NO DECOMPOSITION IN NON-REDUCING ATMOSPHERES

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SUMMARY OF TECHNICAL PROGRESS

The overall goal of this research is to establish the fundamental science needed to develop catalysts that will exhibit high activity and selectivity in the decomposition of NO into N_2 and O_2 . This project is centered on the preparation, characterization, and testing of transition metal exchanged catalysts, especially Co(II) zeolites. Additional Co(II) exchanged A zeolite samples have been prepared in aqueous solution at pH = 5.0-6.1 that contain different exchange levels of Co(II). Some of these have been analyzed for Na and Co contents by chemical methods and by X-ray photoelectron spectroscopy. It was shown that preparation of the samples by ion exchange between pH $\approx$ 6 and 7 tended to give stoichiometric ion exchange of Co(II) for Na^+ . However, ion exchange at lower pH tended to lead to exchange with H^+ , while ion exchange at higher pH tended to lead to the presence of excess Co(II), probably by precipitation of a basic Co phase.

Systematic analyses of Na A zeolite, Co(II) A zeolites, and Co(II)/Ce(III) A zeolites, as well as Na X zeolite, Na Y zeolite, and Na mordenite for comparison purposes, have been carried out by X-ray photoelectron spectroscopy and Auger spectroscopy methods. Complete data analysis has not yet been carried out, but trends in some parameters have been noted, e.g. the relative intensity of the O $KL_{2,3}L_{2,3}$ line in the O 1s spectral region increases as the Si/Al ratio of the Na zeolites increases.

TECHNICAL PROGRESS

Preparation and Characterization of Co(II) A Zeolites

Additional Co(II) exchanged A zeolite samples have been prepared in aqueous solution at pH = 5.0-6.1 that contain different exchange levels of Co(II). In general, 10 g of the dry Na A zeolite was equilibrated in ≈ 200 ml of aqueous $\text{Co}(\text{NO}_3)_2$ solution, typically at 80°C , that contained a known quantity of $\text{Co}(\text{NO}_3)_2$. After a set period of equilibration, the sample was filtered, washed with hot water, and dried in air.

Some of these samples have been analyzed for Na and Co contents by chemical methods (by Galbraith) and by X-ray photoelectron spectroscopy (XPS). Comparison of the available analytical data is made in Table 1, which includes these recently prepared samples and previously prepared samples that were usually ion exchanged with Co(II) in aqueous solutions at higher pH.

It was shown that preparation of the samples by ion exchange between pH ≈ 6 and 7 tended to give stoichiometric ion exchange of Co(II) for Na^+ . However, ion exchange at lower pH tended to lead to exchange with H^+ , while ion exchange at higher pH tended to lead to the presence of excess Co(II), probably by precipitation of a basic Co phase. These observations are reflected by the comparisons in Table 1. Samples that were stoichiometrically exchanged with Co(II) gave approximately the same wt ratios for the bulk chemical analyses and for the surface XPS analyses. However, the samples that contained excess Co(II), e.g. Sample 12 prepared at high pH, gave a much higher Co/Na wt ratio by XPS analysis than for bulk chemical analysis. In contrast, samples prepared at pH 5.2-5.4 gave a lower total content of $(\text{Co(II)} + \text{Na}^+)$ by chemical analysis and a lower Co/Na wt ratio by XPS analysis than by chemical analysis. These latter observations indicate that the

A zeolite was partially ion exchanged with H^+ and that the surface of the zeolite particles were probably enriched with H^+ ions relative to $Co(II)$ (enhanced migration of $Co(II)$ into the zeolite particles).

Ion exchange experiments were also initiated with sodium exchanged zeolites in which the Na^+ ions are being exchanged with K^+ cations for subsequent XPS experiments. The parent zeolites consisting of Na^+ exchanged A, X, and Y zeolites, plus Na mordenite, were first examined by XPS analysis for relative Al content and Na content. The results are shown in Table 2.

TABLE 2. The Si/Al and Na/Al atomic ratios as determined by XPS line intensities for the A, X, and Y zeolites and mordenite that were used in this study. The estimated error in intensity ratios is ± 0.2 .

Zeolite	Si/Al ^a	Na/Al ^b
Na A	1.0	1.0
Na X	1.5	1.0
Na Y	4.3	0.9
Na Mordenite	12.3	1.0

^aEstimated from Al 2p and Si 2s photoelectron line intensities.

^bMean value estimated from the Na 2s/Al 2p and Na 1s/Al 2p photoelectron line intensity ratios.

Auger spectroscopy analysis of the Na^+ zeolites was carried out for all four of the zeolites as self-supporting pellets. The C 1s line (284.4 eV) was used as a calibration point. The O 2s Auger spectrum for the Na A zeolite was shown in the previous quarterly progress report [1], and it is shown again in Figure 1. The oxygen Auger spectra of the other zeolites were also obtained, and the intensities of the $KL_{23}L_{23}$ (1D_2) lines were compared with one another. It was observed that the relative intensity of this oxygen line increased as the Si/Al

ratio increased for the zeolites, as shown in Figure 2. At the same time, the relative intensity of the oxygen KL_1L_1 line decreased in the same series. Thus, the ratio of these two lines exhibited a significant increase at the Si/Al ratio increased, as also shown in Figure 2. Further analysis of the extensive Auger spectroscopy data needs to be carried out.

References:

1. K. Klier, R. G. Herman, and I. Jirka, Technical Progress Report DOE/PC/93222-5, 9 pp (January 1995).

FIGURE 1. Auger spectrum of Na A zeolite in the oxygen 2s region (obtained in ≈ 18 min). The curve resolution and fitting is typical for the Na zeolite samples.

FIGURE 2. (a) Relative intensities of the oxygen 2s KLL Auger spectral lines (normalized relative to the intensities of the photoelectron O 2s lines) for Na⁺ exchanged A zeolite, X zeolite, Y zeolite, and mordenite. (b) The ratios of intensities for O (KL_{2,3}L_{2,3})/(KL₁L₁) Auger lines for the four zeolites.