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Hydrogen Isotope Equilibration of HD on MgO below Room Temperature

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Synopsis. MgO pretreated at ca. 823 K in vacuo showed the highest catalytic activity for an isotope equilibration reaction, $2HD=H_2+D_2$, at 195 K. This reaction proceeds through an interaction of dissociatively adsorbed hydrogen on a pair site consisting of lowly coordinated ions, Mg^{2+}_{LC}-O^{2-}_{LC}, with a residual OH^- at the nearest lattice position.

Boudart et al.[1] found that MgO could catalyze an H_2-D_2 isotope-exchange reaction, even at 77 K, and proposed that the active site for this reaction comprised a specific site, $(O^-)_3$, with a nearby OH^-. Since this finding, many investigators in both theoretical and experimental fields have become interested in this topic and have supported the above mechanism.[2] On the other hand, recent experimental[3–5] and theoretical[6–8] work has revealed that MgO is able to heterolytically dissociate H_2 into H^- and H^+. In this case, lowly coordinated surface ions, O^{2-}_{LC} (and Mg^{2+}_{LC}), but not O^-, play a central role. If the H^- (or H^+), thus produced, interacts with either H^+ (or H^-) arising from another similarly-adsorbed hydrogen molecule or a residual surface OH^-, the H_2-D_2 exchange reaction may proceed. Recent theoretical studies based on the ab initio method have supported this view.[6–8] The present paper gives experimental evidence for participation of a heterolytically dissociated hydrogen species in H_2-D_2 exchange on MgO at low temperatures.

Experimental

The main catalyst used was MgO-JM, supplied by Johnson-Matthey Chemicals, with specific surface areas (SSA) of 61—133 m^2g^{-1} after use. Another sample, MgO-JRC-2, supplied by The Catalysis Society of Japan, was also used. The latter had a larger SSA of 356 m^2g^{-1} after use. The catalysts were always pretreated in vacuo at prescribed temperatures of 673—1123 K before each run and the same sample was repeatedly used in a series of runs. H_2 and D_2 (Takachiho, >99.999 and >99.5 mol%, respectively) and HD (Merck Sharp & Dohme, 98 atom% D) were used through a trap at 77 K. An equilibration reaction of $2HD=H_2+D_2$ was carried out in a flow system by feeding HD gas at ca. 0.1 Pa over MgO at low temperatures. Isotopic composition of the exit gas was monitored by an ANELVA-AGA-100 quadrupole mass spectrometer at a prescribed interval. A relative rate constant, k, for the above reaction was estimated by an equation, $k=-\ln(1-f)$, where f is the exchange fraction, defined as $\{([HD]_i-[HD]_o)/([HD]_i-[HD]_e)\}$, and $[HD]_i$, $[HD]_o$, and $[HD]_e$ are molar fractions of HD in the inlet and outlet gases and a completely equilibrated mixture, respectively. When the reactant HD was diluted in the deuterium concentration with surface OH^- during the reaction, [HD] was corrected for this dilution.

Results and Discussion

Though the catalytic activity for the equilibration reaction was below the detectable limit at 77 K, the reaction was observable at 195 K. Table 1 shows the variation of f as a function of the reaction temperature observed on MgO pretreated at 823 K, indicating that at 273 K the reaction already proceeds near to equilibrium under the experimental conditions used. The pretreatment temperature markedly influenced the catalytic activity and, as shown in Fig. 1, pretreatment at a moderate temperature of around 823 K gave the highest activity; this is consistent with Boudart's results.[1]

Figure 2 shows the time course of the deuterium concentration in the exit gas during HD flow at 195 K, indicating that it was initially low but gradually

Table 1. Reaction Temperature Dependence of f[a)]

Reaction temp/K	f
77	0.0
195	0.43
273	0.88
343	1.0

a) MgO-JM (0.31 g, SSA 61 m^2g^{-1}) pretreated at 823 K.

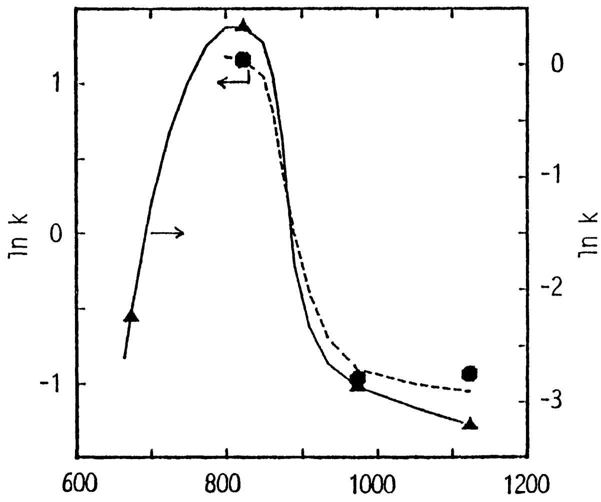


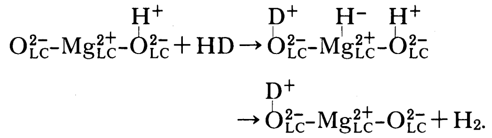
Fig. 1. Pretreatment temperature dependence of k at 195 K on MgO-JM (0.39 g, SSA 133 m^2g^{-1}, ······) and MgO-JRC-2 (0.30 g, SSA 356 m^2g^{-1}, ——).

increased and approached a value of the reactant HD (47.9%). This strongly suggests that surface OH^- takes part in the HD equilibration. The amounts of OH^-, n_{OH}, remaining after the pretreatment in vacuo were estimated by admitting a dose of D_2 onto the surface at 373 K. With an increase in the pretreatment temperature, n_{OH} was monotonously, but remarkably, decreased in accordance with Anderson's results.[9] The MgO-JM (0.39 g, SSA 100 $m^2 g^{-1}$) pretreated at 823 K gave a value of 82×10^{16} m^{-2} for n_{OH}.

On the other hand, H_2 is known to adsorb with heterolytic dissociation on a pair site consisting of Mg_{LC}^{2+}-O_{LC}^{2-}.[3-5] At least seven kinds of adsorbed species, W_i (i=2—8), of which adsorption states were fundamentally similar one another, were produced upon adsorption below room temperature.[5] Among them the most abundant species, W_2, was partly reversible at 195 K,[5] which was a temperature mainly used in the present HD equilibration. The numbers of W_2 sites, n_{W2}, estimated from the saturated adsorption amount, have already been reported to monotonously increase with an increase in the pretreatment temperature.[5] A value of 0.7×10^{16} m^{-2} was obtained for the present MgO-JM (0.39 g, SSA 133 $m^2 g^{-1}$) pretreated at 823 K.

We now consider the role of the adsorbed hydrogen species for the equilibration reaction. First, the W_i sites (especially W_2 in the present case) seem to be isolated from each other, since an H-D exchange between two HD molecules adsorbed on two W_i sites is substantially negligible at 195 K, as has already been reported.[10] If two W_i sites were actually present in the nearest lattice position, an H-D exchange on these sites would be possible (as has already been pointed out by us based on ab initio MO calculations[7]). Note that the surface migration of adsorbed W_i species requires a relatively high activation energy.[7] No significant contribution from the two nearest sites was also supported by the results obtained in this study that molar ratios among H_2, HD, and D_2 in the gas desorbed at 195 K in a TPD run after HD adsorption at 77 K were the same as those in the original HD.

Second, it is pointed out that an H-D exchange between an HD molecule adsorbed at a W_i site and a residual OH^- present at the neighboring position becomes possible when this adsorbed molecule is again desorbed. This is revealed by the TPD curves shown in Fig. 3, where H_2 was adsorbed at 77 K on the surface with either residual OH^- or OD^-. The desorption rate of m/z=3 from the W_2 species formed on the H_2/OD^- surface was higher than that on the H_2/OH^- surface by ca. 15%, while both the surfaces showed almost the same desorption rates for m/z=2. This difference for m/z=3 indicates that a small amount of HD was desorbed from the H_2/OD^- surface. Since no H-D exchange could occur during the adsorption at 77 K, it is believed that this HD was formed between H^-, produced by H_2 adsorption, and OD^-, previously present on the surface, upon their desorption from a W_2 site. This means that only the W_i species which is *reversible* at the reaction temperature (e.g., W_2, or more strictly a part of W_2, for the reaction at 195 K) can take part in the HD equilibration:



$$O_{LC}^{2-}\text{-}Mg_{LC}^{2+}\text{-}\overset{H^+}{O_{LC}^{2-}} + HD \rightarrow \overset{D^+}{O_{LC}^{2-}}\text{-}\overset{H^-}{Mg_{LC}^{2+}}\text{-}\overset{H^+}{O_{LC}^{2-}}$$

$$\rightarrow \overset{D^+}{O_{LC}^{2-}}\text{-}Mg_{LC}^{2+}\text{-}O_{LC}^{2-} + H_2.$$

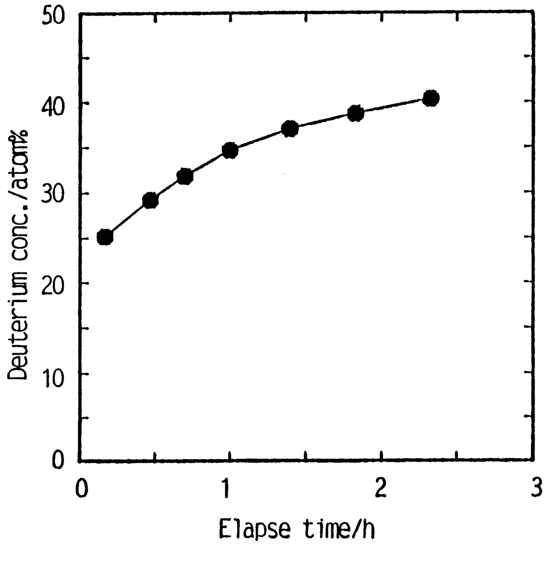


Fig. 2. Time course of deuterium concentration in the exit gas during HD flowing at 195 K over MgO-JM (0.39 g, SSA 133 $m^2 g^{-1}$) pretreated at 823 K. The abscissa indicates elapse time after starting HD flowing.

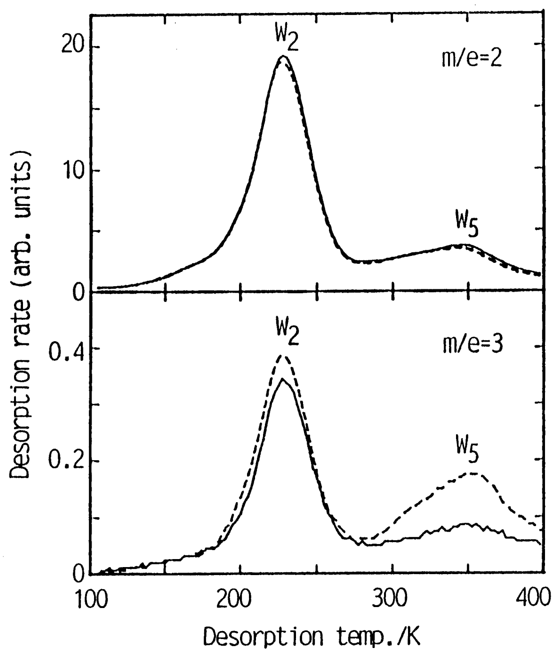


Fig. 3. TPD curves of hydrogen which were produced by H_2 adsorption at 77 K on MgO-JM (0.31 g, SSA 61 $m^2 g^{-1}$) with residual OH^- (——), and OD^- (……), respectively. The MgO was pretreated at 823 K. (Note that m/z=3 from H_2/OH^- surface is due to H_3^+ ions, while that from H_2/OD^- is due to H_3^+ and HD^+.)

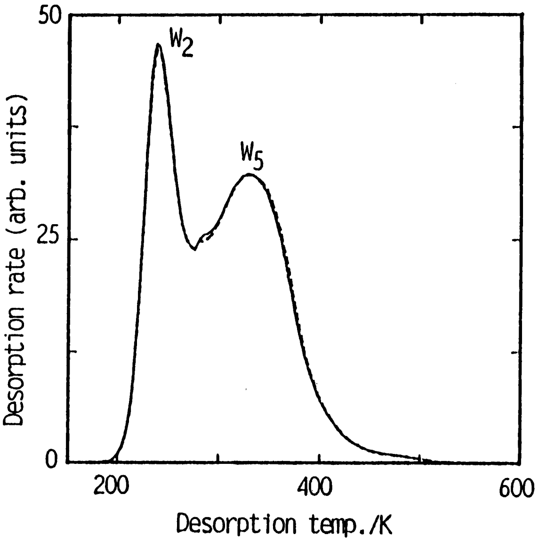


Fig. 4. TPD curves of D_2 from the MgO-JM surface (0.31 g, SSA 61 $m^2 g^{-1}$) which was covered with D_2 adsorbed at 195 K, evacuated at the same temperature, and finally exposed to H_2(——) and He (······), respectively. The MgO was pretreated at 823 K. (Note that a considerable part of W_2 species is irreversible at 195 K.)

This view is supported by the TPD curves shown in Fig. 4, where either H_2 or He (as a reference) was admitted at 195 K onto a surface which had been covered with D_2 *irreversibly* preadsorbed at this temperature. TPD curves of m/z=4 from both surfaces were the same, indicating that no exchange reaction between gaseous H_2 and *irreversibly* adsorbed W_i, i.e., D^- or D^+, was possible, even if there was a neighboring OH^-. The proposed mechanism illustrated by the above reaction scheme has also been supported theoretically.[6]

We can at least qualitatively understand, based on the porposed model, the dependence of k on the pretreatment temperature shown in Fig. 1. This model indicates that k should depend on both n_{OH}, which monotonously decreases with an increase in the pretreatment temperature, and n_{W2}, which monotonously increases; hence, k has a maximum at a moderate pretreatment temperature. Although the proposed mechanism well explains the observed results, minor contributions from other mechanisms,[1,7,8] which also lead to HD equilibration, may be allowed.

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