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CVD Preparation of Vanadium-oxide Supported on Silica Catalyst and Its Structure

Kei INUMARU, Toshio OKUHARA,* and Makoto MISONO
Department of Synthetic Chemistry, Faculty of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Elementary processes of the formation of vanadium-oxide on SiO_2 by CVD of $VO(OC_2H_5)_3$ were studied. All Si-OH groups on the SiO_2 reacted with $VO(OC_2H_5)_3$ to form either $Si\text{-}O\text{-}V(=O)(OC_2H_5)_2$ or $(Si\text{-}O)_2\text{-}V(=O)(OC_2H_5)$. By the repeated CVD, highly dispersed V_2O_5 overlayer was formed as confirmed by XPS and XRD. This catalyst was much more active than V_2O_5/SiO_2 prepared by an impregnation method for oxidative dehydrogenation of ethanol.

Recently, preparation and catalysis of thin films of metal oxides formed on supports have attracted much attention.[1a-f] CVD (Chemical Vapor Deposition) is a useful method to prepare them.[2a-e] Bond et al.[1a] reported that V_2O_5/TiO_2 obtained by CVD of $VOCl_3$ showed a high selectivity for the oxidation of o-xylene. It has been reported that V_2O_5 on SiO_2 prepared by the impregnation method is present as large crystallites.[1f,3] Here, we attempted to prepare highly dispersed V_2O_5/SiO_2 by the CVD method. The elementary reactions of $VO(OC_2H_5)_3$ with OH groups on the SiO_2 surface, the key steps determining the structure of vanadium-oxide overlayer, were examined mainly by IR. The structure of the vanadium-oxide overlayer was characterized by XRD and XPS.

Two different types of vanadium oxide supported on SiO_2 were prepared. The first was obtained by the CVD method. After SiO_2 (Aerosil 200, 203 $m^2 \cdot g^{-1}$) was evacuated at 523 or 773 K in a high vacuum system,[4] the vapor of $VO(OC_2H_5)_3$ (1×10^{-1} Torr, 1 Torr = 133.3 Pa) was introduced at 423 K. Then the sample was heated up to 723 K at a rate of 10 $deg \cdot min^{-1}$. Hereafter, this adsorption-desorption cycle is called "CVD". By changing the number of the CVD cycles, the loading amount was varied. The catalysts thus prepared are designated as V_2O_5/SiO_2(CVD) (as described below, XPS shows that the valence of vanadium is 5+). The second was prepared by the impregnation method (V_2O_5/SiO_2(Imp)) according to the literature.[3] All samples were calcined in air at 623 K for 1 h.

Figure 1 shows the changes of IR spectra of the SiO_2 surface in the OH stretching region. A sharp peak due to isolated Si-OH groups appeared at 3745 cm^{-1} for SiO_2, together with a broad peak at around 3600 cm^{-1} after evacuation at 773 K. The latter is due to the OH group in the solid bulk, because this did not exchange upon contact with D_2O vapor as in the literature.[5)] After the introduction of $VO(OC_2H_5)_3$, the sharp peak disappeared (Fig. 1b), and ethanol was evolved in the gas phase.

In Table 1, the amounts of gas phase products during the CVD are summarized. The amounts of Si-OH were determined by sodium naphthalene titration method[6)] and were similar to those in the literature.[7)] The amounts of ethanol evolved were in agreement with the amounts of the surface Si-OH, indicating that all Si-OH groups reacted with the $VO(OC_2H_5)_3$. The adsorption of ethanol on the original SiO_2 at this temperature was confirmed to be negligibly small.

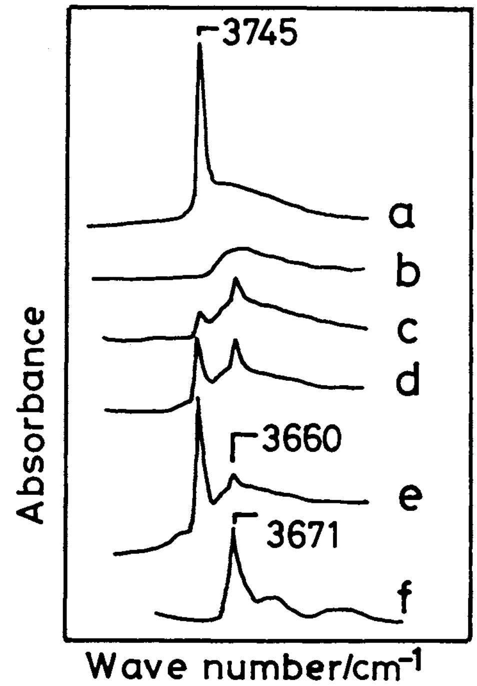


Fig. 1. Changes in the IR spectra in the OH region of SiO_2 during CVD.
(a) Pre-evacuated at 773 K, (b) After introduction of $VO(OC_2H_5)_3$ at 423 K, (c) Evacuated at 523 K, (d) 623 K, (e) 723 K, (f) V_2O_5 (evacuated at 573 K).

The fact that the amounts of ethanol evolved were greater than those of vanadium atom (Table 1) indicates that $(Si\text{-}O)_2\text{-}V(=O)(OC_2H_5)(SiOH/V = 2)$

Table 1. Amount of Gas Phase Product in the First Cycle of CVD (423 K)

Temp[a)] /K	Si-OH[b)]	Amount of gas phase product[c)]				Amount of V[d)] /atom nm^{-2}	n[e)]	Φ[f)]
		$A(C_2H_5OH)$	A(others)	B	Total			
523	4.2	4.34	0.28	2.55	7.17	2.52	1.72[g)]	0.72[g)]
							1.82[h)]	0.82[h)]
773	1.7	1.91	0.13	1.61	3.65	1.20	1.59[g)]	0.59[g)]
							1.57[h)]	0.57[h)]

a) Pretreatment temperature of SiO_2. b) Density of OH groups; nm^{-2}. c) Number of molecule nm^{-2}, A; products when $VO(OC_2H_5)_3$ was adsorbed, B; products during TPD up to 723 K. d) Measured by ICP. e) The average number of Si-OH reacted with one $VO(OC_2H_5)_3$ molecule. f) The fraction of $(Si\text{-}O)_2\text{-}VO(OC_2H_5)$ (**2**), see text. g) From method 1. h) From method 2.

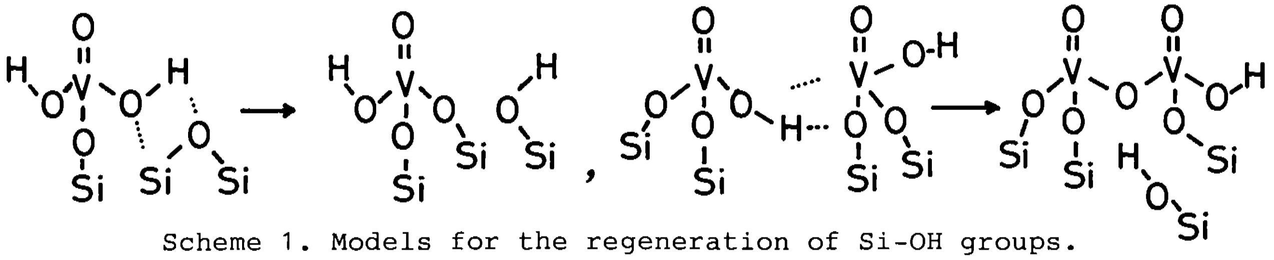
and/or $(Si\text{-}O)_3\text{-}V(=O)$ (SiOH/V = 3) were formed in addition to $Si\text{-}O\text{-}V(=O)(OC_2H_5)_2$(SiOH/V = 1). Considering the models of SiO_2 surface by Peri[8)] and Sindorf,[9)] the reaction of one $VO(OC_2H_5)_3$ molecule with three Si-OH groups to form $(Si\text{-}O)_3\text{-}V(=O)$ may be excluded by steric reasons. So, the following two reactions (Eqs. 1 and 2) can be proposed.

$$Si\text{-}OH + VO(OC_2H_5)_3 \longrightarrow Si\text{-}O\text{-}VO(OC_2H_5)_2\ (\mathbf{1}) + C_2H_5OH \qquad (1)$$

$$2Si\text{-}OH + VO(OC_2H_5)_3 \longrightarrow (Si\text{-}O)_2\text{-}VO(OC_2H_5)\ (\mathbf{2}) + 2C_2H_5OH \qquad (2)$$

If the fraction of the species **2** is Φ ($= \mathbf{2}/(\mathbf{1} + \mathbf{2})$) and the average number of OH groups reacted with one molecule of $VO(OC_2H_5)_3$ is n, n is expressed as $2\,\Phi + 1\,(1-\Phi) = \Phi + 1$. The value of n can be estimated by either N(ethanol evolved)/N(vanadium atom deposited)(method 1) or 3 x N(ethanol evolved)/N(total of gas phase products (based on C_2))(method 2), independently, where N's denote the amounts of molecules (or atoms). The two methods gave very similar values, indicating the validity of the values estimated. From the amounts of gas phase products and vanadium atom, Φ was determined to be 0.72 - 0.82 and 0.59 - 0.57 for SiO_2 pretreated at 523 and 773 K, respectively (Table 1). It is reasonable that Φ increased as the density of Si-OH groups increased.

As shown in Fig. 1c, a new peak at 3660 cm^{-1} appeared after 523 K-evacuation, together with the regeneration of Si-OH groups. This new peak is assigned to V-OH, based on the peak position that is close to the OH of V_2O_5 surface (3671 cm^{-1})(Fig. 1f). Upon heating, the V-OH peak increased initially and then decreased, while the intensity of the Si-OH peak continued to increase. This fact shows that Si-OH is regenerated by the reaction of V-OH probably with Si-O or Si-O-V as illustrated in the Scheme 1.



Scheme 1. Models for the regeneration of Si-OH groups.

In subsequent CVD cycles, similar spectral changes were observed. While the amount of Si-OH regenerated decreased by repeated CVD (after 7th run, only 20% of the initial Si-OH was regenerated), the amounts of V_2O_5 deposited did not decrease much (the first run; 3.6wt%, 2nd to 10th run; about 2.5 wt%). This indicates that both the Si-OH and V-sites are active for the adsorption of $VO(OC_2H_5)_3$.

Figure 2 shows the changes of XPS intensity ratio (I_V/I_{Si}) as a function of the amount of V_2O_5 loading, where I_V and I_{Si} are integrated peak intensities of vanadium ($2p_{3/2}$; 517.9 eV, which corresponds to V^{5+}) and silicon ($2p_{1/2}$ + $2p_{3/2}$; 103.6 eV), respectively. The XPS peak ratios for V_2O_5/SiO_2(CVD) increased linearly to higher levels than those for V_2O_5/SiO_2(Imp). This result clearly shows that the V_2O_5 obtained by CVD are highly dispersed as compared with those by the impregnation. XRD data support the conclusion deduced by XPS; no diffraction lines were found for V_2O_5/SiO_2(CVD) with less than 9.1wt% of V_2O_5 (very weak lines were detected at 19.4wt%), while even 6.8wt%V_2O_5/SiO_2(Imp) gave clear peaks due to V_2O_5 crystallites.

Oxidative dehydrogenation of ethanol was performed at 493 K in a closed circulation system (initial pressures of ethanol and O_2 were both 25 Torr). It was found that acetaldehyde was formed selectively, and the catalytic activity of 19.4wt%V_2O_5/SiO_2(CVD) was 3 - 4 times that of 19.4wt%V_2O_5/SiO_2(Imp) and about 50 times (per weight of V_2O_5) that of the bulk V_2O_5. The high catalytic performance is probably due to the high surface area of the V_2O_5 on the surface.

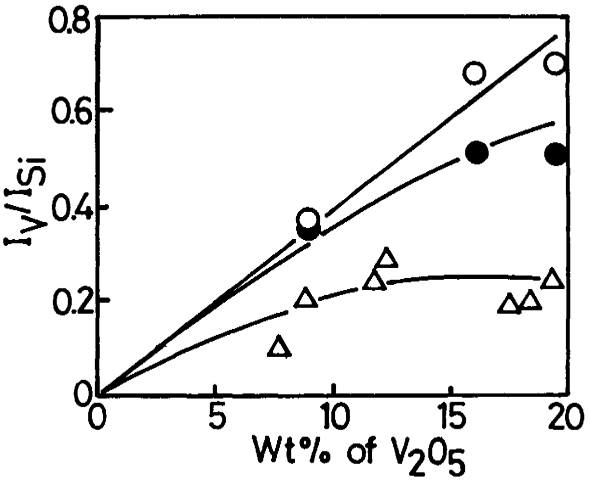


Fig. 2. XPS intensity ratio (I_V/I_{Si}) as a function of the amount of V_2O_5.
○: V_2O_5/SiO_2(CVD) decomposed at 723 K
●: V_2O_5/SiO_2(CVD) calcined at 623 K
△: V_2O_5/SiO_2(Imp).

References

1) a) G. C. Bond and K. Bruckman, Faraday Discuss. Chem. Soc., 72, 235 (1981); b) G. C. Bond and P. Konig, J. Catal., 77, 309 (1982); c) J. Kijenski, A. Baiker, M. Grinski, P. Dollenmeier, and A. Wokaun, J. Catal., 101, 1 (1986); d) Y. Iwasawa and M. Yamagishi, J. Catal., 82, 373 (1983); e) I. E. Wachs, R. Y. Saleh, S. S. Chan, and C. C. Chersich, Appl. Catal., 15, 339 (1985); f) F. Roozeboom, M. C. Mittelmeijer-Hazelger, J. A. Moulijn, J. Medema, V. H. J. de Beer, and P. J. Gellings, J. Phys. Chem., 84, 2783 (1980).
2) a) M. Niwa, M. Kato, T. Hattori, and Y. Murakami, J. Phys. Chem., 90, 6233 (1986); b) S. Sato, H. Sakurai, K. Urabe, and Y. Izumi, Chem. Lett., 1985, 277; c) M. Anpo, M. Sunamoto, and M. Che, J. Phys. Chem., 93, 1187 (1989); d) T. Okuhara and J. M. White, Appl. Surf. Sci., 29, 223 (1987); e) Y. Imizu and A. Tada, Chem. Lett., 1989, 1793.
3) Y. Murakami, M. Inomata, K. Mori, T. Ui, K. Suzuki, A. Miyamoto, and T. Hattori, "Preparation of Catalysts III," Elsevier (1983), p.538.
4) K. Inumaru, T. Okuhara, and M. Misono, Shokubai, 32, 51 (1990).
5) V. Ya. Davydov, A. V. Kiselev, S. A. Kiselev, and V. O.-V. Polotnyuk, J. Colloid Interface Sci., 74, 378 (1980).
6) J. Kijenski, R. Hombek, and S. Malinowski, J. Catal., 50, 186 (1977).
7) J. J. Fripiat and J. Uytterhoeven, J. Phys. Chem., 66, 800 (1962).
8) J. B. Peri and A. L. Hensley, Jr., J. Phys. Chem., 72, 2926 (1968).
9) D. W. Sindorf and E. Maciel, J. Am. Chem. Soc., 105, 1487 (1983).

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