Nitric Oxide Decomposition over Cu Exchanged Zeolites and 

Cu/CeO$_2$

by

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Abstract

Nitrogen oxides (NO$_x$), which include nitrous oxide (N$_2$O), nitric oxide (NO) and nitrogen dioxide (NO$_2$), are some of the most dangerous exhaust gases emitted from automobile engines and industries. NO$_x$ is responsible for acid rain, photochemical smog and harmful effects on human health. The large binding energy of the N–O bond impedes the abatement of NO$_x$ exhaust to occur at low temperature. Efficient catalysts for the mitigation of NO$_x$ are pressingly needed for meeting future emission standards.

Copper-substituted zeolites have been investigated extensively for NO decomposition due to their excellent activity and stabilities. Direct decomposition of NO to N$_2$ and O$_2$ is a robust strategy for NO$_x$ removal. Interestingly, the activity of NO decomposition on Cu-exchanged catalysts exhibit “volcano-type” dependence on temperature, which is different from common reaction behavior. A new adsorption model is hence required to explain this behavior.

In the present thesis, the adsorption compression theory and the Ono-Kondo coordinate was implemented in experiments to examine the interactions between neighboring molecules adsorbed on proximal active sites. The average Cu–Cu distance in Cu-exchanged zeolites, compression energy and catalytic activities were comprehensively studied to elucidate the influence of distances of proximal active sites on Cu based catalysts for NO$_x$ decomposition. It was observed that compression energy is inversely proportional to the Cu–Cu distance of different Cu-zeolites. At low temperatures (less than 400 °C), compression effect can facilitate catalytic NO decomposition by adding an extra potential energy for the reactants to overcome energy
barrier. Meanwhile, at high temperatures (greater than 400 °C), such effect leads to low coverage of adsorbed NO molecules, which results in decrease in catalytic activities.

Inspired by the study on adsorption compression effect of Cu dimers in Cu-exchanged zeolites, a robust Cu/CeO$_2$ catalyst has been developed to achieve efficient abatement of NO$_x$ at low temperatures. For the first time, catalytic direct NO decomposition at room temperature has been observed. Other conditions for NO decomposition such as NO+CO reaction have also been tested with excellent performance. This Cu/CeO$_2$ catalyst represents a promising material for low-temperature NO mitigation.

Committee: Dr. Chao Wang (Advisor)

Dr. Marc Donohue
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Chapter 1. Introduction

1.1 Motivation

Thanks to rapid social and economic development, the demands for energy, transportation and industrial products are escalating worldwide. Meanwhile, significant attention is paid to the subject of environmental protection. The abatement of toxic air pollutants, including carbon monoxide (CO), volatile organic compounds (VOCs), nitrogen oxides (NOx) and so on, plays a key role in achieving future environmental sustainability.1-3

NOx, which include nitrous oxide (N2O), nitric oxide (NO) and nitrogen dioxide (NO2), are some of the most dangerous exhaust gases emitted from automobile engines and industries. During the combustion of fossil fuel at high temperature, nitrogen reacts with oxygen atoms to create nitric oxide (NO), which can further combine with oxygen to create nitrogen dioxide (NO2). On the other hand, nitrous oxide (N2O) is mainly release from the production of adipic acid and nitric acid. As illustrated in Fig. 1, based on the statistics of United States Environmental Protection Agency (EPA), more than 10 million tons of NOx pollutants were emitted by the US in the year of 2016.4 The large amount of NOx emission gave rise to a series of environmental issues. In the presence of sunlight, NOx is a main constituent in the formation of ground-level ozone and smog, which is detrimental to the human respiration system. The chemistry of this process can be described as: 5

\[ \text{NO}_2 + \text{hv} (\lambda < 415 \text{ nm}) \rightarrow \text{NO} + \text{O} \]  \hspace{1cm} (1)  

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]  \hspace{1cm} (2)
Moreover, NO and NO\textsubscript{2} are responsible for the formation of acid rain, which can cause severe damage to waterways, forests and buildings, they are also predominant sources of fine particulate matter (PM), which causes harmful effects on the respiratory system.\textsuperscript{6} In addition, N\textsubscript{2}O has a global warming potential (GWP) of 310, meaning it is 310 times more effective in trapping heat than CO\textsubscript{2}. Furthermore, N\textsubscript{2}O is also considered as one of the major stratospheric ozone-depleting substances.\textsuperscript{7}

![Estimated Total NOx Emissions by US\textsuperscript{4}]

**Figure 1.** Estimated total amount of NO\textsubscript{x} emissions by the US in the year from 2010 to 2016.\textsuperscript{4}

Automobiles and fuel combustion industries are known as the typical mobile and stationary sources of NO\textsubscript{x}, respectively. Fig. 2 shows the contribution from various sources to the total emissions of NO\textsubscript{x} in the U.S. in 2016.\textsuperscript{4} From which we can easily distinguish that the combination of highway vehicles and fuel combustion industries are responsible for more than 50% of the total NO\textsubscript{x} emissions while highway vehicles produce 35% of the total. At stationary sources, NO\textsubscript{x} reduction approaches employing different reducing agents such as ammonia, urea and hydrocarbons have been well-
established. The conversions are usually high due to the utilization of efficient chemical redox reactions. Previous research works indicated many types of catalysts were able to achieve > 90% conversion for NO at low temperatures through selective catalytic reduction (SCR) pathway. For instance, it is reported that NH\textsubscript{3}-SCR over Cu-SSZ-13 catalysts can reach 90% conversion of NO at temperatures higher than 200 °C.\textsuperscript{8} Recently, Liu et al. designed a novel Mn-Ce-Ti mixed-oxide catalysts which is capable of achieving 90% conversion at 150 °C.\textsuperscript{9} At stationary sources, it is also much easier for SCR reactions to reach steady state since the conditions are under strict monitoring and controls. The details regarding SCR reactions is demonstrated in the next section. On the contrast, abatement of NO\textsubscript{x} from automobiles emission is much more challenging since the reaction conditions (e.g. temperature, flow rate and composition of the exhaust gas) were constantly changing.\textsuperscript{10} In addition, as more efficient combustion engines are being designed for transportation to minimize the amount of heat wasted in the exhaust gas, the temperature for NO\textsubscript{x} reduction reaction to take place in automobiles is further decreased. An advanced catalyst that is capable of achieve more than 90% conversions of hazardous gas at low temperatures (< 150°C) is required to meet future emission regulations. This standard has been recently established by U.S. Department of Energy (DOE) as the “150 Challenge.”\textsuperscript{11}
Although the three major components (NO, NO₂ and N₂O) of NOₓ are almost equally harmful to the environment, nitric oxide (NO) attracts the most concern in NOₓ reductions for automobiles among the three. The reason is that the dominant component composition of NOₓ in exhaust gas is the thermodynamically stable NO. NO₂ was then produced when NO react with oxygen in the air at a mild rate. Therefore, the strategy towards NOₓ reduction from automobile sources should focus on catalytic reduction of NO at low temperature.

Catalytic decomposition of NO has attracted research attentions for decades. Efficient catalysts for the efficient removal of NO at low temperatures are pressingly needed with the goal of meeting the DOE “150 Challenge.” In addition, some interesting phenomena (e.g. the volcano behavior) in the mechanisms of NO decomposition have not been ascribed with comprehensive discussions in previous
research. Hence, the object of the present thesis is to explain the unconventional volcano behavior through an innovative adsorption-compression theory as well as design advanced catalysts using the conclusions from exploring the catalytic NO decomposition mechanism.

1.2 NO\textsubscript{x} decomposition pathways and catalysts

Direct NO Decomposition

Direct NO decomposition is a pathway which directly convert NO to N\textsubscript{2} and O\textsubscript{2} It is considered as an ideal and reasonable route for NO removal robust strategy for NO\textsubscript{x} removal because a co-reactant is not required.\textsuperscript{10} The reaction formula for direct NO decomposition can be written as Equ. 3 below:

\begin{equation}
2\text{NO} \rightarrow \text{N}_2\text{O}_2 \quad E_a = 364 \text{ kJ mol}^{-1} \quad (3)
\end{equation}

The issues which impede this pathway from practical applications include (a) the huge energy barrier for NO dissociation, which makes direct NO decomposition reaction very challenging to occur at low temperature; and, (b) oxygen formed as a product during the reaction is usually hard to release, which can poison the catalyst.\textsuperscript{3} In practical applications, very few exhaust streams only contain NO as the reactant. Usually other components also participate to have competing reactions occur over the catalyst, or react with NO. However, the study of direct NO decomposition is still of interest since the performance of catalyst gives us valuable information regarding its activity towards N–O dissociation.

In this thesis, direct NO decomposition is used as a model reaction to examine the performance of catalysts in N-O dissociation as well as to illustrate the effect of Cu–
Selective Catalytic Reduction (SCR)

The selective catalytic reduction (SCR) of NO by ammonia and/or urea is considered as one of the most effective pathway to reduce nitric oxide from stationary sources\textsuperscript{12,13} and diesel cars,\textsuperscript{14} which has now been widely used in practical applications due to the high conversion of NO\textsubscript{x}. The abatement of NO\textsubscript{x} using NH\textsubscript{3}-SCR approach follows standard SCR mechanism as well as fast SCR mechanism which described in the equations below:\textsuperscript{7,15}

\begin{align*}
\text{Standard SCR: } & 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \\
\text{Fast SCR: } & 4\text{NH}_3 + 2\text{NO} + 2\text{NO}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}

Selective catalytic reduction of NO involves NH\textsubscript{3}-SCR pathway needs to be carefully controlled based on reaction stoichiometry. Otherwise the unreacted NH\textsubscript{3} can cause extra pollution. Hence, using SCR approaches with stable, nontoxic compound that selectively release ammonia are more practical. Solutions of urea (usually 32.5 wt\%) dissolved in water are widely used in typical exhaust aftertreatment setups for heavy duty vehicles. The formation of ammonia from urea solution is described as the following equations:\textsuperscript{16}

\begin{align*}
\text{H}_2\text{N-CO-NH}_2 & \rightarrow \text{HNCO} + \text{NH}_3 \\
\text{HNCO} + \text{H}_2\text{O} & \rightarrow \text{NH}_3 + \text{CO}_2
\end{align*}
Three-Way Catalysts (TWC)

The invention of three-way converters for catalytic exhaust aftertreatment was marked as a breakthrough in NOx abatement systems for automobiles. The reason this technique is called “three-way” is that it can simultaneously convert three hazardous components: carbon monoxide (CO), hydrocarbons (CHx) and nitrogen oxide (NOx) into nonhazardous CO2, H2O and N2. The chemical formula for three-way conversion is described as below:\(^7\)

\[
\begin{align*}
\text{CO} + \frac{1}{2}\text{O}_2 & \rightarrow \text{CO}_2 \quad (8) \\
\text{NO} + \text{CO} & \rightarrow \frac{1}{2}\text{N}_2 + \text{CO}_2 \quad (9) \\
\text{C}_x\text{H}_y + (x+y/4)\text{O}_2 & \rightarrow x\text{CO}_2 + y/2 \text{H}_2\text{O} \quad (10) \\
(2x+y/2) \text{NO} + x\text{C}_x\text{H}_y & \rightarrow (x+y/4) \text{N}_2 + x\text{CO}_2 + y/2\text{H}_2\text{O} \quad (11)
\end{align*}
\]

Typical catalysts used in three-way converters are noble metal such as Pt, Pd and Rh supported on Al2O3 or SiO2. There has been a growing interest in designing catalysts using less-expensive metals to replace the noble metals. In the present thesis, the Cu/CeO2 catalyst has been demonstrated with excellent activities in NO+CO reaction, which achieves 100% conversion of NO and 100% selectivity towards N2 at 100 °C.

1.3 NO Decomposition over Cu-Exchanged Zeolite Catalysts

Copper-substituted zeolites have been investigated extensively for NO decomposition due to their excellent activity and stabilities. Ever since the superior activity of CuZSM-
5 in direct NO decomposition was discovered by Iwamoto and co-workers,\textsuperscript{18,19} great efforts have been devoted to discover the performance Cu-containing zeolites in NO reductions. A variety of Cu-containing zeolites, including CuZSM-11,\textsuperscript{20,21} CuMOR,\textsuperscript{17} CuBEA,\textsuperscript{22} CuSSZ-13,\textsuperscript{23} have been demonstrated as excellent catalysts for NO decomposition. The active sites on Cu-containing zeolites for direct NO decomposition and the associated catalytic mechanisms have been comprehensively studied. According to previous literatures,\textsuperscript{24} one of the most widely accepted mechanisms of direct NO decomposition over Cu exchanged zeolites include two NO molecules first adsorbed on a Cu dimer site on CuZSM-5, two proximal NO molecules then react to form the N–N bond and produce intermediate N\(_2\)O, which is the rate-limiting step. The N\(_2\)O molecule reacts with the [Cu\(^{2+}\)–O–Cu\(^{2+}\)]\(^{2+}\) site and subsequently form N\(_2\) and O\(_2\) as final products. Therefore, the distance between two Cu active sites can be critical for the formation of N–N bond. In Cu-containing zeolites prepared by ion exchange method, Cu ions are expected to connect with framework Al sites and the distances between Al sites significantly depend on Si/Al ratios or Al distributions in zeolites with different topologies. Therefore, as expected, Cu–Cu distances are different in CuZSM-5 with different Si/Al ratios or other Cu-containing zeolites. Meanwhile, it is well-known that the activity of NO decomposition on Cu-exchanged catalysts exhibited interesting “volcano-type” dependence on temperature, which is different from common reaction behaviors (i.e., generally the conversion increased with increasing temperature, then levels off at high temperature). So far, only few works discussed this phenomenon. Iglesia et al.\textsuperscript{25} and Lee\textsuperscript{26} ascribed the decrease in NO decomposition rates at high
temperatures to unfavorable NO adsorption thermodynamics. However, no systematic investigation was conducted to explain the unconventional “volcano-type” behavior. It is hypothesized that a compression effect can be imposed on NO molecules to favor the N–N bond formation. Therefore, the distance of Cu dimer sites plays a significant role in catalytic direct NO decomposition over Cu-exchanged zeolites.

1.4 Insights from Adsorption-Compression Theory into Mechanism of Catalytic NO Decomposition over Cu-exchanged Zeolites

The most widely used classical adsorption model is based on Langmuir theory, which only takes adsorbate-adsorbent interactions into account and ignores adsorbate-adsorbate interactions. Adsorption-compression theory and the Ono-Kondo coordinate developed by two of the current authors provided strong tools to understand the interactions between neighboring molecules adsorbed on proximal active sites, e.g., NO molecules adsorbed on Cu dimers in Cu-exchanged zeolites, which is the preliminary and rate-limitation step for NO decomposition. In 2007, Dr. Gertard Ertl discovered that CO adsorption on Pd(111) surface can induce the (2*2) O overlayer to be compressed into a (2*1) O layer on Pd(111) surface, which increases the CO oxidation activity. Since compression between two adsorbates strongly relied on the distances between them, by understanding the way that distance affecting the compression effect could help us discover the influence of distances of proximal active sites on catalytic reactions and hence develop efficient strategies to design Cu based catalysts for NOx removal.
Herein, this thesis includes the research outcome in aim of investigating adsorption and compression effects of Cu-exchanged zeolites in direct NO decomposition reaction. The contents include establishment of catalytic reaction setup, synthesis and characterizations of Cu-exchanged zeolites. Reaction performance and kinetics studies of direct NO decomposition, analysis of adsorption isotherm for NO in Ono-Kondo coordinates and illustration of adsorption compression effect in direct NO decomposition over Cu-exchanged zeolites. Inspired by the study on adsorption compression of Cu dimers in Cu-exchanged zeolites, a robust Cu/CeO₂ catalyst has been developed to achieve efficient abatement of NOₓ at low temperatures, preliminary data of NO decomposition over this catalyst was also provided.
Chapter 2. Experimental Section

2.1 Experimental Setup

The catalytic evaluation system was established as shown in Fig. 3. NO decomposition and isothermal NO adsorption were performed in this setup. In a typical experiment, different reactant gases were adjusted at desired ratios with mass flow controller (MFC) and pass over the catalyst. The catalytic reaction was conducted in a fixed-bed flow reactor at atmospheric pressure. The catalyst was loaded into a microflow quartz reactor (7 mm i.d.) and reaction temperature was monitored by a Carbolite GERO vertical tube furnace system. To determine the conversions of reactants and the formation of products, a Fourier-transform infrared spectroscopy (FTIR) equipped with a 5 m gas cell and a MCT detector (Nicolet 6700, Thermo Electron Co.) as well as a gas chromatograph (GC) equipped with a barrier ionization discharge (BID) detector (GC-2010 plus, Shimadzu) were employed. Particularly, NO, N₂O, and NO₂ were determined by FTIR at 1905 cm⁻¹, 2237 cm⁻¹ and 1630 cm⁻¹ respectively with resolution of 8 cm⁻¹. N₂ was determined by GC using HP-POLT Molesieve column.
Figure 3. Experimental setup of catalyst evaluation system.

2.2 Synthesis of Cu Substituted Zeolites

Three types of zeolites with different frameworks including Zeolite Socony Mobil-5 (ZSM-5), Mordenite (MOR) and SSZ-13 were prepared. Copper was exchanged into the zeolite frameworks utilizing an ion-exchange method. The schematic illustration of zeolite preparation was shown in Fig. 4.

![Schematic illustration of Cu-zeolites preparation.](image)

The pristine ZSM-5 with different Si/Al molar ratios (Si/Al = 11.5, 20, 30,
measured by X-ray fluorescence spectrum)\(^\text{21}\) as well as SSZ-13 (Si/Al = 11)\(^\text{29}\) were synthesized by hydrothermal method. Mordenite was purchased from Zeolyst Co. (CBV 21A, Si/Al = 10).

In zeolite structures, the substitution of Al for Si in zeolites introduced anionic coordination sites (AlO\(_4^-\)), the negative charges were balanced by weakly held Na\(^+\) or H\(^+\). Cu-containing zeolites can be prepared by ion-exchange method. It is reported that Cu-exchanged zeolites showed better activity of NO decomposition when using Na-type zeolites as precursor.\(^\text{20,30}\) Hence, in this work, before Cu exchanging, all the zeolites were converted into Na-type zeolites using NaNO\(_3\) solution. The Na-type zeolites were further exchanged with Cu\(^{2+}\) using Cu(acac)\(_2\) solutions three times to obtain the Cu-exchanged zeolites.

### 2.3 Synthesis of Cu/CeO\(_2\) Catalyst

Besides Cu-exchanged zeolites, the performance of Cu/CeO\(_2\) was also evaluated in this thesis. The preparation of Cu/CeO\(_2\) followed a common impregnation-precipitation method and is shown in Fig. 5.\(^\text{31}\) In a typical synthesis, first the CeO\(_2\) was dispersed in water under sonication. Then, Cu(NO\(_3\))\(_2\) solution was introduced to the CeO\(_2\)-water mixture. Under robust stirring, NaCO\(_3\) solution was slowly added. The mixture was then kept under stirring for 90 min and the CuCO\(_3\)/CeO\(_2\) solid was collected with centrifugation. The obtained green solid was washed with water and ethanol, dried and calcined at 400 °C to obtain the Cu/CeO\(_2\) catalyst. ICP-MS analysis indicates actual Cu loading agreed well with nominal amount. A patented pretreatment process is
implemented to activate the Cu/CeO$_2$ catalyst before using it for NO decomposition reaction.

![Preparation steps for Cu/CeO$_2$ catalyst.](image)

**Figure 5.** Preparation steps for Cu/CeO$_2$ catalyst.
Chapter 3. Characterizations of Cu-Exchanged Zeolites

Scanning electron microscopy (SEM) images were taken on a JEOL 6700F field emission electron scanning microscope operating at 10.0 kV. The representative SEM image of each type of zeolite was shown in Fig. 6. ZSM-5 exhibited rectangular parallelepiped shapes with the length of 1.4 μm, and the width of 1 μm (Fig. 6a). Commercial mordenite (Si/Al = 10) exhibited small particles with the diameter of 100-200 nm, and some large granules around 400 nm can also be observed, which were aggregates of those small particles (Fig. 6b). For SSZ-13 (Si/Al = 11), the particles were individual cube-shaped crystals measuring approximately 400 nm in size, agglomerated by many smaller particles (Fig. 6c).

![Figure 6. SEM images of (a) ZSM-5, (b) MOR-10 and (c) SSZ-13.](image)

X-ray diffraction (XRD) patterns were obtained from a PANalytical X’Pert X-ray diffractometer equipped with a Cu Kα radiation source (λ = 1.5406 Å). Comparing XRD patterns of the samples of each zeolite with corresponding standard reference, the characteristic reflections of each zeolite topology were demonstrated, i.e. MFI (JCDPS No. 37-0359) for ZSM-5 (Fig. 7a), MOR (JCDPS No. 29-1257) for Mordenite (Fig. 7b), and CHA (JCDPS No. 47-0762) for SSZ-13 (Fig. 7c). It was also revealed in XRD patterns that ion exchanging with Cu²⁺ did not change the crystal structures of zeolites as the diffraction patterns of Cu exchanged zeolites are almost
identical to Na type zeolites. Additionally, no CuO (JCDPS No. 34-1354) or CuO (JCDPS No. 44-0706) peaks can be distinguished from XRD patterns of Cu-exchanged zeolites, which indicates Cu exist as pure cationic form within the zeolite pores.

Figure 7. XRD patterns of (a) CuZSM-5 with different Si-Al ratios and Cu loadings, (b) CuMOR-10 and (c) CuSSZ-13 with comparisons to the database.

Bulk Si/Al ratios of the prepared ZSM-5 and SSZ-13 samples and commercial Mordenite were measured by X-ray fluorescence (XRF) on a Bruker-AXS S4. The Cu and Al contents were determined by inductively coupled plasma mass spectrometry (ICP-MS) using a PerkinElmer Elan DRC II Quadrupole ICP-MS. Hydrofluoric acid was used to dissolve the Cu-exchanged zeolite. The solution was further diluted in 2% hydrochloric acid for ICP-MS measurements. Nitrogen adsorption measurements were measured on a Micromeritics ASAP 2010 instrument. The samples were first degassed under vacuum at 300°C for 4 h prior to the measurements. Specific surface area (SSA) was calculated using the Brunauer-Emmett-Teller (BET) theory. Table 1 summarizes the Cu content measured by ICP-MS and BET surface area measured by N₂ adsorption-desorption isotherm of each Cu zeolites. The nitrogen adsorption-desorption isotherm plots of all Cu-exchanged zeolites are shown in Fig. 8.
Table 1. Summary of Cu Content and BET Surface Area of Cu-zeolites

<table>
<thead>
<tr>
<th>Cu exchanged zeolites(^a)</th>
<th>Cu content (wt%)(^b)</th>
<th>BET surface area (m(^2)/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZSM-5-11.5 (0.51)</td>
<td>3.10</td>
<td>373</td>
</tr>
<tr>
<td>CuZSM-5-20 (0.51)</td>
<td>2.64</td>
<td>373</td>
</tr>
<tr>
<td>CuZSM-5-30 (0.42)</td>
<td>2.21</td>
<td>406</td>
</tr>
<tr>
<td>CuMOR-11 (0.50)</td>
<td>3.02</td>
<td>401</td>
</tr>
<tr>
<td>CuSSZ-13-11 (0.59)</td>
<td>3.98</td>
<td>593</td>
</tr>
</tbody>
</table>

\(^a\) The Si/Al ratio of each zeolite was determined by XRF.

\(^b\) The Cu content of each zeolite was measured by ICP-MS.

Figure 8. Nitrogen adsorption-desorption isotherms of Cu-zeolites. (a) CuZSM-5-11.5 (0.51). (b) CuZSM-5-20 (0.51). (c) CuZSM-5-30 (0.42). (d) CuMOR-10 (0.50). (e) CuSSZ-13-11 (0.59).
Chapter 4. Catalytic Studies of Direct NO Decomposition and “Volcano Type” Dependence on Temperature.

4.1 Performance of CuZSM-5, CuMOR and CuSSZ-13 in Direct NO Decomposition

Catalytic direct NO decomposition reactions over Cu exchanged zeolites were conducted in a pre-described flow reactor system at atmospheric pressure. 1 g of each Cu-zeolite (40–60 mesh) was loaded into a microflow quartz reactor as catalyst. The Cu-zeolite was pretreated at 500 °C in He before each reaction. The catalytic performance was evaluated using 500 ppm NO balanced by He and at different temperatures range from 350 °C to 550 °C. NO conversion, N₂ yield and rate of N₂ formation was evaluated with every 50 °C increment. The reaction was carried out at each temperature for at least 45 mins to allow reaction to reach equilibrium and conversion of NO remain constant before the measurements were taken. The NO conversion and N₂ yield were calculated using the following equations:

\[
\text{NO conversion} = \frac{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}}} \times 100\% \tag{12}
\]

\[
\text{N}_2 \text{ yield} = \frac{2[\text{N}_2]_{\text{outlet}}}{[\text{NO}]_{\text{inlet}} - [\text{NO}]_{\text{outlet}}} \times 100\% \tag{13}
\]

[NO]_{inlet} refers to the concentration of NO in the inlet, and [NO]_{outlet} or [N₂]_{outlet} refers to the concentration of NO or N₂ in the outlet. In catalysis, ultimately the reaction rate should be normalized by the number of active sites and converted to “turnover frequencies” because such term expresses the rate at which the catalytic cycle is completed over the active sites.\(^{32}\) In this work, since N₂ is the desired product indicating complete reduction of NO, also Cu sites were demonstrated as the active
sites for direct NO decomposition over Cu-exchanged zeolites by many previous works, we normalize the amount of N₂ formation by reaction time and number of Cu sites.

NO conversion, N₂ yield and rate of N₂ formation over each Cu-zeolite at the temperature range from 350 °C to 550 °C was measured and the results were shown in Fig. 9. As it’s exhibited, direct NO decomposition over all Cu substituted zeolites shows typical volcano-type behavior, which agrees with previous literatures.²⁵,²⁶ The NO conversion, N₂ yield and the rate of N₂ formation reached a maximum value at 450 °C and then showed a decreasing trend between 450 °C to 550 °C. The rate of N₂ formation over the three Cu exchanged ZSM-5 catalysts exhibited volcano slopes increasing from 350 °C to 450 °C and decreasing from 450 °C to 550 °C. For CuSSZ-13 and CuMOR, the rate of N₂ formation reached maximum at 400 °C and slowly reduce after reaching maximum. The catalytic activity of all Cu substituted zeolites in the present study follows the trend of CuZSM-5-11.5 (0.51) > CuZSM-5-20 (0.51) > CuZSM-5-30 (0.42) > CuMOR-10 (0.50) > CuSSZ-13-10 (0.59).

Figure 9. Catalytic activities of direct NO decomposition over different Cu-zeolites at temperatures from 350 °C to 550 °C. (a) NO conversions. (b) N₂ yields. (c) Rate of N₂ formation. NO concentration: 5000 ppm, balance gas: He, contact time: 0.05 min * g₉cat/ml.
In order to prove that the reduction in catalytic activity of Cu-zeolites at high temperature is not due to the decomposition of the zeolite structure, a hysteresis activity test was performed on Cu-ZSM-5-11.5, which was illustrated in Fig. 10. As shown in the figure, there was a slight increase in activity when Cu-ZSM-5-11.5 was tested when temperature decrease from 550 °C to 350 °C, indicating the structure of Cu-zeolite was unchanged even at the highest temperature that was tested, which is 550 °C. Hence, it is suggested that reduce in activity of Cu-zeolites at higher temperatures is related to the adsorption process and catalytic mechanism.

![Hysteresis loop of rate of N\textsubscript{2} formation](image)

**Figure 10.** Hysteresis loop of rate of N\textsubscript{2} formation from 350 °C to 500 °C and from 500 °C to 350 °C. The recovery of catalytic activity indicates the loss of activity at high temperature regime is not due to catalyst deactivation.
4.2 Kinetics Studies of Direct NO Decomposition over Cu Substituted Zeolites

Fig. 11 showed the Arrhenius plot of NO decomposition over different Cu-exchanged zeolites. The apparent activation energy ($E_{\text{app}}$) could be obtained from the slope in the Arrhenius plot where ($\ln K$) was plotted against the reciprocal temperature (Fig. 11a). Comparing the apparent activation energies over different Cu-exchanged zeolites, it is obvious that activation energies in low temperature followed the sequence of CuZSM-5-11.5 (0.51) < CuZSM-5-20 (0.51) < CuZSM-5-30 (0.42) < CuMOR-10 (0.50) < CuSSZ-13-10 (0.59), which suggests that adsorption-compression effect is beneficial to facilitate the catalytic direct NO decomposition reaction over Cu-exchanged zeolites at low temperature (< 400 °C). Meanwhile, the apparent activation energies (Fig. 11b) at high temperature is negative and followed the invertible sequence of CuZSM-5-11.5 (0.51) > CuZSM-5-20 (0.51) > CuZSM-5-30 (0.42) > CuMOR-10 (0.50) > CuSSZ-13-10 (0.59), suggesting that adsorption-compression plays a prohibitive role in direct NO decompositions reaction at high temperature (> 400 °C), exhibiting as the decreasing slope of the unusual “volcano” behavior.
Figure 11. (a) Arrhenius plot of apparent activation energies of direct NO decomposition over different Cu-zeolites. (b) Calculated apparent activation energies at low temperature (<400 °C, red) and high temperature (>400 °C, blue) regimes of direct NO decomposition over different Cu-zeolites.
Chapter 5. Isothermal NO Adsorption Analysis Using Generalized Ono-Kondo Coordinates

5.1 Theories of Generalized Ono-Kondo Coordinates

In the previous chapter, our experimental results indicated that direct NO decomposition over all Cu-substituted zeolites exhibit the unconventional “volcano-type” behavior, which agrees well with previous literatures. The kinetics study suggests adsorption-compression effect can play a critical role in catalytic process. Hence, a new adsorption is needed to take the adsorption-compression effect in to account. The Ono-Kondo Coordinates, developed by two contributors: Dr. Donohue and Dr. Aranovich, is able to consider taking an adsorbate molecule and moving it to the bulk. First, when a molecule is adsorbed on a vacant catalytic site,

\[ M_a + V \rightarrow V_a + M_b \quad (14) \]

where \( M \) is the adsorbate molecule, and \( V \) is the vacancy that it fills. If this exchange occurs at equilibrium, then:

\[ \Delta H - T\Delta S = 0 \quad (15) \]

where \( \Delta H \) and \( \Delta S \) are the enthalpy and entropy changes, and \( T \) is the absolute temperature.

Consider \( \Delta H \) in the form of Taylor expansion in powers of density,

\[ \frac{\Delta H}{kT} = \frac{\varepsilon_s}{kT} + A_1 x_a + A_2 x_a^2 + A_3 x_a^3 + \cdots \quad (16) \]

where \( A_n = \frac{1}{n!} \frac{\partial^n \Gamma_A}{\partial x_a^n} \), \( \Gamma_A \) is the energy of intermolecular (adsorbate-adsorbate) interactions, \( \varepsilon_s \) is the energy of adsorbate-adsorbent interaction, and \( x_a \) is the average normalized density of adsorbed phase, representing the ratio of adsorbed
amount, \( a \), to the adsorption capacity, \( a_m \):

\[
x_a = \frac{a}{a_m}
\]  \hspace{1cm} (17)

Also, in the framework of Ono-Kondo approach,\(^{14}\)

\[
\Delta S = k \ln[x_a (1 - x_b)/(1 - x_a) x_b]
\]  \hspace{1cm} (18)

Where \( x_a \) is the same average normalized density of adsorbed phase \( x_b \) is the average normalized density in the bulk. At the condition of isothermal NO adsorption experiments (80 °C, atmosphere pressure), both \( x_a \) and \( x_b \) should be much smaller than 1. Plugging \( \Delta H \) and \( \Delta S \) from equations (16) and (18) into equation (15) gives:

\[
\ln \frac{x_a (1 - x_a)}{(1 - x_a) x_b} + \frac{\varepsilon_s}{kT} + A_1 x_a + A_2 x_a^2 + A_3 x_a^3 + \ldots = 0
\]  \hspace{1cm} (19)

Which can be presented in the following form:

\[
\ln \frac{x_a (1 - x_b)}{(1 - x_a) x_b} = -\frac{\varepsilon_s}{kT} - x_a \Gamma(x_a)
\]  \hspace{1cm} (20)

where \( \Gamma(x_a) = \Gamma(0) + \frac{1}{2!} \frac{\partial \Gamma}{\partial x_a} x_a + \frac{1}{3!} \frac{\partial^2 \Gamma}{\partial x_a^2} x_a^2 + \ldots \), and \( \Gamma \) is the energy of adsorbate-adsorbate interactions.

We can simplify equation (20) into a linear form: \( Y = k x_a + b \), where:

\[
Y = \ln \frac{x_a (1 - x_b)}{(1 - x_a) x_b}
\]  \hspace{1cm} (21)

Plotting \( Y \) versus \( x_a \) gives information about \( \Gamma(x_a) \), the intermolecular interactions in adsorbed phase. For example, if the initial slope is negative, then there are repulsions between nearest neighbors at small \( x_a \); if this slope is positive, there are attractions between nearest neighbors at small \( x_a \). For larger \( x_a \), the slope can vary and indicate changes of adsorbate-adsorbate interactions.

As seen from equation (20), the slope in the plot of \( Y \) versus \( x_a \) gives the
energy of lateral interactions, $E_{lat}$, in units of $kT$ and the intercept gives $\frac{\varepsilon_s}{kT}$. When $E_{lat}$ is negative, it is the energy of adsorption compression, $E_c = E_{lat}$.

For $x_b << 1$ and $x_a << 1$, equation (21) can be simplified to:

$$Y = \ln \frac{x_a}{x_b}$$  \hspace{1cm} (22)

So, in the range of small densities, plotting $Y = \ln \frac{x_a}{x_b}$ versus $x_a$ gives information about $\Gamma(x_a)$: the slope gives the energy of adsorption compression (in units of $kT$) and the intercept gives $\frac{\varepsilon_s}{kT}$.

5.2 Isothermal NO Adsorption Measurements

Isothermal NO adsorption on different Cu-containing zeolites catalysts was conducted in the fixed-bed flow reactor at atmospheric pressure using similar method and conditions reported in the previous literature.\(^{33}\) The same pretreatment (He, 500 °C) was implemented. After pretreatment, the temperature was cooled down to 80 °C under pure He atmosphere and kept the temperature at 80 °C for adsorption measurement. The feed concentrations of NO were adjusted to 300 ppm, 500 ppm, 800 ppm and 1500 ppm by mixing pure He and 0.5% NO/He gas. The NO/He mixture (201 h\(^{-1}\)) was fed to the catalyst. The composition of the effluent stream was continuously monitored for the entire length of the experiment until all concentrations of different gas species (NO, $N_2O$, $N_2$) were stable. The detection system was the same experimental setup as above. The profile of measured outlet concentration of NO, $N_2O$ and $N_2$ in the time on stream during NO isothermal adsorptions of different NO concentrations on CuZSM-5-11.5 (0.51) at 80 °C was chosen as an example and was shown in Fig. 12. Since the
production of $\text{N}_2\text{O}$ and $\text{N}_2$ followed the two equations below and the stoichiometries of $\text{N}_2\text{O}$ and $\text{N}_2$ to $\text{NO}$ are both 1 to 2. The moles of $\text{NO}$ consumed for the production of $\text{N}_2\text{O}$ and $\text{N}_2$ should be double of the moles of $\text{N}_2\text{O}$ and $\text{N}_2$ produced.

$$4\text{NO} \rightarrow 2\text{N}_2\text{O} + \text{O}_2 \quad (23)$$

$$2\text{NO} \rightarrow 2\text{N}_2 + 2\text{O}_2 \quad (24)$$

Hence, the amount of NO adsorbed on the catalyst at the end of the adsorption measurement was evaluated by measuring the overall uptake of NO and the quantities of $\text{N}_2\text{O}$, $\text{NO}_2$ and $\text{N}_2$ transiently produced, as follows:

$$\text{NO}_{\text{ads}} = \text{NO}_{\text{uptake}} - 2\text{N}_2\text{O}_{\text{prod}} - 2\text{N}_2,\text{prod} - \text{NO}_{\text{hold up}} \quad (25)$$

Where:

- $\text{NO}_{\text{ads}}$ represents NO totally adsorbed (as calculated from mass balance in the gas phase);
- $\text{NO}_{\text{uptake}}$ represents the amount of NO consumed (directly measured in the gas phase);
- $\text{N}_2\text{O}_{\text{prod}}$ represents the amount of $\text{N}_2\text{O}$ produced (directly measured in the gas phase);
- $\text{N}_2,\text{prod}$ represents the amount of $\text{N}_2$ produced (directly measured in the gas phase);
- $\text{NO}_{\text{hold up}}$ represents the amount of NO necessary to fill the dead volumes of the experimental set-up (evaluated in the opportune blank tests).

The amounts of these adsorbed species were estimated by integrating the corresponding signals as a function of time; all these quantities are reported in Table 2 for CuZSM-5-11.5 (0.51).
Figure 12. Outlet concentrations of NO, N\textsubscript{2}O and N\textsubscript{2} during NO isothermal adsorptions of different NO concentrations on CuZSM-5-11.5 (0.51) at 80 °C. (a) 300 ppm NO. (b) 500 ppm NO. (c) 800 ppm NO. (d) 1500 ppm NO.
Table 2. Amounts of Gaseous Species Evaluated by the Integration of the Signals during the Adsorption of Different Concentrations of NO on CuZSM-5-11.5 (0.51) in Ono-Kondo Coordinates

<table>
<thead>
<tr>
<th>Concentrations of NO</th>
<th>NO\textsubscript{ads}</th>
<th>NO\textsubscript{uptake}</th>
<th>N\textsubscript{2}O\textsubscript{prod}</th>
<th>N\textsubscript{2}prod</th>
<th>NO\textsubscript{hold up}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>μmol g\textsuperscript{-1}</td>
<td>μmol g\textsuperscript{-1}</td>
<td>μmol g\textsuperscript{-1}</td>
<td>μmol g\textsuperscript{-1}</td>
<td>μmol g\textsuperscript{-1}</td>
</tr>
<tr>
<td>300 ppm</td>
<td>199</td>
<td>527</td>
<td>125</td>
<td>36</td>
<td>6</td>
</tr>
<tr>
<td>500 ppm</td>
<td>305</td>
<td>703</td>
<td>154</td>
<td>40</td>
<td>10</td>
</tr>
<tr>
<td>800 ppm</td>
<td>441</td>
<td>903</td>
<td>160</td>
<td>63</td>
<td>16</td>
</tr>
<tr>
<td>1500 ppm</td>
<td>686</td>
<td>1188</td>
<td>170</td>
<td>70</td>
<td>22</td>
</tr>
</tbody>
</table>

Fig. 13 shows the plot of $Y = ln \frac{x_a}{x_b}$ versus $x_a$. From the plot, first we can observe the slopes for the plot of each Cu-exchanged zeolite is negative, which is indicative of the repulsion between adsorbed NO molecules. The compression energies can be calculated following the principles introduced in the previous chapter from the slopes in Fig. 12. From the data provided in previous literature, the average Cu–Cu distances of each Cu substituted zeolites were obtained and summarized in Table 3. From the works that were selected, the authors used EXAFS technique to characterize the average Cu–Cu distances of Cu-exchanged zeolites with the same frames and very similar Cu loadings and Si/Al ratios compare to the ones used in the present thesis. The calculated compression energy and average Cu–Cu distance have been related and listed in Table 3. It can be found that calculated compression energy followed the sequence of CuZSM-5-11.5 (0.51) > CuZSM-5-20 (0.51) > CuZSM-5-30 (0.42) >
CuMOR-10 (0.50) > CuSSZ-13-10 (0.59), which agrees well with the order of catalytic activity at low temperature regime (< 400 °C).

![Diagram](Figure 13. Plot of $Y = \ln \frac{x_a}{x_b}$ versus $x_a$. $Xa$ was obtained from adsorption isotherms for NO on Cu-Zeolites at 80 °C in Ono-Kondo coordinates. Compression energy of adsorbed.)
Table 3. Summary of Compression Energy Calculated from Ono-Kondo Coordinates and Average Cu-Cu Distances of Cu Dimers in Cu Zeolites in Present Study

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Cu···Cu distances (Å)</th>
<th>Compression Energy (kCal mol(^{-1}))(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuZSM-5-11.5</td>
<td>2.84(^34)</td>
<td>7.77</td>
</tr>
<tr>
<td>CuZSM-5-20 (0.51)</td>
<td>2.94(^35)</td>
<td>7.05</td>
</tr>
<tr>
<td>CuZSM-5-30 (0.42)</td>
<td>3.13(^36)</td>
<td>6.51</td>
</tr>
<tr>
<td>CuMOR-11 (0.50)</td>
<td>3.34(^37)</td>
<td>6.02</td>
</tr>
<tr>
<td>CuSSZ-13-11 (0.59)</td>
<td>3.76(^38)</td>
<td>5.38</td>
</tr>
</tbody>
</table>

\(^34\) J. Am. Chem. Soc. 125 (2003) 7629-7640

\(^35\) J. Phys. Chem. 98 (1994) 10832-10846

\(^36\) Catal. Lett. 5 (1990) 189-196

\(^37\) J. Mater. Chem. 7 (1997) 1917–1923


\(^a\) Obtained from NO isothermal adsorption measurements
Chapter 6. Effect of Cu···Cu Dimer Distances on Catalytic Activity of NO Decomposition over Cu Substituted Zeolites

In the previous chapter, Cu–Cu distance and compression energy of each Cu-exchanged zeolite were obtained from literature and calculated by Ono-Kondo Coordinate, respectively. Here, by plotting the calculated compression energy at T < 400 °C versus Cu–Cu distance (Fig. 14a), it can be revealed that the compression energy of NO adsorbed in Cu-exchanged zeolites is inversely proportional to the average Cu–Cu distance. Hence, it can be deduced that shorter Cu-Cu distance gave rise to larger compression energy in Cu-exchanged zeolites. Also, by plotting the rate of N₂ formation at T < 400 °C versus compression energy (Fig. 14b), we can see the rate of N₂ formation increases as compression energy increases. Hence, it is concluded that the compression energy can be bridged to the average Cu–Cu distance of each Cu-zeolite, which is crucial for catalytic activity of direct NO decomposition.

![Graph showing dependence of compression energy on Cu-Cu distance and rates of N₂ formation on compression energy.](image)

**Figure 14.** (a) Dependence of compression energy on Cu-Cu distance. (b) Dependence of rates of N₂ formation at 400 °C on compression energy.
The relation for reaction rate with temperature and compression energy in Ono-Kondo modified Langmuir-Hinshelwood mechanism is shown in Equ. 26. Also, in Fig. 15, the parameter which determines the performance of each Cu-exchanged zeolite in direct NO decomposition reaction – the apparent activation energy was plotted versus the compression energy. It can be illustrated that at low temperature regime (< 400 °C), the apparent activation energy is smaller for Cu-zeolite with larger compression energy, which further indicates that compression energy helps reduce the energy barrier of direct NO decomposition at low temperatures. However, at high temperature (>400 °C), the activity of NO decomposition decreases as temperature increases, the apparent activation energy become negative. Observations from this thesis suggest that compression effect causes coverage $a(T)$ decreases with T increases. Cu-zeolite with shorter Cu-Cu distance exhibits stronger compression and larger decrease in $a(T)$.

$$r = -k_0 \cdot \exp \left( -\frac{E_0 - E_c}{RT} \right) \cdot [a(T)]^n$$

(26)

Where:

$E_0$ is intrinsic activation energy without compression effect;

$E_c$, is the compression energy,

$a(T)$ is the coverage of reactants, which was relevant with temperature.

Combination of $E_0-E_c$=Apparent activation energy ($E_{app}$).
Figure 15. Plot of calculated apparent activation energy \( (E_{\text{app}}) \) of each Cu-exchanged zeolite at low temperature regime \(< 400 \, ^{\circ}C\) and high temperature regime \(> 400 \, ^{\circ}C\) versus compression energy.

The observations in the adsorption-compression effect in direct NO decomposition reaction can be combined with the commonly believed mechanism of direct NO decomposition over Cu-zeolites, which have been summarized and demonstrated in Fig. 16. This mechanism involves adsorption of two NO molecules on adjacent Cu sites in Cu-zeolites. Formation of N–N bond and production of N\(_2\)O as a precursor of N\(_2\) was believed as the rate limiting step. Previous computational study
indicated that the distance of Cu dimer sites plays a significant role in catalytic direct NO decomposition over Cu-zeolites. The present thesis further demonstrated that Cu-Cu distance in Cu-zeolite determines the compression energy which greatly affect the behavior in direct NO decomposition reaction. Shorter Cu-Cu distance can give higher compression energy which serves as an extra potential energy which helps the NO molecules to overcome the energy barrier and form N₂O intermediates.

Figure 16. Illustration of mechanism for direct NO decomposition over copper dimers and effect of compression.

The behavior of adsorbed NO molecules on Cu active sites in Cu-exchanged zeolites can be illustrated in Fig. 17. It can be revealed that under compression effect,
an adsorbate-adsorbate interaction can shorten the distance of the two adsorbed molecules, which favors the reaction between them. However, beyond a certain limit, (e.g. the compression effect is too strong caused by increase in temperature), the strong interaction might cause one molecule to desorb and thus reduce the coverage of adsorbed molecules on the catalyst surface. The reaction activity will then dramatically decrease.

![Diagram of adsorption-compression effect](image)

**Figure 17.** Illustration of adsorption-compression effect on adsorbed molecules on catalyst surface.

Generally, the energy profiles of classical reaction (black line) and the reaction involving compression adsorption between adsorbed reactants (red line) can be illustrated in Fig. 18. The compression between adsorbates could activate reactants with certain compression energy (Ec), thus decreased classical kinetic energy (Ea) to lower value (Ea’), eventually made reactants overcoming reaction barrier easier.
Figure 18. Comparison of classical reaction activation pathways (black) with reaction activation pathways involves compression energy (red).
Chapter 7. NO Decomposition over Cu/CeO$_2$

7.1 From Cu-exchanged Zeolites to Cu/CeO$_2$

With the rise of the DOE “150 Challenge”, Cu-zeolites, as well as many conventional deNO$_x$ catalysts, fail to fulfill the requirements due to the lack of low temperature activities. Cant et al. studied the performance of typical Rh, Pt and Pd based three-way catalyst in NO decomposition with a mixture of CO, C$_3$H$_6$, C$_3$H$_8$, H$_2$ and O$_2$, it was observed that 100% conversion can be easily achieved at 200 $^\circ$C over Rh/Al$_2$O$_3$, over Pt/Al$_2$O$_3$ and Pd/Al$_2$O$_3$, the temperature to reach 100% conversion is 325 $^\circ$C and 400 $^\circ$C, respectively. However, at 150 $^\circ$C there was only about 5% conversion of NO.$^{40}$ Based on the conclusions obtained from study on Cu-zeolites, Cu–Cu distance plays an essential role in catalytic NO decomposition. However, in Cu-zeolites, Cu–Cu distance is limited by number of exchangeable sites as well as structure of zeolites.$^{30}$ Previous literature also demonstrated oxygen formed during reaction can poison the catalyst. The release of adsorbed oxygen requires careful design on the catalysts to be feasible at low temperature.$^{19}$

Recently, a series of research works demonstrated that cerium oxide can provide oxygen vacancies for absorption and release of oxygen as well as the regeneration of catalytic active sites, which is ideal for NO$_x$ decomposition.$^{41,42}$ Inspired by the conclusion of our studies on Cu-zeolites and previous literatures, it is believed CeO$_2$ can serve as a better support for Cu(I) dimers, which can give rise to robust catalytic ability in NO decomposition. To the best of our knowledge, no catalyst which can achieve direct NO decomposition at room temperature has yet been reported.
7.2 Characterization of Cu/CeO$_2$ catalyst

TEM images of the CeO$_2$ support and 5% Cu/CeO$_2$ were obtained. Representative images are shown in Fig. 19. and Fig. 20, respectively. No significant difference can be distinguished by comparing the two images, especially no particles can be observed at the edge of the plate-like CeO$_2$ support. Which indicates Cu species are highly dispersed. High-resolution TEM (HRTEM) images of the 5% Cu/CeO$_2$ catalyst were also taken and a representative image was shown in Fig. 21. Even at high resolution, no Cu species can be identified. At high resolution, two lattice spacings of CeO$_2$ can be observed, 0.31 nm which represents the presence of (111) phase and 0.27 nm which represents the presence of (110) phase. ICP-MS characterization was also performed to verify the Cu loading on CeO$_2$ and it’s observed that the impregnation-precipitation method gave very accurate loading of Cu compare to the nominal amount.

Figure 19. TEM image of the CeO$_2$ support.
**Figure 20.** TEM image of 5% Cu/CeO$_2$.

**Figure 21.** HRTEM image of 5% Cu/CeO$_2$. 
7.3 Performance of Cu/CeO$_2$ in Various NO Decomposition Pathways

Here as shown in Fig. 22, we report the 5% Cu/CeO$_2$ catalyst after a pretreatment technique was capable of achieve direct NO decomposition at room temperature with almost 100% conversion and 100% selectivity to N$_2$ and O$_2$. The catalyst was active for around 500 min. By far, this catalyst is the first which achieves direct NO decomposition with total conversion of NO at room temperature. The details of the pretreatment technique were patented and should be kept confidential in the present thesis.

![Figure 22. Performance of direct NO decomposition over 5% Cu/CeO$_2$ at 30 °C.](image)

Although the 5% Cu/CeO$_2$ have demonstrate great activity for direct NO decomposition, the eventual deactivation of the catalyst indicate the reaction of direct NO decomposition did not reach steady state. Also, analysis of effluent stream indicating O$_2$ concentration is much lower than the theoretical stoichiometry amount.
Hence, it can be hypothesized that oxygen intermediate was hard to release, which cause to deactivation. However, if CO as a reducing agent was introduced, the catalyst was able to reach steady state, 100% conversion of NO and 100% selectivity to N₂ was achieved at 100 °C (Fig. 23).

**Figure 23.** Performance of NO+CO reaction over 5% Cu/CeO₂.
Chapter 8. Conclusions and Future Directions

In conclusion, in the first part of the present thesis, a series of Cu-exchanged zeolites have been synthesized, including Cu-ZSM-5, CuMOR and CuSSZ-13. The Cu-exchanged zeolites were characterized with SEM, XRD, ICP-MS, XRF and evaluated for the direct NO decomposition reaction. The effect of adsorption and compression in direct NO decomposition reactions was tested. The results obtained from theoretical calculation agreed well with experimental observation. The Ono-Kondo correction to the Langmuir-Hinshelwood (OK-LH) model was applied to take adsorbate-adsorbate interactions into account. By relating the Cu–Cu distance and compression energy, it can be proved that compression energy of NO on Cu-exchanged zeolites is inversely proportional to Cu–Cu distance. The unconventional volcano behavior of direct NO decomposition activity at different temperatures was then explained by adsorption-compression theory. At low temperature (< 400 °C), compression energy gives an extra potential energy which helps the reactant to overcome the reaction energy barrier. However, at high temperature (> 400 °C), the compression results in low coverage of reactants which causes decrease in reaction activity.

In the second part of the thesis, a Cu/CeO₂ catalyst has been designed and synthesized. High resolution TEM images indicate that Cu species are highly dispersed on CeO₂ surface. After a patented pretreatment technique, 5% Cu/CeO₂ was able to achieve 100% conversion of NO in direct NO decomposition at room temperature with 100% selectivity. The catalyst was not deactivated for nearly 500 min. Excellent activity was observed in NO+CO reaction over Cu/CeO₂ catalyst as well.
Based on the superior performance of Cu/CeO$_2$ in NO decomposition reaction, some future directions are suggested for exploring the Cu/CeO$_2$ system. First, DRIFTS of NO chemisorption on Cu/CeO$_2$ catalyst should be performed to determine the active sites for NO decomposition. Spectroscopies studies such as X-ray adsorption (XAS), UV-Vis and Raman should also be conducted to examine the effect of pretreatment on the Cu/CeO$_2$ catalyst. It is observed that 5% Cu/CeO$_2$ deactivated after 500 mins in direct NO decomposition reaction at room temperature. Analysis of the effluent stream suggests that oxygen was stored in the catalyst which caused the deactivation. Hence, increasing oxygen release ability can be a suggestion for improving the stability of the catalyst, which can be done by doping other metal oxides into the CeO$_2$ support or alloying Cu with other active metals. The optimized deNO$_x$ catalyst should be tested in real exhaust condition. Additional modifications on the design of this catalyst might also be necessary to overcome the interference of oxygen and water vapor that are presented in the real automobile exhaust.
References


1483–1492.


Curriculum Vita

Tiancheng Pu was born in Nanjing, China in 1994 and was raised there before his college education. He came to the US in 2011 and studied Chemical and Molecular Engineering at Stony Brook University. During his undergraduate career, Tiancheng’s research interests were in magnetic properties of coordinated complexes as well as biomass conversion using metal oxide catalysts. Following the completion of his bachelor’s degree, Tiancheng began his MSE in Chemical and Biomolecular Engineering department at The Johns Hopkins University. He joined Dr. Chao Wang’s nano energy lab in 2016 and became Dr. Wang’s first graduate student in the field of heterogeneous catalysis. Tiancheng focused on the synthesis and characterizations of advanced catalysts for future energy and environmental sustainability. Under Dr. Wang’s supervision, his research efforts include nitric oxide decomposition, methane conversion and CO oxidation over Cu and Pt based catalysts.

Publications:


