BINDING AND CATALYTIC REDUCTION OF NO BY TRANSITION METAL ALUMINOSILICATES

Technical Progress Report for the Period
March 1992-May 1992

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June 1992

PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-FG22-89PC89784

MASTER

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JUN 30 1992

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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_a 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

Na, Co^{2+} , Ce^{3+} , and $\text{Co}^{2+}\text{Ce}^{3+}$ exchanged A type zeolite have been tested for NO and N_2O adsorption and decomposition at room temperature. Dynamic temperature programmed desorption (TPD) studies were also carried out with these four zeolites, as well as with CeO_2 and CoA zeolite mixed with CeO_2 . It was demonstrated that NO was especially decomposed into N_2 , with some N_2O , over the doubly ion exchanged CoCeA zeolite that contained 1.77 Co and 2 Ce per unit cell. Some segregation of CeO_2 occurred during these experiments, and a lower content of Ce in the the CoCeA zeolite might be utilizable.

TECHNICAL PROGRESS

Adsorption and desorption of NO and N₂O were studied over the parent NaA zeolite and the Co and Ce ion exchanged NaA zeolites using isothermal adsorption and thermal desorption techniques. The addition of Ce to CoA zeolite enhanced direct NO decomposition. The higher activity might be ascribed to the redox property of Ce.

Experimental

The transition metal- and cerium-containing zeolites were prepared by ion exchange method described in previous reports. The starting material was sodium type A zeolite with 12 Na cations per unit cell. The Co²⁺, Ce³⁺, and Co²⁺Ce³⁺ exchanged A zeolites were prepared as 1.77 per Co per unit cell, about 3 Ce per unit cell, and 1.77 Co and 2 Ce per unit cell, respectively.

The behavior of NO and N₂O over sodium and metal cation-containing zeolites was investigated by the temperature programmed desorption (TPD) method in a conventional vacuum system. The apparatus for the TPD experiments consisted of a quadrupole mass spectrometer as a detector, a reactor within a furnace, thermocouple, and a temperature programmer. A turbopump was used to maintain the high vacuum. The NO was purified by a cold trap at -135°C maintained by a pentane slurry, and the gas phase before adsorption was checked by mass spectrometry. NO was the only component detected before contacting with zeolites. After evacuating the system overnight at 110°C and then for 2 hr at 350°C to a residual pressure less than 10⁻⁵ torr, the samples (each about 100 mg) were cooled to room temperature and were exposed to 50 torr NO or N₂O for 0.5 hr, followed by further evacuation for another 0.5 hr. TPD was subsequently carried out with a heating rate 10°C

min⁻¹. The desorbed species were analyzed by mass spectrometry by monitoring mass units at 30(NO), 44(N₂O), 28(N₂), 32(O₂), and 46(NO₂).

Results and Discussion

The monitoring of gas-phase species by the mass spectrometry after adsorption of NO on CoA and CoCeA zeolites at 25°C showed the presence of both N₂O and N₂. The appearance of N₂O and N₂ in the gas phase demonstrated that the decomposition of NO occurred even during NO adsorption at 25°C. After incorporating Ce into the CoA zeolite, the activity of this NO decomposition was further enhanced as shown by increased N₂ formation.

Under the dynamic conditions for which the catalytic reactions proceed, reaction intermediates are generally so unstable that they are difficult to clarify. Thus temperature-programmed desorption was applied here to the various zeolite systems to determine the nature of the intermediates. The vacuum system was used to prevent the readsorption of products, and a small amount sample was used to make sure the sample was heated homogeneously without the presence of carrier gas.

The typical NO desorption patterns for NaA, CoA, CeA, and CoCeA are shown in Figures 1-4. The components of desorbed gases are shown in Table 1.

For the metal ion exchanged zeolites, the NO desorption peaks tended to be broader than that of the parent NaA zeolite. The NO TPD peaks are all centered around 100-200°C. However, the CeA zeolite (Figure 3) showed two overlapped peaks at 100 and 200°C. After incorporating Ce into CoA, the NO peak became broader and the peak maximum shifted toward higher temperatures, i.e. from ≈100-150°C to ≈130-190°C. The major difference is that in CoCeA, the amount of N₂ desorbed was appreciably greater than

TABLE 1. Desorbed gas phase species observed during dynamic TPD over various zeolites after NO adsorption.

Sample	Gases
NaA	NO
CoA	NO, N ₂ O(small), N ₂ (very small)
CeA	NO, N ₂ O(small)
CoCeA	NO, N ₂ , N ₂ O(very small)

that in the case of CoA, while the amount of desorbed N₂O decreased compared with that in CoA but shifted to higher TPD temperatures.

In order to understand the production of N₂O from NO and subsequent desorption, N₂O was adsorbed on various zeolites at 25°C under identical conditions used for the NO adsorption experiments. The TPD patterns for N₂O desorption are shown in Figure 5-8. The observed components of the desorbed gases are shown in Table 2.

TABLE 2. Desorbed gas phase components observed by dynamic TPD after N₂O adsorption on various zeolites.

Sample	Gases
NaA	N ₂ O
CoA	N ₂ O, N ₂ (small), O ₂ (small)
CeA	N ₂ O
CoCeA	N ₂ O, NO(very small)

There were no desorbed gases other than N_2O observed with the NaA and CeA zeolites. However, there was a difference in the cases of CoA and CoCeA zeolites. For CoA, N_2 was desorbed beginning at $150^\circ C$, while O_2 was desorbed in significant quantities beginning at $\approx 275^\circ C$. These results indicate that N_2O was decomposed by this catalyst into N_2 and O_2 at $150^\circ C$ but that O_2 was held by the zeolite until it was released at higher temperature. For CoCeA, there were two TPD peaks observed for NO centered at $\approx 150^\circ C$ and $\approx 300^\circ C$ and a very small amount of N_2 desorbed above $300^\circ C$. This indicated that N_2O did not decompose into N_2 and O_2 under the same conditions on CoCeA as for the CoA zeolite.

Since the X-ray diffraction pattern of the used CoCeA zeolite showed CeO_2 formation after the NO adsorption/desorption experiments, the dynamic NO TPD studies were carried out with CeO_2 and with CoA zeolite mixed with CeO_2 . The TPD patterns are shown in Figures 9 and 10. Clearly, there was no large amount of N_2 desorbed from either one of the two samples.

Under the dynamic vacuum reaction conditions employed in these TPD experiments, the CoCeA zeolite enhanced the direct decomposition of NO into N_2 , relative to the singly ion exchanged A zeolites. The decomposition pathway apparently does not involve N_2O as an intermediate state. Since some CeO_2 was formed outside the zeolite cages as a separate phase during these TPD experiments, lower concentrations of Ce ion exchanged into the CoA zeolite may be favorable.

FIGURE 1

TPD of NO adsorbed on NaA at R.T.

FIGURE 2

TPD of NO adsorbed on CoA at R.T.

FIGURE 3

TPD of NO adsorbed on CeA at R.T.

FIGURE 4

TPD of NO adsorbed on CoCeA at R.T.

FIGURE 5

TPD of N₂O adsorbed on NaA at R.T.

FIGURE 6

TPD of N₂O adsorbed on CoA at R.T.

FIGURE 7

TPD of N₂O adsorbed on CeA at R.T.

FIGURE 8

TPD of N₂O adsorbed on CoCeA at R.T.

FIGURE 9

TPD of NO adsorbed on CeO₂ at R.T.

FIGURE 10

TPD of NO adsorbed on CoA/CeO₂ at R.T.

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