Infrared Reflectance Spectra of Adsorbed Species on Opaque Metal Oxides

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Summary The i.r. diffuse reflectance method can be applied successfully to the study of adsorption on opaque metal oxides.

MUCH work on the i.r. spectra of chemisorbed species deals predominantly with transmission techniques.[1] I report that the diffuse reflectance method can be applied to the study of adsorption on opaque metal oxides, without the use of any support.

Experiments were carried out in a similar manner to those described elsewhere.[2] The catalysts used were ferric oxide (prepared from ferric oxalate) and chromic oxide (Nakarai Chem. Ltd., Guaranteed grade). These were placed in a cell (2 mm in depth and 7 mm in diameter) and were heated at 300° in a stream of helium. Thereafter, formic acid or deuterium oxide vapour (saturated at room temperature) was carried with the helium stream and was adsorbed at 80°. The spectra were obtained at room temperature. These were recorded with a Nippon Bunko (Japan Spectroscopic Co. Ltd.) Model IR-G i.r. spectrophotometer to which a Model DR-3 diffuse reflectance apparatus was attached. The experimental arrangement used is shown schematically in the Figure. White light from the source was initially reflected on a spheroidal mirror and was brought to focus upon the sample. The reflected light from the sample was detected by the spectrophotometer.

When ferric oxide was heated at 300° in the helium stream, the sharp absorbtion band due to the OH stretching vibration occurred at 3670 cm^{-1}. After the adsorption of formic acid, this band disappeared and bands due to carboxylate stretching vibrations were observed near 1550 and 1360 cm^{-1}, together with bands due to CH stretching vibrations at 2940 and 2865 cm^{-1}. The reflectance spectrum of ferric formate showed absorption bands near 2950, 2870, 1560, and 1370 cm^{-1}. This coincides fairly well with

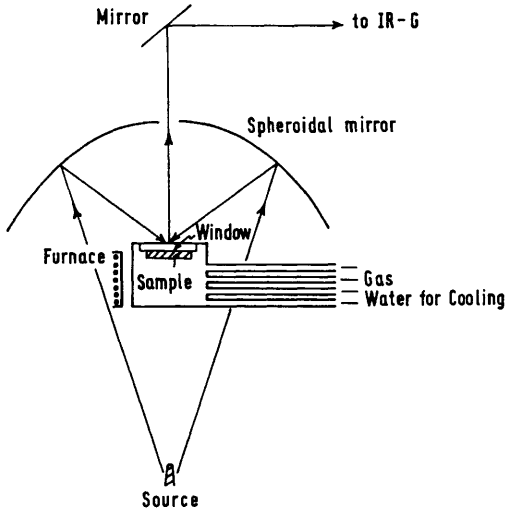

FIGURE. *Schematic diagram of the reflectance apparatus*

the spectrum of adsorbed formic acid, indicating that surface formate is formed during the adsorption.

When deuterium oxide was adsorbed, the 3680 cm^{-1} band decreased in intensity, and a new band due to the deuteroxy-group was observed at 2730 cm^{-1}. Surface hydroxy-groups may thus be replaced by deuteroxy-groups.

The adsorption of gaseous formic acid on chromic oxide was attempted, but no change in the spectrum was observed. However, when liquid formic acid was brought in contact with chromic oxide and the solid was evacuated at 80° for 1 h, bands due to carboxylate stretching vibrations were observed.

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[1] For example, see "Infrared Spectra of Adsorbed Species," L. H. Little, Academic Press, New York, 1966.
[2] G. Kortuem and H. Delfs, *Spectrochim. Acta*, 1964, **20**, 405; N. Takezawa, K. Miyahara, and I. Toyoshima, *J. Res. Inst. Catalysis, Hokkaido Univ.*, 1971, **19**, 56; N. Takezawa, to be published in *Bull. Chem. Soc. Japan*, 1972, **45**, No. 1.