The Solvent-like Function of Zeolites. Comparison of the Catalytic Reduction of Nitric Oxide by Ammonia over Cobalt Amine Complexes in Y-Zeolites and in Solution

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Summary It has been demonstrated that the catalytic reduction of nitric oxide by ammonia proceeds over Co(LL) complexes (LL = NH_3, en = ethylenediamine, and trien = triethylenetetra-amine) in Y-type zeolites with the same mechanism as that in solution, indicating a solvent-like function of zeolites.

IT has been reported that Co^{III}–dinitro-bis(diamine) complexes catalyse the reduction of nitric oxide by ammonia to form nitrogen and nitrous oxide in solution in water, alcohol, dimethylformamide (DMF), or dimethyl sulphoxide at room temperature.[1] A large solvent effect is observed in this reaction, and the kinetics in DMF are quite different from those in aqueous solution, indicating the important role of the solvent. N.m.r. spectroscopic studies during the reaction seem to suggest that dissociation of the $-NH_2$ group of the diamine is required for the co-ordination of NO, which would be assisted by the solvent. This reaction, however, does not proceed over complexes supported on silica or alumina, probably because of the lack of the dissociation process.

Here we demonstrate that a zeolite can function in the same way as a solvent, *i.e.*, the NO–NH_3 reaction proceeds catalytically over Co^{III} $(LL)_{1-2}$ (LL = ethylenediamine or triethylenetetra-amine) complexes impregnated in Y-type zeolites, in a similar manner to that in solution. Lunsford *et al.* have reported the catalytic reduction of NO by NH_3 over Co^{II} and Co^{III} ions in zeolites and have proposed cobalt–amine dinitrosyl complexes $[Co(NH_3)_n(NO)_2]^{2+}$ as active intermediates.[2] Accordingly it is possible to study the effect of various ligands (NH_3, en, or trien) on the selectivity and mechanism of this reaction, and compare it with the reaction in solution.

When NO and NH_3 were introduced onto the surface of $Co(en)_2$ or Co(trien) complexes in zeolites in the temperature range 25—95 °C, a decrease in the concentrations of NO and NH_3 was accompanied by the formation of N_2 and N_2O after several hours. The order of the dependence of the rate of N_2 formation upon the partial pressures of NO and NH_3 (30—300 Torr) was estimated to be unity and zero, respectively, indicating that the reaction between the adsorbed NH_3 and weakly held NO on the surface is the rate-determining step. This was supported by an i.r. study. When NO was introduced onto the disc of $Co(en)_2$ complex in the zeolite, three new bands were observed which were assigned to the NO dimeric (1880 and 1800 cm^{-1}) and NO monomeric (1700 cm^{-1}) adsorbed species. On adding <20 Torr of NH_3, these bands shifted to lower frequencies and their intensities diminished. However, under higher partial pressures of NH_3, they disappeared completely and only the bands corresponding to adsorbed NH_3 were observed, which indicates that only a small amount of NO is adsorbed on the surface during the NO–NH_3 reaction. In the case of Co(trien) complexes in zeolites, the NO dimeric species was more weakly held than with $Co(en)_2$ complexes and also, no NO monomeric species was detected under various conditions. However, NO is able to co-ordinate competitively with NH_3 on the Co^{II}–zeolite system and both NO dimeric and monomeric species were observed even under higher partial pressure of NH_3.

TABLE. Selectivities and reaction orders in the catalytic reduction of NO by NH_3 over Co(LL) complexes in zeolites, H_2O, and DMF [a]

LL	Zeolite	H_2O	DMF
NH_3	$S(N_2) = 0{\cdot}6$—$0{\cdot}7$ $m = 0{\cdot}3, n = 0$		
en	$S(N_2) = 0{\cdot}3$—$0{\cdot}4$ $m = 1, n = 0$	$S(N_2) = 0{\cdot}4$—$0{\cdot}5^b$ $m = 1, n = 1$	$S(N_2) = 0{\cdot}4$—$0{\cdot}5^b$ $V(N_2) = kKP_{NO}[NH_3]/(1 + KP_{NO}[NH_3])$
trien	$S(N_2) = 0{\cdot}05$—$0{\cdot}1$ $m = 1, n = 0$	$S(N_2) = 0{\cdot}05$—$0{\cdot}1^b$ $m = 1, n = 1$	$S(N_2) = 0{\cdot}05$—$0{\cdot}1^b$ $V(N_2) = kKP_{NO}[NH_3]/(1 + KP_{NO}[NH_3])$

[a] Selectivity: $S(N_2) = N_2/(N_2 + N_2O)$ formed in 2 h at room temperature. ($P_{NO} = 200$ Torr, $P_{NH_3} = 50$ Torr). Reaction order: $V(N_2) = kP_{NO}{}^{m}P_{NH_3}{}^{n}$ ($P_{NO} = P_{NH_3} = 30$—300 Torr). [b] The amount of N_2O dissolved in solution (50 ml) is not included in the estimation.

Consequently, the relative strengths of NO dimeric and monomeric species adsorbed on the Co(LL) complexes in zeolites is estimated to be LL = $NH_3 >$ en $>$ trien, which corresponds well with the selectivity for N_2 formation as shown in the Table. The reaction orders with different ligands in the zeolites and in solution (H_2O and DMF) are also summarized in the Table. In aqueous solution, they are unity with respect to both NO and NH_3, which suggests that the dissociation of the amine ligands is the slow step. In DMF, the slow step is the reaction between the coordinated NO and NH_3. Over Co(NH_3) complexes in the zeolite, both NO and NH_3 can be co-adsorbed and the reaction between adsorbed NO and NH_3 is the slow step, which is a similar situation to that in DMF solution. In the case of en and trien complexes in zeolites, the surface is saturated with NH_3, and the reaction proceeds between adsorbed NH_3 and very weakly held NO.

As no reaction takes place with complexes supported on silica or alumina, it is reasonable to suppose that the state of the complexes in zeolites is similar to that in solution. Different selectivities, reaction orders, and the large solvent effect are understandable because of the changes of stability of the intermediates and the rate determining steps with different ligands and solvents.

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[1] S. Naito, *J.C.S. Chem. Comm.*, 1978, 175.
[2] T. Iizuka and J. H. Lunsford, *J. Amer. Chem. Soc.*, 1978, **100**, 6106.