BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

Technical Progress Report for the Period

September 1991–November 1991

Kamil Klier
Richard G. Herman
and
Shaolie Hou

Zerlemoyer Center for Surface Studies
and Department of Chemistry
Lehigh University
Bethlehem, PA 18015

December 1991

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-89PC89784

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DEC 23 1991

BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

Disclaimer

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States DOE, nor any of their employees, nor any of their contractors, subcontractors, of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

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 catalysts 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.

BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

SUMMARY OF TECHNICAL PROGRESS

Adsorption and desorption experiments with NO have been carried out on sodium type A zeolite. The volumetric measurement showed that 1 g of zeolite could hold about 20 mg NO at a pressure of 700 torr at room temperature. Although the amount of desorbed NO was up to 95% around 623K, the diffuse reflectance optical spectrum of the sample was not recovered completely after desorption up to 623K.

Zeolite catalysts containing the rare-earth element cerium have been obtained via a solid state ion exchange method. Both CeNaA and CeCoA zeolites were prepared, and these catalysts were characterized by X-ray powder diffraction. Optical studies are in progress.

TECHNICAL PROGRESS

NaA zeolite is the parent material of the CoA zeolites being investigated in this research. The 12 sodium ions can be replaced by transition metal cations and rare-earth cations such as Co^{2+} and Ce^{3+} . In this research, $\text{Co}_{1.3}\text{A}$ has 9.4 Na^+ per unit cell and $\text{Co}_{3.9}\text{A}$ has 4.2 Na^+ per unit cell. The study of NO adsorption on NaA zeolite will provide useful baseline information about the behavior of CoA and CeCo exchanged A zeolite catalysts.

NO Adsorption and Desorption on NaA Zeolite

Experimental

The apparatus utilized for the optical measurements and for the adsorption and desorption experiments was described in our earlier report.¹

The sample of about 2 g NaA zeolite was dehydrated first. NaA was outgassed for 6 h at 373K and gradually heated up to 600K at the rate of 50K per half hour. Finally, the sample was kept at 600K for another 6 h under vacuum of about 10^{-5} torr pressure.

The NO was purified by passing the gas through a trap maintained at the melting temperature of pentane at 143K before adsorption. The pressure and temperature of the gas were kept the same as for CoA. After evacuation at room temperature, the sample was heated at the rate of 5K/min from 323K up to 623K. The gas phase analysis was carried out by the Micro Mass Spectrometer coupled to the vacuum line. The mass units monitored were 14, 16, 28, 30, 32, 44, and 46.

The optical measurements were performed after the sample was cooled to room temperature. The optical measurements were repeated after NO adsorption and desorption.

Results

Dehydration. The spectrum of the hydrated sample NaA showed two intense peaks corresponding to water absorption bands at 5,300 and 7,000 cm^{-1} and some broaden peaks at about 12,000 cm^{-1} . After dehydration, all the water bands were eliminated and the spectrum (Spectrum 1 in Figure 1) only gave a very broad peak around 39,000 and an edge at 47,000 cm^{-1} . In the range from 4,700 cm^{-1} up to 35,000 cm^{-1} , there is no optical adsorption at all.

Adsorption. Upon adsorption of NO, there is no color change and the volumetric measurement showed that 1.31×10^{-3} mol NO was held by 1.85 g dehydrated NaA. This corresponds to 1.2 mole NO per unit cell or 20 mg NO per g zeolite.

The spectrum after NO adsorption is shown in spectrum 2 (Figure 1). There is no major change except the broaden peak and the adsorption edge were shifted toward smaller wavenumber by 10,000 and 5,000 cm^{-1} , respectively.

Desorption. After evacuation at room temperature, the desorption was performed in the range from 323 to 623K. The thermal programmed desorption (TPD) profile is shown in Figure 2. There is a major peak around 423K and a small peak around 573K.

The optical spectra during the desorption showed that the intensity of the small peak around 29,000 cm^{-1} decreased as the temperature increased and the adsorption edge shifted back toward larger wavenumbers, but the 623K spectrum (Spectrum 3 in Figure 1) showed there was incomplete recovery compared with the starting dehydrated sample. Even after the sample was heated in the presence of H_2 up to 423K, the spectrum (Spectrum 4 in Figure 1) did not completely recover.

The gas phase analysis indicated there was only NO principally involved in these adsorption and desorption processes. When the temperature was raised up to 500K, there was only a trace of NO_2 found.

Discussion

The NO adsorption on NaA was not very weak since the desorption had to be done at the elevated temperatures. The optical spectra showed that there was some strong charge transfer during the adsorption since the edges were shifted. This kind of shifting was also found in the case of NO adsorption on CoA. However, compared with NO adsorption on CoA, there was no decomposition of NO associated with the adsorption and desorption processes. The reactant remained as the NO molecule, and there was only a trace of NO₂ detected at 500K.

The TPD profiles indicated there was one major peak around 423K, which was related to the desorption of NO held by NaA. The small peaks at high temperatures seem to be due to NO₂ formation.

Solid State Ion Exchange

Introduction

Cerium oxide is generally added to automotive three-way catalysts as a promotor or as an oxygen storage component under cycled air-fuel ratio conditions. It has been reported² that cerium stabilizes the alumina support against thermally induced surface area loss and increases and stabilizes the dispersion of noble metals. In addition to these beneficial effects, cerium can alter the kinetic behavior of automotive catalyst as a result of its interaction with supported noble metals. Oh³ reported that the addition of cerium to a low-loaded Rh/Al₂O₃ catalyst gave rise to the following changes in the CO-NO reaction kinetics: suppression of N₂O formation, decreased apparent activation energy, and a shift to a positive-order dependence of the rate on NO partial pressure. These cerium-induced modifications of the kinetics lead to enhancement of the NO reduction activity at low temperature. Here, we introduced Ce into NaA and CoA zeolites by solid ion exchange in order to examine the behavior of catalyst under

NO adsorption and CO-NO reaction.

For A type zeolite, ion exchange equilibrium have involved mostly univalent and divalent counter ions. Attempts to exchange with trivalent Ce ions were unsuccessful by conventional aqueous solution at 363K. Subsequently, the solid-state ion exchange between CeCl_3 and A type zeolite (hydrogen and sodium forms and also coexchanged with Co^{2+}) has been studied. Results indicate that CeA zeolite can be obtained by this method by mixing NaA and CeCl_3 at ambient temperature. Cerium also can be exchanged into CoNaA zeolite successfully. However, the hydrogen-form zeolite was structurally destroyed when heated with CeCl_3 during the reaction.

General Procedure

The general procedure for carrying out solid-state ion exchange is simple. Finely dispersed powders of the zeolite and a salt or oxide of the in-going cation are carefully mixed and heated, either in a stream of inert gas or in high vacuum. In fact, the temperature required for achieving a certain degree of exchange usually depends on the nature of the cations and anions involved. In some cases, a portion of the cations is exchanged even during grinding of the salt-zeolite mixtures at ambient temperatures. The effect of the duration of heat treatment is less pronounced.

Solid state ion exchange may be carried out in stoichiometric mixtures of salts or oxides and zeolites, as related to the Al content of the zeolite framework (the ion exchange capacity). However, this ion exchange process also works with sub- or super-stoichiometric mixtures. In the latter case, the excess salts may be removed by brief extraction of the solid-state reaction product with water; also salts occlusion may occur during heat treatment. Thus, with many important salt(oxide)-zeolite systems, the desired degree of exchange, even a 100% exchange, can be achieved in a one-step procedure.

There are quite a number of experimental techniques to prove qualitatively, and determine quantitatively, the extent of solid-state ion exchange such as chemical analysis, ESR, IR, XRD, MAS-NMR, etc.

Experimental

A. Exchange with Hydrogen Form Zeolite

The ammonium-exchanged A zeolite was prepared by treating 10 g NaA zeolite with 50 ml of 0.1N NH_4Cl solution at 343K for 30 min. The NH_4Cl solution was then decanted and a new portion of 0.1N NH_4Cl solution was added to the zeolite (repeated 5 times) leaving the zeolite in contact with the NH_4Cl solution for a total of 2.5 h. Then the NH_4A sample was washed with deionized water and dried at room temperature. The ammonium A zeolite was treated with aqueous $\text{Co}(\text{NO}_3)_2$ solution at 353K for 2.5 h. After filtration the resulting cobalt, ammonium-exchanged A zeolite (CoNH_4A) was rinsed and dried at room temperature. CoNH_4A zeolite was then placed in a tube that was coupled to a vacuum line, evacuated for 30 min, and then treated by raising its temperature to 623K for 1 h to obtain the hydrogen form of the zeolite (CoHA).

The H^+ form of the zeolites and $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ were intimately ground together in air. The mixture contained 1 Ce^{3+} per 3 Al of the zeolite structure, and it was placed in a quartz tube and cautiously heated to 423K for 2 h and then to 623K for another 2 h. The evolved hydrogen chloride was trapped in the vacuum line.

B. Exchanged with Sodium Form Zeolites

Both the NaA and CoNaA zeolites were mixed with stoichiometric $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ with 1 Ce^{3+} per 3 Al of the zeolite structure. Then the mixture was mechanical ground in a mortar for 30 min at room temperature in the presence of moisture. The CoNaA zeolite was prepared with the conventional solution ion exchange and contained about 1 Co per unit cell.

Results and Discussion

The samples were studied by the X-ray powder diffraction and the X-ray powder diffraction patterns for NaA is shown in Figure 3. Typical X-ray powder diffraction patterns for NH_4A and CoNH_4A zeolites are shown in Figures 4 and 5. Both the ion exchanged samples were obtained by conventional ion exchange. The crystallinity was not changed significantly although the intensity of some peaks are different. For example, the intensity of the peaks with Miller index (220) is larger than that of the peak (222) in the case for NaA. However, the two intensities became equal in the case of NH_4A and the intensity of the peak (220) even became smaller than that of (222) in CoHA zeolite. The unit cell constant increased from 12.30 Å for NaA to 12.32 and 12.38 Å for NH_4A and CoNH_4A , respectively.

After heating the mixture of CoHA and cerium chloride, the HCl evolved was detected by the mass spectrometer that is coupled to the vacuum line. However, the X-ray powder diffraction pattern (Figure 6) showed the amorphous feature of the final zeolites. The peaks at $2\theta = 28.67, 33.23, 35.27, 47.71$ and 56.54 degrees have d-spacings of 3.11, 2.70, 2.54, 1.90 and 1.62 Å, respectively. It is the typical X-ray powder diffraction pattern for CeO_2 . It indicated that the zeolite was destroyed by this treatment. The evolved hydrogen chloride may be the cause, for A type zeolite belongs to low Si/Al zeolite group and it is not stable in the presence of a strong acid. However, the destruction may be caused by the reaction between the Ce and Co ions at elevated temperature.

The X-ray powder diffraction patterns for mixtures of CeCl_3 with NaA and with CoNaA are shown in Figure 7 and 8. The major peaks of A type zeolite still appeared though the crystallinity was decreased a little bit. The most important information is that in both cases, the reflection peaks of crystalline NaCl were observed. The NaCl peaks that were not overlapped with zeolite peaks are located at $2\theta = 28.1, 31.7$, and 45.4 degrees, having d-spacing of 3.17, 2.82

and 1.99 Å, respectively. The most likely explanation for the observation is that a fraction of the sodium cations, which were expelled from the cation sites by Ce^{3+} , formed NaCl crystallites at the outer surface of the zeolite particles. Another fraction of the sodium cations or the remaining CeCl_3 may be dissolved in the intracrystalline water that can not be detected by XRD. However, the Ce^{3+} must be at least partially exchanged into zeolite. This result agrees well with some other reported work on solid ion exchange between Na type zeolite and various metal cations.⁴

References:

1. Klier, K., Herman, R.G., and Hou, S., Technical Progress Report DOE/PC/89784-6 (March 1991).
2. Harrison, B., Diwell, A. F., and Hallett, C., Platinum Met. Rev., 32, 73 (1988).
3. Oh, S. H., J. Catal., 124, 477 (1990).
4. Beran, S., Wichterlova, B., and Karge, H. G., J. Chem. Soc. Faraday Trans. I, 86, 3033 (1990).

FIGURE 1

FIGURE 2

TPD profiles of NO on NaA

FIGURE 3

Sample: NaA File: SY00: SHU1J02.SM

FIGURE 4

Sample: NH4A File: SY00: SHU2J02.SM

Sample: CoA File: SY00: SHU3J02.SM

FIGURE 5

Sample: CeCoA File: SY00: SHU4J02.SM

FIGURE 6

FIGURE 7

Sample: CeNaM File: SHU5.SM

FIGURE 8

Sample: CECOM File: SHU10J03.SM

END

DATE
FILMED

4 102 192

I