NOTES

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Comparison of the Catalytic Activities of Metal Oxides for Hydrogen-Deuterium Equilibration and Ortho-Parahydrogen Conversion

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Synopsis. The corrected activities, rates divided by square of spin magnetic moment of a metal ion, in ortho-parahydrogen conversion on first series transition metal oxides at 77 K were shown to give a very similar activity pattern to that obtained in hydrogen-deuterium equilibration.

In order to find the relation between catalytic activity and the character of the catalysts, considerable work has been done to examine the activities of the first series transition metal oxides in reactions such as hydrogen-deuterium equilibration,[1] dehydrogenation and disproportionation of cyclohexene,[2] dehydrogenation of propane,[3] hydrogenation of ethylene,[4] isotopic mixing in ethylene[5] and dehydrogenation of cyclohexane.[6] It is noteworthy that a similar activity pattern was obtained in the above reactions.

Systematic studies have not yet been carried out on the activities in ortho-parahydrogen conversion, one of the simplest of catalytic reactions. We thought it of interest to see if an activity pattern similar to that in the above reactions also holds in this conversion. In the present work, we show the activity sequences of the first series transition metal oxides in ortho-parahydrogen conversion at 77 K, and in hydrogen-deuterium equilibration at 178 K.[7]

Experimental

Preparation of Oxides. V_2O_5 was prepared by the decomposition of NH_4VO_3 at 773 K in an oxygen flow. V_2O_3 was obtained by the reduction of V_2O_5 with hydrogen at 873 K. Cr_2O_3, Mn_2O_3, Fe_2O_3, Co_3O_4, NiO, CuO, ZnO, and CdO were prepared by the calcination of the respective hydroxide at 773 K for 5 hr in air. The hydroxide was precipitated with ammonia from the aqueous solution of the corresponding nitrate. Mn_3O_4 was prepared similarly and calcined at 1223 K. FeO was prepared by the reduction of Fe_2O_3 at 1473 K with an equimolar mixture of hydrogen and carbon dioxide. CoO was prepared by the decomposition of Co_3O_4 at 1073 K. SiO_2 and Al_2O_3 were prepared by the calcination of the corresponding hydroxide obtained by the hydrolysis of ethyl-ortho-silicate and that of alminum isopropoxide, respectively. MoO_3 was obtained by the oxidation of ammonium molybdate with the addition of concd. HNO_3. TiO_2 and CrO_3 were obtained from Wako Pure Chemical Industries, Ltd. The oxides, TiO_2 (anatase), V_2O_3, $Cr_2O_3(\alpha)$, Mn_2O_3, Mn_3O_4, $Fe_2O_3(\alpha)$, FeO, Co_3O_4, CoO, NiO, and CuO were confirmed to be well crystallized from X-ray diffraction patterns.

Materials. Hydrogen gas was purified by diffusion through a heated palladium thimble. Deuterium gas (D_2 99.3%, HD 0.7%, Takachiho Chemical Co.) was used without further purification.

Apparatus and Procedure. The reactor attached to the glass-made gas circulation system capable of achieving a vacuum to 10^{-6} Torr was used. The rates of the conversion and the equilibration were measured at temperatures 77—90 K and 77—300 K, respectively, under the total pressure of 100 Torr. Prior to individual runs, the catalyst in the reactor was outgassed at high temperature for more than 4 hr *in vacuo* below 5×10^{-5} Torr. The catalyst thus treated was cooled down to room temperature in herium gas, and the reaction vessel was immersed in a coolant to establish the required temperature for the reaction. The catalyst after being used once for the reaction was substituted by a fresh one before each run.

Results and Discussion

Both the conversion and the equilibration obeyed first order kinetics in the whole temperature range for all the oxides studied. The reaction rate, R_m, was calculated from the first order rate constant k_e to be

$$R_m = k_e N/S \quad \text{molecule}\cdot\text{s}^{-1}\cdot\text{cm}^{-2} \qquad (1)$$

where N is the number of molecules in the reaction system and S the surface area of the catalyst. The rates of conversion at 77 K over paramagnetic oxides and diamagnetic ones are shown in Tables 1 and 2, respectively. The former oxides have magnetic moment due to free spins in their metal ions, but the latter none. The rates of equilibration at 178 K are also shown in Table 3. In the temperature range 77—90 K, the conversion over paramagnetic oxides proceeds rapidly with a small apparent activation energy. However, the equilibration does not take place except over Co_3O_4 in this temperature range. The rates of the conversion over paramagnetic oxides are greater than those over diamagnetic oxides by a factor of $\sim 10^3$. This shows that the low-temperature conversion proceeds *via* a paramagnetic mechanism.

Activity Order in the Equilibration and Conversion. The activity order in the equilibration at 178 K is seen from Table 3 to be

$$Co_3O_4 > CoO > NiO > Cr_2O_3 \gg ZnO > V_2O_3, Mn_2O_3, Mn_3O_4, Fe_2O_3, FeO, CuO.$$

A similar activity sequence was presented in the same reaction[1] and many other different types of reaction.[2-6]

The activity order of the paramagnetic oxides for the conversion at 77 K is seen from Table 1 to be

$$Co_3O_4 > Cr_2O_3 \simeq Mn_3O_4 > CoO > NiO > Fe_2O_3 > V_2O_3 > FeO > Mn_2O_3 > CuO.$$

Table 1. Rates of conversion over paramagnetic oxides

Oxides	Outgassing Temp. (K)	Surface area (m^2/g)	Activation energy at 77—90 K (kcal/mol)	$R_m \times 10^{-14}$ (molecule $\cdot s^{-1} \cdot cm^{-2}$) 77K, 100 Torr
V_2O_3	773	4.85	—	2.01
Cr_2O_3	773	27.4	0.2	13.5
Mn_2O_3	773	28.7	—	0.66
Mn_3O_4	773	1.01	−0.2	13.4
Fe_2O_3	773	29.0	0.2	2.78
FeO	773	0.10	−0.2	1.34
Co_3O_4	773	13.5	0.5	31.9
CoO	773	3.69	—	7.46
NiO	773	16.4	0.2	6.73
CuO	673	1.04	−0.2	0.15

Table 2. Rates of conversion over diamagnetic oxides

Oxides	Outgassing Temp. (K)	Surface area (m^2/g)	Activation energy at 77—90 K (kcal/mol)	$R_m \times 10^{-11}$ (molecule $\cdot s^{-1} \cdot cm^{-2}$) 77K, 100 Torr
TiO_2	773	10.2	−0.2	2.83
V_2O_5	773	4.91	—	6.18
CrO_3	373	4.69	—	0.5
ZnO	673	0.98	−0.2	4.55
Al_2O_3	773	189.0	—	3.12
SiO_2	773	296.0	—	0.5
MoO_3	773	2.20	—	2.46
CdO	673	2.24	—	2.63

Table 3. Rates of equilibration at 178 K

Oxides	Activation energy at 100—300 K (kcal/mol)	$R_m \times 10^{-12}$ (molecule $\cdot s^{-1} \cdot cm^{-2}$) at 178 K
V_2O_5	—	0.00
V_2O_3	—	0.00
Cr_2O_3	6.3	2.00
Mn_3O_4	—	0.00
Fe_2O_3	—	0.00
FeO	—	0.00
Co_3O_4	0.76	1260.00
CoO	—	460.00
NiO	1.7	60.00
CuO	—	0.00
ZnO	5.9	0.03

As in the usual paramagnetic mechanism, the conversion proceeds by the interaction of adsorbed hydrogen molecules with the inhomogeneous magnetic field of a metal ion on the surface. The rate of the conversion can be given by

$$R_m = k \cdot f_a \cdot f_m \cdot n_a \tag{2}$$

where f_a is a measure of the interaction strength of a catalyst with hydrogen molecule, f_m a measure of the strength of the magnetic field of a metal ion on an oxide, n_a the number of active sites per surface area of an oxide and k the transition probability of hydrogen from para- to ortho-hydrogen or *vice versa,* which is constant over various oxides. It was shown that the probability of the transition depends on the square of the spin magnetic moment of an ion or molecule.[8] The rate of the low temperature conversion on the rare earth metal oxides was confirmed to increase in proportion to the square of the spin magnetic moment of a metal ion in the corresponding metal oxides.[9] Thus, we assume here that f_m can be substituted by μ_M^2 in Eq. (2).[10] The corrected rates of the conversion, *i.e.*, R_m divided by the square of the spin magnetic moment of a metal ion in the corresponding metal oxide, are shown in Fig. 1. The rates of the conversion thus eliminated by the magnetic field contribution give a very similar activity pattern to that obtained in the equilibration.

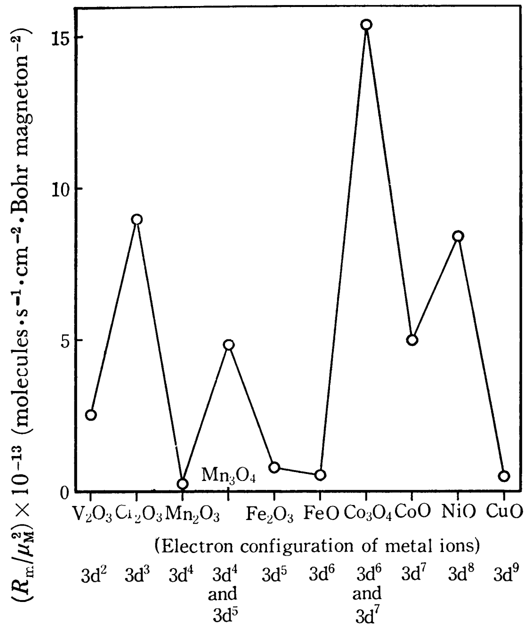

Fig. 1. Comparison of R_m/μ_M^2 for the paramagnetic oxides of the first series transition metal elements.

References

1) D. A. Dowden, N. Mackenzie, and B. M. W. Trapnell, *Proc. Roy. Soc., Ser. A*, **237**, 245 (1956).

2) G. M. Dixon, D. Nicholls, and H. Steiner, "Proc. 3rd Intern. Congr. on Catalysis," Amsterdam, North-Holland Pub. Co. (1965), p. 815.

3) D. A. Dowden, *Endeavour*, **24**, 69 (1965).

4) D. L. Harrison, D. Nicholls, and H. Steiner, *J. Catal.*, **7**, 359 (1967).

5) A. Ozaki, H. Ai, and K. Kimura, Forth Intern. Congr. on Catalysis, Moscow, No. 40 (1968).

6) P. C. Richardson and D. R. Rossington, *J. Catal.*, **14**, 175 (1969).

7) Hereafter, ortho-parahydrogen conversion and hydrogen-deuterium equilibration will be referred to as the conversion and the equilibration, respectively.

8) E. Wigner, *Z. Phys. Chem.*, **B23**, 28 (1933).

9) D. R. Ashmead, D. D. Eley, and R. Rudham, *J. Catal.*, **3**, 280 (1964).

10) The values of spin magnetic moments, μ_M, are given by $\mu_M = \sqrt{n(n+2)}$, where n is the number of free spins of a corresponding metal ion. The value of Co_3O_4 ($Co^{2+}Co_2^{3+}O_4$) or Mn_3O_4 ($Mn^{2+}Mn_2^{3+}O_4$) is given as $\mu_M^2 = (2\mu_{M^{3+}}^2 + \mu_{M^{2+}}^2)/3$.