A Study of the Exchange Reaction between Water and Surface Hydroxyl Groups on Magnesium Oxide by Means of Infrared Diffuse Reflectance Spectroscopy

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Infrared diffuse reflectance spectroscopy was applied to the study of the exchange reaction between water and surface hydroxyl groups on magnesium oxide. The results led to the conclusion that (i) no reaction occurs *via* the combination of hydroxyl groups, and (ii) the hydroxyl groups react with adsorbed water reversibly. Two types of hydroxyl groups present on the surface are involved in the rate determining step.

A study of adsorption by means of diffuse reflectance spectroscopy provides valuable information on the state of the adsorbed species.[1-3] In an earlier stage of investigation, experiments were carried out in the visible and ultraviolet regions. Little work had been done in the infrared region until Kortuem and Delfs published their work in this spectral region.[4] Since then, it has been applied to the study of adsorption or inorganic analysis,[5-11] but no kinetic study has been carried out on catalytic reactions.

Some infrared spectral studies of the adsorption were conducted on alkaline earth metal oxides.[8,9,12-16] We have applied the infrared diffuse reflectance method to the exchange reaction between water and surface hydroxyl groups on magnesium oxide.

Experimental

Experiments were carried out in a manner similar to that in the previous work.[7-9] About 50 mg of magnesium oxide* in powder form** (J. T. Baker Co., Ltd.) was packed in a cell to a thickness of about 2 mm. The cell was attached to a Nippon Bunko model DR-3 diffuse reflectance apparatus (Japan Spectroscopic Co., Ltd.), the spectra being recorded with a Nippon Bunko Model IR-G infrared spectrophotometer.

Prior to the experiments, the sample was heated at 310 °C for 5 hr in a stream of purified nitrogen. Deuterium oxide vapor saturated at room temperature or at 0 °C was allowed to flow over the sample with a nitrogen stream to react with surface hydroxyl groups at 240—310 °C. The reaction between water and surface deuteroxyl groups was also carried out in a similar manner.

The reflectivity of the sample was practically independent of its amount for a sample weighing more than 35 mg.*** No. emission band was observed.

Results and Discussion

Water Adsorption. Part of the original sample was in the form of magnesium hydroxide, as confirmed by the presence of a strong absorption band at 3700 cm^{-1}.[8,9] When the sample was heated at 310 °C for 5 hr, the band disappeared and two new absorption bands were observed at 3730 and 3610 cm^{-1}. These bands were previously assigned to the OH stretching vibrations of different types of surface hydroxyl groups.[8,9,17] According to Anderson *et al.*,[17] the model for chemisorbed water consists of hydroxyl group adsorbed on a surface magnesium ion, the remaining hydrogen forming another hydroxyl group with an adjacent surface O^{2-} ion. The former (referred to as OH_h) gives rise to the absorption band at 3730 cm^{-1} and the latter that at 3610 cm^{-1} (referred to as OH_l). After the sample is once heated as described above, the intensities of these bands change no more by further heating at 240—310 °C. It was confirmed that no water was desorbed under these conditions. The positions and the intensities of these bands remained unchanged in the presence of water vapor (H_2O).

Adsorption of water was carried out with a conventional adsorption apparatus. It was found that the adsorption of water is initially rapid followed by slow adsorption. The adsorbed amount slightly increases with time in the latter stage of the adsorption. Finally, 0.09 ml STP/g MgO of water was held on the sample at 23 mmHg 290 °C after 2 hr. Over 90% of adsorbed water was rapidly desorbed upon degassing. The amount of the reversibly adsorbed water is roughly proportional to 0.25 th power of the partial pressure of water. The retention volume of water was determined as a function of the temperature of the gas chromatographic column in which magnesium oxide was packed. The heat of adsorption of water was estimated to be 6.9 kcal/mol from the temperature dependence of the retention volume.

Thus, it is concluded that water is reversibly adsorbed on magnesium oxide. The amount of spectroscopically active hydroxyl groups on magnesium oxide was kept constant irrespective of the presence or absence of water vapor.†

The Reaction between Water and Surface Hydroxyl Groups. In contrast to the above results, the intensities of the absorption bands due to the hydroxyl groups decreased appreciably when deuterium oxide vapor was brought into contact with magnesium oxide. New bands due to surface deuteroxyl groups appeared at 2760 (OD_h) and 2670 (OD_l) cm^{-1}. The positions of OH_h and OH_l remained unchanged in the course of the reaction. When water vapor (H_2O) was allowed to flow

* The average particle size of the sample was about 12 μ.

** The surface area of magnesium oxide was 16 m^2/g.

*** The reflectivity of the sample should be independent of its amount for a quantitative analysis of the diffuse reflectance spectra.

† The total amount of hydroxyl groups was estimated from that of water released by heating at 750 °C for 1 hr. It was found that the water amounted to 0.92 ml STP/g MgO.

over the sample which had been partially deuterated, the bands due to the deuteroxyl groups decreased, whereas those due to hydroxyls increased according to the reaction between H_2O and OD. The reaction proceeded at a faster rate as compared to the reaction of D_2O with OH. When the partial pressure of water vapor was lowered to one fifth of that in the former run, the rate was reduced by 34%. The rate is, therefore, proportional to 0.25 power in the partial pressure of water, indicating that the reaction proceeds in proportion to the amount of reversibly adsorbed water.

Evaluation of the Rate of the Reaction. For estimating the rate of the reaction, the relation between the reflectivity and the adsorbed amount should be obtained. According to Frei *et al.*,[18] total reflectivity R at given wave number $\tilde{\nu}$ of binary system can be written with reference to the Kubelka-Munk equation[19] as

$$(1-R)^2/2R = k_1/s_1 + k_2/s_2, \quad (1)$$

where k_1 and k_2 are the absorption coefficients and s_1 and s_2 the scattering coefficients. The reflectivity R can be determined with reference to the standard material of $R=1$. Mamiya[7] recently pointed out that alkali halide particles can be used as a standard meterial and that its reflectivity decreases by only 4% with an increase in its size from 1—5 μ to 40—80 μ. Potassium bromide with an average particle size of 15 μ was therefore employed. It is assumed that the term k_1/s_1 in the right hand side of Eq. (1) is the reflectance function of the sample itself whereas k_2/s_2 is that due to hydroxyl or deuteroxyl groups. Since the value of k_1/s_1 can be estimated from the background spectrum by means of the Kubelka-Munk equation $(1-R_1)^2/2R_1=k_1/s_1$ (R_1: the reflectivity of the sample), the k_2/s_2 value is readily estimated from Eq. (1). The integrated intensity n_iI_i of surface species i can thus be given by the following equation, assuming that s_2 is independent of wave number for the absorption band in question:

$$n_iI_i = \int k_2/s_2 \mathrm{d}\nu = \int\left[\frac{(1-R)^2}{2R} - \frac{(1-R_1)^2}{2R_1}\right]\mathrm{d}\tilde{\nu} \quad (2)$$

where n_i is the amount of the species i and I_i its intensity per unit amount.

Figure 1 illustrates the plot of the n_iI_i-values for OH_h and OD_h against the time of the reaction D_2O+OH at 290 °C. We see that the intensity of OH_h monotonically decreases with time whereas that of OD_h increases. Similar results were obtained for OH_l and OD_l, whereas these trends were reversed for the reaction between OD and H_2O.

The difference $I_i\Delta n_i$ between the n_iI_i-values at $t=0$ and $t=t$ is proportional to the change in the amount of the species i in the course of the reaction. Figure 2 shows the relation between these difference for OH_h and OD_h. The linear relationship indicates that OH_h was replaced by OD_h in the course of the reaction. On the assumption that one OH_h was replaced by one OD_h, the slope α of the plot gives the ratio I_{OD_h}/I_{OH_h}. The total intensity $n_{OH_h}I_{OH_h}+n_{OD_h}(I_{OD_h}/\alpha)$ which is proportional to the sum of the

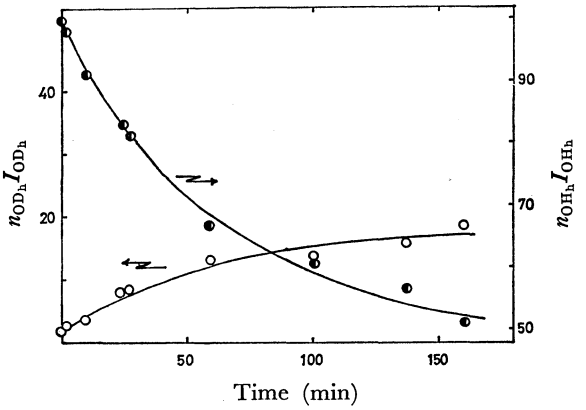

Fig. 1. The change in the intensities of surface OH_h and OD_h in the course of the reaction D_2O+OH at 290 °C.
◐: OH_h ○: OD_h

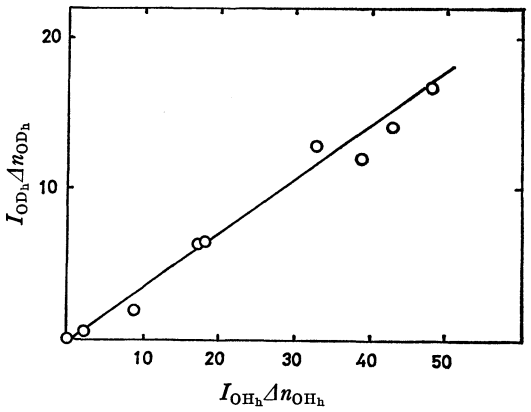

Fig. 2. The plots of the change in OH_h, $I_{OH_h}\Delta n_{OH_h}$ *versus* that in OD_h, $I_{OD_h}\Delta OD_h$.

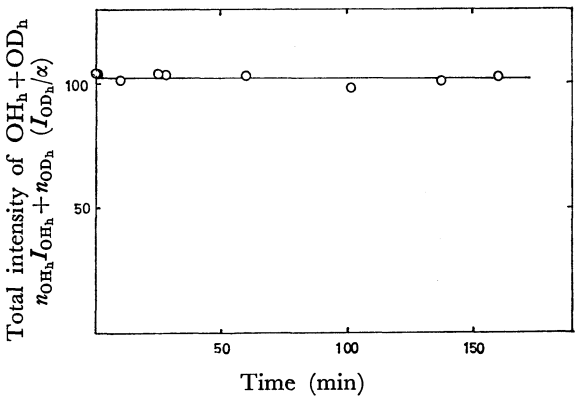

Fig. 3. Total intensity of OH_h+OD_h *versus* time of the reaction D_2O+OH at 290 °C.

amount of OH_h and OD_h was therefore determined from Eq. (2) and the value of α. Figure 3 shows the plot of the total intensity against the time of the reaction. This indicates that the sum of the amount of OH_h and OD_h remained practically constant during the course of the reaction. It is also valid for OH_l and OD_l although the intensities of these species could not be determined as accurately as those of OH_h and OD_h. The results were, therefore, consistent with those described above, indicating that the amount

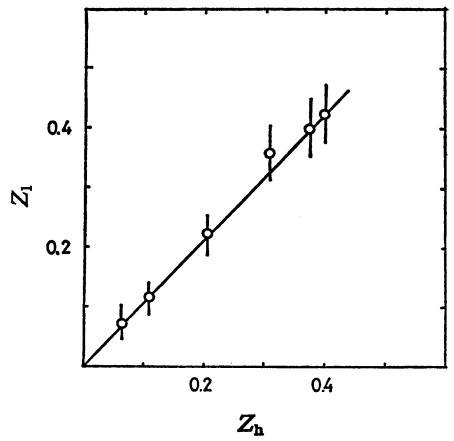

Fig. 4. Relation between the atomic fraction Z_l of OD_l and Z_h of OD_h in the course of the reaction D_2O+OH at 290 °C.

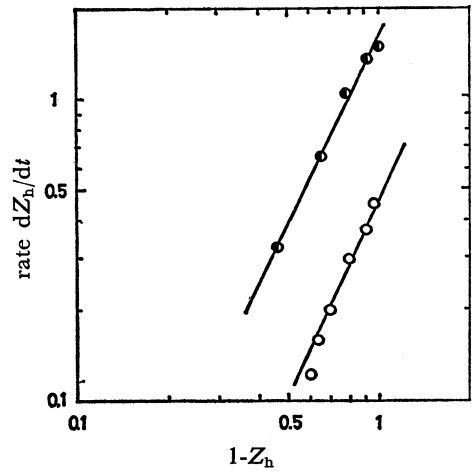

Fig. 5. Rate dZ_h/dt of the increase in the atomic fraction of OD_h *versus* atomic fraction $(1-Z_h)$ of OH_h. The reaction D_2O+OH was carried out at 290 °C(○) and at 310 °C(◐).

of hydroxyl groups can be determined by the Kubelka-Munk equation (1). The ratio of $n_{OD_h}(I_{OD_h}/\alpha)$ to the total intensity gives the atomic fraction of OD_h. Similarly, the atomic fraction of OD_l can be determined.

Mechanism of the Reaction. The amount of surface hydroxyl groups did not change unless deuterium oxide was present in ambient gas. No reaction occurred *via* the combination of a pair of hydroxyl groups. The exchange reaction proceeded at a rate proportional to the amount of reversibly absorbed deuterium oxide.

Figure 4 illustrates the relation between the atomic fractions Z_h of OD_h and Z_l of OD_l in the course of the reaction between D_2O and OH. The results indicate that the atomic fraction of OD_l is practically the same as that of OD_h in the course of the reaction. The rate of the reaction of D_2O with OH_h is illustrated as a function of the atomic fraction $(1-Z_h)$ of OH_h (Fig. 5). It is evident that the rate is proportional to $(1-Z_h)^2$. On the other hand, the rate of the reaction between H_2O and OD is proportional to Z_h^2 and is not proportional to $(1-Z_h)$ or Z_h as is often the case in exchange reactions. We conclude that two hydroxyl groups participate in the reaction. Since the atomic fraction of OH_h is the same as that of OH_l, both species might be simultaneously involved in the reaction. Under the present experimental conditions, reversibly adsorbed deuterium oxide reacts with both species in the rate determining step.

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