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BRIEF COMMUNICATION

The Concentration of Surface V=O Species on Oxidized Vanadium Oxide Catalysts

AKIRA MIYAMOTO, ATSUSHI HATTORI, AND YUICHI MURAKAMI

Department of Synthetic Chemistry, Faculty of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464, Japan

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On the basis of an oxidized surface state model of vanadium oxides, Andersson has theoretically shown that the concentration of surface V=O species on oxidized V_6O_{13} or V_2O_4 catalyst is higher than that on V_2O_5 catalyst (*1*). The purpose of this study was to confirm the validity of this inference experimentally.

V_2O_5 was prepared by the thermal decomposition of ammonium metavanadate at 773 K for 3 hr in a stream of O_2 (*2–4*). V_6O_{13} and V_2O_3 were prepared by the reduction of the V_2O_5 in a stream of H_2 for 1 hr at 703 and 763 K, respectively (*2, 3*). The stoichiometries were confirmed by means of a Rigaku D-3F x-ray diffractometer. The number of surface V=O species (L) was determined by using the rectangular pulse technique described previously (*4, 5*). This technique is based on the following reactions:

$$\mathrm{V{=}O + NO + NH_3 \rightarrow V\text{-}OH + N_2 + H_2O}, \quad (1)$$

$$\mathrm{V\text{-}OH \xrightarrow{\text{bulk } V=O} V{=}O + \tfrac{1}{2}H_2O}, \quad (2)$$

together with the introduction of NO and NH_3 mixture in a rectangular pulse shape onto the preoxidized catalyst and detection of the concentration profile of N_2 produced by Eq. (1). The separation of N_2 due to the initial surface V=O species from that due to the V=O species reproduced by Eq. (2) leads to the determination of L, whereas the analysis of the concentration profile of N_2 due to the V=O species formed in Eq. (2) gives information on the bulk V=O species. The preoxidation of the catalyst was conducted in a stream of O_2 under conditions shown in Table I. The BET surface area of the catalyst (S_{BET}) was determined by using a conventional flow type apparatus using N_2 as an adsorbate. XPS spectra of the preoxidized catalysts were obtained Shimazu ESCA 750 photoelectron spectrometer.

On the basis of the XPS spectra of V_6O_{13}, V_2O_3, and V_2O_5, the vanadium ion on the catalyst surface was found to be in the highest oxidation state, V^{5+}, for all catalysts. This agrees with the surface model adopted by Andersson, that an oxidized vanadium oxide forms V^{5+} ions on its surface while the bulk oxidation state decreases with decreasing O/V ratio of the oxide (*1*). Figure 1 shows examples of concentration profiles of N_2 produced by Eq. (1) for oxidized

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TABLE I

RESULTS OF THE NUMBER OF SURFACE V=O SPECIES (L), THE BET SURFACE AREA (S_{BET}), AND THE CONCENTRATION OF SURFACE V=O SPECIES (C)

	Preoxidation[a]				
Catalyst	Temp (K)	Time (min)	L (μmole/g)	S_{BET} (m^2/g)	C (μmole/m^2)
V_2O_5[b]	773	15	22	5.4	4.1
V_6O_{13}[c]	549	1	74	9.0	8.2
	583	1	67	9.0	7.4
	570	5	95	9.0	10.6
	548	5	91	9.0	10.1
	558	10	94	9.0	10.4
V_2O_3[c]	573	1	33	9.4	3.5
	574	5	70	9.4	7.4
	568	5	69	9.4	7.3
	568	10	67	9.4	7.1

[a] The flow rate of O_2 was 125 cm^3-STP/min.

[b] The value of L did not change with the preoxidation condition.

[c] The concentration of the surface V=O species on the nonoxidized V_6O_{13} or V_2O_3 was much lower than that on V_2O_5: 0.8 μmole/m^2 for V_6O_{13} and 0 μmole/m^2 for V_2O_3.

V_2O_5, V_6O_{13}, and V_2O_3 catalysts measured under various preoxidation conditions. As shown, the profile was composed of two parts—the initial sharp N_2 and the tailing N_2. As precisely described in previous papers (*4*, *5*), the initial sharp N_2 can be separated from the tailing N_2 by the dotted line shown in Fig. 1, and the number of surface V=O species is given by the number of the initial sharp N_2. Table I shows results of L and S_{BET} together with the concentration of surface V=O species (C). Here, C is defined as L/S_{BET}. As shown in Table I, C for the oxidized V_6O_{13} and V_2O_3 catalysts was considerably higher than C for the V_2O_5. Although the results support the validity of the theoretical inference obtained by Andersson (*1*), the following points should be noted with respect to the concentration profiles of N_2. As shown in Fig. 1, the concentration of N_2 at the tailing part for the V_6O_{13} catalyst was much lower than that for the V_2O_5 catalyst. Similarly the tailing of N_2 was barely observed for the oxidized V_2O_3 catalyst. According to Eqs. (1) and (2) these results indicate that the reoxidation of the surface V–OH species by the bulk V=O species scarcely takes place for V_6O_{13} or V_2O_3. This is reasonable since by using infrared spectroscopy (*2*, *3*) the amount of

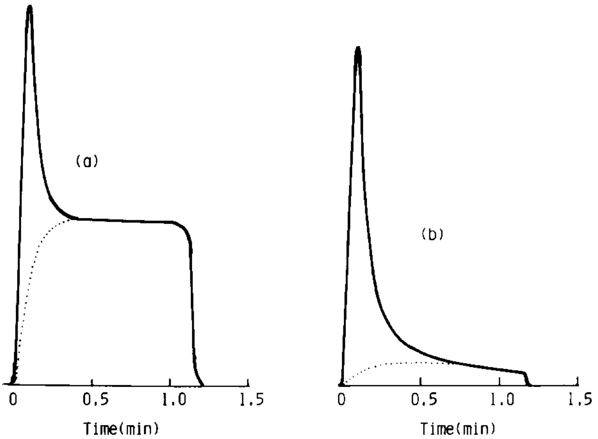

FIG. 1. Examples of concentration profiles of N_2 produced by the reaction of the rectangular pulse of NO and NH_3 mixture with preoxidized V_2O_5 (a) and V_6O_{13} (b) catalysts. Preoxidation condition: 773 K for 15 min for V_2O_5 and 583 K for 1 min for V_6O_{13}. Condition of the rectangular pulse experiment: 567 K for V_2O_5 and 583 K for V_6O_{13}; other experimental variables were the same as those employed in previous studies (*4*, *5*).

bulk V=O species for V_6O_{13} or V_2O_3 has been found to be much smaller than that for V_2O_5.

In conclusion, the concentration of surface V=O species on the oxidized V_6O_{13} or V_2O_3 catalyst was found to be significantly higher than that on the V_2O_5 catalyst. This provides experimental evidence for the validity of the oxidized surface state model proposed by Andersson (*1*).

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