Development of Sol-Gel Prepared Palladium-Based Sulfated Zirconia Catalysts for Nitrogen Oxides Reduction with Methane

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Abstract

Nitrogen oxides (NOx) have brought serious environmental and human health issues, and more and more attention has been focused on effective removal of NOx. While current catalytic aftertreatments are effective for present engines, they do not work well for next generation high efficient combustion engines which operate with high oxygen concentrations. Methane-based selective catalytic reduction (CH4-SCR) is a potential technology for lean burn engine NOx reduction. However, a significant challenge appears in CH4-SCR: rather than selectively reducing NOx under lean burn conditions, the reducing agent CH4 tends to be oxidized by O2. To overcome this problem, our group proposed a dual-catalyst system (mixed bed catalyst) which contains both reduction catalyst and oxidation catalyst. In this system, NO is first oxidized to NO2 which is more easily reduced over the oxidation catalyst, and then NO2 is reduced to N2 over the reduction catalyst. This work focused on the study of the reduction catalyst, palladium based zirconia (Pd/SZ).

Pd/SZ was prepared by one step sol-gel method. Parameters of preparation, such as concentration of zirconium propoxide and the ratio of zirconium-to-sulfur, were changed in this study, and their effects on physical characteristics and catalytic activities of Pd/SZ were investigated. Zirconium propoxide concentration did not obviously affect surface area and sulfate retention of Pd/SZ catalysts. Surface area and sulfate retention of the catalysts with the same zirconium propoxide concentration first
increased with the increasing sulfate loading, and then decreased. Surface areas showed maxima at sulfate ratio of 1, while sulfate retentions reached maxima at sulfate ratio of 2. XRD and Raman were used to identify the crystalline phases in the sol-gel prepared Pd/SZ catalysts, and both monoclinic and tetragonal structures were observed. For each series of catalyst with the same zirconium propoxide concentration, tetragonal phase was dominant at low sulfate loading while monoclinic phase became more obvious with increased sulfate loading. Highly active catalysts were screened out by steady state reaction tests, and N₂ yield as high as 77% was achieved over Pd/SZ (1/2). DRIFTS-TPD (pyridine) was adopted to measure the acid sites and their strengths on the surfaces of Pd/SZ, and the results of DRIFTS were consistent with the catalytic activities of Pd/SZ catalysts.

Experiments aiming to measure the hydrothermal stabilities of prepared Pd/SZ catalysts were carried out to test their potentials for practical applications. NOₓ SCR switch during NOₓ oxidation and CH₄ combustion experiment showed that CH₄ combustion resulted in a permanent activity loss in NOₓ reduction over Pd/SZ catalyst. In water resistance experiments, oxidation catalyst Co/ZrO₂ was proved to have high resistance to water vapor, while the reduction catalyst Pd/SZ deactivated in the presence of H₂O. However, the deactivation of Pd/SZ was recoverable and its catalytic activity returned back after H₂O was removed. Reversible competitive adsorption of NO, CH₄, and H₂O on the active sites was proposed to explain the recoverable activity loss of Pd/SZ in the wet/dry switch experiments. NO₂ is a stronger oxidizer than NO and is more easily reduced. The addition of Co/ZrO₂ to Pd/SZ greatly increased NO
conversion and N\textsubscript{2} yield, because the re-oxidation of NO which resulted from the partial reduction of NO\textsubscript{2} provided more chances for NO\textsubscript{2} to be reduced to N\textsubscript{2}. A high N\textsubscript{2} yield of 90% was achieved over mixed bed (physical mixture of Co/ZrO\textsubscript{2} and Pd/SZ) with CH\textsubscript{4}. A small amount of Co/ZrO\textsubscript{2} was proved to be enough in the mixed bed to re-oxidize NO and more Co/ZrO\textsubscript{2} did not further increase N\textsubscript{2} yield. In addition, the mixed bed exhibited high stabilities for NO reduction with both CH\textsubscript{4} and simulated streams in the absence and presence of H\textsubscript{2}O. Meanwhile, CO, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8}, which also appeared in the exhaust streams, were completely converted over mixed bed, showing very good potential for practical applications for natural gas reciprocating engine NO\textsubscript{x} reduction.
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Chapter 1 Introduction

Nitrogen oxides (NO\textsubscript{x}, including NO and NO\textsubscript{2}) are gases that bring serious air pollution. They mainly come from the combustion of fossil fuels, such as coal, petroleum, and natural gas, which are the primary sources of world energy. NO\textsubscript{x} has many harmful effects on both the environment and human health: NO\textsubscript{x} helps generate acid rain, contributes to global warming, and promotes ground level ozone which causes human respiratory diseases and reduces plant growth [1]. Therefore, more and more attention and actions have been addressed to effective removal of NO\textsubscript{x} emissions.

There are two kinds of NO\textsubscript{x} produced during the process of fuel combustion: NO\textsubscript{x} from the oxidation of molecular nitrogen in the combustion air at high temperature, known as thermal NO\textsubscript{x}; and NO\textsubscript{x} from the combustion of nitrogen contained in the fuel, known as fuel NO\textsubscript{x} [2]. To reduce thermal NO\textsubscript{x} emissions, combustion control technology is used; while to decrease the amount of fuel NO\textsubscript{x}, fuels with less nitrogen content, such as hydrocarbons, are preferred.

Current combustion control aiming to decrease thermal NO\textsubscript{x} emissions is achieved through modifying combustion chamber design or reducing temperatures in the combustion cylinder through gas recirculation [3]. The field of engine design is quite developed, whereas exhaust gas recirculation causes efficiency loss making it not a promising solution [3].
Lower hydrocarbons, without organically bound nitrogen and sulfur, could significantly reduce fuel NO\(_x\) as cleaner fuels than conventional fossil fuels. Due to its large availability and attractive price, methane, the principle component of natural gas, has become the most popular hydrocarbon fuel. Natural gas reciprocating engines are widely used in stationary power generation, where they can be operated under both lean and rich burn conditions. Due to its obvious advantages, lean burn operation is favored: it greatly increases engine efficiency and reduces exhaust pollutants, such as NO\(_x\) emissions, which are reduced because of a lower combustion temperature. However, the level of NO\(_x\) emissions still attracts attention and stringent emission control legislations have been increasingly imposed [4].

In addition to combustion control and adopting low-nitrogen fuel, exhaust treatment is a widely used technology. Although it costs more, exhaust treatment is more effective to reduce NO\(_x\) pollutions than combustion control [2]. Catalytic aftertreatment is the most developed and widely used exhaust treatment technology currently [2]. Catalytic aftertreatment technology is easily retrofitted with no associated efficiency losses. Current catalytic NO\(_x\) reduction control technologies contain Three Way Catalysts (TWCs) and ammonia-based selective catalytic reduction (NH\(_3\)-SCR). TWCs reduce nitrogen oxides, and oxidize carbon monoxide and unburned hydrocarbons in the exhausts. While TWCs are highly effective for current combustion engines, they are not suitable for the next generation of high fuel-efficient lean burn engines [5]. Lean burn engines are operated in rich oxygen concentrations, and under this condition TWCs quickly deactivate [5]. NH\(_3\)-SCR is
another widely applied technology, and it is also highly effective for removing NOx emissions. Unfortunately, NH3-SCR has some disadvantages, such as ammonia storage and delivery, and ammonia slipstream issues [6], and these disadvantages limit the applications and further development of NH3-SCR.

While neither TWCs nor NH3-SCR is competent for next generation engine NOx reduction, hydrocarbon, especially methane-based selective catalytic reduction (CH4-SCR), has become one of the most promising potential solutions for removing NOx emissions from lean burn engines. In CH4-SCR technology, CH4 is not only used as fuel gas but also reducing agent. Since CH4 and other hydrocarbons already appear in the exhaust streams, using them as reducing agent definitely decreases fuel penalty costs and exempts reducing agent injection controls. However, a principle challenge that exists in CH4-SCR technology is that CH4 tends to combust under rich oxygen conditions rather than selectively reduce the NOx species. To overcome this challenge, a two-stage system (mixed bed catalyst) has been proposed for the reduction of NOx under lean burn conditions by our group [7]. This approach is based on the principle that NO2 is a stronger oxidizer than NO, and therefore, can compete better with oxygen for reaction with the reducing agent CH4. The two-stage system contains two catalysts which are physically mixed together but perform separate functions. The two catalysts are the oxidation catalyst and the reduction catalyst, and the reactions in this system could be described as: NO is first oxidized to NO2 over the oxidation catalyst followed by reduction of NO2 to N2 over the reduction catalyst.

The work of this study is focused on the development of NOx reduction catalysts,
palladium based sulfated zirconia (Pd/SZ) which are prepared by a modified one-step sol-gel method. Preparation parameters were modified, and related physical characteristics and catalytic activities for NOx reduction under lean conditions were investigated. High N₂ yields were achieved, and highly effective reduction catalysts for NOx reduction with CH₄ were screened out. In addition, thermal and hydrothermal evaluations of the sol-gel prepared Pd/SZ and the two-stage catalyst aftertreatment system under both test and simulated exhaust streams were performed.
Chapter 2 Literature Review

2.1 NO\textsubscript{x} Reduction with Hydrocarbons

NO\textsubscript{x} reduction with hydrocarbons (CH) exhibits great potential for reciprocating engines which are applied in stationary power generation sites under lean burn conditions. CH-SCR technology possesses many advantages for practical applications, for example, it is less corrosive than NH\textsubscript{3}- or urea-SCR, and it avoids other problems such as ammonia slip and direct ammonia oxidation [6]. Additionally, the composition of the reducing gas is similar to that of the exhaust, therefore, CH-SCR technology is relatively easily to build-in.

Various hydrocarbons including ethylene, propane, propene, n-hexane, and n-octane [8-12] have been studied for NO\textsubscript{x} reduction. While higher hydrocarbons above have been proven effective for reducing NO\textsubscript{x}, methane was regarded as a nonselective reductant due to its strong C-H bond which is difficult to activate without high reaction temperature [13-15]. However, as the main component of natural gas, CH\textsubscript{4} is an extremely attractive reducing agent for NO\textsubscript{x} reduction because of its large availability and attractive price. Therefore, intensive research is required on the catalytic reduction of NO\textsubscript{x} with CH\textsubscript{4}, especially under lean burn conditions.

2.2 NO\textsubscript{x} Reduction over Zeolite-Based Catalysts with CH\textsubscript{4}

Large amounts of catalysts for NO\textsubscript{x} reduction with CH\textsubscript{4} have been studied in
literatures. Zeolite-based catalysts are the most intensively investigated categories of these catalysts.

Zeolites are microporous aluminosilicate minerals containing interlocking tetrahedrons of SiO₄ and AlO₄, and metals can be introduced into their frameworks by ion exchange [16]. Li and Armor studied on Co/ZSM-5 catalyst for NO reduction by CH₄ and reported that the catalytic activity is related to the Co²⁺ exchange level [17, 18]. They also found that the presence of water vapor in the reaction feed significantly decreased NO reduction and they proposed that the water effect was due to competitive adsorption between NO and H₂O [19]. In subsequent work they replaced the support with a ferrierite zeolite and NO conversion increased twofold. However, water still severely reduced NO conversion since it apparently increased the activation energies of NO reduction and CH₄ oxidation [20]. They also investigated NO reduction over Co-ZSM-5 and Ga-H-ZSM-5 with CH₄, respectively, and pointed out that the former has higher NO conversion while the latter has higher CH₄ selectivity. Thus, H⁺ acid sites were proposed to promote NO reduction [21].

Loughran and Resasco [22] studied several H- and Na-ZSM-5 zeolites for NO reduction with CH₄. They suggested a mechanism for NO reduction with CH₄ in which NO decomposes first and then CH₄ reacts with O₂ to regenerate the active site. Meanwhile they found that Pd/ZSM-5 was active for NO decomposition but deactivated quickly. They also studied palladium-based acidic and non-acidic catalysts for NO reduction and indicated that both palladium and acid sites were necessary for high catalytic activity. On Pd/H-ZSM-5, catalytic activity and
selectivity were observed to pass through a maximum with increasing palladium loading. Besides H-ZSM-5 they also found other acidic supports on which palladium was supported were effective to enhance the activity and selectivity of NO reduction. Additionally, mechanical mixture of acidic materials and inactive Pd/SO₂ was observed to promote the activity. A bifunctional mechanism in which both palladium and acidic sites contribute to NO reduction was proposed [23]. Their further study indicated that Pd²⁺ ions which were stabilized by surface acidity were selective for NO reduction. When Pd loading was increased, Pd²⁺ was transformed to PdO which was not selective for NO reduction but favored CH₄ combustion [24].

Bell et al. [25, 26] investigated Pd-H-ZSM-5 for NO reduction with CH₄, and found that the state of Pd depended on the reaction temperature and the presence of O₂ in the feed gas. Pd remained dispersed as Pd²⁺ below 610K when O₂ was absent, while in the presence of O₂ Pd remained highly dispersed as Pd²⁺ species up to 873K. The activity of Pd-H-ZSM-5 for NO reduction with CH₄ was much higher than that of H-ZSM-5, indicating that Pd²⁺ was the active component. They also claimed that CN species were intermediates of NO reduction in their studies on Co-ZSM-5 [27], Mn-ZSM-5 [28], and as well as Pd-ZSM-5.

The studies on zeolite-based catalysts are extensive, however, the main disadvantage of these catalysts is their poor hydrothermal stability due to dealumination when they are exposed to wet exhaust streams at high temperatures [29]. This made zeolite-based catalysts not practical for applications to actual combustion exhausts. Although efforts have been made to improve the hydrothermal
stability of zeolites, alternative supports with higher stability such as metal oxides with acid properties are required.

2.3 NO$_x$ Reduction over Sulfated Zirconia Catalysts with CH$_4$

Surface acidity in catalysts has been identified as a key to activity in the reduction of NO$_x$ with CH$_4$ [20, 30-32], and solid superacids have been wildly explored. Superacids refer to acids whose Hammett acidity is stronger than 100% sulfuric acid [33], and the most extensively researched solid superacid is sulfated zirconia (SZ). Arata et al. reported that zirconia, after proper treatment with sulfuric acid or other sulfates, exhibits extremely strong acidity, $10^4$ times stronger than 100% sulfuric acid [34, 35]. The superacidity of SZ is controversial though, as some researchers [36-39] pointed out that SZ is only a strong solid acid whose acidity is comparable to that of sulfuric acid. However, sulfated zirconia is still an active catalyst and commonly used in acid-catalyzed organic reactions such as the difficult isomerization of n-butane to isobutene at room temperature [34]. Moreover, sulfated zirconia is a safe and environmentally friendly catalyst. Current strong acid catalysts such as H$_2$SO$_4$ or HF have many shortcomings including extreme corrosivity and high toxicity, as well as the inherent risk of handling these hazardous acids in large amounts [33].

Song and Sayari [33] reported that although sulfated zirconia has shown extremely high activity for acid catalyzed reductions, it deactivates fast which is possibly due to coke deposition on the strong acid sites. To overcome this problem,
several groups developed SZ catalysts containing small amounts of transition metals, such as Pt, Pd, Au, Ga or Mn [40, 41]. Consequent metal-promoted SZ catalysts were found to contain both Bronsted and Lewis acidities with superior acid strengths [37]. Among these metal-promoted SZ catalysts, Pd/SZ was found to be the most active for NO\textsubscript{x} reduction with CH\textsubscript{4} [42]. Pd/SZ has been demonstrated to be able to increase NO\textsubscript{x} reduction activity and selectivity by stabilizing Pd\textsuperscript{2+} ions which is selective for NO\textsubscript{x} reduction [43]. More attractive than zeolite-based catalysts, Pd/SZ is less sensitive to water vapor and SO\textsubscript{2} poisoning and exhibits higher reversibility after water or SO\textsubscript{2} is removed [43].

Many groups have been working on the mechanism of the activity of Pd/SZ. Bifunctional mechanism is the mechanism which has been commonly accepted [44]. In this mechanism, both sulfate incorporation and palladium dispersion contribute to NO\textsubscript{x} reduction. In Pd/SZ catalyst, sulfate ions are known to relate to its strong acid properties. It is revealed that the oxidation state of sulfur in Pd/SZ showing high activity was S\textsuperscript{6+} based on XPS and IR data [33], and Figure 2.1 shows one of the probable structures of Pd/SZ. Tanabe [45] and Jin [46] et al. proposed that the strong acidity resulted from the electron induction effect of two covalent S=O bonds, which increased the electron deficiency of the metal atom attached to the sulfate group, therefore the acidity was strengthened. Lopez \textit{et al.} claimed that sulfur was incorporated into the solid through an anionic exchange between the HSO\textsubscript{4}\textsuperscript{-} anions from the solution and the OH groups on the solid [47]. Therefore, the acidity of sulfated zirconia can be controlled by the presence of OH groups on the original
material.

Figure 2.1 One of proposed structures of Pd/SZ (cited from[33])

It has been generally reported that sulfation results in changes to the surface area and the crystalline structure of zirconia. Comparing to pure zirconia, sulfated zirconia has higher surface area and more stable tetragonal phase [48-51].

Two main methods have been reported in the literature for the preparation of sulfated zirconia catalysts: two-step method and one-step method [33]. Two-step method firstly prepares zirconium hydroxide and then sulfates the zirconium hydroxide. Figure 2 shows the schematic illustration of its process [33]: a zirconium salt, such as ZrOCl₂, ZrO(NO₃)₂, ZrCl₂, Zr(NO₃)₄, or Zr propoxide [Zr(OC₃H₇)₄], etc. is first hydrolyzed with aqueous ammonia or urea or water to produce zirconium hydroxide, and then a H₂SO₄, (NH₄)₂SO₄ or SO₂, H₂S, CS₂, or SO₂Cl₂, etc. solution is used to sulfate the zirconium hydroxide. The obtained sulfated zirconium hydroxide is calcined in air at high temperature during which the sulfur containing species are
transformed into the form of sulfate $\text{SO}_4^{2-}$ to generate strong acidity. In the one-step method, sulfuric acid solution is added to the zirconium alkoxide precursors during the formation of the gel. In this way the sulfate was included in the gel network, leading to a zirconium-sulfate cogel. Catalysts prepared by one-step method exhibit higher surface areas and homogeneous distribution of components [52].

Figure 2.2 Schematic illustration of the two-step method for the preparation of sulfated zirconia (cited from [33]).

It is widely reported that preparation parameters play great roles on the properties of Pd/SZ catalysts. Davis et al. [53] claimed that the salt used to prepare zirconium hydroxide significantly affects the crystalline phase of the zirconia obtained after calcination. Calcination temperature also has great impacts on surface
area, sulfur retention, crystalline phase and catalytic activity of Pd/SZ [54]. In earlier work by our group, Pd/SZ was calcined at 500, 600 and 700°C respectively, and it was found that samples calcined at 700°C exhibited the highest activity, although the samples calcined at 600°C showed the highest surface area [3]. Chen et al. [54] found that calcinations between 400 and 500°C generated increased catalytic activity while sulfur content did not change much. They claimed that the nature of the sulfate was more important than the sulfate content, and appropriate calcination temperature resulted in the proper configuration of sulfur species which generated a high activity. Our group also compared the samples pretreated under He only and 10% O_2/He respectively, and found that the added sulfate to the catalyst was more thermally stable under 10% O_2/He pretreatment.

Palladium based sulfated zirconia catalysts have been reported highly effective for NO_x reduction with CH_4. After working on acidic zeolite catalysts, Resasco et al. intensively investigated Pd/SZ catalysts for NO_x reduction with CH_4. Although similar to acidic zeolites isolated Pd^{2+} ions which were selective for NO reduction were stabilized by acidic sites, Pd/SZ catalysts were found to be less sensitive to structural damage under hydrothermal conditions [43]. In their study, Pd/SZ catalysts showed high activity and selectivity for NO reduction. One of their most significant characteristics was that they were remarkably more resistant to H_2O and SO_2 than zeolite-based catalysts during the investigated 40hs, and they also exhibited higher reversibility of activity after H_2O and SO_2 was removed [55]. White et al. [56] claimed that the deactivation of these catalysts were due to the change of acidic sites
on the surface in the presence of water.

Ohtsuka et al. [42] found that Pd/SZ was the most active catalyst for NO$_x$ reduction with CH$_4$ after they impregnated various precious metals into sulfated zirconia supports. In their study, NO$_2$ showed higher N$_2$ yield than NO did in the reduction tests. Subsequently they developed a highly active bimetallic catalyst, Pd-Pt/SZ, based on their former observation that Pt was active to oxidize NO to NO$_2$. This bimetallic catalyst was found to be still active in the presence of 9% H$_2$O [57]. However, a gradual deactivation appeared in long-term activity tests. Ohtsuka et al. suggested that this resulted from the conversion of tetragonal to monoclinic phase of zirconia, which generated sulfate loss and so decreased the catalytic activity [58].

Our past group members prepared Pd/SZ catalysts by the incipient wetness impregnation (IWI) method and found that these catalysts were very active for NO$_x$ reduction with CH$_4$ under lean burn conditions, especially when they were mixed with the oxidation catalyst Co/ZrO$_2$. Our group also studied the effect of Pd content on the NO reduction and found that 0.3% Pd/SZ possessed the best catalytic activity. In addition, our group started the research on sol-gel prepared Pd/SZ catalysts which showed high activity for NO reduction and found that the sol-gel catalysts calcined at 700°C exhibited the best performance [3].
Chapter 3 Experimental Methods

3.1 Catalyst Synthesis

The catalysts used in this study were prepared by incipient wetness impregnation (IWI) or sol-gel (SG) synthesis techniques. IWI technique relates to the physical mixing of an unloaded porous catalyst support and a solution containing a dissolved metal salt. IWI technique was used to prepared oxidation catalyst Co/ZrO$_2$ in this study and water was used as the solvent. Metal salt of the active component is dissolved and then impregnated onto the support. The solution is introduced drop by drop to the support and the total volume of the solution introduced to the support is equal to the pore volume of the support. The catalyst is then dried at 110°C overnight to evaporate the solvent, and the metal is left on the catalyst support. Multiple impregnation steps are used if needed to make better impregnation or to impregnate multiple metals onto the support. After the final impregnation step, the catalysts are calcined in air at 500°C with a ramp rate of 10°C/min and held at 500°C for 3 hours. The sol-gel preparation method can allow better control of support characteristics such as pore volume and pore diameter and can achieve higher surface area and better metal dispersion. In this study, sol-gel method was used for synthesizing reduction catalyst Pd/SZ. Acetic acid was used as hydrolysis agent for all sol-gel preparations in this study, and the catalyst structure was built by the controlled hydrolysis of metal alkoxide precursor by using acetic acid. The alkoxide precursor is put in an organic
solvent containing the dissolved active metal salt, and then under stirring hydrolysis agent is added to the mixture of alkoxide precursor, organic solvent and active metal salt. After hydrolysis the gel is dried at 110°C overnight. The dried gel was then ground using a mortar and pestle, and then the powder obtained is calcined in air at 700°C with a ramp rate of 10°C/min and held at 700°C for 3 hours.

3.2 Steady-State Reaction Studies

The reaction system used in this study is depicted in Figure 3.1. Five mass flow controllers are equipped into the system and a wide range of feed gas mixtures can be introduced to the reactor. Water can be added to the feed by passing He in the stream through a heated bubbler and the tubing is heated using heating tape to prevent water from condensing. Feed gases are mixed and sent through two three-way valves which can allow gas to bypass the reactor for feed analysis. The reactor is a 1/4” outer diameter stainless steel tube and it is located in a homemade resistively heated furnace whose maximum temperature is 700°C. The catalyst sample is packed in the reactor between two quartz wool plugs, and the reactor is set in the center of the furnace. The reaction temperature is monitored and controlled by an Omega 1/16” k-type thermocouple and an Omega CN4400 temperature controller. The thermocouple is inserted into the reactor and touches the upper quartz wool of the catalyst bed. The gases out of the reactor are measured by the analysis part of the system.

The concentrations of N₂, O₂, CH₄, CO₂, CO, N₂O, C₂H₆, and C₃H₈ are analyzed by a Varian CP-4900 micro gas chromatograph. Sample gas is drawn for 30 seconds
by the micro-GC to flush the injection ports, and then is injected to a Molecular Sieve 5A (test for N₂, O₂, CH₄, and CO) and a Porapak Q (test for CO₂, N₂O, C₂H₆, C₃H₈) GC column. The two columns are placed in parallel to decrease analysis time which is 60 or 70 seconds (depending on the gas composition) in this study. Gas concentrations are calculated from peak areas and response factors determined by using gases of known concentrations.

![Figure 3.1 Schematic of NOₓ steady-state reaction system](image)

The other portion of gas flow which is not sucked into the micro-GC passes through a Thermo Environmental Model 42H Chemiluminescence NOₓ analyzer which continuously measures NO and NO₂. The operation principle of the NOₓ
analyzer is that NO and O₃ react to produce a characteristic luminescence with an intensity linearly proportional to the NO concentration. NO₂ has to be first transformed into NO to be measured, and the conversion of NO₂ to NO happens in a stainless steel converter. Sample gas is pulled into the NOₓ analyzer by an external pump, and then is routed either straight to the reaction chamber (NO mode) or through the NO₂-to-NO converter and then to the reaction chamber (NOₓ mode). The NO and NOₓ concentrations are calculated in the NO and NOₓ modes, and the difference between the two concentrations is the NO₂ concentration.

3.3 Physisorption for BET Surface Area Analysis

Nitrogen physisorption was performed on a Micromeritics ASAP 2010 accelerated surface area and porosimetry instrument. A sample tube was sealed, degassed, and weighed followed by loading 200-250 mg catalyst into it and degassing the catalyst overnight at 130°C under a vacuum of 3 μm Hg. Then the sample tube holding the catalyst was weighed and the degassed catalyst weight was calculated from the mass differences of the empty sample tube and the sample tube holding the catalyst. The sample tube was then moved to the analysis port where it was submerged in liquid nitrogen and the catalyst inside the tube was exposed to injections of nitrogen gas. The instrument measures the pressure during nitrogen physisorption and the ASAP 2010 software to determine the surface area and pore volume of the catalyst.

During the analysis process, the amounts of nitrogen molecules adsorbed or
desorbed are determined by the pressure variations due to the adsorption or desorption of nitrogen molecules on the catalyst. Various amounts of nitrogen molecules are adsorbed or desorbed at different pressures. Given the area occupied by one nitrogen molecule (\(\sigma = 16.2 \text{ Å}^2\) for nitrogen), the ASAP 2010 adopted the most widely used adsorption model, BET method (developed by Brunauer, Emmett, and Teller) [59], to calculate the surface area of the catalyst:

\[
\frac{P}{n(P_0 - P)} = \frac{1}{cn_m} + \frac{c - 1}{cn_m} \frac{P}{P_0}
\]

In which, \(P\) is the adsorption pressure, \(P_0\) is the saturation vapor pressure, \(c\) is a constant, \(n\) is the amount adsorbed (moles per gram of catalyst) at the relative pressure \(P/P_0\), and \(n_m\) is the monolayer capacity (moles of molecules needed to carry out a monolayer coverage on the surface of one gram of catalyst). By plotting \(P/[n(P_0-P)]\) against \((P/P_0)\), the slope and intercept of the linear equation gives \(n_m\). Then the specific surface area, \(S\), can be calculated as:

\[
S = N_A n_m \sigma
\]

Where \(N_A\) is Avogadro’s number.

3.4 X-ray Photoelectron Spectroscopy (XPS)

XPS is an important surface chemical analysis technique for catalysis research. It can offer quantitative measurements of elemental composition, chemical state and electronic state of the elements on the catalyst surface. In this study, XPS spectra were
obtained under ultra high vacuum conditions by irradiating the catalyst with a beam of monochromatic X-ray while measuring the kinetic energy $KE$ and number of electrons which escaped from the surface atoms of the catalyst at the same time. The energy of a particular Al X-ray wavelength is known, therefore the electron binding energy $BE$ of the emitted electron can be calculated by the following equation:

$$BE = h \nu - KE - \phi$$

Where $h \nu$ is the energy of the X-ray photons being used, $KE$ is measured by the instrument, and $\phi$ is the work function of the spectrometer.

$BE$ is a characteristic of an element so could be used to determine the element. The peak area of the element is dependent on the atomic concentration in the sample, and the atomic concentration of an element, $C_i$, can be calculated as:

$$C_i = \frac{A_i}{\sum_i \frac{A_i}{S_i}}$$

Where $A_i$ is the peak area of element $i$, and $S_i$ is the sensitivity factor for the peak $i$.

A Kratos Axis Ultra instrument with an aluminum anode was used in this study. Catalysts were first placed in a high-vacuum preparation chamber, and they were degassed to $10^{-6}$ torr overnight there. Then catalysts were moved to the analysis chamber, and the operation there was under the conditions of an ultra-high vacuum of $10^{-9}$ torr. A survey scan that covered the complete binding energy range was carried out to check expected peaks, and then higher resolution scans that covered the binding
energy ranges of the elements of interest were carried out. The location of the carbon 1s peak was used to correct charge shift.

3.5 X-ray Diffraction (XRD)

XRD is a non-destructive technique that can exhibit detailed information about the crystalline structure of catalyst samples. A sample is exposed to monochromatic X-rays, which constructively interfere at certain scattering angles to generate diffraction as they scatter from two atomic planes in the crystalline sample. Constructive interference occurs when the atomic lattice spacing (d) of the sample is an integer multiple (n) of the X-ray wavelength (λ), and thus the angles (θ) at which constructive interference occurs show up in a characteristic pattern which can help determine the crystalline phases of the sample. The equation being used to calculate the angles of diffraction is:

\[ n\lambda = 2d \sin \theta \]

In this study, XRD was carried out on a Bruker D8 Advance X-ray diffractometer equipped with a CuKα source whose wavelength is 1.54 Å. The instrument is fitted with a controlled atmosphere/temperature chamber and a position sensitive detector. The temperature can range from cryogenic to 1200°C. The sample was loaded in the shallow sample holder and a glass microscope slide was used to press the sample to obtain a flat surface. Diffraction patterns were gotten over a range of two-theta equal to 20-70°.
3.6 Laser Raman Spectroscopy

Raman spectroscopy is a powerful technique which is highly suitable for \textit{in situ} studies for catalysis research. In this study Raman spectroscopy was used to measure the crystalline phase of the catalyst samples. Raman spectroscopy is based on the inelastic scattering of photons from a laser. The laser light interacts with photons in the sample and this results in the energy of the laser photons being shifted up or down. This shift in energy provides information about the photon modes of the sample. Laser Raman spectra were obtained over a Horiba Jobin-Yvon LabRam HR800 spectrometer with a 632.81 nm argon ion laser and a $\times 50$ microprobe in the back scattering geometry.

Two-point calibration was daily used to calibrate the spectrometer, which were based on white light with no grating and silicone with 1800 grating. The laser power was originally 7.0 mW at the sample, but neutral density filters were used to decrease the laser power on some samples to get better spectra.

3.7 Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS)

DRIFTS is an infrared spectroscopy technique that is well developed for the analysis of catalyst powder. Incident light in DRIFTS is divides into two parts, diffuse reflectance light and specular reflectance light, after its interaction with the sample. DRIFTS spectra are based on the diffuse reflectance light which has interacted intimately with the sample particles and the adsorbed surface species as well. The specular reflectance light has not undergone the same interaction with the sample and
is blocked, thus it does not contribute to the spectra. An environmental chamber is able to monitor the sample surface under different feed gases and temperature ramps by adjusting the surrounding atmosphere and sample temperature. The chamber is furnished with ZnSe windows, and a diffuse reflectance cell is equipped inside of it. The cell is the place to perform in-situ measurements, and a thermocouple mount in it is used to directly measure the sample temperature. In this study a Nicolet 6700 DRIFTS was used, and it was equipped with a liquid N\(_2\) cooled MCT detector and KBr beamsplitters. Spectra were obtained over 500 scans in the mid-IR range (400-4000 cm\(^{-1}\)) at a resolution of 4 cm\(^{-1}\).
Chapter 4 NO\textsubscript{x} Reduction over Palladium Based Sulfate Zirconia with Methane

4.1 Catalysts Synthesis

4.1.1 Background and Past Group Work on Pd/SZ

As introduced before, there are mainly two methods for preparing Pd/SZ reported in the literature: two-step method and one-step method. Two-step method first prepares zirconium hydroxide and then sulfates the zirconium hydroxide, while in the one-step method sulfuric acid solution is added to the zirconium alkoxide precursors during the sol-gel formation. Pd/SZ prepared by the one step sol-gel method exhibits higher surface areas and homogeneity [52].

Our past group members prepared Pd/SZ by the incipient wetness impregnation (IWI) method and verified its high catalytic activity for NO\textsubscript{x} reduction with CH\textsubscript{4} under lean burn conditions, especially when it was mixed with an oxidation catalyst Co/ZrO\textsubscript{2}. They also started the research on sol-gel prepared Pd/SZ catalysts which showed even higher activity for NO\textsubscript{x} reduction. They found that when the Pd content was 0.3 wt% and the calcination temperature was 700°C, the catalysts exhibited the best performance. However, there are still other parameters which are supposed to affect catalytic activity of sol-gel prepared catalysts and need to be investigated. Therefore, in this work, more preparation parameters for sol-gel prepared Pd/SZ catalysts, as well as their physical characteristics and catalytic activities were intensively studied.
4.1.2 One Step Sol-Gel Preparation of Pd/SZ

Since small changes during the preparation of Pd/SZ would affect the number and the strength of acid sites so as to alter the catalytic properties [9], we focused on the effects of preparation parameters on the physical characteristics and catalytic performances of Pd/SZ catalysts. After optimizing Pd content and calcination temperature by our past group members, we changed the concentration of zirconium propoxide ([ZrPr]) and the ratio of zirconium-to-sulfur (Zr/S) to screen the highly active catalyst in this study.

Pd/SZ catalysts were prepared using a one step sol-gel method. The process of preparation is given below: Acetic acid was used as a controlled hydrolysis agent and n-propanol was used as a solvent. Pd acetate (purchased from Sigma-Aldrich, grade 98%) was first weighed to the desired final loading of 0.3 wt% Pd and then dissolved in n-propanol (purchased from Fisher Scientific) under constant stirring. 30 minutes later zirconium propoxide 70 wt% solution in n-propanol (purchased from Aldrich) and sulfuric acid (purchased from Fisher Scientific, assay 95.6%) precursors were added to the solution to achieve the desired final concentrations listed in Table 4.1. After stirring the solution for 5 minutes, acetic acid (purchased from Fisher Scientific, assay 100.2%) was added as the hydrolyzing agent by using a syringe pump at a hydrolysis ratio of 4. This solution was gently stirred, and the gelation time was recorded. The resultant gel was kept stirring for another 2 hours after its formation. Then the gel was dried in a drying oven overnight at 110°C. The obtained dry powder was ground and calcined at 700°C in air for 3 hours. After calcination the sample was
ground again and stored in a vial.

Table 4.1 listed the parameters of preparation of Pd/SZ catalysts. We named the sample in the form of Pd/SZ (X/Y), in which X is the molar concentration of zirconium propoxide ([ZrPr]) in the sol, and Y is the ratio of zirconium-to-sulfur (Zr/S). Thus, smaller X means lower zirconium concentration while smaller Y means higher sulfate loading.

<table>
<thead>
<tr>
<th>Sample</th>
<th>[ZrPr]</th>
<th>Zr/S</th>
<th>Hydrolysis ratio*</th>
<th>Gelation time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd/SZ 1.3/3</td>
<td>1.3</td>
<td>3</td>
<td>4</td>
<td>44</td>
</tr>
<tr>
<td>Pd/SZ 1.3/2</td>
<td>1.3</td>
<td>2</td>
<td>4</td>
<td>56</td>
</tr>
<tr>
<td>Pd/SZ 1/3</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>71</td>
</tr>
<tr>
<td>Pd/SZ 1/2</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>10</td>
</tr>
<tr>
<td>Pd/SZ 0.6/3</td>
<td>0.6</td>
<td>3</td>
<td>4</td>
<td>87</td>
</tr>
<tr>
<td>Pd/SZ 0.6/2</td>
<td>0.6</td>
<td>2</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>Pd/SZ 0.6/1</td>
<td>0.6</td>
<td>1</td>
<td>4</td>
<td>20</td>
</tr>
<tr>
<td>Pd/SZ 0.3/3</td>
<td>0.3</td>
<td>3</td>
<td>4</td>
<td>105</td>
</tr>
<tr>
<td>Pd/SZ 0.3/2</td>
<td>0.3</td>
<td>2</td>
<td>4</td>
<td>70</td>
</tr>
<tr>
<td>Pd/SZ 0.3/1</td>
<td>0.3</td>
<td>1</td>
<td>4</td>
<td>50</td>
</tr>
<tr>
<td>Pd/SZ 0.3/0.5</td>
<td>0.3</td>
<td>0.5</td>
<td>4</td>
<td>70</td>
</tr>
</tbody>
</table>

* Hydrolysis ratio = \( \frac{n_{\text{HAc}}}{n_{\text{ZrOPr}} \times 4} \)

Water content in the solution during the preparation plays a significant role for the texture, structure and catalytic activity of Pd/SZ catalysts. Zirconium propoxide \((\text{Zr(OPr)}_4)\) is very sensitive to water and it reacts with water quickly. This makes it difficult to control the hydrolysis of Zr(OPr)_4, so that few amount of sulfur is held at the surface resulting in decreased catalytic activity. In our study, acetic acid was used...
as controlled hydrolysis agent to reduce the amount of water in the sol so as to slow down the gelation and to obtain a better sulfur retention on the surface of the catalysts. During the preparation, acetic acid replaced –OPr group on Zr and generated *in-situ* the needed hydrolysis water, and both of these two reactions helped control the hydrolysis process [60, 61]. Main reactions in the preparation are given below:

\[
\begin{align*}
Zr(O\text{Pr})_4 + xCH_3\text{COOH} & \rightarrow Zr(O\text{Pr})_{4-x}(CH_3\text{COO})_x + x\text{Pr OH} \\
CH_3\text{COOH} + \text{Pr OH} & \rightarrow H_2O + CH_3\text{COO Pr} \\
Zr(O\text{Pr})_4 + xH_2O & \rightarrow Zr(O\text{Pr})_{4-x}(OH)_x + x\text{Pr OH} \\
Zr(O\text{Pr})_4 + Zr(O\text{Pr})_{4-x}(OH)_x & \rightarrow Zr_2(O\text{Pr})_{8-2x} + x\text{Pr OH}
\end{align*}
\]

4.2 Surface Area of Pd/SZ

BET surface areas of the prepared Pd/SZ catalysts are presented in Figure 4.1. The concentration of zirconium propoxide did not have obvious effects on surface areas of the catalysts; therefore, four graphs were drawn to correspond to four series of samples in which each series of samples was prepared with the same concentration of zirconium propoxide. A comment on notation is warranted here: the samples prepared with a concentration of zirconium propoxide of 1.3 mol/L were represented as 1.3/ and so on for other molarities. It was obvious that surface areas of series 1.3/, 1/, and 0.6/ increased with increased sulfate loading. For series 0.3/, surface areas increased with increased sulfate loading until the ratio of zirconium-to-sulfur, or sulfate ratio, was unity and then decreased with increased sulfate loading. This presence of a maximum of surface areas at sulfate ratio of unity may correspond to
monolayer coverage of sulfate on the surface. In addition, pyrosulfuric or higher pollysulfuric acids were reported to exist on the surface when sulfate loading was increased [62-64], and this may also be the reason why surface areas decrease at high sulfate loading. Surface areas of series 1.3/, 1/ and 0.6/ did not exhibit a maximum, which may be because the investigated sulfate loadings were not high enough to allow them to show the trend. Later in this study, similar to the discussion of sulfate loading and surface area above, sulfate loading was correlated with the variation of sulfur retention and crystalline structure of the samples as well.

Figure 4.1 Surface areas of Pd/SZ catalysts
4.3 Sulfate Retention on Pd/SZ

The concentrations of sulfate and zirconium in Pd/SZ catalysts were obtained from XPS, and sulfate retentions of Pd/SZ were calculated as:

\[
\text{S/Zr ratio from XPS} \times \frac{\text{theoretical S/Zr ratio}}{100}\%
\]

Figure 4.2 shows the sulfate retentions of samples with the same concentration of zirconium propoxide. The sulfate retentions of series 1.3/ and 1/ increased with increased sulfate loading in the investigated range respectively. For series 0.6/ and 0.3/, their sulfate retentions increased with increased sulfate loading first and then decreased, and both of their sulfate retentions reached maximums at sulfate ratio of 2. Sulfate retention is the sulfate content of the catalyst after calcinations during which parts of sulfate species are lost, therefore, it is understandable that sulfate retentions vary from nominal sulfate loadings. Figure 4.3 also indicates that sulfate retention of Pd/SZ after calcinations had a maximum and adding more sulfate acid did not help increase actual sulfate retention on the catalyst after a certain amount of sulfate loading. In addition, the differences between sulfate retentions and nominal sulfate loadings may because at that high sulfate loadings parts of sulfate species migrate into the bulk of the sample [65] where they were not measured.

Comparing the samples with different concentrations of zirconia propoxide, we found that zirconium propoxide concentrations did not affect sulfate retentions much. At the sulfate ratio of 3, sample 0.3/3, 0.6/3, 1/3 and 1.3/3 almost had the same sulfate retention (27%, 30%, 29%, and 28% respectively), while at sulfate ratio of 2, sulfate retentions of 0.3/2, 0.6/2, 1/2, and 1.3/2 were also very close (46%, 46%, 39%, 46%
Although both of surface areas and sulfate retentions of Pd/SZ samples showed maximums with increased sulfate loadings, they reached maximums at different sulfate loadings: surface areas arrived at maximum at sulfate ratio of 1, while sulfate retentions reached maximum at sulfate ratio of 2. Since sulfate retention is the final

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1 Courtesy of Dr. Burcu Mirkelamoglu.
sulfate content on the sample surface after calcinations, it may not impact the surface area of the sample in the same way as the initial sulfate loading, i.e. nominal sulfate loading, did. Most likely the nominal loading had much to do with the surface area and crystal structure of the sample during the process of the gel formation.

4.4 XRD of Pd/SZ

Crystalline structures of Pd/SZ catalysts were examined by XRD, and the XRD patterns of catalysts were shown in Figure 4.3, in which the samples with the same zirconium propoxide concentration were arranged in the same graph. Diffraction peaks at 30.2, 50.2, and 60.2° are assigned to be tetragonal zirconia phase, while the peaks at 24.2, 28.2, 31.5, 41.1, 54.1, and 55.6° are the characteristics of monoclinic zirconia [66]. Although many papers reported that sulfation helped stabilize the tetragonal phase and retard the transformation from the tetragonal to the monoclinic phase [48-51], both tetragonal and monoclinic zirconia phases were observed in our sol-gel prepared Pd/SZ catalysts. Since small changes in the preparation could significantly affect the properties of sulfated zirconia catalysts, we think the differences of the crystalline structures may result from some unnoticed experimental factors in different laboratories.

Additionally, in our study crystalline structures exhibited the same trend with the increased sulfate loading for each series of samples with the same zirconium propoxide concentration, and here we chose the series 0.3/ as an example to discuss the trend. At low sulfate loading such as Pd/SZ 0.3/3, tetragonal phase was the
dominant phase although monoclinic structure was also observed. As sulfate loading was increased, for example Pd/SZ 0.3/1 and 0.3/0.5, the intensities of monoclinic peaks increased and more peaks representing monoclinic phase appeared.
Figure 4.3 XRD patterns of Pd/SZ catalysts²

² Courtesy of Dr. Burcu Mirkelamoglu.
Figure 4.3 Continued
Figure 4.3 Continued

![Graph showing X-ray diffraction patterns with labels M and T.](image-url)
Figure 4.3 continued
4.5 Raman of Pd/SZ

Raman Spectra were also used to investigate the crystalline structures of prepared Pd/SZ catalysts. Figure 4.4 exhibits the Raman spectra of the samples with the same zirconium propoxide concentration. Sample spectra of monoclinic and tetragonal zirconia were given on the bottom of each graph in Figure 4.4. Comparing the spectra of Pd/SZ catalysts with those of monoclinic and tetragonal zirconia samples, we found that: consistent with XRD results, except for Pd/SZ 0.3/3, the prepared Pd/SZ catalysts contained both tetragonal and monoclinic phases. Similarly, for each series of catalysts with the same zirconium propoxide concentration, the tetragonal phase was the dominant structure at low sulfate loading while as the sulfate loading was increased the monoclinic phase became more obvious.
Figure 4.4 Laser Raman spectra of Pd/SZ catalysts
Figure 4.4 continued
Figure 4.4 continued
Figure 4.4 continued
4.6 Steady-State CH₄-SCR over Pd/SZ

The NOₓ reduction activities of Pd/SZ catalysts were carried out on the system introduced before (Chapter 3), and the reactions were performed based on an equal surface area of 13.4 m². The catalyst sample was loaded between two plugs of quartz wool in a 1/4” O.D. stainless steel reactor tube. Feed conditions used for the steady-state reaction studies in this part were 1000 ppm NO₂, 3000 ppm CH₄, and 10% O₂ in balance He. Total flow rate of feed gas was 45 cm³/min. Catalysts samples were pretreated at 400°C for 30 minutes in 10% O₂/He before the beginning of steady-state reactions. Reactant (NO₂, NOₓ, and CH₄) conversions were calculated as

\[
\text{Conversion} = \frac{\text{Inlet Concentration of } X - \text{Outlet Concentration of } X}{\text{Inlet Concentration of } X},
\]

while product (N₂, N₂O, and NO₂) yields were calculated as

\[
\text{Yield} = \frac{\text{Concentration of } N \text{ in Desired Product}}{\text{Inlet Concentration of } N}.
\]

Prepared Pd/SZ catalysts exhibited similar trends of reactant conversions and product yields across the examined temperature range. The steady-state reaction results of NO₂ reduction with CH₄ over Pd/SZ (1/2) were shown in Figure 4.5 as an example to illustrate the performance of Pd/SZ catalysts for NO₂ reduction with CH₄. As shown in Figure 4.5, yield of N₂ was observed to increase with reaction temperature up to a maximum, and then decreased. This is a typical trend in NOₓ reduction with hydrocarbon reducing agents under lean conditions, and this results from the consumption of the hydrocarbon due to its combustion in rich oxygen at high
temperatures. The yield of N\textsubscript{2} over Pd/SZ (1/2) reached a maximum of 77\% between 450 and 500\textdegree C, and then N\textsubscript{2} yield decreased due to the combustion of CH\textsubscript{4}. NO\textsubscript{x} conversion was very close to N\textsubscript{2} yield, although a small amount of N\textsubscript{2}O was produced. CH\textsubscript{4} conversion increased with temperature, showing a sharper light-off above 450\textdegree C which corresponded to N\textsubscript{2} yield maximum. Complete conversion of CH\textsubscript{4} was achieved above 550\textdegree C. NO\textsubscript{2} conversion also increased quickly with temperature and NO\textsubscript{2} was completely converted above 400\textdegree C, which revealed a significant side reaction: NO\textsubscript{2} was partially reduced to NO. NO yield increased first and then decreased and exhibited a trough when N\textsubscript{2} yield reached its maximum.
Figure 4.5 Steady-state reaction results from the reduction of NO$_2$ with CH$_4$ over Pd/SZ (1/2). Reaction conditions: 1000 ppm NO$_2$, 3000 ppm CH$_4$, and 10% O$_2$ in balance He, flow rate=45 cm$^3$/min, 200 mg Pd/SZ (1/2).
To compare catalytic activities of Pd/SZ catalysts, N₂ yields or CH₄ conversions were plotted on the same graph for the catalysts with the same zirconium propoxide concentration in Figure 4.6. The trends of both N₂ yields and CH₄ conversions of the samples could be explained as those of Pd/SZ (1/2) which were discussed above. Yields of N₂ over these eleven samples were observed to reach maximums between 450 and 550°C, which ranged from 50% to 80%, and then N₂ yields decreased. CH₄ conversions in each graph were similar except for those over Pd/SZ (1/2) and Pd/SZ (0.3/2). CH₄ conversions over these two samples were similar to the other samples at low temperatures, but were not observed to take off until above 450 and 500°C respectively. Lower CH₄ conversion at high reaction temperatures could explain the observed higher or shift maximums observed in the N₂ yields over the Pd/SZ (1/2) and Pd/SZ (0.3/2).

Figure 4.6 Steady-state reaction N₂ yields and CH₄ combustions from the reduction of NO₂ with CH₄ over Pd/SZ catalysts. Reaction conditions: 1000 ppm NO₂, 3000 ppm CH₄, and 10% O₂ in balance He, flow rate=45 cm³/min.
Figure 4.6 continued
A correlation of catalytic activity with sulfate retention was less satisfactory. Among the eleven samples, activities of Pd/SZ (0.3/1), Pd/SZ (1/2), and Pd/SZ (1.3/3) were obviously higher than others: their maximum N₂ yields were 77, 76 and 74%, respectively. We found that high activities did not relate to high sulfate retention, and thought that the relationship between catalytic activity and sulfate retention was not a simple one. Possibly the activity kept increasing after some sulfates had migrated into the bulk, since some of the sulfates which appeared in the underlying layer of the sample may contribute to the reduction of NOₓ by CH₄ as well [65]. Additionally, the nature of the sulfur species would probably be important for catalytic activity, rather than the sulfate content itself [54], therefore, the configurations of the sulfur species incorporated in the samples should be investigated in further study. Moreover, the catalytic activity of sulfated zirconia was generated by the interaction of sulfate groups with the metal palladium without changing the acidity [44], and the incorporation of metal palladium into SZ greatly increased its catalytic activity. Therefore, full coverage of the surface with sulfate species, which actually transformed the surface into zirconium sulfate, would destroy the catalytic activity [65].

4.7 DRIFTS- Temperature Programmed Desorption (TPD) of Pyridine of Pd/SZ

To study the acidic sites and their strength on the surface of Pd/SZ catalysts, Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used. Catalyst sample was loaded into an environmental chamber and pretreated at 400°C
in 10% O$_2$/He for 30 mins. Background spectra were taken every 50°C from 600°C to 50°C. Pyridine vapor was fed to adsorb on the sample surface at 50°C for 30 mins, and then the sample was flushed with He for another 30 mins. Desorption spectra were taken every 50°C from 50°C to 600°C.

Figure 4.7 Lewis and Bronsted acid structures in sulphated zirconia catalysts (cited from [67])

As introduced in Chapter 2, sulfur is incorporated into zirconia by exchanging OH groups of zirconium hydroxide with SO$_4^{2-}$ or HSO$_4^-$ anions [47]. The incorporation of sulfur into zirconia induces two kinds of acidic sites: Lewis site and Bronsted site, whose structures are given in Figure 4.7. Lewis site is the highly covalent configuration of the surface sulfates, and the catalytic activity of Pd/SZ catalysts is a maximum when the amount of strong Lewis acidity at the surface is maximum, while that of Bronsted acidity is a minimum [68]. Two kinds of probes
have been reported to determine the acid strength at solid surfaces: weak bases such as benzene or CO, they interact only with stronger acid sites; while strong bases such as acetonitrile, ammonia or pyridine also interact with weaker acid sites [69]. In this study, we used pyridine to probe the acid sites.

Figure 4.8 and Figure 4.9 exhibit the temperature programmed pyridine desorption spectra of Pd/SZ (0.3/1) catalyst. Since prepared Pd/SZ samples exhibited very similar trends as the temperature was increased, here we only gave the pyridine desorption spectra of Pd/SZ (0.3/1) as an example to discuss the spectra changes of Pd/SZ catalysts during the temperature program. Because we used the sample at the same temperature before the adsorption of pyridine as its background, the spectra collected showed interactions between base probe molecule pyridine and different acid (Lewis and Bronsted) sites. As shown in Figure 4.8, the broad band between 1340 and 1400 cm\(^{-1}\) is the characteristic vibration of S=O, and its exact position lies on the covalency of the double bond [47]. The band at 3648 cm\(^{-1}\) is S-OH vibration, together with S=O band they evidence the sulfation of zirconia. The band at 3741 cm\(^{-1}\) was assigned to the terminal OH on the zirconia surface. Moreover, pyridine-Lewis acid sites (Py-L) were indicated as vibrations at 1609, 1575, 1475 and 1444 cm\(^{-1}\), while pyridine-Bronsted acid sites (Py-B) were referred to the peak at 1632 cm\(^{-1}\). The peaks at 2334 and 2362 cm\(^{-1}\) are the characteristics of CO\(_2\). As seen in Figure 4.8, increasing the temperature from 300 to 600°C resulted in evolution of CO\(_2\), which was due to part of adsorbed pyridine was oxidized to CO\(_2\) at high temperature. In the low wave range of the spectra of Pd/SZ (0.3/1) Figure 4.9,
depletions of Py-L were observed when temperature was increased, while no obvious change of Py-B was present. This indicated that it was the covalently bound pyridine, i. e. Py-L, that was oxidized to form CO$_2$. In addition, with the increase of temperature the S=O band became less negative. When Pd/SZ catalyst was exposed to pyridine, its S=O bonds reduced and SO$_3$ were formed. The increase of S=O during pyridine desorption indicated that the initial loss of S=O did not solely result from the decomposition of sulfate, but at least partially resulted from an interaction of the sulfate species with the pyridine molecule which generated a change to the chemical bonding [70]. When pyridine was removed, S=O groups came back.
Figure 4.8 DRIFTS spectra of Pd/SZ (0.3/1)-full wave range

Figure 4.9 DRIFTS spectra of Pd/SZ (0.3/1)-low wave range
Figure 4.10 – Figure 4.13 exhibit the DRIFTS spectra of Pd/SZ catalysts with the same zirconia propoxide concentration taken at 50°C. As shown in the spectra of 0.3/ series Pd/SZ Figure 4.10, the spectra of Pd/SZ (0.3/1) is quite different from that of the others: Its S=O group has higher wave length; Moreover, it has more Py-L peaks and its Py-L sites are stronger, while its Py-B sites are much weaker. Therefore, based on the results of DRIFTS, the catalytic activity of Pd/SZ (0.3/1) was supposed to be much higher than those of the others in 0.3/ series catalysts. This was confirmed by the steady-state NO_x SCR results which were discussed in 4.6. Additionally, in the other three spectra Pd/SZ (0.3/3) is the one whose Py-L sites are stronger while the Py-B peak is weaker. This is also consistent with Pd/SZ (0.3/3) having the second highest activity in 0.3/ series catalysts. It is the same for series 0.6/, 1/, and 1.3/ (Figure4.11 – Figure 4.13) as well, the sample with more and stronger Py-L sites and weaker Py-B sites and higher wave length S=O group corresponds to higher catalytic activity.
Figure 4.10 DRIFTS spectra of Pd/SZ (0.3/ series) at 50°C

Figure 4.11 DRIFTS spectra of Pd/SZ (0.6/ series) at 50°C
Figure 4.12 DRIFTS spectra of Pd/SZ (1/) series at 50℃

Figure 4.13 DRIFTS spectra of Pd/SZ (1.3/) series at 50℃
4.8 Conclusions

A one step sol-gel method was used to prepare palladium based sulfated zirconia, and with changing the concentration of zirconium propoxide and sulfate loading, eleven samples were synthesized. For each series of samples with the same zirconia propoxide concentration, both surface areas and sulfate retentions increased with increased sulfate loading first and then decreased, although they reached maximums at different sulfate loadings. XRD and Raman results showed that the prepared Pd/SZ samples contain both tetragonal and monoclinic structures. Tetragonal phase was dominant at low sulfate loading while monoclinic phase increased with increased sulfate loading. Steady-state reaction tests did not show a clear correlation of catalytic activity with sulfate retention, but screened out that Pd/SZ (0.3/1), Pd/SZ (1/2), and Pd/SZ (1.3/3) were highly active NO\textsubscript{x} reduction catalysts whose N\textsubscript{2} yields were close to 80%. DRIFTS spectra confirmed the sulfation of zirconia catalysts and explained the catalytic activities of the prepared samples in terms of acidic sites and their strengths.
Chapter 5 Hydrothermal Stability of Palladium Based Sulfated Zirconia for NO\textsubscript{x} Reduction

As shown in the previous chapter, prepared Pd/SZ catalysts exhibited very high activity for NO\textsubscript{x} reduction with CH\textsubscript{4}. However, the exhaust stream from combustion engines usually contains a certain amount of water. Therefore, industrial NO\textsubscript{x} reduction catalysts must remain stable at high temperature with water vapor at the operating conditions. In this study, to prove the potentials of sol-gel prepared Pd/SZ catalysts for practical applications, a series of experiments aiming to test their hydrothermal stability were performed.

5.1 Influence of Methane Combustion to the Stability of Pd/SZ

NO\textsubscript{x} SCR switch during NO\textsubscript{x} oxidation and CH\textsubscript{4} combustion over Pd/SZ catalyst was carried out with NO\textsubscript{x} reaction system. Pd/SZ (1/2) was used as a probe to test the influence of CH\textsubscript{4} combustion on Pd/SZ catalysts, and the same equal surface area of 13.4 m\textsuperscript{2} as that used for steady-state NO\textsubscript{x} SCR tests was adopted. The catalyst sample was pretreated at 400°C for 30 minutes in 10\% O\textsubscript{2}/He before the switch experiments. Total flow rate of feed gas was 45 cm\textsuperscript{3}/min. Feed conditions were 1000 ppm NO\textsubscript{2}/NO and 10\% O\textsubscript{2} in balance He, 1000 ppm NO\textsubscript{2}/NO and 3000 ppm CH\textsubscript{4} and 10\% O\textsubscript{2} in balance He, 3000 ppm CH\textsubscript{4} and 10\% O\textsubscript{2} in balance He, 1000 ppm NO\textsubscript{2}/NO and 3000 ppm CH\textsubscript{4} and 10\% O\textsubscript{2} in balance He in sequence. The switch experiments were performed at 400°C.
Figure 5.1 gives the results of NO$_2$-SCR switch during NO$_2$ oxidation and CH$_4$ combustion over Pd/SZ (1/2). During the first stage in which only NO$_2$ and O$_2$ were fed, around 44% of NO$_2$ was converted, but the total nitrogen oxides, the sum of NO and NO$_2$, were not reduced much. Experiment data showed that NO$_2$ was partially reduced to NO but not N$_2$ (which are not given here) during this stage. During the second stage when NO$_2$ SCR happened, almost all NO$_2$ was reduced over the Pd/SZ catalyst while NO$_x$ conversion is about 80%. The difference between NO$_2$ and NO$_x$ conversions mainly resulted from NO$_2$ partial reduction. During the third stage, CH$_4$ combustion, no NO$_2$ and NO$_x$ reduction happened. When the feed was switched to the last stage NO$_2$ SCR again, NO$_2$ was still almost totally converted, however, only 60% NO$_x$ conversion was achieved which is a 20% decrease compared to the NO$_2$ SCR before CH$_4$ combustion. The unrecoverable catalytic activity in NO$_x$ reduction indicated that CH$_4$ combustion possibly permanently deactivated the Pd/SZ catalyst. Figure 5.1.2 shows the same unrecoverable reduced catalytic activity in NO SCR switch during NO oxidation and CH$_4$ combustion. The differences of Figure 5.2 from Figure 5.1 are NO was oxidized to NO$_2$ during the first stage and no partial reduction of NO$_2$ during the SCR stages.

Resasco et al. also observed the similar phenomena of decreased activity of NO$_x$ reduction catalysts. They pointed out that Pd$^{2+}$ is selective for NO$_x$-SCR, while PdO is active for CH$_4$ combustion. Parts of the Pd$^{2+}$ ions which are stable under CH$_4$ + NO + O$_2$ might be converted to PdO under the CH$_4$ + O$_2$ condition [24].
Figure 5.1 NO$_2$-SCR switch during NO$_2$ oxidation and CH$_4$ combustion over Pd/SZ (1/2). Conditions: 0/1000 ppm NO$_2$, 0/3000 ppm CH$_4$, 10% O$_2$, He balance, total flow rate=45 cm$^3$/min, 400°C and 200mg Pd/SZ (1/2).
Figure 5.2 NO-SCR switch during NO oxidation and CH$_4$ combustion over Pd/SZ (1/2). Conditions: 0/1000 ppm NO, 0/3000 ppm CH$_4$, 10% O$_2$, He balance, total flow rate=45 cm$^3$/min, 400°C and 200mg Pd/SZ (1/2)
5.2 Effect of Water Vapor on NO\textsubscript{x} Reduction over Pd/SZ

Besides NO\textsubscript{x} species and unburned hydrocarbons, exhaust streams from natural gas reciprocating engines contain a significant amount of water vapor (2-15\%) [71]. The water vapor mainly comes from two sources: atmospheric water and the combustion products of hydrocarbons. Although the actual level of H\textsubscript{2}O in an exhaust gas depends on several factors and would vary significantly, a level of 6 vol\% H\textsubscript{2}O which was adopted in this study is appropriate to simulate the water content in realistic operating conditions.

5.2.1 NO Oxidation with H\textsubscript{2}O Switch Away from NO-NO\textsubscript{2} Equilibrium

NO oxidation with H\textsubscript{2}O switch experiment was performed on the NO\textsubscript{x} system. 25 mg 10\% Co/ZrO\textsubscript{2}, which proved to be the most active for NO oxidation by our past group members, was used as the oxidation catalyst in this experiment. The catalyst was pretreated at 400\( ^\circ \)C for 30 minutes in 10\% O\textsubscript{2}/He. The feed conditions for reaction were: 1000 ppm NO, 10\% O\textsubscript{2}, 0/6\% H\textsubscript{2}O in balance He. Total flow rate was 45 cm\textsuperscript{3}/min and the experiment was carried out at 400\( ^\circ \)C.
Figure 5.3 NO oxidation with H$_2$O switch over Co/ZrO$_2$ catalyst. Conditions: 1000 ppm NO, 10% O$_2$, 0/6 % H$_2$O, He balance, total flow rate=45 cm$^3$/min, 400°C and 25 mg 10% Co/ZrO$_2$. 
Figure 5.3 gives the results of NO oxidation with H₂O switch over Co/ZrO₂ catalyst. Under the dry feed conditions NO conversion was around 48% which was slightly below the equilibrium value under the same conditions calculated by our past group members (refer to Appendix B). This indicated that the reaction under these conditions was controlled by kinetics. Additionally, as shown in Figure 5.3, NO conversion under the wet feed conditions was almost the same as that when the feed was dry, demonstrating that the oxidation catalyst Co/ZrO₂ has high resistance against water vapor. NOx conversion was close to zero, meaning NO was oxidized to NO₂ and no other products were formed.

5.2.2 Wet/Dry Feed Switch Experiments

To study the effects of water vapor on reduction catalyst and mixed bed catalyst for NO and NO₂ reduction, we performed wet/dry feed switch experiments on NO reduction with CH₄ over Pd/SZ, NO₂ reduction with CH₄ over Pd/SZ, and NO reduction with CH₄ over Pd/SZ-Co/ZrO₂ mixed bed, respectively.

Wet/Dry feed switch experiments were performed on the NOₓ system. 200 mg Pd/SZ (1/2) or 200 mg Pd/SZ (1/2) mixed with 25mg Co/ZrO₂ was used as the catalyst and was pretreated at 400°C for 30 minutes in 10% O₂/He. The feed conditions for reaction were: 1000 ppm NO/NO₂, 3000 ppm CH₄, 10% O₂, 0/6% H₂O in balance He. Total flow rates were 45 cm³/min and the reaction temperatures were 500°C.
5.2.2.1 NO Reduction with CH\(_4\) over Pd/SZ

Figure 5.4 shows the results of wet/dry feed switch during NO reduction with CH\(_4\) over Pd/SZ (1/2). NO conversion and NO\(_x\) conversion overlapped, and both were 82\% under dry feed condition and decreased to 50\% when water vapor was introduced. This trend remained the same during the three cyclic performances. The decrease of NO conversion under wet feed condition indicated that H\(_2\)O deactivated the Pd/SZ catalyst for NO reduction (Scheme 5.1), however, the catalytic activity was recoverable when the feed was switched to dry gas, which meant the active sites for NO reduction were not permanently deactivated. Competitive adsorption of NO, CH\(_4\) and H\(_2\)O on the active sites which was reversible [3] was considered to result in the decrease and recoverability of the catalytic activity on NO reduction.

\[
\text{NO} \quad \xleftrightarrow{\text{H}_2\text{O}} \quad \text{N}_2
\]

Scheme 5.1 Effect of water vapor on NO reduction with CH\(_4\) over Pd/SZ catalyst

Note: ↓ means water vapor deactivated the NO reduction to N\(_2\).
Figure 5.4 Wet/Dry feed switch during NO reduction with CH\textsubscript{4} over Pd/SZ (1/2).

Conditions: 1000 ppm NO, 3000 ppm CH\textsubscript{4}, 10% O\textsubscript{2}, 0/6% H\textsubscript{2}O, balance He, total flow rate 45 cm\textsuperscript{3}/min, 500°C and 200 mg Pd/SZ (1/2).
5.2.2.2 NO\textsubscript{2} reduction with CH\textsubscript{4} over Pd/SZ

Figure 5.5 gives the results of wet/dry feed switch during NO\textsubscript{2} reduction with CH\textsubscript{4} over Pd/SZ (1/2). NO\textsubscript{2} conversion was almost 100\%, indicating that water vapor played no roles on NO\textsubscript{2} reduction over Pd/SZ catalyst. NO\textsubscript{x} conversion was lower than NO\textsubscript{2} conversion and it decreased from 83\% to 64\% when water vapor was introduced to the feed. This resulted from the fact that NO\textsubscript{2} was partially reduced to NO and NO reduction over Pd/SZ was depressed when the feed was switched to wet gas, which was elucidated in Scheme 5.2. The same as Figure 5.2, the decrease in NO\textsubscript{x} reduction over Pd/SZ catalyst was recoverable, which was due to the reversible competitive adsorption of NO, CH\textsubscript{4} and H\textsubscript{2}O on the active sites for NO reduction, but rather permanent deactivation of active NO reduction sites. Additionally, a comparison of NO\textsubscript{x} conversions in Figure 5.4 and 5.5 indicated that NO\textsubscript{2} is easier to reduce than NO over Pd/SZ reduction catalyst.

![Scheme 5.2 Effect of water vapor on NO\textsubscript{2} reduction with CH\textsubscript{4} over Pd/SZ catalyst](image)

Note: ↓ means water vapor deactivated the NO reduction to N\textsubscript{2}.
Figure 5.5 Wet/Dry feed switch during NO₂ reduction with CH₄ over Pd/SZ (1/2).

Conditions: 1000 ppm NO₂, 3000 ppm CH₄, 10% O₂, 0/6% H₂O, balance He, total flow rate 45 cm³/min, 500 °C and 200 mg Pd/SZ (1/2).
5.2.2.3 NO Reduction with CH$_4$ over Pd/SZ-Co/ZrO$_2$ Mixed Bed

The results of wet/dry feed switch during NO reduction with CH$_4$ over mixed bed catalyst were given in Figure 5.6. Decrease and recoverability of NO and NO$_x$ reduction during the switch of water vapor were also observed in Figure 5.6. Since water vapor does not affect the oxidation catalyst Co/ZrO$_2$ which was discussed in 5.2.1, the recoverable activity loss resulted from reversible competitive adsorption of NO, CH$_4$ and H$_2$O on the active sites of Pd/SZ reduction catalyst. Compared to Figure 5.4 and 5.5, NO conversion (dry 97%, wet 88%) and NO$_x$ conversion (dry 94%, wet 71%) during NO reduction over mixed bed were much higher than NO/NO$_x$ conversion (dry 82%, wet 50%) during NO reduction over only reduction catalyst and NO$_x$ conversion (dry 83%, wet 64%) during NO$_2$ reduction over only reduction catalyst. The explanation is: During the NO$_2$ reduction over reduction catalyst, a certain amount of NO$_2$ was partially reduced to NO which is harder to reduce to N$_2$ than NO$_2$. When oxidation catalyst was added, some NO which resulted from the partial reduction of NO$_2$ was oxidized back to NO$_2$. The re-oxidation of NO increased the chances for NO$_2$ reduction to N$_2$ so that increased NO$_x$ conversion. Scheme 5.3 exhibits the reactions in the wet/dry feed switch during NO reduction with CH$_4$ over mixed bed experiment.

![Scheme 5.3 Effect of water vapor on NO reduction with CH$_4$ over mixed bed](image)

Note: ↓ means water vapor deactivated the NO reduction to N$_2$. 

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Figure 5.6 Wet/Dry feed switch during NO reduction with CH$_4$ over mixed bed catalyst. Conditions: 1000 ppm NO, 3000 ppm CH$_4$, 10% O$_2$, 0/6% H$_2$O, balance He, total flow rate 45 cm$^3$/min, 500°C and 200 mg Pd/SZ (1/2) mixed with 25 mg Co/ZrO$_2$. 
5.2.3 Effect of the Amount of Co/ZrO₂ on Water Resistance of the Mixed Bed

As discussed above, the re-oxidation of NO by Co/ZrO₂ increased NOₓ conversion over the mixed bed. Therefore, will more Co/ZrO₂ promote NO re-oxidation and consequently increase NOₓ conversion and N₂ yield in the presence of H₂O? To answer the question, NO reductions with CH₄ over mixed bed with different amounts of Co/ZrO₂ while the amount of Pd/SZ was kept constant were carried out in the absence or presence of water vapor.

Figure 5.7-5.9 exhibit the results of NO reduction with CH₄ over mixed bed in the absence of H₂O, NO reduction with CH₄ over mixed bed in the presence of H₂O, and NO reduction with CH₄ over mixed bed with increased amount of Co/ZrO₂ in the presence of H₂O, respectively. As shown in Figure 5.7, an extremely high N₂ yield of 90% and a wide temperature window of maximum activity were observed, indicating the promising potential of mixed bed catalyst for NOₓ reduction. A comparison of Figure 5.7 and 5.8 showed that in the presence of H₂O, N₂ yield was decreased from 90% to 78% and the temperature window of maximum activity was narrowed. Moreover, the conversion of CH₄ was depressed as well. As discussed above, this resulted from the competitive adsorption of NO, H₂O and CH₄ on the Pd/SZ reduction catalyst. Compared to Figure 5.8, the experiment in Figure 5.9 increased Co/ZrO₂ from 25mg to 50 mg with all other conditions the same. As shown in Figure 5.9, although the amount of Co/ZrO₂ was increased, N₂ yield (67%) was about 11% less than that with less Co/ZrO₂. After increasing the amount of oxidation catalyst, more N₂O oxidized from NO was produced whereas total NOₓ conversion decreased.
Therefore, based on N balance, $N_2$ yield decreased. On the other hand, NO$_2$ was observed during the whole investigated temperature range even for the smaller amount of oxidation catalyst (Figure 5.8), indicating that NO oxidation over the small amount of Co/ZrO$_2$ was faster than the NO$_2$ reduction over Pd/SZ catalyst. Therefore, $N_2$ yield in this system was not limited by NO oxidation, and 25 mg Co/ZrO$_2$ was sufficiently to be mixed with 200 mg Pd/SZ for NO reduction with CH$_4$. 
Figure 5.7 Steady-state reaction results from the reduction of NO with CH₄ over mixed bed (200 mg Pd/SZ (1/2), 25 mg Co/ZrO₂). Reaction conditions: 1000 ppm NO, 3000 ppm CH₄, and 10% O₂ in balance He, flow rate=45 cm³/min.
Figure 5.8 Steady-state reaction results from the reduction of NO with CH$_4$ over mixed bed (200 mg Pd/SZ (1/2) and 25 mg Co/ZrO$_2$) in the presence of H$_2$O.

Reaction conditions: 1000 ppm NO, 3000 ppm CH$_4$, 6% H$_2$O, and 10% O$_2$ in balance He, flow rate=45 cm$^3$/min.
Figure 5.9 Steady-state reaction results from the reduction of NO with CH₄ over mixed bed (200 mg Pd/SZ (1/2) and 50 mg Co/ZrO₂) in the presence of H₂O.

Reaction conditions: 1000 ppm NO, 3000 ppm CH₄, 6% H₂O, and 10% O₂ in balance He, flow rate = 45 cm³/min.
5.3 Stability of the Mixed Bed System for NO reduction in the Absence or Presence of Water Vapor

Many current active NO\textsubscript{x} reduction catalysts such as zeolite-based catalysts which were introduced in Chapter 2 deactivate quickly when exposed to actual combustion exhaust which is wet and at high temperature. Therefore, long-term stability of NO\textsubscript{x} reduction catalyst is a significant index for its practical applications. To test the durability of our mixed bed, time on stream of NO reduction with CH\textsubscript{4} over mixed bed and NO reduction with simulated exhaust stream over mixed bed were carried out respectively.

5.3.1 Stability of Mixed Bed for NO Reduction with CH\textsubscript{4}

Time on stream experiments of NO reduction with CH\textsubscript{4} over mixed bed were performed at 500 °C in absence and presence of H\textsubscript{2}O respectively, and Figure 5.10-5.11 show their results. Under dry conditions, NO\textsubscript{x} conversion and N\textsubscript{2} yield were stable and very high during the investigated 33 hours. Although the catalytic activity of mixed bed under wet conditions decreased around 15% compared to that under dry conditions, the losses of NO\textsubscript{x} conversion and N\textsubscript{2} yield as time during the investigated period were very small. NO\textsubscript{x} conversion and N\textsubscript{2} yield were still as high as 71% and 63% respectively 33 hours after the beginning of the experiment. The fluctuations came from the effects of water vapor on the NO\textsubscript{x} analyzer but the actual activity does not vary.
Figure 5.10 Stability of mixed bed for NO reduction with CH₄ in the absence of H₂O.

Conditions: 1000 ppm NO, 3000 ppm CH₄, 10% O₂, in balance He, total flow rate = 45 cm³/min, 500 °C, 200mg Pd/SZ and 25mg Co/ZrO₂
Figure 5.11 Stability of mixed bed for NO reduction with CH₄ in the presence of H₂O.

Conditions: 1000 ppm NO, 3000 ppm CH₄, 10% O₂, 6% H₂O, in balance He, total flow rate = 45 cm³/min, 500 ºC, 200mg Pd/SZ and 25mg Co/ZrO₂
5.3.2 Stability of the Mixed Bed System for NO Reduction with Simulated Exhaust Stream

In addition to NO\textsubscript{x}, CH\textsubscript{4} and O\textsubscript{2}, actual lean-burn natural gas engine exhausts contain many other species, such as C\textsubscript{2}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{8}, CO, CO\textsubscript{2} and H\textsubscript{2}O, and the exhaust composition varies remarkably based on the actual operation conditions of the engine. Under typical operation conditions of current engines, NO concentration in the exhaust varies between 90-900 ppm and unburned hydrocarbons (mainly CH\textsubscript{4}, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8}) are present between 1500-2500 ppm [3]. In this study, we use 400 ppm NO, 1700 ppm CH\textsubscript{4}, 200 ppm C\textsubscript{2}H\textsubscript{6}, 100 ppm C\textsubscript{3}H\textsubscript{8}, 600 ppm CO, 6% CO\textsubscript{2} and 10% O\textsubscript{2}, 6% H\textsubscript{2}O, in balance He to simulate exhaust condition which is in the realm of actual lean-burn natural gas engine exhaust compositions.

Figure 5.12 exhibits the results of time on stream of NO reduction with dry simulated exhaust over mixed bed. N\textsubscript{2} yield was as high as 85% at the first couple of hours. Although it decreased a little as time went on, N\textsubscript{2} yield was still high (64%) 50 hours after the beginning of the experiment. Additionally, as shown in Figure 5.12, CO, C\textsubscript{2}H\textsubscript{6}, and C\textsubscript{3}H\textsubscript{8} were completely oxidized in dry simulated exhaust steam.
Figure 5.12 Stability of mixed bed for NO reduction with simulated exhaust stream in the absence of H₂O. Conditions: 400 ppm NO, 1700 ppm CH₄, 200 ppm C₂H₆, 100 ppm C₃H₈, 600 ppm CO, 6% CO₂, 10% O₂, in balance He, total flow rate = 45 cm³/min, 500°C, 200 mg Pd/SZ, 25 mg Co/ZrO₂, and 175 mg quartz powder.
Figure 5.13 Stability of mixed bed for NO reduction with simulated exhaust stream in the presence of H₂O. Conditions: 400 ppm NO, 1700 ppm CH₄, 200 ppm C₂H₆, 100 ppm C₃H₈, 600 ppm CO, 6% CO₂, 10% O₂, 6% H₂O, in balance He, total flow rate = 45 cm³/min, 500°C, 200 mg Pd/SZ, 25 mg Co/ZrO₂, and 175 mg quartz powder.
Figure 5.13 shows the results of time on stream of NO reduction over mixed with simulated exhaust in the presence of H₂O. Compared to the NO reduction with dry stimulate exhaust feed, NOₓ reduction and N₂ yield under wet simulate exhaust conditions decreased approximately 10% and 20% respectively. However, they reached a stable level several hours later and NOₓ reduction and N₂ yield still achieved 58% and 47% respectively 50 hours. As mentioned before, the fluctuations came from the effects of water vapor on NOₓ analyzer but the actual activity does not vary. Another point to be emphasized is that CO, C₂H₆, and C₃H₈ were completely oxidized even under wet simulated exhaust conditions. Since CO, C₂H₆, and C₃H₈ which are harmful gases present in lean-burn engine exhausts, their complete conversions greatly help reduce exhaust pollution. Additionally, using unburned hydrocarbons as reducing agents has significant benefits, such as no fuel penalty and simplifying engine design, compared to injecting a new reducing agent to the exhaust stream.

5.4 Conclusions

Hydrothermal stability of Pd/SZ and mixed bed catalyst were intensively studied in this chapter. The unrecoverable catalytic activity of Pd/SZ after CH₄ combustion indicates it permanently deactivated the active sites for NOₓ reduction. Water vapor did not effect NO oxidation much, indicating that the oxidation catalyst Co/ZrO₂ has high resistance to water vapor. Recoverable catalytic activity was observed during wet/dry feed switch in NOₓ reductions, and this resulted from reversible competitive
adsorption of NO, CH₄, and H₂O on Pd/SZ catalyst without permanent loss of active sites on the catalytic surface. With the addition of oxidation catalyst, re-oxidation of NO was promoted which increased N₂ yield over the mixed bed. However, in the investigated range more oxidation catalyst did not result in higher N₂ yield. At last, mixed bed catalyst exhibited high stability for NO reduction with both CH₄ and simulated exhaust stream. Meanwhile, mixed bed completely converted CO, C₂H₆, and C₃H₈ present in the exhaust steam, which could decrease both exhaust pollutions and fuel penalty and as well as simplify engine design.
Chapter 6 Conclusions and Recommendations

6.1 Conclusions

Reduction of NO\textsubscript{x} emissions has attracted more and more attention due to their environmental and health hazards. The most significant barrier in NO\textsubscript{x} reduction with hydrocarbons is the competitive combustion of hydrocarbons under lean burn conditions. A dual-catalyst system (mixed bed) containing both reduction catalyst and oxidation catalyst was proposed to solve this barrier. In this system NO is first oxidized to NO\textsubscript{2} which is more easily reduced, and then NO\textsubscript{2} is reduced to N\textsubscript{2}. The oxidation catalyst has been intensively investigated by our past group members, and this study focused on the reduction catalyst Pd/SZ prepared by the one step sol-gel method.

Parameters of the preparation have significant effects on the activity of sol-gel prepared catalysts, and in this study the roles of the concentration of zirconium propoxide and the ratio of zirconium-to-sulfur on the catalytic activity of Pd/SZ were investigated. The catalysts with the same zirconium propoxide concentration exhibited maximum surface area at a zirconium-to-sulfur ratio of 1, while the sulfate retention reached a maximum at a zirconium-to-sulfur ratio of 2. Both monoclinic and tetragonal phases were observed in prepared Pd/SZ catalysts. Tetragonal structures were dominant at low sulfate loadings and monoclinic structures increased with increased sulfate loadings. No obvious relationship between catalytic activity and
sulfate retention was observed. However, highly active reduction catalysts were screened out, and over 80% N₂ yield was achieved. DRIFTS spectra exhibited acidic sites and their strength on Pd/SZ samples, and they were consistent with the activities of prepared Pd/SZ catalysts.

Thermal and hydrothermal stabilities of Pd/SZ were studied to test their potentials for practical applications. The unrecoverable activity loss of Pd/SZ for NOₓ reduction showed that CH₄ combustion possibly deactivated Pd/SZ catalyst permanently. Oxidation catalyst in the mixed bed promoted the re-oxidation of NO so as to provide more opportunities for N₂O reduction and increase N₂ yield to more than 90%. Water vapor did not deactivate the oxidation catalyst Co/ZrO₂, and a small amount of Co/ZrO₂ in the mixed bed was enough to re-oxidize NO. The reduction catalyst Pd/SZ deactivated in the presence of H₂O. However, the catalytic activity was recoverable after H₂O was removed, indicating the activity loss resulted from reversible competitive adsorption of NO, H₂O and CH₄ on active sites of Pd/SZ. The mixed bed containing both reduction catalyst Pd/SZ and oxidation catalyst Co/ZrO₂ proved to have high durability for NOₓ reduction with both test stream and simulated exhaust stream.

6.2 Recommendations

While sol-gel prepared Pd/SZ catalyst as a component of mixed bed has exhibited high activity for NOₓ reduction and its thermal and hydrothermal stability have been tested, its resistance to SO₂, another component present in actual engine
exhausts which could seriously poison NO$_x$ reduction catalyst, should be investigated. Future work should focus on the resistance of Pd/SZ catalyst to SO$_2$ and continue to increase their water resistance and long term stability as well.
References


Appendix A

List of Acronyms

NOx  —  Nitrogen Oxides
SCR  —  Selective Catalytic Reduction
SZ  —  Sulfated Zirconia
Pd/SZ  —  Palladium Based Sulfated Zirconia
TWC  —  Three Way Catalyst
IWI  —  Incipient Wetness Impregnation
SG  —  Sol-Gel
GC  —  Gas Chromatograph
XPS  —  X-ray Photoelectron Spectroscopy
XRD  —  X-ray Diffraction
DRIFTS  —  Diffuse Reflectance Infrared Fourier Transform Spectroscopy
TPD  —  Temperature Programmed Desorption
Appendix B

Equilibrium Curve for NO Oxidation to NO₂

NO oxidation to NO₂ Equilibrium Curve.

Conditions: 1000 ppm NO, 10% O₂ in balance He.

Oxidation reaction: \( NO + \frac{1}{2} O₂ \leftrightarrow NO₂ \)

It is obvious that the NO/NO₂ equilibrium greatly depends on temperature: at lower temperature NO₂ is thermodynamically favored, while at high temperature NO is preferred.
Appendix C

Sample Calculations

Concentrations of NO and NO₂ were directly read from the NOₓ analyzer.

Concentrations of N₂, O₂, CH₄, CO₂, CO, N₂O, C₂H₆, and C₃H₈ were analyzed by the gas chromatograph (GC). Gas concentrations were determined as:

\[
\text{Concentration} = (\text{GC Peak Area of Species X}) \times (\text{GC Response Factor of Species X})
\]

In which:

\[
\text{GC Response Factor of Species X} = \frac{\text{Known Concentration of X}}{\text{GC Peak Area of X}}
\]

Conversion of reagent (NO, NO₂, NOₓ, or CH₄) was calculated as:

\[
\text{Conversion} = \frac{\text{Inlet Concentration of X} - \text{Outlet Concentration of X}}{\text{Inlet Concentration of X}}
\]

Yield of N₂, N₂O, and NO₂ was calculated based on nitrogen atom as:

\[
\text{Yield} = \frac{\text{Concentration of N in Desired Product}}{\text{Inlet Concentration of N}}
\]