Hydrogen–Deuterium Equilibration over Synthetic Faujasites. The Role of Impurities

By CHRIS F. HEYLEN, PETER A. JACOBS, and JAN B. UYTTERHOEVEN

(*Centrum voor Oppervlaktescheikunde en Colloidale Scheikunde, Katholieke Universiteit Leuven, De Croylaan* 42, B-3030 *Heverlee, Belgium*)

Summary Evidence is provided for the catalytic importance of zeolitic impurities during reactions involving the activation of the hydrogen molecule.

RECENTLY, attention was devoted to the catalytic role of zeolitic impurities.[1,2] Lombardo *et al.*[1] pointed out the influence of group IIA cation impurities in carbonium-ion catalysed reactions. Imai *et al.*[2] suggested the role of transition-metal ion impurities as electron donors in zeolites. Turkevich *et al.*[3] found that for the H_2–D_2 equilibration over zeolites the concentration of active centres was considerably less than that of "decationated" sites. The centres of activity were considered to be Lewis sites close to each other or impurities located near an acid centre.

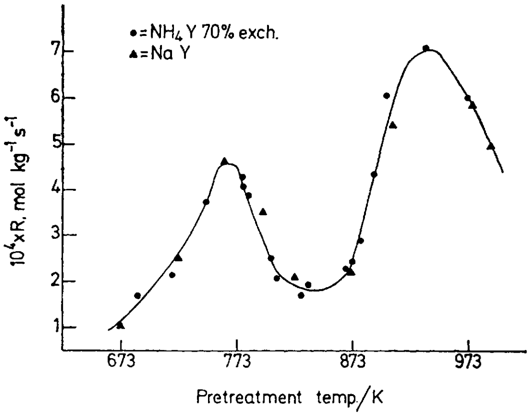

FIGURE. Absolute first-order rate constant for H_2–D_2 equilibration at 673 K against the pretreatment temperature.

We have now compared the influence of the pretreatment temperature of NaY and NH_4Y samples on the H_2–D_2 equilibration rate. Heat treatment of the NH_4Y sample results in the formation of OH groups below 773 K and dehydroxylated sites (Lewis sites) above this temperature.[4] The same thermal treatment given to NaY does not create either Brönsted or Lewis sites. In the Figure, the absolute first-order rate constant for H_2–D_2 equilibration at 673 K is plotted against the pretreatment temperature. For both samples, the experimental points coincide after different pretreatment temperatures. This rules out the possibility that the formation of deammoniated or dehydroxylated sites contributes in any way to the equilibration rate and we believe that impurities can be the active sites for the reaction.

Two maxima are observed, one after pretreatment at 763 K, another at 938 K. The maximum in activity at 938 K corresponds well with the maximum in electron-donor power of an NH_4Y sample as measured by the formation of trinitrobenzene anion radicals.[5] Flockhart *et al.*[5,6] conclude that closely adjacent aluminium centres must be involved. Comparison with our results suggest that also in this case impurities can play a role in the redox behaviour of the zeolite. However, more experiments are needed to verify these ideas.

The decrease of the reducing and oxidizing properties above 973 K was ascribed to crystal deterioration of the NH_4Y zeolites at higher pretreatment temperatures.[6] The similar decrease in H_2–D_2 equilibration rate cannot be ascribed to crystal collapse since NaY remains still crystalline above 1073 K and this perhaps reflects changes in the chemical nature of the impurities with the pretreatment temperature.

C.F.H. acknowledges a research grant from I.W.O.N.L. Belgium. P.A.J. is grateful to N.F.W.O. (Belgium) for a grant.

(*Received*, *2nd November* 1973; *Com.* 1510.)

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