The Adsorbed State of Oxygen on Vanadium Pentoxide Catalyst

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ESR studies on the adsorbed state of oxygen on metal oxides have been reported, the most extensive works being performed with the adsorbed oxygen on zinc oxide and titanium oxide.[1)]

We[2)] observed three kinds of ESR signals (α, β and γ) for oxygen adsorbed on vanadium oxide supported on silica. One of these signals, β-signal, is similar to that which was recently reported by Kasansky.[3)] The present communication is concerned with the ESR spectra of the adsorbed oxygen and their stability.

Vanadium oxide catalyst was prepared as follows. Synthetic silica which was prepared by hydrolysis of ethyl ortho silicate was impregnated with aqueous solution of ammonium meta vanadate, followed by drying at 100°C and calcination in air at 500°C. The content of vanadium oxide was 5 wt%.

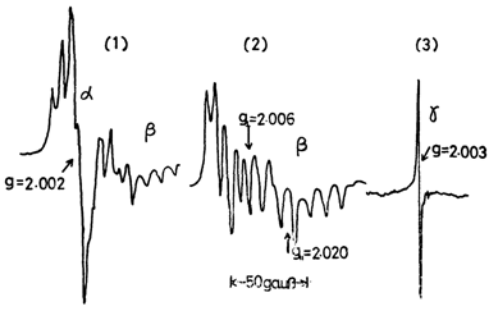

Fig. 1. ESR spectra of the oxygen adsorbed on $V_2O_{5-\delta}$-SiO_2.
(1) measured at −80°C. (P_{O_2} ; 20 Torr)
(2) measured at room temperature. (P_{O_2} ; 20 Torr)
(3) measured at room temperature. $V_2O_{5-\delta}$-SiO_2 was treated by O_2 at 200°C for 30 min and followed by evacuation at the same temperature.

Prior to the adsorption of oxygen, the catalyst was treated with hydrogen at 350°C in a glass reactor which had a quartz tube for ESR measurement as a side arm. This treated catalyst can be expressed as $V_2O_{5-\delta}$-SiO_2 ($\delta \simeq 0.1$).

ESR measurements were carried out at various temperatures by a 3BSX type spectrometer manufactured by Japan Electron Optics Co.

Some observed ESR spectra are shown in Fig. 1. Spectrum (1) is composed of two kinds of absorption signals. One (β-signal) is essentially the same as spectrum (2) which has h.f.s. due to interaction with ^{51}V ($I=7/2$),[3)] and the other (α-signal) is a singlet signal. At temperatures higher than −60°C, this α-singal is very unstable and disappears to leave β-signal. Spectrum (3) is a narrow singlet signal (γ-signal) observed for the catalyst treated with oxygen at 200°C. In Table 1, the temperature range in which each signal can be observed in spectra is shown together with characteristic parameters of signals.

By comparing these signals with those of the adsorbed oxygen on zinc oxide and titanium oxide, we tentatively assigned α-, β- and γ-signal as adsorbed $O_2^-(\alpha)$, $O_2^-(\beta)$ and O^- respectively. Preliminary studies on the reactivity of these adsorbed species reveal that $O_2^-(\beta)$ reacts with ethylene at room temperature and O^- reacts with sulfur dioxide at 200°C.

TABLE 1. CHARACTERISTICS OF SIGNALS

Signal	Observed temperature	g	A or ΔH_{msl} (gauss)
α	from −120°C to −60°C	2.002	$\Delta H=8.0$
β	from −120°C to 150°C	$g_{\parallel}=2.020$	$A_{\parallel}=9.4$
		$g_{\perp}=2.006$	$A_{\perp}=5.8$
γ	from 20°C to 350°C	2.003	$\Delta H=0.96$

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3) V. A. Shvets, M. E. Sarichev and V. B. Kasansky, *J. Catalysis*, **11**, 378 (1968).