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Protium–Deuterium Exchange Mechanism between Hydrogen in Gas Phase and Hydrogen Sorbed by Mg_2Ni Modified by Chloranil

INTRODUCTION

Klier *et al.* (*1*) have presented a very impressive theory that describes the isotopic exchange reactions. By this theory, three possible reaction mechanisms could be distinguished kinetically, and more detailed discussion on the reaction mechanism could be made; the participation of the two-atom exchange (R'') mechanism and the one-atom exchange (R') mechanism could be evaluated. This theory was tested by the time dependences of the concentrations of $O^{18}O^{18}$, $O^{16}O^{18}$, and $O^{16}O^{16}$ molecules over magnesium oxide. Tsuchiya *et al.* (*2*) first applied the theory to the systems consisting of gaseous hydrogen and anthracene–sodium and -potassium complexes, where the hydrogen atoms of the EDA complexes were exchanged. Cavalier and Chornet (*3*) reported the results applying the theory to the protium–deuterium exchange on iron catalysts. For the sake of simplicity, the word "hydrogen atom" in the present paper hereafter stands for both isotopes, protium and deuterium, and where necessary, the individual isotopes are designated as H and D.

Imamura *et al.* (*4–7*) found that the surface property of such hydrogen storage materials as Mg_2Ni and $SmMg_3$ could be varied by treating its surface with some organic compounds, to enhance the rate of sorption of hydrogen markedly. On the surface of Mg_2Ni, the formation of EDA complex was suggested. The hydrogen sorption mechanism of the hydrogen storage intermetallics has hardly been investigated. The protium–deuterium exchange over the intermetallics has not been reported, either. In general hydrogen molecules are dissociatively sorbed by the hydrogen storage materials (*8*), and the exchange reaction between protium–protium might take place during the course of the protium adsorption. Accordingly, the informations on the contribution of R'- and R''-mechanism obtained from the protium–deuterium exchange reaction may be useful to characterize the surface properties of the intermetallics. If the EDA complex is formed on the intermetallics surface as was suggested previously (*6, 7*), the theory presented by Klier *et al.*(*1*) would be applicable, and it would be expected that the same three reaction types would be discernible. The Mg_2Ni modified by chloranil (tetrachloro-*p*-benzoquinone), CHL–Mg_2Ni, has been employed as the catalyst, because the enhancement observed in the rate of sorption of hydrogen was great (*7*). In this paper, the interest was centered on the protium–deuterium exchange reaction mechanism between gaseous hydrogen molecules and sorbed hydrogen molecules and/or atoms.

These three mechanisms may be described by the following scheme where the symbols for the reaction rates R, R', and R'' have analogous meanings to those applying in Ref. (*1*) for the corresponding oxidation exchange reactions:

$$D_2 + H_2(g) \rightleftarrows 2HD(g) \quad R$$

$$\left.\begin{array}{lllll} D_2(g) & + & H(s) & \rightleftarrows & HD(g) + D(s) \\ HD(g) & + & H(s) & \rightleftarrows & H_2(g) + D(s) \end{array}\right| R'$$

$$\left.\begin{array}{lllll} D_2(g) & + & 2H(s) & \rightleftarrows & H_2(g) + 2D(s) \\ HD(g) & + & 2H(s) & \rightleftarrows & H_2(g) + D(s) \\ & & & & \qquad\quad + H(s) \\ HD(g) & + & 2D(s) & \rightleftarrows & D_2(g) + D(s) \\ & & & & \qquad\quad + H(s) \end{array}\right\} R''$$

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H(s) or D(s) means hydrogen atom sorbed by the CHL–Mg_2Ni; index (g) relates to the gaseous phase.

The hydrogen molecule either exchanges one (R') or two (R'') of its hydrogen atoms per reactive collision with the CHL–Mg_2Ni or exchanges between gaseous molecules take place without detectable participation of hydrogen atoms sorbed by the CHL–Mg_2Ni (R). In order to measure the value of R'' for an actual system, where all three reactions might simultaneously take place, it is useful to study the exchange between a preequilibrated gas mixture of H_2, D_2, and HD, and the hydrogen sorbed by CHL–Mg_2Ni. We define $[HD]^2/[H_2][D_2] = \psi$. If only the R and R' reactions operate, $d\psi/dt = 0$. However, if R'' reaction operates, $d\psi/dt$ would be varied with time. The contribution of R'' would accordingly be shown (*1*).

EXPERIMENTAL

A closed recirculating system with a U-shaped glass tube reactor was used to follow the reaction. H_2 and D_2 were supplied from Taiyo Sanso Ltd., and dried by the passage of a molecular sieve 13X trap and a liquid nitrogen trap. The CHL–Mg_2Ni sample used was prepared in a manner similar to that described elsewhere (*7*).

The equilibrated isotope mixture of hydrogen isotopes (H_2, D_2, and HD) was prepared by the protium–deuterium equilibration reaction over Pt/SiO_2 at a selected temperature for a day. The selected temperature was the same as that employed in the subsequent protium–deuterium exchange with the CHL–Mg_2Ni. The composition of the reactant mixture was confirmed to be in the equilibrium by gas chromatography.

In a typical experiment, the CHL–Mg_2Ni was first evacuated at 423 K for 2 h. Then ca. 3×10^4 Pa of H_2 (or D_2) was introduced into the reaction system in order to be presorbed by CHL–Mg_2Ni for a day. The hydrogen presorbed CHL–Mg_2Ni was evacuated for a few minutes, and the equilibrated mixture was immediately introduced. The composition of gas phase was occasionally analyzed by gas chromatography at suitable time intervals.

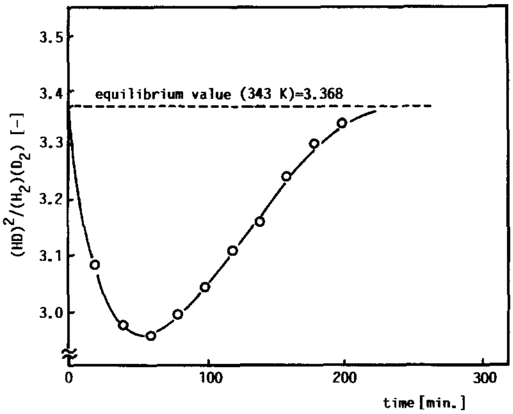

FIG. 1. $[HD]^2/[H_2][D_2]$ vs time at 373 K. The amount of CHL–Mg_2Ni used was 0.1733 g. Total pressure of hydrogen isotope mixture at initial stage was 1.26×10^4 Pa.

RESULTS AND DISCUSSION

Figure 1 shows a typical result for the protium–deuterium exchange reaction between hydrogen in the gas phase and that sorbed by CHL–Mg_2Ni at 373 K. The ratio, $[HD]^2/[H_2][D_2]$, decreases from the initial equilibrium value and passes through a minimum before returning, finally, to the equilibrium value again. It is clear that the contribution of R'' in the total exchange is important. The isotope effect for R'-mechanism may be considered in the protium–deuterium system. However, Cavalier and Chornet (*3*) could not observe the minimum in the time dependence of protium-deuterium exchange over the (110), (100), and (111) surface of iron, where R''-mechanism did not contribute to the reaction. Over the polycrystalline surface of iron catalyst, on the other hand, the minimum in the time dependence was observed. Therefore the minimum is not due to the isotope effect for R'-mechanism.

The values for the rates R, R', and R'' calculated by a manner similar to that employed previously (*1, 2*) are summarized in Table 1. They confirm the significant contri-

TABLE 1

The Rates of *R*, *R*′, and *R*″ Reaction for CHL–Mg_2Ni

Series:	A-1	A-2	A-3	B-1	B-2	B-3
Presorbed hydrogen:	H_2	H_2	H_2	D_2	D_2	D_2
Amount of CHL–Mg_2Ni/g:	0.0964	0.1733	0.1199	0.1517	0.1128	0.089
Reaction temperature/K	343	373	403	343	373	403
m/atoms	1.48×10^{20}	6.69×10^{19}	4.75×10^{19}	1.10×10^{20}	7.58×10^{19}	1.05×10^{20}
R/molecules min^{-1}	0	0	0	0	0	0
R′/molecules min^{-1}	5.0×10^{17}	6.0×10^{17}	1.0×10^{18}	1.0×10^{17}	3.0×10^{17}	2.3×10^{17}
R″/molecules min^{-1}	4.6×10^{17}	4.5×10^{17}	2.6×10^{17}	1.2×10^{17}	4.3×10^{17}	5.9×10^{17}
R′/*R*″	1.09	1.33	3.84	0.83	0.70	0.38

bution of *R*″ and show that the homomolecular *R*-mechanism is negligible. Although the amount of hydrogen sorbed is the function of the ambient pressure, the temperature, and the time of sorption, it was very difficult to control the amount of hydrogen sorbed. We could not accordingly make it constant among the runs, and the values of *m*, the number of exchangeable hydrogen atoms, are shown in Table 1.

Since the amounts of CHL–Mg_2Ni and the number of exchangeable hydrogen atoms are different among the runs, the discussion based on the ratios, *R*′/*R*″, are reasonable. The *R*′/*R*″ in the case of protium presorbed increases with increasing the reaction temperature. The fact suggests that the contribution of *R*″-mechanism decreases with increasing the reaction temperature. The *R*′/*R*″ in the case of deuterium presorbed, on the other hand, decreases with increasing the reaction temperature. This suggests that the contribution of *R*″-mechanism increases with increasing the reaction temperature. Although Klier *et al.* (*1*) did not take into the account the isotope effect, the effect would be considered in the *R*′-mechanism of hydrogen, since the mass number difference between protium and deuterium is great. The ratios, *R*′/*R*″, for the protium presorbed surface were seemingly larger than unity, while those for deuterium presorbed surface were less than unity. This different tendency of contribution of *R*′- and *R*″-mechanism may be attributed to the sort of isotope effect.

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S. TSUCHIYA[1]
H. MORISHIGE
H. IMAMURA

Department of Industrial Chemistry
Faculty of Engineering
Yamaguchi University
Tokiwadai, Ube, 755, Japan

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[1] To whom correspondence should be addressed.