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The Observation of Surface Hydroxyl Groups on Metal Oxides by Means of Infrared Reflectance Spectroscopy

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Much work has been carried out applying the transmission method to the infrared spectral study of adsorption.[1-3] In most cases, the catalyst used as an adsorbent has been supported on a carrier which transmitted the infrared radiation, and has been pressed into a disc. However, since the activity of the catalyst is occasionally affected by the presence of the carrier[1] and the pressure applied on the disc,[4] we cannot simply compare the results with those obtained on a powdered catalyst without a carrier.

Recently, it has been shown, however, that the diffuse reflectance method can be applied to the study of the powdered bulk compounds without using any carrier such as KBr or nujol mull.[5] In this respect, we attempted to study the adsorption on metal oxides in powder form. There have already been a few reports studying the adsorption.[6,7]

Experimental

A Nippon Bunko (Japan Spectroscopic Co. Ltd.) Model DR-1 reflectance apparatus was modified so that the catalyst could be prepared in a cell at an elevated temperature without exposing it to air. The optical system was similar to that used by Mamiya,[7] but the cell could be placed horizontally.

The catalysts used were magnesium oxide (J. T. Baker Chem. Co.), silica (Aerosil, Degussa Co.), stannic oxide (Koso Chemical Co.), zinc oxide (Kanto Chemical Co.), germanium oxide (Nakarai Chem., Ltd.), and titanium oxide (E. Merck A. G.). They were placed in a cell (2 mm in depth and 7 mm in diameter) in the form of a powder without using the disc technique. The average particle size of each sample was as follows: silica ($<1\ \mu$), stannic oxide ($8\ \mu$), zinc oxide ($25\ \mu$), germanium oxide ($7\ \mu$), and titanium oxide ($20\ \mu$).

The spectra during the dehydration and the adsorption of water or deuterium oxide were recorded with a Nippon Bunko Model IR-G infrared spectrophotometer. The dehydration was carried out at temperatures ranging from 50 to 310°C in a stream of prepurified nitrogen. Prior to the experiments, it was determined that the reflectivity of the catalysts was unaffected by the amount of the catalysts.[8]

Water or deuterium oxide vapor saturated at room temperature was carried with the nitrogen stream into the cell during the adsorption experiments.

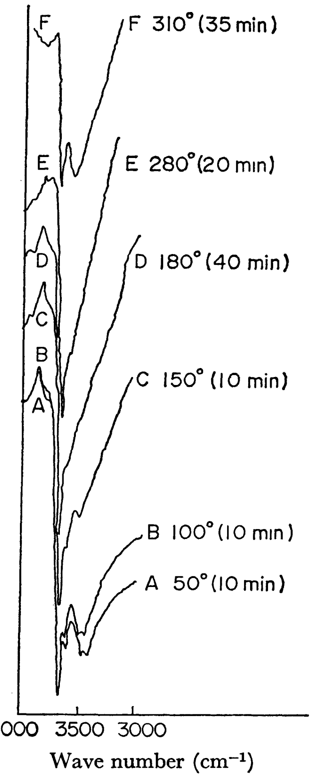

Fig. 1. Dehydration of magnesium oxide at various temperatures.
In brackets in the figure, the time for the dehydration is indicated. (The ordinates are displaced to avoid overlapping of traces.)

Results and Discussion

Figure 1 illustrates the spectra during the dehydration of magnesium oxide at various temperatures. The absorption bands were observed near 3700, 3630, 3500, 3450, and 1630 cm^{-1} at 50°C.[9] When the catalyst was heated at 150°C, the 3450 and 1630 cm^{-1} bands disappeared simultaneously. Since the bands occurred at 3445 and 1627 cm^{-1} in liquid water[10]

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2) L. H. Little, "Infrared Spectra of Adsorbed Species," Academic Press, New York (1966).

3) N. Takezawa and M. J. Low, to be published.

4) W. Osanami, S. Baba, T. Kawakami, and Y. Ogino, Preprints for the 22nd Annual Meeting of the Chemcal Society of Japan, Tokyo (1969), No. 06424.

5) M. Mamiya, *Hyomen (Surface)*, **7**, 45 (1969).

6) G. Kortuem and H. Delfs, *Spectrochim. Acta*, **20**, 405 (1964).

7) M. Mamiya, Preprint for the Analytical Chemistry Meeting, Japan (1968), 11307.

8) With reference to the reflectance of magnesium oxide, the relative reflectivities of the samples were estimated to be 1.78, 1.06, 1.52, 1.78, and 1.48 for silica, stannic oxide, zinc oxide, germanium oxide, and titanium oxide respectively at the wave number of 4000 cm^{-1}.

9) The catalyst was heated to 50°C by infrared radiation.

10) J. E. Hibben, *J. Chem. Phys.*, **5**, 166 (1937).

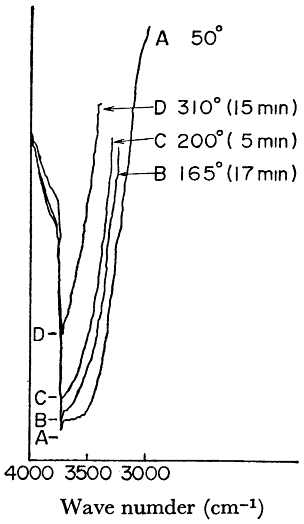

Fig. 2. Dehydration of silica at various temperatures.
In brackets in the figure, the time for the dehydration is indicated.

for its O–H stretching and bending vibrations respectively, the bands observed near 3450 and 1630 cm^{-1} are probably due to water physically adsorbed on magnesium oxide. All the bands other than that at 3700 cm^{-1} decreased on heating at 180°C. The 3700 cm^{-1} band finally disappeared at 310°C, and new bands occurred at 3730 and 3610 cm^{-1}. This observation was in fair accordance with that made by the transmission method.[11] The former band was assigned to the stretching vibration of the surface hydroxyl, whereas the latter was assigned to that of the hydroxyl in the lower-lying layer of the surface of magnesium oxide.[11]

According to the work by Benesi,[12] the 3700 cm^{-1} band can be assigned to the hydroxyl group of magnesium hydroxide, while the bands at 3630 and 3500 cm^{-1} may be due to combinations of the stretching with the librational modes of the hydroxyl of the hydroxide.

Table 1. Surface hydroxyl groups on various oxides

Oxides	Hydroxyl(OH) cm^{-1}	Deuteroxyl(OD) cm^{-1}
MgO	3730, 3610[13] (3752, 3610)[11]	2760, 2670 (2760, 2615)
SiO_2	3735, 3600 (3730, 3580)[14]	2750, 2650 (2760, 2620)
SnO_2	3550 (—)	— (—)
ZnO	3600 (3500)[15]	— (—)
GeO_2	—, 3550 (3673, 3550)[16]	—, 2620 (2710, 2630)
TiO_2	3690, 3350 (3680, 3320)[17]	2730, 2430 (2725, 2475)

- or (—); not determined. The numerical values in the brackets represent the positions of the bands which were determined by other workers using transmission method. The value in the brackets for zinc oxide was obtained as a result of hydrogen adsorption.

In Fig. 2, some results on silica are illustrated; the bands due to surface hydroxyl groups were also observed. When deuterium oxide was adsorbed, bands due to surface deuteroxyl groups were observed. Table 1 lists the positions of these bands as observed on various oxides. In the brackets in the table we list the positions of the bands which were determined by the transmission method. As is evident from the table, the results on silica, zinc oxide, germanium oxide, and titanium oxide also accord with those obtained by the transmission method.

In the present work, we have briefly shown that the infrared reflectance method is applicable to the study of hydroxyl groups on metal oxides.

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