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NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
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SUMMARY OF TECHNICAL PROGRESS

Studies have been carried out with Co(II) A zeolites having 1.3, 1.8, and 3.9 Co(II) cations per unit cell. All of the samples were thermally dehydrated under vacuum in *in situ* diffuse reflectance optical cells, and the optical spectra were obtained in a broad spectral range of 4,500 to 45,000 cm^{-1} . Subsequently, the samples were exposed to excess NO, and the optical spectra were again obtained. The results show that the Co(II) cations in the dehydrated zeolites were only coordinated to the zeolite lattice in the 6-ring windows (with trigonal symmetry), and that multiple NO molecules adsorb onto each Co(II) cation upon exposure to excess NO.

During this quarter, we were in the process of arranging for a new researcher to work under the sponsorship of this research project.

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TECHNICAL PROGRESS

Research Objective

The objective of this research is to obtain the fundamental knowledge required for significant technological advancement in design of catalysts for conversion of NO_x to N_2 and O_2 under oxidizing or neutral environments that exist in exhaust gases and emissions of sources such as power stations. This goal presents a well-recognized fundamental scientific challenge with high practical impact for the world environment since it would alleviate the necessary addition of reducing chemicals such as ammonia to the flue gas that is common in many other processes currently in use or under development. The *redox* functions in our system would be provided by the redox transition metal/lanthanide cations in porous zeolite catalysts, and the net reaction would be decomposition of NO rather than its reduction by a gas phase reducing agent.

These studies involve the preparation, testing, and characterization of catalysts, e.g. Co(II) A zeolite, that might be more practical in terms of thermal stability, resistance to deactivation, and ability to stabilize promoters. In addition to Co(II) and Co(II)/Ce(III) A zeolites, Mn(II), Ni(II), and Cu(II) zeolites based on the more structurally stable X and Y zeolites, ZSM-5, and mordenite will be explored. Knowledge of the specific reaction kinetics and mechanistic pathways of NO conversion will result in the development of catalysts that are efficient in the active and selective decomposition of NO.

Preparation of the Co(II) A Zeolites

Following the research carried out in our earlier U.S. DOE-sponsored research, we have carried out dehydration and NO adsorption studies with Co(II) A zeolite to confirm and reproduce our previous results. The zeolites utilized consisted of ion exchanged A zeolites containing 1.3, 1.8, and 3.9 Co(II) cations per unit cell.

The preparation typically involved 5 g of Na A zeolite, obtained from Union Carbide Corp., slurried in 500 ml of distilled water, to which a known volume of 0.14 M $\text{Co}(\text{NO}_3)_2$ solution was added at room temperature. The resultant solution was heated to 80°C and continuously stirred for 2.5 hr, at which time the pH of the solution was ≈ 6 for the Co(II) preparation. The equilibrated slurry was filtered while hot, washed with hot distilled water, air-dried, and stored in closed sample bottles.

The optical spectral measurements were performed in the diffuse reflectance mode by using an Apple computer-controlled Varian 2300 spectrophotometer. The spectral measurements could be obtained in the range of 4,000 to 50,000 cm^{-1} , and spectral measurements are referenced to a Lab Sphere Spectralon standard. The resultant spectra were evaluated by transformation according to the Schuster-Kubelka-Munk relationship, $K/S = (1 - R_\infty)^2 / 2R_\infty = F(R_\infty)$, that gives the ratio of the absorption coefficient (K) to the scattering coefficient (S) as a function of $F(R_\infty)$ of the measured reflectance (R_∞).

The quartz sample cell used for obtaining the optical spectra had a 5 mm thick x 28 mm diameter infrasil window. The cell was connected *via* a flexible stainless steel tube and a Cajon VCR fitting to a small UHV line, which consisted of two parts. One was the UHV chamber with CF flanges mounted on a Balzer TPU 050 turbomolecular pump. Gas analysis was carried out by a VG Micromass 100F quadrupole mass spectro-meter *via* a leak valve. The other part of the UHV line was a gas chamber with 0.5 inch Cajon VCR fittings

that connected to the diffuse reflectance cell. It also contained a gas inlet (Nupro soft seal valves not bakeable $> 150^{\circ}\text{C}$), an ionization gauge, and a differential membrane manometer. The vacuum line permitted volumetric measurements, if desired.

Dehydration of the Samples

The optical experiments were carried out using ≈ 2.5 g of sample contained in the diffuse reflectance cell. Gentle evacuation of the cell and the zeolite was initially carried out at ambient temperature, and then the sample was heated to 100°C and evacuated for 6 hr. The sample was further heated by increasing the temperature to 350°C at the rate of 50°C every 30 min., and then the 350°C dehydration treatment was maintained for 6 hr under a vacuum of $\approx 10^{-5}$ torr. After cooling the light blue sample, indicative of dehydrated Co(II), to ambient temperature, the optical spectrum was obtained. The spectra, designated as **A**, of the dehydrated Co(II) A zeolite samples are shown in Figures 1-3. The two peaks located at $\approx 25,000\text{ cm}^{-1}$ are characteristic of trigonal Co(II) cations held in the zeolite windows, without being coordinated by any other ligand such as water.

Adsorption of NO by Co(II) A Zeolites

The adsorption of NO was carried out by expansion of the NO gas from the gas reservoir chamber (483 ml) into the individual optical cells (≈ 47 ml) containing the ion exchanged zeolites. For exposures to excess NO as carried out here, this resulted in ≈ 700 torr of NO being equilibrated with the zeolite samples. The resultant spectra, **B**, are shown in Figures 1-3. It is evident that the two peaks located at $\approx 25,000\text{ cm}^{-1}$ were no longer present, indicating the bare trigonal Co(II) has been complexed by NO. In addition, a strong band at $\approx 20,000\text{ cm}^{-1}$ has appeared, along with a strong charge transfer band at $\approx 37,000\text{ cm}^{-1}$. Brief evacuation at ambient temperature of the Co(II) A zeolite containing

1.8 Co cations per unit cell did not alter the features of the optical spectrum, as shown by spectrum C in Figure 2.

These spectra reproduce the results obtained in our earlier study. In addition, the spectra have been obtained to higher wavenumbers and on an intensity scale to show that the charge transfer band is actually a band centered at $\approx 37,000\text{ cm}^{-1}$ and not only an edge shifted by some $10,000\text{ cm}^{-1}$. The spectra indicate that more than one NO molecule is coordinated to the Co(II) centers because the spectra do not resemble that of 4-coordinate Co(II) cations in a distinct T_d environment, which is expected if the Co(II) centers were coordinated to the three oxygens in the 6-ring window of the zeolite and one NO molecule.

FIGURE 1. Optical spectra of the Co(II) A zeolite sample having 1.3 Co(II) cations per unit cell [A] after dehydration and [B] after exposure of the sample to excess NO.

FIGURE 2. Optical spectra of the Co(II) A zeolite sample having 1.8 Co(II) cations per unit cell [A] after dehydration, [B] after exposure of the sample to excess NO, and [C] after evacuation at ambient temperature.

FIGURE 3. Optical spectra of the Co(II) A zeolite sample having 3.9 Co(II) cations per unit cell [A] after dehydration and [B] after exposure of the sample to excess NO.

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