J. Res. Inst. Catalysis, Hokkaido Univ., Vol. 19, No. 1 pp. 56 to 61 (1971)

(Note)

INFRARED DIFFUSE REFLECTANCE SPECTRA OF SURFACE HYDROXYL GROUPS ON MAGNESIUM OXIDE

By

Nobutsune TAKEZAWA,*) Koshiro MIYAHARA*)
and Isamu TOYOSHIMA*)

(Received January 5, 1971)

Infrared spectroscopy is one of the most powerful experimental techniques to gain information on the state of adsorbed species.

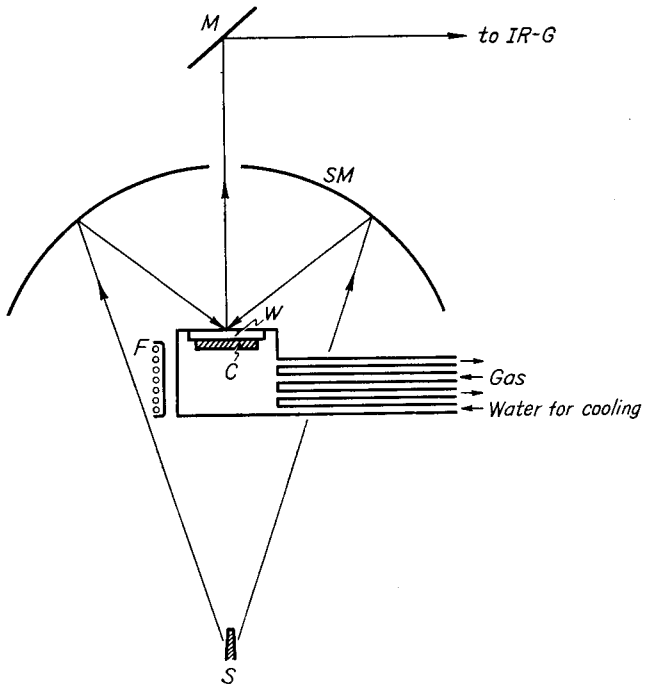
In most cases, the transmission method is employed in which the catalyst is pressed into a thin wafer-like disc.[1-3] However, it is technically difficult to prepare a disc which exhibits adequate transmission of infrared beam. Furthermore, the activity of the catalyst is, in some cases, sensitively affected by the pressure whch is exerted on the disc. In this respect, the present authors aimed to apply the diffuse reflectance method to the study of the species adsorbed on the catalyst in powder form.

Experimentals

A Nippon Bunko (Japan Spectroscopic Co. Ltd.) Model DR-1 diffuse reflectance cell was modified so that the catalyst could be prepared at elevated temperatures without exposing it to air. The arrangement of the cell is shown in Fig.1.

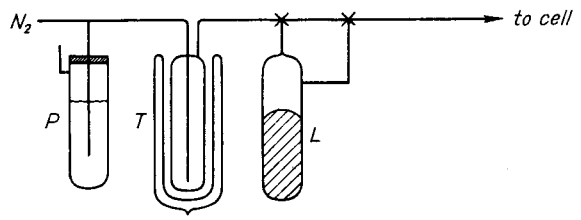
The catalyst used was magnesium oxide (J. T. Baker Chem. Co.)[3] and it was placed in the cell in a form of powder without any press technique. The spectra during the dehydration, the adsorption of water or the exchange with deuterium oxide were determined on a Nippon Bunko Model IR-G infrared spectrophotometer. The de hydrationwas carried out at different temperatures in a stream of prepurified nitrogen. Saturated water or deuterium oxide vapor at room temperature was carried by nitrogen stream into the catalyst bed during the experiments of the adsorption of water or the exchange with deuterium oxide. The apparatus for vapor dose is schematically illustrated in Fig. 2.

*) Research Institute for Catalysis, Hokkaido University, Sapporo, Japan.



C: Catalyst S: Sourve
F: Furnance SM: Spheroidal Mirror
M: Mirror W: Window (KBr)

Fig. 1. The arrangement of the diffuse reflectance cell.



L: A Vessel containing Water or Deuterium Oxide
P: Pressure Regulator T: Trap (Dry-ice)

Fig. 2. The apparatus for vapor dose.

Results and Discussion

Fig. 3 shows the spectra during the dehydration of magnesium oxide at various temperatures. The absorption bands were observed near 3700, 3630, 3500, 3430 and 1630 cm^{-1} at 50°C.*) With the rise of the temperature the latter three bands

*) The temperature of the catalyst was increased to 50°C by infrared radiation.

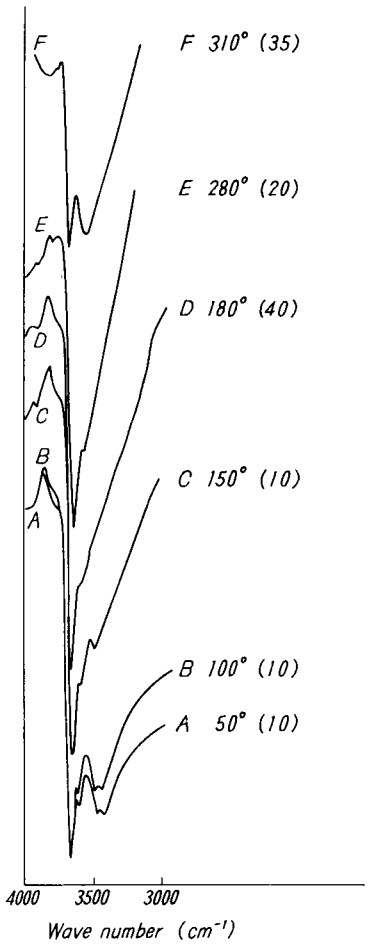


Fig. 3. Dehydration at various temperatures.
Numbers in the brackets indicate the time (min) for the dehydration.
(The ordinates are displaced to avoid overlapping of traces).

weakened appreciably at 100°C, and at 150°C both the bands at 3430 and 1630 cm^{-1} disappeared simultaneously. Since liquid water absorbs at 3445 and 1627 cm^{-1}[14] due to its O-H stretching and bending vibrations respectively, the bands observed near 3430 and 1630 cm^{-1} are due to water on magnesium oxide. On heating at 180°C, the 3500 cm^{-1} band weakened whereas the intensity and the position of the 3700 cm^{-1} band remained unchanged. The latter band, however, finally disappeared at 310°C and new bands were observed at 3730 and 3610 cm^{-1}. From the observations by the transmission method, these two bands were assigned to the stretching vibration of free hydroxyl groups.[5] The former band was attributed

to the surface hydroxyl whereas the latter to the hydroxyl in the second layer of magnesium oxide surface. The 3700 cm^{-1} band, on the other hand, could be assigned to the stretching vibration of the hydroxyl group of magnesium hydroxide according to the work by BENESI.[6] It is therefore concluded that at 50°C magnesium oxide was partly in the state of hydroxide with water. When it was heated, water wss removed at 150°C. Hydroxide decomposed at 310°C and new hydroxyl groups were formed. In this respect, the present results fairly accorded with the previous observations by the transmission method.[4] The bands observed at 3630 and 3500 cm^{-1} could not be assigned at present. These may arise from combinations of the stretching with librational modes of the hydroxyl of the hydroxide.[6]

Fig. 4 shows the spectra during the dehydration at 310°C, from which it

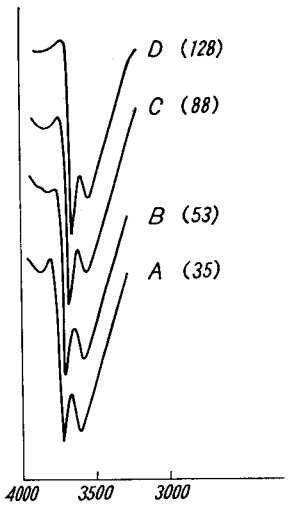


Fig. 4. The dehydration at 310°C. Numbers in the brackets indicate the time (min.) for the dehydration. (The ordinates are displaced to avoid overlapping of traces).

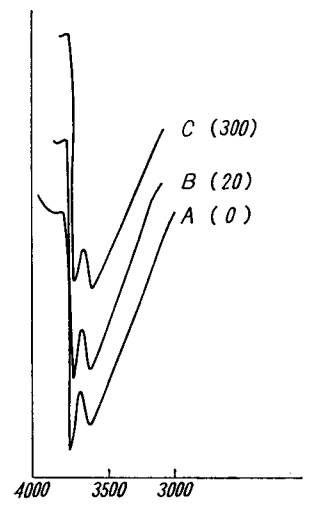


Fig. 5. The adsorption of water at 150°C. Numbers in brackets indicates the time (sec.) for the dehydration. (The ordinates are displaced to avoid overlapping of traces).

is seen that the intensity of the 3700 cm^{-1} band remains unchanged whereas 3610 cm^{-1} band decreases.

From Fig. 5, the former band is found to produce no appreciable change whereas the latter increased during the adsorption of water at 150°C. It is thus confirmed that these two bands arise from the different hydroxyl groups.

Fig. 6 shows the spectra of magnesium oxide at 310°C during the exchange of the hydroxyl groups with deuterium oxide vapor. The adsorption of deuterium

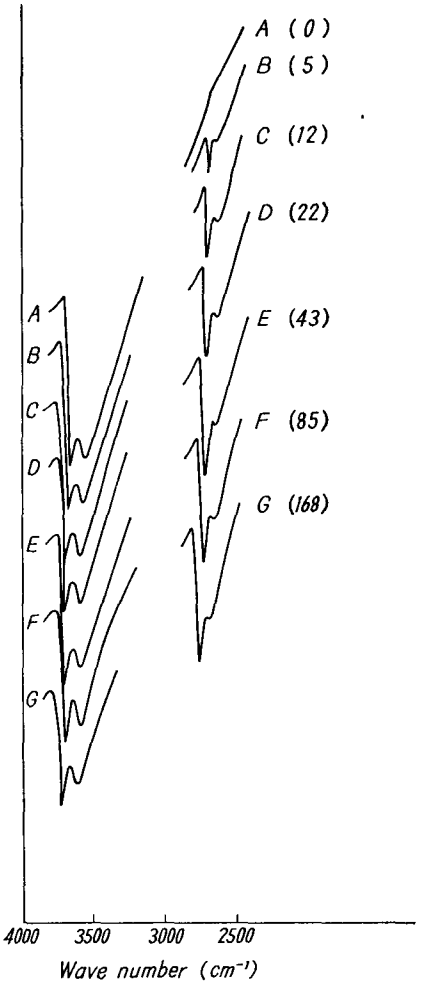


Fig. 6. The exchange of the hydroxyl groups with deuterium oxide.
Numbers in brackets indicate the time (min) for the exchange.
(The ordinates are displaced to avoid overlapping of traces).

oxide produced new bands at 2760 and 2670 cm^{-1} which were assigned to the stretching vibration of free deuteroxyl groups, corresponding to the bands at 3730 and 3610 cm^{-1} on hydroxylated magnesium oxide. The former two bands grew and the latter two weakened, indicating that the hydroxyl groups were replaced by the deuteroxyls.

From the present work, we showed that the diffuse reflectance method could be applicable to the study of the reaction on the surface of oxide.

This work was supported in part by the Incentive Grant for Scientific Research of Ministry of Education to which one of the present authors (N.T.) gratefully acknowledged. The authors express thanks to Prof. T. NAKAMURA for his careful reading of the manuscript. Thanks are also extended to Nippon Bunko Co. Ltd. in the construction of the diffuse reflectance cell.

References

1) R. P. EISCHENS and W. A. PLISKIN, Adv. in Catalysis, W. G. Frankenburger, ed. Academic Press, New York, Vol. X, 1 (1958).
2) L. H. LITTLE, "*Infrared Spectra of Adsorbed Species*", Academic Press, New York, 1966.
3) N. TAKEZAWA and M. J. D. LOW, to be published.
4) J. H. HIBBEN, J. Chem. Phys., **5**, 166 (1937).
5) P. J. Anderson, R. F. HORLOCK and J. F. OLIVER, Trans. Faraday Soc., **61**, 2754 (1964).
6) H. A. BENESI, J. Chem. Phys., **30**, 852 (1959).