparticles
Figure 5.3 (a) TGA curves and (b) corresponding derivative curves for as-prepared colloidal Cu, Ni and Ni@Cu nanoparticles heated in air at 7°C/min.
5.3.2 Characterization of Supported WGS Catalysts

X-ray diffraction patterns of supported Cu@Ni and Ni@Cu core-shell nanoparticles are shown in Figure 5.4. The diffraction peaks of the Cu phase were observed in XRD patterns of the Cu@Ni core shell nanoparticles, while those of Ni phase were only visible in the X-ray diffraction patterns of Ni@Cu core shell nanoparticles. These observations can be explained by assuming that the outer layer is too thin and/or disordered to be detected by X-ray diffraction. These results are also in agreement with UV-vis and TGA observations.

![XRD patterns of supported Ni@Cu and Cu@Ni nanoparticles.](image)

**Figure 5.4** XRD patterns of supported Ni@Cu and Cu@Ni nanoparticles.
CO chemisorption on transition metal surfaces is a useful tool to characterize active surface sites present in heterogeneous catalysts.\cite{22} This technique is particularly valuable for the surface characterization of current CuNi core-shell catalysts, because XPS is expected to provide essentially bulk chemical composition due to small size of CuNi nanoparticles. While Ni surfaces are characterized by a large value of irreversible CO uptake, Cu surfaces in supported catalysts exhibit a significantly lower irreversible CO uptake.\cite{22,23} Therefore, the magnitude of CO uptake in bimetallic CuNi catalysts can be used to characterize the nature of such surfaces. Table 5.1 shows the irreversible CO uptake on the supported nanoparticles. Supported Cu catalysts showed significantly lower CO uptake normalized to the surface area of active metal (2.0 \( \text{\mu mol/m}_m^2 \)) than supported Ni catalysts (13.6 \( \text{\mu mol/m}_m^2 \)). In the case of the core-shell catalysts, supported Cu@Ni nanoparticles exhibited the CO uptake of 7.8 \( \text{\mu mol/m}_m^2 \) indicating that their surfaces are likely terminated by both Ni and Cu. Moreover, our CO chemisorption data for the pure Cu and Ni catalysts allowed estimation of surface Cu atomic fractions as 0.48 in the supported Cu@Ni. On the other hand, the CO uptake of 1.9 \( \text{\mu mol/m}_m^2 \) in supported Ni@Cu nanoparticles was similar to that in the pure Cu catalyst indicating that the Ni core in this catalyst was covered by essentially pure Cu shell. Band-structure measurements and ab initio calculations conducted by Held et al. showed weak electronic coupling and practically no shift in the d band center for 1ML Cu/Ni(111). Therefore, the CO-surface bond is similar to that with a surface Cu atom. These results are
also in agreement with our CO chemisorption and reactivity data for core-shell nanoparticles

Therefore, CO chemisorption data suggested surface segregation of Cu in the supported Cu@Ni catalysts, which is in agreement with our previous observations of mixed Cu-Ni surface termination in the bimetallic alloy catalysts.

**Table 5.1** CO chemisorption and CO consumption rate of supported Cu@Ni and Ni@Cu catalysts at 230°C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Active metal content (wt.%)</th>
<th>COirr uptake (μmol/gM)</th>
<th>COirr uptake (μmol/mM²)</th>
<th>CO consumption rate (μmol/gM)</th>
<th>CO consumption rate (μmol/mM²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
<td>Cu</td>
<td>Ni</td>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>Cu5@Ni5</td>
<td>3.2</td>
<td>3.5</td>
<td>1117</td>
<td></td>
<td>7.8±0.8</td>
</tr>
<tr>
<td>Ni5@Cu6.5</td>
<td>3.2</td>
<td>4.1</td>
<td>239</td>
<td></td>
<td>1.9±0.3</td>
</tr>
<tr>
<td>Cu5Ni5</td>
<td>3</td>
<td>3.2</td>
<td>295</td>
<td></td>
<td>23±3.0</td>
</tr>
<tr>
<td>Cu10</td>
<td>--</td>
<td>7.5</td>
<td>260</td>
<td></td>
<td>2.0±0.7</td>
</tr>
<tr>
<td>Ni10</td>
<td>6.5</td>
<td>--</td>
<td>1673</td>
<td></td>
<td>13.6±3.6</td>
</tr>
</tbody>
</table>

a. gM defined as total mass of active metals.
b. Metal surface area (mM²/g) was calculated by the following equation: 6×10³/ρd, where ρ is active metal density (g/cm³) and d is given in nm.

5.3.3 WGS activity

CO conversion in the WGS reaction over supported Cu and Ni nanoparticles shown in Figure 5.5 (a) was reported previously[16, 17] and is shown here for comparison with the WGS activity of the core-shell nanoparticles. Supported Cu nanoparticles showed a light-off temperature of 125°C, which is lower than that of the supported Ni nanoparticles (200°C). Supported Ni catalysts were more active than Cu catalysts above 275°C. However, up to 12
mol. % CH$_4$ yield was observed during the WGS reaction over the Ni catalysts due to a methanation side reaction (Fig. 5.5 (b)). Supported Cu@Ni catalysts showed comparable activity to the Ni catalysts, while supported Ni@Cu catalysts exhibited activity similar to the Cu catalysts. This suggests that the surfaces of Cu@Ni and Ni@Cu nanoparticles contain mostly Ni and Cu, respectively. The methanation reaction was suppressed for the Cu@Ni catalysts as compared to Ni catalysts. Since the Ni shell structure in Cu@Ni nanoparticles is thermodynamically unfavorable because of the lower surface energy of Cu, the Cu component tends to segregate to the surface at elevated temperatures, which suppresses the methanation reaction.$^{[10, 16]}$ The CH$_4$ yield was negligible for the Cu10 and Ni5@Cu6.5 catalysts at all reaction temperatures employed.

According to Nørskov and co-workers,$^{[24]}$ the characteristics of the $d$-band center ($\epsilon_d$) play an important role in determining surface reactivity. Previous DFT studies showed that compressive and tensile strains caused by a mismatch in lattice parameters tend to downshift and upshift the $d$-band center, respectively, thus influencing the catalytic activity.$^{[24]}$ For instance, a highly enhanced activity in the preferential oxidation of CO in hydrogen over Ru@Pt core-shell nanoparticles as compared to monometallic components and annealed Ru-Pt alloy has been demonstrated by Alalyoglu et al.$^{[2]}$ In this case, the interaction of the Pt shell with the Ru core tended to downshift the $d$-band center of surface Pt atoms. This downshifting due to significantly mismatched Ru and Pt lattice parameters (ca. 45%) resulted
in decreased CO binding and much lower CO saturation coverages on Ru@Pt surface, which in turn enhanced catalytic activity. However, the WGS activity is not significantly affected by the core-shell structure of bimetallic Cu-Ni nanoparticles due to a small mismatch (ca. 2.5%) between the Cu and Ni lattice parameters. The small mismatch between the Cu and Ni lattice parameters probably resulted in a small surface strain and a slight change in activity based on CO conversion.\textsuperscript{[25]} The CO consumption rates over Cu, Ni, and bimetallic Cu-Ni nanoparticles possessing core-shell and alloy structures (Cu5Ni5) are summarized in Table 5.1. The Cu-Ni alloy prepared by co-reduction showed higher specific reaction rate per active metal surface area as compared to monometallic and core-shell catalysts. The reaction rate over the Ni@Cu core-shell nanoparticles was similar to that for the Cu catalysts, while the reaction rate over the Cu@Ni system was lower than for the Ni catalyst. The Ni shell layer on Cu particles is expected to expand as compared to bulk Ni. Accordingly, the $d$-band center should shift upward and the binding energy of CO should increase, resulting in high CO saturation coverage at a low temperature (230°C). Therefore, Cu@Ni catalyst was expected to show a lower reaction rate as compared to Ni catalysts, which was indeed confirmed by experimental observations (Table 5.1).
Figure 5.5 (a) CO conversion and (b) methane yield during WGS reaction over alumina-supported colloidal Cu, Ni, and Cu-Ni core-shell nanoparticles. Feed composition: 10% CO-20% H₂O in He.
CO conversion over colloidal (Cu and Ni) and impregnated (Cu10I and Ni10I) catalysts at 275 and 300°C and GHSV = 12,500 and 25,000 h⁻¹ is shown in Figure 5.6. Supported colloidal Cu and Ni catalysts showed slightly decreased CO conversion at high GHSV. At 300°C and GHSV = 25,000 h⁻¹, supported Cu5@Ni5 showed high CO conversion of up to 90% and a CH₄ yield of only 2 mol. %. The similar trend for supported Cu5@Ni5 catalysts was observed at 300°C and GHSV = 12,500 h⁻¹. At 275°C and GHSV = 25,000 h⁻¹, supported colloidal Ni was more active than supported colloidal Cu, Cu@Ni, and Ni@Cu catalysts, demonstrating a CO conversion of ca. 90%. However, up to 4 mol. % CH₄ yield was observed over the colloidal Ni catalyst. At 275°C and low GHSV = 12,500 h⁻¹, Cu5@Ni5 catalyst showed comparable activity to Ni catalysts, but a lower methane yield of 2 mol. %. Therefore, the supported Cu@Ni nanoparticles prepared from metal colloids are promising as WGS catalysts at moderately high temperatures (275-400°C).
Figure 5.6 CO conversion and methane yield (two values shown for each plot) over WGS catalysts at (a) 275°C and (b) 300°C at GHSV of 12,500 and 25,000 h⁻¹. Feed composition: 10%CO-20%H₂O in He
5.4 Conclusions

We employed a successive reduction route to synthesize Cu@Ni and Ni@Cu core-shell nanoparticles and deposited them onto alumina support to obtain well-defined supported bimetallic catalysts. The XRD, UV-vis and CO chemisorption data suggested that Cu@Ni and Ni@Cu nanoparticles possessing core-shell structures were synthesized. Supported Cu@Ni nanoparticles showed similar WGS activities to supported Ni nanoparticles, but lower methanation activity. Suppressed methanation activity observed for Cu@Ni nanoparticles may be due to Cu segregation to the surface. Supported Ni@Cu nanoparticles displayed WGS activity comparable to supported Cu nanoparticles. Both supported Cu@Ni and Ni nanoparticles showed the highest conversion of CO (ca. 90%), while the Ni nanoparticles showed higher methanation activity (8 mol. % CH₄ yield) as compared to Cu@Ni (2 mol. % CH₄ yield) at GHSV=12,500 and 275°C. The WGS activity was not significantly affected by the formation of core-shell structures due to a small mismatch (2.5%) in lattice parameters of Cu and Ni.
5.5 References


CHAPTER VI

Conclusions and Recommendations for Future Research

6.1 Conclusions

A series of model Cu, Ni nanoparticle catalysts and three sets of bimetallic Cu-Ni catalysts, namely, (a) Cu-Ni mixed alloy (CuNi), (b) Cu core and Ni shell (Cu@Ni), and (c) Ni core and Cu shell (Ni@Cu) nanoparticle catalysts were prepared, and investigated as WGS catalysts. For comparison, traditional catalysts prepared by incipient wetness impregnation were also investigated. The model Cu, Ni nanoparticle catalysts employed in this research are highly promising for the development of rules of rational design of novel supported bimetallic catalysts displaying desirable structural, morphological and compositional properties for the WGS catalysis.

Supported Cu and Ni nanoparticles prepared from metal colloids were 2.5 times more active per unit mass of active metal in the WGS reaction at 230°C as compared to traditional impregnated catalysts. The important result of this study is the improvement of the dispersion and catalytic activity of supported Cu catalysts in the presence of CTAB. In the case of Ni catalysts, well-dispersed Ni/Ni(OH)₂ nanoparticles were obtained due to electrostatic stabilization effect of the surface OH⁻ groups and reduced mutual attractions of magnetic dipoles of the Ni/Ni(OH)₂ particles. Another significant finding of this study was the demonstration of the bimetallic effect on the WGS activity. Bimetallic mixed alloy catalysts
showed strong inhibition of methane yield and high activity in the medium to high temperature range (above 350°C). Moreover, the Cu5Ni5 catalyst exhibited the WGS reaction rate that was higher than that observed over colloidal Cu and Ni catalysts. Therefore, the presence of Cu in these bimetallic catalysts induced favorable structural and electronic effects not only for enhancing the WGS activity, but also for suppressing methane yield. In the case of core-shell catalysts, supported Cu@Ni nanoparticles showed similar WGS activities to supported Ni nanoparticles, but lower methanation activity. Suppressed methanation activity observed for Cu@Ni nanoparticles may be due to Cu segregation to the surface. However, the WGS activity was not significantly affected by the formation of core-shell structures due to a small mismatch (2.5%) in lattice parameters of Cu and Ni.

6.2 Recommendations for Future Research

The lifetime of WGS catalysts according to DOE technical targets is > 5000 h. Therefore, in future research, the long-term stability (up to 5000 h on-stream) for Cu-Ni bimetallic catalysts should be addressed.

As this thesis research demonstrated, supported bimetallic Cu-Ni nanoparticles are highly promising novel WGS catalysts. They displayed higher specific reaction rate as compared to monometallic Cu and Ni catalysts. However, the model bimetallic Cu-Ni catalysts reported in Chapter IV suffered from relatively large particle size (~50 nm). Therefore, future research on this catalytic system should focus on the formation and
characterization of bimetallic Cu-Ni mixed alloy nanoparticles smaller than 10 nm. In Chapter II, we reviewed synthesis methods of bimetallic Cu-Ni nanoparticles which illustrated that the fabrication of Cu-Ni alloy nanoparticles smaller than 10 nm is challenging at present time.\cite{1-8} However, we have already successfully synthesized Cu@Ni and Ni@Cu core-shell nanoparticles smaller than 10 nm. Therefore, small Cu-Ni mixed alloy nanoparticles may be prepared by annealing Cu@Ni and Ni@Cu core-shell nanoparticles above 354°C, since the bulk Cu-Ni system is completely miscible over the entire range of compositions above this temperature. It may even be possible to control to some extent the degree of Cu and Ni mixing in these nanoparticles by exploring the differences in atomic diffusivity of these metal species. Cu atoms are more mobile than those of Ni as reflected in its lower Tamman temperature of \(~405°C\) vs. \(~590°C\) for Ni.\cite{9, 10} Therefore, the extent of mixing is expected to increase as the annealing temperature is raised in the 350-600°C range. This method is expected to result in a series of model Cu-Ni catalysts where the extent of mixing may be kinetically controlled by properly choosing the annealing temperature and time. However, despite kinetic control over spatial distributions of the Cu and Ni components in these catalysts, these distributions could be “locked in” since the optimal temperatures of using these supported nanoparticles in WGS catalysis are well below the Tamman temperatures of Cu and Ni.
Ni-based catalysts have been recognized as alternative catalysts for the WGS reaction, because they are potentially used in a single stage instead of the usual two-stage WGS process. However, the methanation side reaction observed over the Ni catalysts and their lower activity at low temperatures are serious drawbacks for a WGS catalyst. Cu-based catalysts are widely used as low temperature WGS catalysts. However, the deactivation of Cu at high temperature due to sintering limits its application in small mobile fuel processors. Recently reported core-hollow shell structures (metal@metal oxide) are advantageous as high temperature WGS catalysts, because the particle aggregation is essentially prevented by the presence of metal oxide hollow shells.\cite{11} For example, Park et al. prepared a Ni@SiO$_2$ yolk-shell nanoreactor framework comprising Ni cores inside hollow silica shells (Scheme 6.1). This novel catalyst is remarkably stable at high temperature up to 973K during steam methane reforming. Borrowing this idea, highly stable Cu@metal oxide catalysts can be prepared similarly as alternative WGS catalysts.

\textbf{Scheme 6.1} Fabrication of Ni@SiO$_2$ yolk-shell nanoreactor framework
The WGS reaction is an integral step bridging a fuel gasifier and downstream H₂ purification. A variety of impurities can be found in the syngas from coal gasification, among which sulfur compounds are major impurities. Under WGS reaction conditions, sulfur is most likely to be present in the form of H₂S.¹² Poisoning of WGS catalysts in sulfur-containing fuels can be attributed to (1) physical adsorption/chemisorption of H₂S, i.e., reactions (a) and (b) at surface active sites (dissociation of sulfur atoms from H₂S) that lead to the reduction of surface area shown below, (2) sulfidation of active metals, i.e., reaction (c) due to reaction between sulfur and active metals resulting in a loss of catalytic activity.¹³

\[ M + H_2S \rightarrow M-H_2S \]  
\[ M(s) + H_2S(g) \rightarrow M-HS(ads) + M-H(ads) + M-S(ads) + M-S(ads) + H_2 \]  
\[ xM + H_2S \rightarrow MxS + xH_2 \]

Bimetallic catalysts are among some of the most important industrial catalysts. The potential for synergy between constituent metals by ensemble and electronic effects offers the possibility to manipulate and design catalysts for specific function. Although colloidal Cu and Ni and Cu-Ni are promising as WGS catalysts, they are still susceptible to poisoning by sulfur-containing compounds through the formation of the sulfur-metal bonds.¹⁴ Theoretical DFT studies predicted alloying Cu with Ni to yield less sulfur resistant catalysts than monometallic Cu.¹⁵ Recently, Inoglu et al. examined the sulfur
tolerance of binary combinations of 10 different late transition metal atoms (Fe, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, and Au) using DFT to predict the S-adsorption energy.\cite{16} Their findings suggested that Pd alloyed with Cu would possess improved S tolerance characteristics as compared to pure Pd and Cu systems. The Cu/Pd alloys have received much attention in recent years as sulfur-resistant H\textsubscript{2} separation membranes.\cite{17-19} The Cu/Pd system was shown to be more resistant to H\textsubscript{2}S poisoning than pure Pd when the Cu/Pd alloy structure is in the face-centered cubic (fcc) region of the Cu/Pd phase diagram. Therefore, synthesis of supported Cu/Pd alloy nanoparticles with an fcc structure is highly promising as the next step to develop highly active, sulfur-resistant WGS catalysts.

Indeed, our preliminary data indicated that Pd\textsubscript{2.5}Cu\textsubscript{20} catalysts possessing an fcc structure are more sulfur-tolerant than supported Cu\textsubscript{20} catalysts (Figure 6.1 and 6.2). The XRD patterns of the Cu and CuPd catalysts prepared by alumina support impregnation after reduction at 400\textdegree{}C are shown in Figure 6.1. The XRD pattern of the CuPd catalyst indicated that the diffraction peaks shifted to lower 2\theta values as compared to that of Cu, indicating the formation of an fcc CuPd alloy. Figure 6.2 shows CO conversion over Cu and CuPd catalysts. The CO conversion over the Cu catalyst quickly declined from an initial 22\% to 0\% within 8 h following its exposure to 50 ppm H\textsubscript{2}S at 300\textdegree{}C, whereas the CuPd catalyst showed slower deactivation as compared to the pure Cu catalyst. These
preliminary results support earlier findings that Cu/Pd catalysts are highly promising as sulfur-resistant WGS catalysts.

**Figure 6.1** XRD diffraction patterns of supported Pd2.5Cu20 and Cu20 catalysts after reduction in hydrogen at 400°C 2h.
Figure 6.2 CO conversion in the presence of 500 ppm of H$_2$S over supported Cu20/Al$_2$O$_3$ and Pd2.5Cu20/Al$_2$O$_3$ catalysts. Feed composition: 10% CO, 20% H$_2$O, 70% He with 50 ppm of H$_2$S. Reaction conditions: 300°C and GHSV = 25,000

On the other hand, according to Nørskov et al.,\textsuperscript{[20]} the characteristics of the $d$-band center ($\epsilon_d$) play an important role in determining surface reactivity. Previous DFT studies showed that compressive and tensile strains caused by a mismatch in lattice parameters tend to downshift and upshift the $d$-band center, respectively, thus influencing the catalytic activity.\textsuperscript{[20]} For instance, a highly enhanced activity in the preferential oxidation of CO in hydrogen over Ru@Pt core-shell nanoparticles as compared to monometallic components and annealed Ru-Pt alloy has been demonstrated by Alalyoglu et al.\textsuperscript{[21]} In this case, the interaction of the Pt shell with the Ru core tended to downshift the $d$-band center of surface
Pt atoms. This downshifting due to significantly mismatched Ru and Pt lattice parameters (ca. 45%) resulted in decreased CO binding and much lower CO saturation coverages on Ru@Pt surface, which in turn enhanced catalytic activity. Kundsen et al. using DFT theory to investigate Cu/Pt near surface alloys as WGS catalyst and revealed that Cu/Pt core-shell structure bound CO significantly more weakly than Pt.\textsuperscript{[22]} However, as our studies indicated, the WGS activity was not significantly affected by the core-shell structure of bimetallic Cu-Ni nanoparticles due to a small mismatch (ca. 2.5\%) between Cu and Ni lattice parameters. Therefore, Cu shell covering a metal core with a smaller lattice parameter than that of Cu may experience a compressive strain that would reduce the potential for CO poisoning on the Cu surface, and thus enhance the WGS activity. Unfortunately, the majority of active metals for the WGS catalysis discussed previously exhibit larger lattice parameter than that of Cu. However, one system, i.e., Ru@Cu may be a promising WGS catalyst, since compressive strain in Ru@Pt nanoparticles (Pt and Cu have atomic radius of 135 pm) resulted in decreased CO binding and lower CO saturation energy.\textsuperscript{[21]}

Cu and Fe have been widely explored as LTS and HTS WGS catalysts, respectively. Through the combination of different metals their geometries and electronic structures can be varied over wide ranges that allow tuning their catalytic reactivities. Alloys of Cu with
Fe may be a potential WGS catalyst to replace Cu-Ni alloy catalyst because of the disadvantage of methanation side-reaction displayed by many Ni-containing catalysts.
6.3 References


