Infrared Spectra of Surface V=O Bond of Vanadium Pentoxide

Yoshiya KERA, Shousuke TERATANI and Kozo HIROTA

Fuculty of Science, Osaka University, Toyonaka, Osaka

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With reference to the catalytic activity of vanadium pentoxide, it is interesting to investigate the behavior of the V=O group projecting from the net plane of the oxide, because it is proposed that the oxygen atom of this group is very reactive during the oxidation, and gaseous oxygen changes into the product *via* this combined state.[1] Hence, it is necessary to confirm this state for the "oxidation-reduction mechanism"[2] to be true, especially because there is still an objection to the mechanism.[3]

The present authors attempted to investigate the combined state of the exchangeable oxygen in vanadium pentoxide by means of the infrared spectroscopy and could obtain an affirmative result, which will be reported briefly.

Vanadium pentoxide was treated at 490°C with mixture of oxygen and carbon dioxide,*1 both containing *ca.* 60 atom% of ^{18}O. After 24 hr, isotopic equilibrium between carbon dioxide and V_2O_5 was established. The ^{18}O concentration of carbon dioxide decreased to about 19 atom%, while ^{18}O concentration of oxygen did not change. IR absorption spectrum of this oxide was measured by the KBr-disk method over the range from 1300 to 400 cm^{-1}, by a DS-402G type apparatus of Japan Spectroscopic Co., Ltd. In Fig. 1, the spectrum of the oxide is shown by curve B and the one of the oxide without the treatment by curve A*2 for the sake of comparison. A new

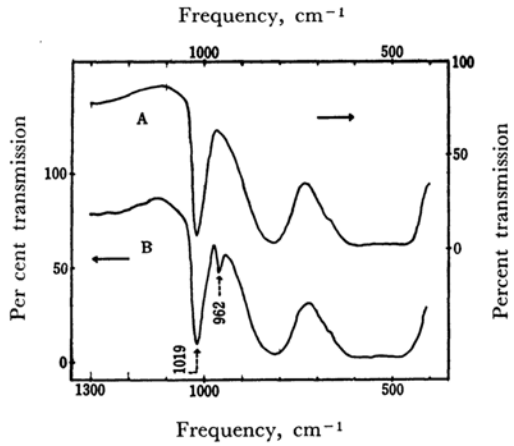

Fig. 1. IR absorption spectra of vanadium pentoxide.

band appears at 962 cm^{-1} near the strong band at 1019 cm^{-1}, which was regarded as the V=O stretching band.[1,4] No other new band can be observed also in the spectral range studied in this research. The new band has reasons to be ascribed to the $V=^{18}O$ stretching band.

If the 1019 cm^{-1} band shifts by isotopic substitution, the calculated $V=^{18}O$ stretching band would appear at 961 cm^{-1} under the assumption that the oxygen atom forms a bond with an atom of infinite mass. This value coincides well with the observed one, 962 cm^{-1}. Secondly, this band appeared, though very weakly, on the oxide which was contacted with heavy carbon dioxide at 370°C. Moreover, the higher was the equilibrium concentration of ^{18}O in carbon dioxide, the more intense was the band.

In short, the above result offers a support to the presence of the exchangeable oxygen in the surface V=O bond.

1) K. Tarama, S. Teranishi, S. Yoshida and N. Tamura, Proc. 3rd Intern. Cong. Catalysis, Amsterdam (1965), p. 262.

2) J. M. Weiss and C. R. Downs, *Ind. Eng. Chem.*, **15**, 965 (1923), *etc.*

3) V. A. Roiter, *Kinetika i Kataliz (SSSR)*, **1**, 63 (1960).

*1 According to the research now in progress, oxygen exchange occurs rapidly between carbon dioxide and vanadium pentoxide above 370°C. (*Cf.* K. Hirota, K. Kishimoto, T. Imanaka and M. Chono, *Shokubai*, **6**, 48 (1964))

*2 The spectrum of the ^{18}O enriched V_2O_5 did not change by standing this sample in the air for two weeks.

4) L. D. Frederickson and D. M. Hausen, *Anal. Chem.*, **35**, 818 (1963).