JOURNAL OF CATALYSIS 38, 488–490 (1975)

Low-Temperature Parahydrogen Conversion on X-Zeolite Containing Paramagnetic Cations

X-Zeolite containing lanthanide ions has been shown to be an active catalyst for the low-temperature conversion of parahydrogen (*1*). The Wigner theory for paramagnetic conversion (*2*) was applicable, since the absolute rates of conversion k_m under constant reaction conditions (930 N m^{-2} and 77 or 90 K) were found to be proportional to the square of the magnetic moment of the lanthanide ion μ. Treatment of these results can be extended by expressing the activity on the basis of an individual ion, k_i in molecules ion^{-1} s^{-1}, but it is first necessary to subtract the value of k_m for zeolite free from lanthanide ions obtained under identical reaction conditions. Values of k_i at 77 K and 10^3 N m^{-2} are given in Table 1. Lanthanide ions in X-zeolite are distributed between a number of possible cation sites, with the actual distribution depending on their concentration, temperature, and the extent of dehydration (*3*). All the lanthanide ions at sites other than S_I are accessible to molecular hydrogen, but their catalytic activity can be expected to vary with position. It follows that k_i is a mean value which includes ions at S_I sites, but fails to take into account their inability to contribute to conversion. The use of a constant concentration of lanthanide ions and a constant outgassing treatment (*1*) results in a single distribution of the four ions studied, and hence a constant value for $k_i\mu^{-2}$.

We have presently extended measurements of low-temperature parahydrogen conversion to X-zeolite containing divalent transition metal ions. The catalysts contained closely similar concentrations of these ions which had been introduced by ion exchange without change of valence (*4*), and were from the identical preparations used in previous catalytic studies (*4–6*). As in the earlier work (*1*), the catalysts were outgassed for 14 hr at 623 K and $\sim 1.3 \times 10^{-4}$ N m^{-2} prior to measurements of parahydrogen conversion at 77 K. Absolute rates at 10^3 N m^{-2} and kinetic orders with respect to hydrogen pressure n over the pressure range 6×10^2–7×10^3 N m^{-2} are given in Table 1. The values of n are either zero or sufficiently close to zero to show that k_m at 10^3 N m^{-2} represents the total activity for conversion. The difference in activity between the unexchanged zeolite and that containing Zn^{2+}, which is less than that between the two samples of unexchanged zeolite determined in two different set-ups, shows that diamagnetic ions have negligible effect on parahydrogen conversion. In calculating the values of $k_i\mu^{-2}$ given in Table 1, spin-only values of μ were used with the exception of Pd^{2+}, where the effective μ is small compared with the spin-only prediction and lies between 0.07 and 0.13 Bohr magneton (μ_B) (*7*). Clearly $k_i\mu^{-2}$ is not constant for divalent transition metal ions, but the results can be expressed in terms of the "activity sequence": $Pd^{2+} > Cu^{2+} > Ni^{2+} > Co^{2+} > Mn^{2+}$. Omitting Pd^{2+}, due to the uncertainty in μ, this sequence cannot be explained solely in terms of differences in the ionic radii, since the dependence required by the Wigner mechanism (*2,8*) should lead to the sequence $Ni^{2+} > Co^{2+} > Mn^{2+} > Cu^{2+}$. Furthermore, differences in the ionic radius are relatively unimportant in practice, since values of $k_i\mu^{-2}$ are effectively constant for both lanthanide and divalent transition metal ions supported on rutile

Copyright © 1975 by Academic Press, Inc.
All rights of reproduction in any form reserved.

TABLE 1

PARAHYDROGEN CONVERSION AT 77 K CATALYZED BY X-ZEOLITE CONTAINING PARAMAGNETIC CATIONS

	Conc (g ion g^{-1})	k_m at 10^3 N m^{-2} (molecules mg^{-1} s^{-1})	n	k_i (molecules ion^{-1} s^{-1})	$k_i\mu^{-2}$ (molecules ion^{-1} s^{-1} μ_B^{-2})
Unexchanged[a]	—	2.76×10^{14}	0.29	—	—
Nd^{3+}	2.04×10^{-4}	4.90×10^{15}	0.00	3.76×10^{-2}	2.78×10^{-3}
Sm^{3+}	2.04×10^{-4}	1.01×10^{15}	0.21	5.94×10^{-3}	2.18×10^{-3}
Gd^{3+}	2.04×10^{-4}	2.10×10^{16}	0.00	1.68×10^{-1}	2.66×10^{-3}
Dy^{3+}	2.04×10^{-4}	3.90×10^{16}	0.00	3.15×10^{-1}	2.80×10^{-3}
Unexchanged[b]	—	1.40×10^{14}	0.12	—	—
Mn^{2+}	4.7×10^{-4}	9.55×10^{15}	0.10	3.3×10^{-2}	9.4×10^{-4}
Co^{2+}	4.3×10^{-4}	1.15×10^{16}	0.00	4.4×10^{-2}	2.9×10^{-3}
Ni^{2+}	4.7×10^{-4}	1.29×10^{16}	0.00	4.5×10^{-2}	5.6×10^{-3}
Cu^{2+}	4.7×10^{-4}	1.51×10^{16}	0.00	5.3×10^{-2}	1.8×10^{-2}
Zn^{2+}	4.7×10^{-4}	1.36×10^{14}	0.13	~0	—
Pd^{2+}	3.9×10^{-4}	6.18×10^{14}	0.14	2.0×10^{-3}	1.2×10^{-1}– 4.1×10^{-1}

[a] Blank for zeolite containing lanthanide ions.

[b] Blank for zeolite containing transition metal ions.

(*9*). The sequence can be explained, however, if the ions vary in their activity due to differing distributions between accessible and inaccessible cation sites within the zeolite structure; an increase in the proportion of the ions located at inaccessible S_I sites will be accompanied by a decrease in the value of $k_i\mu^{-2}$. It follows that the present activity sequence is also that of the preference for location at sites other than S_I.

Relatively little information is available on the location of transition metal ions in X-zeolite (*3*), and it is not possible to construct a series based on the findings of other techniques. EPR measurements show that Cu^{2+} is located at S_I and S_{II} sites (*10*), which is compatible with the high activity of Cu^{2+} in parahydrogen conversion. This is not the case for Mn^{2+}, where EPR suggests that the preferential location is at S_{II} sites (*11*). However, for the structurally similar Y-zeolite, the X-ray investigations of Gallezot and coworkers (*12–14*) suggest a preference for location at sites other than S_I which decreases in the order $Cu^{2+} > Ni^{2+} > Co^{2+}$. In this connexion it is relevant that the sequence presently observed for $k_i\mu^{-2}$ is similar to the activity sequences observed for the identical catalysts in oxidation reactions (*5,6*). The use of simple spin-only values of μ in determining $k_i\mu^{-2}$ is open to criticism, due to the changes in the effective value of μ for Co^{2+} in Y-zeolite which accompany progressive dehydration (*15*). These changes, in which μ is consistently greater than the spin-only value, are interpreted in terms of both the magnetic moment and location of an individual ion varying with the extent of its dehydration. Under such circumstances k_i would be affected, not only by changes in ion accessibility, but also by changes in the effective value of μ and the extent to which hydration controls ion–hydrogen approach distances. Since ions vary in their behavior on zeolite dehydration (*3*), conclusions drawn from comparisons of values of $k_i\mu^{-2}$ can only be accepted with reservation. The case would be much stronger for drawing conclusions on the variation in distribution of a single type of ion from measurements of k_i as a function of either the extent of exchange or the extent of dehydration. We suggest that the measurement of low-temperature parahydrogen conversion offers a method of assessing cation distribution, in which the physical interaction with molecular hydrogen is unlikely to bring about any change in the location of the ions.

REFERENCES

1. Brown, D. E., Eley, D. D., and Rudham, R., *J. Catal.* **29**, 246 (1973).
2. Wigner, E., *Z. Phys. Chem. B* **23**, (1933).
3. Breck, D. W., "Zeolite Molecular Sieves" p. 97. Wiley, New York, 1974.
4. Rudham, R., and Sanders, M. K., *in* "Chemisorption and Catalysis" (P. Hepple, Ed.), p. 58. Inst. of Petrol., London, 1971.
5. Rudham, R., and Sanders, M. K., *J. Catal.* **27**, 287 (1972).
6. Gentry, S. J., Rudham, R., and Sanders, M. K., *J. Catal.* **35**, 376 (1974).
7. Cabrera, B., and Duperier, A., *Proc. Phys. Soc. (London)* **51**, 845 (1939).
8. Pearce, D. R., Richardson, P. C., and Rudham, R., *Proc. Roy. Soc., Ser. A* **310**, 121 (1970).
9. Tullett, A. D., PhD thesis, Univ. of Nottingham, 1973.
10. Leith, I. R., and Leach, H. F., *Proc. Roy. Soc., Ser. A* **330**, 247 (1972).
11. Barry, T. I., and Lay, L. A., *J. Phys. Chem. Solids* **27**, 1821 (1966).
12. Gallezot, P., Ben Taarit, Y., and Imelik, B., *J. Catal.* **26**, 295 (1972).
13. Gallezot, P., and Imelik, B., *J. Phys. Chem.* **77**, 652 (1973).
14. Gallezot, P., and Imelik, B., *J. Chim. Phys.* **71**, 155 (1974).
15. Egerton, T. A., Hagan, A., Stone, F. S., and Vickerman, J. C., *J. Chem. Soc. Faraday I* **68**, 723 (1972).

R. RUDHAM
A. D. TULLETT
K. P. WAGSTAFF

Chemistry Department
University of Nottingham
Nottingham NG7 2RD, England

Received April 5, 1974; revised August 12, 1974