Activity of a $[Co^{III}(NH_3)_nNO]^{2+}$-Y Zeolite for the Catalytic Reduction of Nitric Oxide by Ammonia

By KENNETH A. WINDHORST and JACK H. LUNSFORD*

(*Department of Chemistry, Texas A&M University, College Station, Texas* 77843)

Summary The $[Co^{III}(NH_3)_nNO]^{2+}$ complex within a Y type zeolite is a catalyst for the conversion of NO and NH_3 to N_2 and H_2O at temperatures greater than 50 °C.

THE catalysed reduction of NO_x from effluent gas streams by reduction with ammonia has considerable technological importance.[1] Recent studies have demonstrated that the reactivity of nitric oxide co-ordinated to cobalt(II) in Y-type zeolites can be greatly enhanced by forming complexes with ammonia.[2] The presence of $[\mathrm{Co^{III}(NH_3)}_n\mathrm{NO}]^{2+}$ in a zeolite facilitates the intramolecular reaction between the nitrosyl and ammonia ligands, as well as the disproportionation of NO. The latter reaction, however, results in the formation of N_2O and $[\mathrm{Co^{III}(NH_3)}_n\mathrm{NO_2}]_2{}^{+}$ which terminates the catalytic activity of the cobalt ammine complex.

We report here that the cobalt ammine complex in a Y-type zeolite is indeed an active catalyst for the reduction of NO provided the partial pressure of NO in the gas phase is less than 1 Torr, thus eliminating the disproportionation reaction. The catalyst used was a cobalt(II)-exchanged NaY zeolite with approximately 13 Co^{2+} ions per unit cell. After degassing at 500 °C, 0·8 g of catalyst was cooled to 25 °C and exposed to 200 Torr of NH_3. Gas phase NH_3 was removed by evacuation, and a gas mixture consisting of 0·7 Torr NO, 50 Torr NH_3 and 710 Torr He was passed over the catalyst at a flow rate of 40 $cm^3\ min^{-1}$. The exit gas was analysed for N_2, NO, N_2O and H_2O.

The Figure shows the observed activity as a function of both temperature and time on stream. At temperatures below 50 °C the activity of the catalyst decreased continuously until no activity remained after 48 h on stream. The activity at 75 °C decreased to a steady state level at which 48% of the NO reacted. This corresponds to a rather small turnover number of $0{\cdot}15 \times 10^{-2}$ NO molecules per Co^{2+} ion min^{-1}. At 90 °C, essentially all of the NO initially reacted, and this activity remained constant for more than 70 h on stream. Under all conditions the major products were N_2 and H_2O, with only a trace amount of N_2O being observed; thus, the disproportionation reaction is negligible under the conditions of this experiment.

The mechanism for the reaction of NO with NH_3 *via* the $[\mathrm{Co^{III}(NH_3)}_n\mathrm{NO}]^{2+}$ complex has been discussed previously;[2] however, it was of interest in this work to determine the origin of the loss in activity at the lower reaction temperatures. I.r. spectra of thin zeolite wafers[2] were recorded at 25 °C while the reactants flowed over the catalyst. After 5 and 45 min in the reaction mixture and when $[\mathrm{Co^{III}NH_3)_6}]$ was exchanged into the zeolite, bands at 1360, 1470 and 1640 cm^{-1} were observed. The bands at 1640 and 1470 cm^{-1} are due to ammine and ammonium ion deformation modes respectively.[2] The band at 1360 cm^{-1} which grows slowly with time on stream is attributed to the $[\mathrm{Co^{III}(NH_3)_6}]^{3+}$ complex which forms in the zeolite. The position of the band is consistent with that observed for other salts of $[\mathrm{Co^{III}(NH_3)_6}{}^{3+}$;[3] furthermore, the band may be reproduced by direct exchange of $[\mathrm{Co^{III}(NH_3)_6}]^{3+}$ into a zeolite. Upon heating the $[\mathrm{Co^{III}(NH_3)_6}]^{3+}$-Y zeolite to 100 °C the band at 1360 cm^{-1} disappeared. These results suggest that the slow oxidation of the Co^{II} ammine complex to hexamminecobalt(III) is responsible for the loss in activity at the lower temperatures.

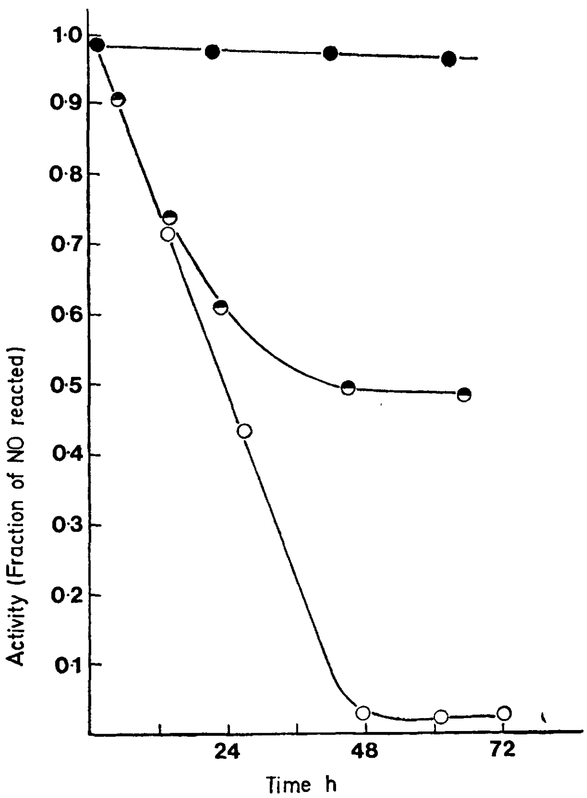

FIGURE. Plot of the activity (fraction of NO reacted) *vs.* time using 0·8 g of a Co-Y zeolite catalyst with reaction temperatures of 50 °C (○), 75 °C (◓), and 90 °C (●).

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