NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

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SUMMARY OF TECHNICAL PROGRESS

During this quarter, a new researcher was employed to work under the sponsorship of this research project. While this researcher was becoming familiar with the research that is being carried out in regard to the activation and decomposition/reduction of NO over metal cation exchanged zeolites, the experimental results previously obtained here were further analyzed and a manuscript was written and submitted for presentation and publication at the International Zeolite Conference that will be held in Germany this summer. This further analysis and summary is given in this progress report. In particular, a clear distinction is made between temperature programmed desorption studies (TPD) carried out under a dynamic vacuum and temperature programmed reaction studies (TPR) that were carried out under static conditions where it was possible for the reaction products to react further with the catalyst. The basic conclusions are consistent with those reported in the final report for our previous research project [1].

In this study probing the conversion of NO to $\text{N}_2 + \text{O}_2$ over Co(II) exchanged A zeolite, it was found that the Co(II) A zeolite adsorbed up to three NO molecules per Co(II) cation. Static and dynamic temperature programmed reaction/desorption (TPR/TPD) experiments demonstrated that the Co(II) enhanced the adsorption and decomposition of NO and that both N_2O and N_2 formed over these catalysts. It was further found that a doubly exchanged Co(II)Ce(III) A zeolite was active in the decomposition of NO under mild reaction conditions, e.g. with desorption and conversion activity during TPD experiments beginning by 75°C. Under static TPR conditions over this doubly promoted catalyst, the principal product was N_2 , while under dynamic vacuum TPD conditions N_2O

was formed as the favored product formed at temperatures less than 250°C. It was shown that N_2O was not decomposed by itself over this catalyst under the reaction conditions employed. Since N_2 was a dominant product when Ce(III) was added to the Co(II) A zeolite, it appears that the presence of Ce(III) induced a new low temperature mechanism for NO decomposition. During NO TPD/TPR studies with these zeolite catalysts, the oxygen tended to be held in the zeolite until higher temperatures were reached. In the presence of excess Ce(III), this oxygen promoted formation and segregation of CeO_2 , which was quite inactive by itself. Monitoring of the catalysts by optical spectroscopy during all stages of these experiments confirmed the accessibility of the trigonally held transition metal cations and that NO adsorption was strong and reversible under ambient conditions.

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TECHNICAL PROGRESS

1. INTRODUCTION

Nitric oxide, NO, is thermodynamically unstable with respect to its decomposition to elements,

and yet it has proven kinetically stable unless a suitable catalyst is used. There are surprisingly few catalysts for the above reaction, among them noble metals Rh, Pd and Pt, from which only rhodium has passed the test of demanding conditions for practical applications such as in the car exhaust catalysis. The mechanism of NO decomposition over these noble metals is simple, beginning with dissociative chemisorption [2], e.g.

followed by recombination of the chemisorbed nitrogen atoms to N_2 and of the chemisorbed oxygen atoms to O_2 . The latter process occurs only at very high temperatures [2], and in real catalytic conditions the surface oxygen still has to be removed by a reaction with reducing gases such as CO or hydrocarbons. The effective catalytic action of rhodium metal is due to its ability to attack the NO molecule from both the nitrogen and the oxygen end, to the weak bonding of the surface nitride, and to the reducibility of surface oxygen. Rhodium catalysts *do not* work in excess oxygen because bulk oxides are formed irreversibly and the catalytic action of the essential metallic phase is lost. There is a well-recognized scientific challenge of decomposing NO in non-reducing, i.e. neutral or oxidizing, atmospheres.

The principal difficulty in decomposing NO over non-metallic catalysts is the tendency of NO to donate its odd π^* electron to its molecular environment,

by which process the bond order of neutral NO, 2.5, increases to that of $\text{NO}^\oplus$, 3, with a concomitant shortening of the N-O distance and stabilization of the undissociated species in the ligand sphere of the electron acceptor. In zeolites, many transition metal ions react with NO in this way, for example

There are, however, surface complexes in zeolites in which NO acts as a neutral ligand, and multiple nitrosyl adducts with a single metal center are formed [3,4]. One such system consists of the $\text{Co}^{\text{II}}\text{-A}$ zeolite. Stoichiometry determinations revealed the existence of di- and tri-nitrosyl complexes with the cobalt ions, and spectroscopy pinpointed the valence state as Co^{2+} in all stages of the complex formation [1]. It was proposed that the $\text{Co}(\text{II})\text{-NO}$ complexes decompose by the pattern summarized in the **Reaction Scheme I** below.

The last step, desorption of oxygen, was incomplete under most reaction conditions, and for that reason it is desirable to find a suitable cation or pair of cations that will bind oxygen more weakly. The $\text{O}^\ominus\text{Co}^{\text{III}}\text{A}$ complexes could be reduced, e.g. by hydrogen, regenerating thus the primary catalytic site $\text{Co}^{\text{II}}\text{A}$ for repeating the cycle above. What

emerges here mechanistically is a bimolecular three-step mechanism (**Reaction Scheme II**) accompanied by an electron transfer in each step, i.e.

A redox system is desirable for this reaction cycle, and the transition metal zeolites are prime candidates as catalysts because there are many ways the transition metals can be introduced (as cation or framework sites) and their redox potentials controlled.

The approach to the initial selection of the cation was based on its having a suitable redox potential. The redox potentials in terms of oxidizabilities calculated with the use of ligand field theory based on observed spectral transition parameters are compared in Figure 1, adapted from Reference [5], for the divalent cations of the first transition series. The dotted area in Figure 1 locates redox potentials around the presently used Co^{II} A system. Oxidation potentials slightly below the dotted area will provide the desired conditions for the weakening of the $\text{O}^{\ominus}\text{-Me}^{\text{III}}$ bond; oxidation potentials well below the dotted area will be prohibitive for the *formation* of the $\text{O}^{\ominus}\text{Me}^{\text{III}}$ adduct; and redox potentials above the dotted area are conducive to the formation of a very stable $\text{O}^{\ominus}\text{Me}^{\text{III}}$ complex from which oxygen will not desorb. In fact, in the case of the Cr^{II} A zeolite, a stable covalent mono-oxygen complex was documented by Kellerman and Klier [6], which goes beyond $\text{O}^{\ominus}\text{Me}^{\text{III}}$ and is formally $\text{O}=\text{Cr}^{\text{IV}}$.

It is conceivable that other than $\text{Me}^{\text{II}}/\text{Me}^{\text{III}}$ redox couples may fall in the desired range. Such a system may be Iwamoto's Cu-ZSM-5 [7]. There are indications that this system utilizes the redox $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ couple [3] but, aside from showing encouraging catalytic results for NO decomposition, this system is not well characterized.

FIGURE 1. One electron ($\Delta E^{(1)}$) and two electron ($\Delta E^{(2)}$) oxidizabilities for the divalent ions of the first transition series in the D_{3h} sites in A zeolite [5]. Also shown is the third ionization potential ($-I_3$) of the metal under consideration. The primary interest is in the one electron oxidation, $M^{II} \rightarrow M^{III}$, especially in the area of the shaded band.

The conditions that a catalyst must satisfy to catalyze NO decomposition by Mechanism II are the following:

- (i) a metal ion center that binds NO into di- or higher coordinated nitrosyl complexes must be present,
- (ii) the metal ion must not be an electron acceptor such that a stable NO^+ ligand would form,
- (iii) the metal ion should have a sufficient but not overly strong potential for electron donation to form N_2O and the surface $O^\ominus$ intermediate, and
- (iv) the binding between the sorbed mono-oxygen and the metal ion must be sufficiently weak in order that the oxygen be removable by desorption rather than by reduction.

2. EXPERIMENTAL

The preparation of the Co(II) cation exchanged zeolites and subsequent pretreatment, characterization, and thermal desorption studies have been described in detail elsewhere [1,8]. Specific sample treatments are given in the following RESULTS section of this report.

3. RESULTS

3.1. Optical Spectra of Dehydrated Co(II) A Zeolites

Most of the studies carried out with respect to thermal dehydration utilized Co(II) A zeolite samples containing 1.3 and 3.9 Co(II) cations per unit cell. Dehydration of the ion exchanged A zeolite samples was carried out in the diffuse reflectance optical cell. Samples of ≈ 2.5 g Co(II) 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 optical measurements were performed after the sample was cooled to room temperature (RT). When samples were heated above 350°C, they exhibited a pale blue color, which is typical of dehydrated Co(II) A zeolites.

The diffuse reflectance spectra (DRS) obtained with the thermally dehydrated (to 350°C) Co(II) A zeolites were very similar to those reported earlier [9,10] and showed three distinguishing groups of peaks centered at $\approx 7,000$ cm^{-1} , 18,000, and 24,500 cm^{-1} , corresponding to d-d* transitions. The Co(II) ions are located almost in the plane of the three proximal oxygens, completing a nearly planar C_{3v} symmetry. A suitable representation for term labels is D_{3h} for which the electronic transitions corresponding to the optical bands are ${}^4E'' \rightarrow {}^4E'$, ${}^4E'' \rightarrow {}^4A_1''$, ${}^4A_2''$, and ${}^4E'' \rightarrow {}^4E''$, respectively [11]. Compared to the

hydrated Co A zeolite spectra (not shown, e.g. see [11]), the disappearance of sharp water and hydroxyl bands at 5,300 and 7,000 cm^{-1} confirm that the dehydration of the Co A zeolites was complete.

In the dehydrated Co(II) A zeolites, the 25,000 cm^{-1} band is a characteristic peak for the bare Co(II) ion with the trigonal symmetry, corresponding to the metal ions being located at or near the center of the 6-membered ring window. This exposed metal cation is the expected adsorption site for guest molecules. Thus, when the Co A zeolites are exposed to NO, the 25,000 cm^{-1} band was expected to be significantly affected by the NO ligand.

3.2. Adsorption and Desorption of NO on Co(II) A and Co(II)Ce(III) A Zeolites

The adsorption measurements were generally 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 NO gas at known pressure at room temperature. From the pressure drop, measured by a differential manometer, the volumetric measurement was achieved with an optimal accuracy of approximately 2-5%.

Upon exposure to purified NO at 700 torr and ambient temperature, the Co(II) A zeolites turned instantaneously gray or nearly black. As determined by desorption, approximately 2.5-3 NO molecules were adsorbed per Co cation. The spectra after NO adsorption showed that the major bands centered at about 24,500-25,000 cm^{-1} for the dehydrated samples disappeared for the NO/Co A samples. The peaks at 17,000-18,500 cm^{-1} were shifted to larger wavenumbers. This was especially shown with the 3.9 Co(II) A zeolite by sequentially increasing the NO pressure from 50 to 750 torr, which caused the optical band at $\approx 25,000 \text{ cm}^{-1}$ to disappear and the broad, strong band at $\approx 19,000 \text{ cm}^{-1}$

appeared and grew in intensity (Figure 2). This was accompanied by the appearance of a charge transfer band initiated at $\approx 31,000\text{ cm}^{-1}$. It is concluded that the Co(II) cations were highly accessible to NO and that the rather strong NO ligand altered the trigonal symmetry of the bare site Co(II) cation upon complexation. In addition, the quantity of NO adsorbed corresponded to more than 1 NO molecule/Co(II), as shown in the insert in Figure 2.

Upon evacuation (either dynamic or by sequential expansion) at RT, about half (≈ 1.5 NO/Co(II)) of the adsorbed NO could easily be desorbed, without significant change in the optical spectrum, and the color of the sample turned a dark blue/purple. Upon careful evacuation at 150°C , additional desorption occurred (corresponding to ≈ 0.5 NO/Co(II)), and the resultant optical spectrum was consistent with T_d mononitrosyl-Co(II) held in the trigonal window of the zeolite, as shown in Figure 3. Two bands located at $\approx 7,000$ and $\approx 17,000\text{ cm}^{-1}$ arise from the ${}^4A_2(F) \rightarrow {}^4T_2(F)$ and ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transitions, respectively, and each is split into three peaks because of the dynamic Jahn-Teller effect [11]. In addition, an intense charge-transfer band initiated at $\approx 25,000\text{ cm}^{-1}$ is observed. This is some $6,000\text{ cm}^{-1}$ wavenumbers lower than that observed when excess NO is adsorbed onto the Co(II) A zeolite, see Figure 2.

Following evacuation at 375°C , the pale blue color of the dehydrated sample was regained, and the optical spectrum corresponded to the original dehydrated near- C_{3v} Co(II), with recovery of the characteristic band at $\approx 25,000\text{ cm}^{-1}$. When the sample was again exposed to 700 torr NO, the optical spectrum indicated NO complexation to the Co(II) cations, and the volumetric results again corresponded to ≈ 3 NO molecules/Co(II). These results indicate that NO adsorption on Co(II) cations is strong but reversible.

FIGURE 2. Optical spectra obtained upon sequentially increasing the pressure of NO at ambient temperature over the dehydrated A zeolite containing 3.9 Co(II)/unit cell.

FIGURE 3. Optical spectrum (A) of the mononitrosyl Co(II) complex (B) in A zeolite.

3.3 Conversion of NO on Co(II) and Co(II)Ce(III) A Zeolites

Both *dynamic* temperature programmed desorption (TPD) and *static* temperature programmed reaction (TPR) experiments were carried out after adsorption of NO, as partly described above. In many cases, N₂O was observed by mass spectrometry (MS) in addition to NO, indicating that some NO decomposition/disproportionation had occurred. The adsorption/desorption experiments were carried out with a Co(II) Na A zeolite sample containing 1.77 Co(II) cations per unit cell and a Co(II) Ce(III) A zeolite containing 1.77 Co(II) and ≈ 2 Ce(III) per unit cell.

TPD/TPR using mass spectrometry detection of gas phase species was carried out after exposure of the samples to NO by using two procedures. In the first procedure, referred to as dynamic TPD treatment, the samples were typically exposed to 50 torr NO for 0.5 hr and evacuated at ambient conditions for 0.5 hr to remove weakly adsorbed NO. Maintaining the dynamic vacuum, TPD to 350°C was subsequently carried out with a heating rate of 10°C/min. Under these conditions, NO desorption exhibited a maximum desorption rate at $\approx 125^\circ\text{C}$ for both Na and Co A zeolites. In addition, over the Co A zeolite, small quantities of N₂ and N₂O were observed (as shown in Figure 4). Analogous experiments after adsorption of N₂O demonstrated that no decomposition occurred over Na A zeolite (90-235°C N₂O desorption peak centered at 170°C), but over the Co A zeolite desorption of the N₂O (broad peak centered at 170°C) was accompanied by some decomposition as evidenced by the larger than trace amounts of N₂ formed at 150-350°C and O₂ released at $> 280^\circ\text{C}$.

Over the Ce A zeolite, double maxima TPD curves of lower intensity were observed for both NO (100 and 200°C) and N₂O (100 and 260°C), as shown in Figure 4. The CoCe

FIGURE 4. Dynamic TPD curves obtained after adsorption of NO at ambient temperature.

A zeolite sorbed much more NO and most of the NO molecularly desorbed to give a broad flat-top peak, accompanied by a smaller amount of N₂O. Formation of the latter increased at temperatures >250°C, as did the formation of N₂, indicating an appreciable quantity of strongly held NO_x. Semi-quantitatively, much more N₂O and N₂ were formed over the CoCe A zeolite than for any of the other zeolites.

The static TPR experiments especially demonstrated the activity of the CoCe A zeolite for decomposition of NO. These experiments involved evacuation of the samples at ambient temperature after NO adsorption, isolation of the optical cell containing the sample from the vacuum manifold, and heating to 350°C at a rate that was typically 100°C/hr. This allowed the desorption/decomposition products to accumulate at low pressure over the catalyst. The products were analyzed approximately every six min by mass spectrometry *via* a leak valve. Under these conditions, NO desorption began at 50°C and exhibited a maximum desorption rate at ≈150-175°C for both Na and Co A zeolites. The dominant product was N₂O, but N₂ became a more important product at the higher temperatures (Figure 5). An analogous experiment after adsorption of N₂O demonstrated that very little decomposition of the N₂O occurred but that N₂O molecularly desorbed in the 150-225°C temperature range.

Most remarkable were the TPR data for the CoCe A zeolite following adsorption of NO. This catalyst was observed to be much more active than the Co A zeolite. The resultant static TPR curves are shown in Figure 5, and it can be seen that much of the NO was converted to N₂. When decomposition of NO occurred, desorption of O₂ was usually observed at high temperatures (>150°C). However, as evident in Figure 5, O₂ desorption was not significant in the temperature range employed. This was also the case during the dynamic vacuum TPD experiments, but here both N₂ and N₂O were observed as products.

FIGURE 5. Static TPR of NO over Co(II) and Co(II)Ce(III) A Zeolites.

Subsequent XRD analysis of the sample after the latter test demonstrated the presence of CeO_2 . Thus, part of the Ce segregated from the zeolite during the test, and perhaps a lower exchange level of Ce should be used. For bulk CeO_2 , dynamic TPD showed only a small NO desorption peak (MS signal = 0.7 a.u. at peak maximum).

Carrying out an analogous dynamic TPD experiment with N_2O on the CoCe A zeolite showed that the N_2O desorbed with a peak maximum at $\approx 150^\circ\text{C}$ and that significant amounts of N_2 were not formed upon TPD. This was in contrast to the results of NO TPR (Figure 5), where N_2 was the principal product. Thus, it appears that long residence times, i.e. TPR conditions, favor the decomposition of NO to N_2 . Possibly the Co^{II} ions are NO binders and the Ce^{III} ions provide the redox binding sites of high temperature oxygen,

4. CONCLUSIONS

Static/dynamic TPR/TPD experiments showed that Co(II) A zeolite adsorbed up to three NO molecules per Co(II) cation and that the Co(II) enhanced the decomposition of NO, where the dominant product tended to be N_2O , with smaller amounts of N_2 . It was found that the Co^{II} A zeolite decomposed NO under both TPD [12] and TPR conditions with greater efficiency if the Co-containing zeolite were co-exchanged with Ce^{III} . Since N_2 was a dominant TPR product over the doubly exchanged Co(II)Ce(III) A zeolite, it appears that the presence of Ce(III) promoted a low temperature process for NO decomposition.

The oxygen formed tended to be held by the zeolite lattice until temperatures $>250^{\circ}\text{C}$ were reached, at which point O_2 was desorbed. During these tests up to 350°C , CeO_2 segregated but was quite inactive by itself. This Ce(III) oxidation, migration, and segregation might be temperature dependent and favored by high reaction temperatures, e.g. $<250^{\circ}\text{C}$. This might be similar to the behavior of Cu(II) in Y zeolite in strongly reducing environments at $250\text{--}400^{\circ}\text{C}$ where reduction, migration, segregation, and agglomeration of Cu° occurs [13,14].

Monitoring of the catalysts by optical spectroscopy during all stages of these experiments confirmed the accessibility of the trigonally held transition metal cations, that NO adsorption is strong, multiple, and reversible under ambient conditions, and leads to NO decomposition under mild reaction conditions. The best *model* system so far investigated has been the Type A zeolite because of the uniformity and open coordination of the transition metal cations [15]. However, more stable zeolites, such as X, Y, ZSM-5, or ZSM-11, also are viable candidates as catalysts^a for NO decomposition if the Co(II) cations can be kept in open coordinated positions similar to those in A zeolite.

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