**BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL
ALUMINOSILICATES**

Technical Progress Report for the Period

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OBJECTIVE AND SCOPE OF WORK

The objective of this research is to provide the scientific understanding of processes that actively and selectively reduce NO in dilute exhaust streams, as well as in concentrated streams, to N₂. Experimental studies of NO chemistry in transition metal-containing aluminosilicate catalysts are being carried out with the aim of determining the chemical rules for NO reduction on non-precious metals.

The catalyst supports chosen for this investigation are A and Y zeolites, mordenite, and monoliths based on cordierite. The supported transition metal cations that will be examined are principally the first row redox metals, e.g. Cr(II), Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Cu(I). The reactions of interest are the reductions of NO by H₂, CO, and CH₄, as well as the disproportionation of NO.

In order to stabilize the transition metal cations in accessible sites and with desired oxidation states so that the resultant activity and selectivity to NO reduction are increased, rare earth cations that possess redox properties will be placed in the more shielded sites, e.g. Site I in Y zeolite, prior to or simultaneously with the exchange procedure with the transition metal cations. The rare earth redox couples that can be utilized include Ce(III)/Ce(IV), Eu(II)/Eu(III), Sm(II)/Sm(III), and Pr(III)/Pr(IV). The prepared catalysts will be tested in batch, pulsed, recycle, and continuous flow reactors with in-line gas chromatographic or mass spectrometric analyses, and they will be fully characterized before and after catalytic testing.

To provide insight into the functioning of the redox cations and guidance in choosing the best transition metal/rare earth combination for the dissociative chemisorption of NO, theoretical calculations of the electronic structure of the transition metal cations in zeolitic sites will be carried out by ab initio methods, such as the scattered wave X_α and Gaussian 86 or 90 packages. The aim of this part of the research is to find the best match between the metal-based antibonding orbitals and the antibonding orbitals of the NO molecule such that the N-O bond is weakened and is readily broken.

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SUMMARY OF TECHNICAL PROGRESS

Extensive series of experiments were carried out with Co(II)A zeolites containing 2.6 and 3.9 Co²⁺ ions per unit cell in which NO and N₂O were separately adsorbed, and subsequent temperature programmed desorption (TPD) and optical spectroscopy analyses were carried out to study the desorption and decomposition behavior of these catalysts toward the adsorbates. The solid phase was monitored by optical diffuse reflectance (UV-Vis-NIR), while the gas phase was monitored by mass spectrometry. The experimental data are summarized here, and interpretation of these results is being carried out.

TECHNICAL PROGRESS

I. Complexation and Decomposition of N₂O on CoA zeolites

1. Room Temperature Isotherms of N₂O on CoA Zeolites

The dehydration of the CoA zeolite samples (2.6 Co²⁺/unit cell) was carried out in the diffuse reflectance cell. Samples of about 2.5 g Co²⁺ A zeolites were outgassed for 6 hr at 100°C and gradually heated up to 350°C at the rate of 50°C per 30 min. Finally, the sample was kept at 350°C for another 6 hr under a vacuum of about 10⁻⁵ torr pressure. The adsorption experiments were performed by gas expansion from the gas chamber (volume of 483 ml) into the cell (volume of 47 ml). The gas chamber was filled with gas at known pressure at room temperature. Following the pressure drop, measured by a differential manometer, the volumetric measurement was carried out with an optimal accuracy of approximately 2-5%.

After the CoA zeolite was dehydrated, N₂O adsorption experiments were carried out at room temperature. The amount of N₂O adsorption depends on the pressure of N₂O (Figure 1). For the sample with 2.6 Co²⁺ per unit cell, there were up to 7 N₂O molecules adsorbed by a unit cell. This corresponds to more than 2 N₂O per Co cation. The adsorption rate became much slower after the CoA zeolite had adsorbed N₂O corresponding to about 2 N₂O per Co²⁺ ion. There was no detectable stable state corresponding to the adsorption of only one N₂O per Co²⁺ cation. Upon evacuation at room temperature, N₂O could be fully desorbed without decomposition.

2. N₂O Decomposition on CoA Zeolite

After exposure of the CoA zeolite to 750 torr of N₂O, followed by brief evacuation of the gas phase, the temperature of the sample was progressively increased to 350°C. As the programmed temperature reached 150°C, adsorbed N₂O began to decompose, which was manifested by the release of N₂. Oxygen is believed to be chemisorbed on the zeolite at the lower temperatures utilized, for when the temperature was increased to 300°C, O₂ was also released (Figure 2). The initial reaction can be written as follows:

CoA-O_{chem} sites with chemisorbed oxygen are rather stable up to 300°C, and they more readily decompose above this temperature with liberation of O₂, i.e

Since the reaction of gas phase O₂ with CoA at 150-350°C does not result in its chemisorption, CoA-O_{chem} sites are apparently formed as a result of chemisorption of O atoms and not the O₂ molecule.

3. UV-VIS-NIR Spectra of N₂O on CoA Zeolites

The most significant spectral change after N₂O adsorption at ambient temperature was that the characteristic peaks for bare site Co²⁺ at 24,000 and 25,000 cm⁻¹ (Figure 3) were completely absent when the Co cation adsorbed more than one N₂O molecule (Figure 4-5). The addition of the 14,500 and 21,000 cm⁻¹ peaks (Figure 6) contributed to the broadening of the original 16,000 and 18,500 cm⁻¹ peaks. Increasing the pressure of N₂O after reaching the level of one N₂O molecule per Co cation level did not change the

spectrum except for only increasing the intensity of those peaks. After evacuation at room temperature, the spectrum corresponded to that of the original bare site Co^{2+} (Figure 3) and was fully recovered.

When CoA was heated in the present of N_2O (750 torr), the background of the optical spectra was increased (Figures 7 and 8). The peaks at 14,500 and 21,000 cm^{-1} gradually disappeared, and the 24,500-25,000 cm^{-1} band appeared as shown in Figure 9 (during this temperature region, N_2 was released, see Figure 10). When the temperature reached above 300°C, the 24,000 and 25,000 cm^{-1} peaks were partially recovered but did not fully recover at 350°C, as shown in Figure 11 (during this temperature region, O_2 was also released as shown in Figure 10). Desorption at lower temperature did not change the spectra, but the profound evacuation at 350°C almost completely regenerated bare site Co^{2+} as indicated by the spectrum shown in Figure 12. Reduction of this sample by H_2 at 350°C fully regenerated the sample, and the products observed were water and nitrogen.

During the heating in the present of N_2O , there was a slight color change noted at 250°C. The sample became a greenish color, and the color became quite intense at 300°C. It changed back to dark blue at 350°C.

II. Complexation and Decomposition of NO on CoA zeolites

1. Room Temperature Isotherms of NO on CoA Zeolites

Prior to these studies, the zeolite samples were dehydrated as described in the previous section of this report. The amount of NO adsorption on CoA zeolites at ambient temperature depends on the pressure of NO (Figure 13). For the sample containing 3.9 Co^{2+} ions per unit cell that was used for these experiments, there were up to 11 NO

molecules adsorbed per unit cell at 750 torr of NO. This corresponds to 2.8 NO per Co^{2+} cation. There was no stable state observed that would correspond to only one NO per Co^{2+} cation. Upon evacuation at room temperature, NO was partially desorbed with some N_2O formation since the latter component was detected in the desorbed gases. This indicated that the adsorption of NO was stronger than that of N_2O and that the NO was much more activated than N_2O .

2. NO Decomposition on CoA Zeolites

After exposure of the CoA zeolite (10 mg) to 50 torr NO, followed by brief evacuation at room temperature to remove the gas phase NO, temperature programmed studies were carried out. As the sample temperature was progressively raised from room temperature up to 350°C , NO began to decompose, which was manifested by the release of N_2 and N_2O (Figure 14). The quantity of N_2O desorbed reached a maximum around 200°C , and the decrease at higher temperatures may be caused by subsequent decomposition of the N_2O over the CoA zeolite. However, there was little oxygen released in this temperature region. The decomposition may be achieved *via* the surface complexes formed. After evacuation of the sample at 350°C , a H_2 reduction treatment was employed. This reduction treatment at 350°C (Figure 15) gave H_2O , N_2 and NO as major products, which indicated that the surface complexes must involve oxygen and a higher valence state nitrogen. When a H_2 and NO mixture was heated over the same zeolites at 350°C , the only products observed were N_2 and H_2O (Figure 16).

3. UV-VIS-NIR Spectra of NO on CoA Zeolites

The most significant spectral change after NO adsorption was the disappearance of the characteristic peaks for bare site Co^{2+} at $24,500$ and $25,000\text{ cm}^{-1}$ when the Co cation

adsorbed more than one NO molecule (Figure 17). At the same time, the absorption edge at $40,000\text{ cm}^{-1}$ moved towards lower wavenumbers, e.g. $36,000\text{ cm}^{-1}$, which indicated that charge transfer occurred. The intensity of the $16,000\text{ cm}^{-1}$ peak decreased with increasing NO pressure and split into two peaks. The $18,500\text{ cm}^{-1}$ peak was broadened by addition of the new peak at $20,500\text{ cm}^{-1}$. Evacuation at room temperature could not regenerate the original spectrum (Figure 18); however, the $16,000\text{ cm}^{-1}$ peak increased in intensity while the $20,500$ peak decreased to form a 1:1 intensity ratio. The thermal desorption experiment extended up to 350°C partially regenerated the spectrum, which gave the original relative peak intensities at $16,000$ and $18,500\text{ cm}^{-1}$ and reappearance of the $24,500\text{-}25,000\text{ cm}^{-1}$ band. However, the intensity of the latter peaks was much lower than the original intensity (the spectra intensity of the original sample to the NO treatment sample was about 4:1, as shown in the Figure 19). After H_2 reduction at 350°C , the spectrum was fully regenerated.

When CoA zeolite was heated in the presence of NO (750 torr), the spectra showed similar features to those of the thermal desorption spectra. However, there was no recovery in the $24,500\text{-}25,000\text{ cm}^{-1}$ region. There was a new peak at $31,000\text{ cm}^{-1}$ when the treatment temperature was above 300°C (Figure 20). Evacuation at 350°C did not eliminate this peak, but the loss of this new peak was achieved by H_2 reduction at the same temperature. The corresponding gas components after exposure of NO on CoA and after hydrogen reduction at various temperatures are shown in Figures 21 and 22, respectively. It is probably reasonable that no oxygen was detected, for oxygen will react with NO to form NO_2 immediately at these reaction conditions. However, in the case of N_2O , the oxygen did not react with N_2O and could recombine to form O_2 . N_2O was not necessarily an intermediate in the NO decomposition.

4. Adsorption of NO₂ on CoA Zeolites

The adsorption of NO₂ on CoA was studied by UV-VIS-NIR spectroscopy. The NO₂ tested sample exhibited strong absorption spectral band centered at $\approx 32,000\text{ cm}^{-1}$ wavenumbers (Figure 23). Thermal desorption at 350°C did not generate the 24,500-25,000 cm^{-1} peaks (Figure 24). This indicated that the adsorption of NO₂ was stronger than that of NO and N₂O. Hydrogen reduction treatment at 350°C gave the same reduction products, H₂O, N₂ and NO, as in the case of the NO treatment sample (Figure 22). Regeneration of the 24,500-25,000 cm^{-1} spectra feature could also be achieved by H₂ reduction at the same temperature. However, complete regeneration required several cycles of hydrogen exposure and evacuation of the reduction products. These experiments indicate that NO₂ may be a surface complex formed during the NO decomposition. The amount of NO₂ formed was small and was strongly held by the surface. Thus, NO₂ was not easily detected in the gas phase but was easily reduced by H₂ in the case of NO decomposition.

FIGURE 1

R.T. isotherms of N₂O on Co_{2.6}(II)A

FIGURE 2

FIGURE 3

Dehydrated $\text{Co}_{2.6}\text{A}$ zeolite

FIGURE 4

$\text{Co}_{2.6} \text{ A zeolite} + 100 \text{ torr } \text{N}_2\text{O} \text{ (} 0.97 \text{ N}_2\text{O/Co}^{2+}\text{)}$

FIGURE 5

Co_{2.6} A zeolite + 750 torr N₂O (2.7 N₂O/Co²⁺)

FIGURE 6

Spectra subtracting from bare site $\text{Co}_{2.6}$ A zeolite

FIGURE 7

Co_{2.6} A zeolite heated up to 200°C at 750 torr of N₂O

FIGURE 8

Co_{2.6} A zeolite heated at 250°C at 750 torr of N₂O

FIGURE 9

Co_{2.6} A zeolite heated at 300°C at 750 torr of N₂O

FIGURE 10

Gases Component of N₂O(750 torr) on CoA
at various temperatures.

FIGURE 11

CO₂. A zeolite heated at 350°C at 750 torr of N₂O

FIGURE 12

CO₂, A zeolite desorption at 350°C

FIGURE 13

FIGURE 14

FIGURE 15

Gases components of H₂ reduction of CoA
at 350C after thermal evacuation.

FIGURE 16

FIGURE 17

FIGURE 18

CO_{3.9} A zeolite desorption at different temperatures
after NO treatment

FIGURE 19

Co_{3.9} A zeolite 1) fresh sample
2) after 1 time NO treatment
3) after 2 time NO treatment

FIGURE 20

$\text{Co}_{3.9}$ A zeolite heated at different temperatures
in the presence of 750 torr

FIGURE 21

Gases components of NO(750 torr)on CoA
at various temperatures.

FIGURE 22

Gases components of H₂ reduction of CoA
at 350C after thermal evacuation.

FIGURE 23

CO_{3.9} A zeolite after NO₂ adsorption at 750 torr at R.T.

FIGURE 24

$\text{Co}_{3.9}$ A zeolite desorption at 350°C after NO_2 adsorption

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