NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

Technical Progress Report for the Period
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SUMMARY OF TECHNICAL PROGRESS

The studies with Co(II) ion exchanged erionite zeolites, with Si/Al molar ratio of 3.6, have been continued. It was found that the paramagnetic moment of Co(II) in erionite (8 wt% Co(II)) dehydrated at 525°C was higher than that obtained after dehydration to only 350°C. This indicated that dehydration temperatures higher than 350°C are needed for the Co(II) erionite to achieve complete dehydration and uniform dispersion of the Co(II) cations into trigonal coordination sites in the zeolite. In contrast, it appears that the Co(II) cations in A zeolite achieve the uniformly dispersed trigonal symmetry state at the dehydration temperature of 350°C. Diffuse reflectance spectroscopy was utilized to monitor the spectral changes that occurred upon adsorption of CO and ethylene on the low Co(II)-containing erionite samples after dehydration at 350°C. This demonstrated that the Co(II) cations were accessible to these ligands and that CO-Co(II) and ethylene-Co(II) complexes were formed in the zeolites.

TECHNICAL PROGRESS

The research during this quarter was centered on the Co(II) erionite zeolite that was previously found to be fairly active at 400°C for the selective reduction of NO by methane in an oxidative atmosphere [1]. Under the conditions employed, the Co(II) erionite catalyst exhibited approximately the same activity (8.7×10^{-6} mol of NO converted /g of zeolite/sec) as the Co(II) ZSM-5 zeolite and double that of the Co(II) A zeolite [1]. In addition to optical studies (diffuse reflectance spectroscopy, DRS) of dehydrated Co(II) erionite samples [2], as well as of Co(II) erionite as a function of NO adsorption at increasing NO pressures [1], paramagnetic moments of the Co(II) ions in these zeolites had previously been measured [3], and a value of 5.0 Bohr Magnetons (BM) was observed for all three zeolites in the hydrated form. However, the value obtained for the Co(II) erionite dehydrated at 300°C was appreciably less (5.2 BM) than that of the Co(II) A zeolite dehydrated at 360°C [3]. Therefore, samples of Co(II) erionite were freshly dehydrated at the higher temperatures of 350°C and 525°C.

Magnetic Properties of Co(II) in Zeolites and Complexes

Dehydration at 350°C was carried out under dynamic vacuum (approximately 7×10^{-3} Torr) in a flask in the following three steps: 100°C for 1 hr, 220°C for 30 min, and 350°C for 3 hr. The heating ramp between these temperatures was 5°C/min. Samples that were dehydrated at higher temperature were then heated to 525°C using a heating ramp of 10°C/min and maintained at this temperature for 8 hr. The observed magnetic moments, obtained by the Gouy method at ambient temperature as described previously [3], are given

in Table 1. The measurements with each sample were repeated 5-10 times to obtain an error of measurement smaller than 5%.

TABLE 1. The magnetic susceptibilities of Co(II) in erionite (8% exchanged with Co(II)) and comparisons with dehydrated zeolite A and with literature reports for octahedral and tetrahedral Co(II) complexes.

Co(II) Cation Environment	Paramagnetic Moment (BM)
Hydrated	5.0
Dehydrated, 350°C	5.2
Dehydrated, 525°C	5.7
Dehydrated Co(II) A	5.6, Ref. 3
Dehydrated Co(II) A	5.65, Ref. 4
$[\text{Co}(\text{H}_2\text{O})_6]^{2+}$	5.1, Ref. 5
Tetrahedral Co(II)	4.4-4.8, Ref. 6

The high values of the magnetic moments of Co(II) in the dehydrated erionite samples indicate a high spin state for the Co(II) cation. The “spin only” magnetic moment for high spin Co(II) is 3.87, as determined by the formula $\mu_S = g\sqrt{S(S + 1)} = 2.00\sqrt{3/2(3/2 + 1)}$, where g is the gyromagnetic ratio and S is the sum of the spins of the unpaired electron [6], i.e. three unpaired electrons for Co(II). Since the experimentally determined magnetic moments in Table 1 are much higher than the expected “spin only” value, appreciable orbital angular momentum is also contributing to the magnetic moments of the Co(II) zeolites. This contribution arises from the motion of the unpaired electrons around the nucleus. The expected magnetic moment of high spin Co(II) taking account of both the spin moment and

the orbital moment can be calculated by the following formula: $\mu_{S+L} = \sqrt{4S(S+1) + L(L+1)}$, where $S = 3/2$ and $L = 3$ for the ground state quantum number of Co(II) [6]. This results in $\mu_{S+L} = 5.20$. The very high value of the magnetic moment of Co(II) in the dehydrated A zeolite has been attributed to the large orbital contribution to the magnetic moment of the Co(II) cation located in 6-ring window sites with trigonal planar symmetry [3]. The lower magnetic moment observed for Co(II) erionite dehydrated at 300 or 350°C indicates that a higher dehydration temperature, such as the 525°C that was utilized, is needed to completely dehydrate the Co(II) cation in this zeolite and to locate the cation in sites having a uniform symmetry environment.

Diffuse Reflectance Studies of the Adsorption of CO and Ethylene on Co(II) Erionite

To clarify the location and accessibility of the Co(II) cations in erionite, adsorption studies with CO and ethylene have been initiated. These studies, centered on changes in the electronic spectra of the zeolites upon formation of Co(II) complexes, are being carried out with the Co(II) erionite dehydrated only to 350°C and to the higher temperature of 525°C. After dehydration, CO (99.0+% from Aldrich Chem. Co.) and ethylene (CP Grade from Linde) were adsorbed at ambient temperature. The CO was dried by the freeze/thaw technique using a trap of liquid nitrogen. The amount of gas adsorbed was controlled by adsorption at various pressures from volumes of 40, 180, or 1400 ml. Pressures of gases before and after adsorption were measured using a Pirani vacuum gauge. Adsorption was complete when no decrease in the pressure of the adsorbing gas was observed during a time interval of 15 min.

Co(II) erionite samples containing 0.2, 1.7, 3.2, 6-8, and >8 wt% Co(II) were prepared by aqueous ion exchange. The first four samples were prepared by single equilibrations with Co(II) solutions, usually the acetate salt, of various molarities. The most highly exchanged sample was prepared using a three-step exchange process. The two more highly exchanged samples have not yet been quantitatively analyzed for Co(II) content.

Diffuse reflectance spectra were obtained at ambient temperature with the zeolites after dehydration at 350°C using a computer controlled Varian 2300 spectrophotometer. The spectra of the samples in the visible (VIS) spectral region are shown in Figure 1, where the spectra have been transformed according to the Schuster-Kubelka-Munk theory using the relationship $F(R_{\infty}) = (1 - R_{\infty})^2 / (2R_{\infty})$, where R_{∞} is the measured reflectance. The characteristic asymmetric absorption band centered at 15,000-18,000 cm^{-1} is evident for each sample. As the Co(II) content of the erionite was progressively increased, a band centered at about 19,000 cm^{-1} increased in intensity.

Accessibility of Co(II) cations in erionite to CO and ethylene was determined by adsorption and monitoring the DRS of the samples. The effect of CO adsorption on the 0.2 wt% Co(II) erionite dehydrated at 350°C is shown in Figure 2. Both the optical spectrum and the second derivative analysis demonstrate that the Co(II) cations were accessible to CO and formed a Co-CO complex with new characteristic bands. Analogous adsorption experiments were carried out with ethylene, and the resultant DRS data for the 0.2 wt% Co(II) erionite are shown in Figure 3. The spectrum of the ethylene-Co(II) complex is clearly different from that of the dehydrated Co(II) erionite and from the CO-Co(II) complex in erionite.

At least in the low ion exchanged samples of Co(II) erionite, the Co(II) cations were accessible to ligands that formed complexes with the cations. More highly exchanged samples will be studied, and experiments will also be carried out after the zeolites have been dehydrated at 525°C.

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FIGURE 1. Diffuse reflectance spectra (VIS DRS) of Co(II) erionite samples containing different Co(II) contents (0.2 to >8 wt% Co(II)) dehydrated at 350°C.

FIGURE 2. Effect of CO adsorption (solid curve) on the VIS DRS of 0.2 wt% Co(II) erionite dehydrated at 350°C (dotted curve). Also shown is the comparison of the second derivative spectral curves.

FIGURE 3. Effect of ethylene adsorption (solid curve) on the VIS DRS of 0.2 wt% Co(II) erionite dehydrated at 350°C (dotted curve). Also shown is the comparison of the second derivative spectral curves.