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Structures and dehydrogenation activities of vanadium oxide overlayers on supports

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EXAFS study clarified the structure of vanadium oxide overlayers on MgO, Al_2O_3 and SiO_2. On MgO, vanadium oxides were present as mixed oxides such as $Mg_3V_2O_8$. Vanadium oxides were in the form of thin films on Al_2O_3 regardless of the preparation method. On the other hand, three different structures were present on SiO_2; isolated species and crystallites by an impregnation method and thin films by chemical vapor deposition (CVD). The thin films on SiO_2 were stable even at 773 K in air. Temperature programmed decomposition of ethanol adsorbed revealed that the dehydrogenation activities were strongly affected by the structure of the overlayers; thin films > crystallites >> isolated species.

Keywords: Vanadium oxide overlayers; thin films; support effects; dehydrogenation

1. Introduction

Catalytic properties of supported vanadium oxides are sensitive to their structures, which depend on the preparation methods and the catalyst supports [1,2]. TiO_2 and Al_2O_3 are good supports for the selective oxidations of xylene and benzene [2]. On the other hand, SiO_2 is a useful support for photo-oxidations [3,4] and the oxidation of benzene to phenol using N_2O [5]. Kung et al. reported that V_2O_5/MgO catalyzed selective oxidative dehydrogenation of butane [6].

Because these overlayers do not possess long-range order in most cases, it was often difficult to analyze the structure by using XRD. In those cases, EXAFS is suitable for the analysis of the structure. In the present study, we attempted to elucidate the effects of the supports on the structure of vanadium oxides by using EXAFS. Chemical properties of vanadium oxide overlayers were examined by temperature programmed decomposition of adsorbed ethanol.

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2. Experimental

As supports, SiO_2 (Aerosil 200, 203 $m^2 g^{-1}$, Al_2O_3 (Aerosil Al_2O_3-C, 93 $m^2 g^{-1}$) and MgO (obtained by decomposition of $MgCO_3$ in vacuo) were used. The catalysts were prepared by two methods. The first was an impregnation method using an aqueous solution of oxalic acid and NH_4VO_3 [7]. After the impregnation, the samples were calcined at 623 K in air (denoted as, e.g., V_2O_5/SiO_2(Imp)). The second was a CVD method [7]. After evacuating the supports at 773 K, $VO(OC_2H_5)_2$ vapor was introduced at 423 K to react with the surface. Then the samples were heated at 723 K in vacuo. By repeating this adsorption–decomposition cycle, V_2O_5 overlayers were grown. These samples were calcined at 623 or 773 K (designated as, e.g., V_2O_5/SiO_2(CVD)). The powder samples were pressed into a pellet in a N_2 atmosphere with a proper thickness for transmission measurements.

The X-ray absorption spectra of V K-edge were measured at room temperature at the Photon Factory (Beam Line 7C). The phase shifts of V and O calculated by Teo and Lee were used for the Fourier transforms of EXAFS [8]. In the present study, a square window (width, 10 Å^{-1}; from 3.5–4.0 Å^{-1} to 13.5–14.0 Å^{-1}) was used as the window function for Fourier transformation and the cutoffs were chosen to be where $\chi(\kappa)$ is small ($\chi(\kappa)$ is EXAFS data with the background subtracted) [9].

3. Results and discussion

Fig. 1 provides the Fourier transforms of vanadium K edge EXAFS. For the bulk V_2O_5 (fig. 1a), peaks appeared at around 1.6, 1.9 and 3.1 Å, which correspond to the V=O, V–O and V–V distances, respectively [10]. It can be seen that the V=O and V–O peaks are well resolved. The peak positions for V=O, V–O, and V–V for the V_2O_5 crystallite agreed well with the bond distances from the crystallographic data [10], indicating that the analysis of the present study is reliable.

As shown in fig. 1b, the spectrum of 9.1 wt% V_2O_5/MgO(Imp) is obviously different from that of bulk V_2O_5; only one peak, at 1.8 Å, was observed for V_2O_5/MgO(Imp). This result indicates that vanadium on MgO is not in the form of V_2O_5. It has been reported that vanadium oxides react readily with the surface of MgO to form new phases such as $Mg_3V_2O_8$ [6] and $Mg_2V_2O_7$ [11]. XRD of 9.1 wt% V_2O_5/MgO(Imp) showed only peaks due to MgO, which is in agreement with the results in the literature [6,11]. $Mg_3V_2O_8$ consists of V ions in tetrahedral sites (V–O; 1.70–1.81 Å) and Mg ions in octahedral sites, and $Mg_2V_2O_7$ has V_2O_7 groups (V=O, 1.63 Å; V–O, 1.70–1.82 Å) [12]. The single peak (at 1.8 Å) in the EXAFS spectrum suggests the formation of a $Mg_3V_2O_8$ phase.

As shown in fig. 1c, 9.1 wt% V_2O_5/SiO_2(Imp) gave a spectrum similar to that of the bulk V_2O_5, indicating that the V_2O_5 overlayers have the same structure as the bulk V_2O_5. XRD confirmed the presence of V_2O_5 crystallites which have a size of

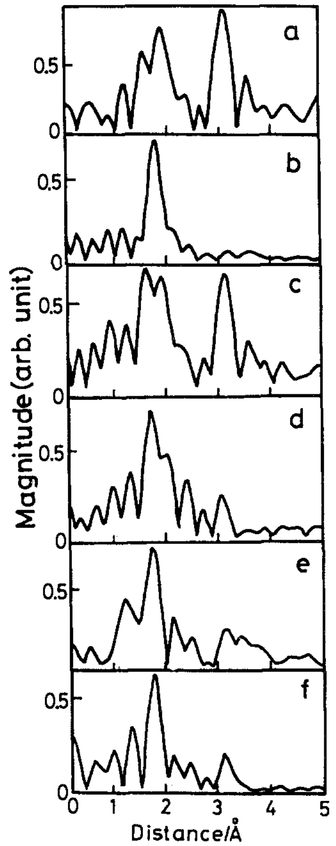

Fig. 1. Fourier transforms of V K-edge EXAFS of (a) V_2O_5, (b) 9.1 wt% V_2O_5/MgO(Imp), (c) 9.1 wt% V_2O_5/SiO_2(Imp), (d) 7.9 wt% V_2O_5/SiO_2(CVD), (e) 9.1 wt% V_2O_5/Al_2O_3(Imp), (f) 7.4 wt% V_2O_5/Al_2O_3(CVD). All samples were calcined at 623 K in air.

about 150 Å. These XRD and EXAFS results are in agreement with those in the literature [1,13,14]. In the present study, crystallites are defined as particles which are detectable with XRD [15]. Since aggregates of vanadium compounds, e.g., oxalates, on the surface before the calcination were detected by EXAFS [15], the formation of V_2O_5 crystallites is attributed to the formation of the aggregates during the impregnation process. Some researchers claimed that isolated vanadium species (i.e., $(V{=}O)O_3$) were formed at low loadings (about 2 wt%) in the impregnation method [1,3,16]. Although a reliable spectrum of 3.2 wt% V_2O_5/SiO_2(Imp) was not obtained due to the low concentration of V, this sample had surface properties different from those of thin films and crystallites, as stated below.

As shown in fig. 1d, 7.4 wt% V_2O_5/SiO_2(CVD) gave a peak at 1.6 Å (V=O) and a weak peak at around 3 Å (V–V), showing that the vanadium oxides were not present as crystallites. As reported previously [7], $VO(OC_2H_5)_3$ reacted with all the surface OH groups of SiO_2 to form $(SiO-)_2VO(OC_2H_5)$ and $(SiO-)VO(OC_2H_5)_2$ in a stoichiometric manner. The ethoxy groups decomposed to give ethylene and V–OH groups by evacuation at elevated temperatures and the V–OH group subsequently reacted with the surface Si–O–Si groups to generate new V–O–Si bonds. The resulting thin films may be stabilized through these V–O–Si bonds. The weakness of the V–V peak at around 3 Å (fig. 1d) is probably due to the strong interaction between the vanadium oxide and SiO_2 surface, which may induce large Debye–Waller factors of V–O–V bonds [15].

Figs. 1e and 1f show the spectra of 9.1 wt% V_2O_5/Al_2O_3(Imp) and 7.4 wt% V_2O_5/Al_2O_3(CVD). In both V_2O_5/Al_2O_3 samples, sharp peaks appeared at 1.7 Å (V=O), while the peaks at 3.3 Å (V–V) were small. These spectra are close to those of V_2O_5 thin films on SiO_2 (fig. 1d), suggesting that vanadium oxides on Al_2O_3 are also present in the form of thin films. The V_2O_5 crystallites were not detected by XRD. Therefore, vanadium oxide thin films were formed on Al_2O_3 not only by the CVD method but also by the impregnation method. Since the isoelectronic point of Al_2O_3 is 6–8 [17] and the pH of the solution of vanadium used for the impregnation was 2, the surface OH groups of Al_2O_3 were protonated, when the solution of vanadium was added to it. Furthermore, the OH group density of the surface of Al_2O_3 (10 OH group/nm^2) was greater than that of SiO_2 (2 OH/nm^2) [7]. Thus, the anions of vanadium in the solution interacted efficiently with the surface of Al_2O_3 to form thin films.

Fig. 2 shows the EXAFS spectra of V_2O_5/SiO_2(CVD) after the calcination at 773 K in air. Except for 16.9 wt% V_2O_5/SiO_2(CVD), the peaks at 3.3 Å (V–V) remained small, as did those observed after the calcination at 623 K. This result means that the vanadium oxide overlayers of V_2O_5/SiO_2(CVD) were thermally

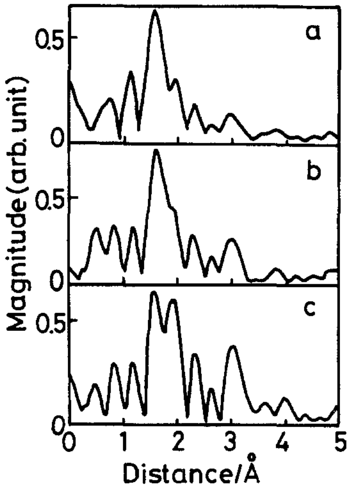

Fig. 2. Fourier transforms of V K-edge EXAFS of (a) 5.4 wt% V_2O_5/SiO_2(CVD), (b) 7.9 wt% V_2O_5/SiO_2(CVD), (c) 16.9 wt% V_2O_5/SiO_2 (CVD). All samples were calcined at 773 K in air.

very stable when the loading level was less than 7.9 wt%. In the case of 16.9 wt% V_2O_5/SiO_2(CVD), a part of the V_2O_5 overlayers was present as crystallites, which were detected by XRD. The surface monolayer of V_2O_5 corresponds to 22 wt% on SiO_2, if the (010) layer of V_2O_5 crystallites may be assumed for the calculation of the monolayer. Although the loading of V_2O_5 for 16.9 wt% V_2O_5/SiO_2(CVD) is less than the calculated monolayer (22 wt%), V_2O_5 which interacts little with the SiO_2 may exist and aggregate after the calcination at the high temperature. In the case of Al_2O_3, the surface monolayer of V_2O_5 corresponds to about 13 wt%. XRD showed that no crystallites were present on V_2O_5/Al_2O_3 when the loading was less than 10.0 wt%, but V_2O_5 crystallites were present on 17.0 wt% V_2O_5/Al_2O_3(Imp).

In the present study, determination of the coordination numbers of oxygen around vanadium by the curve fitting method was not adopted, because it is difficult to obtain reliable values due to the non-uniformity in the bond length for the V_2O_5 overlayers, i.e., the large Debye–Waller factor.

Fig. 3 shows the results of temperature programmed decomposition of ethanol adsorbed on V_2O_5/SiO_2. The decomposition (or desorption) pattern from 16.9 wt% V_2O_5/SiO_2(CVD) is given in fig. 3A. Desorption of ethanol started at 300 K

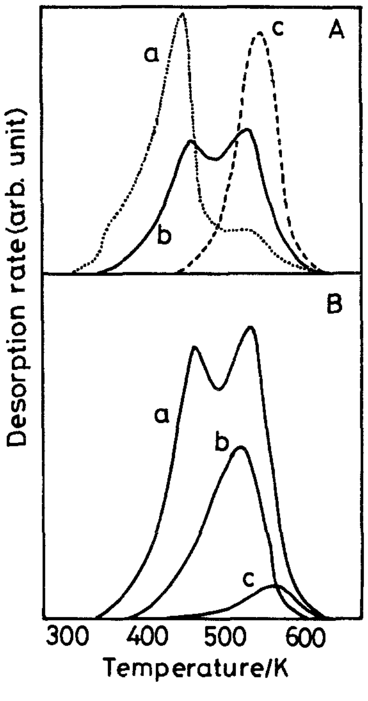

Fig. 3. Temperature programmed decomposition of ethanol adsorbed on V_2O_5/SiO_2. (A): (a) ethanol, (b) acetaldehyde, (c) ethylene from 16.9 wt% V_2O_5/SiO_2(CVD); (B) acetaldehyde from (a) 16.9 wt% V_2O_5/SiO_2(CVD), (b) 14.8 wt% V_2O_5/SiO_2(Imp), (c) 3.2 wt% V_2O_5/SiO_2(Imp).

and gave a peak at 450 K. Acetaldehyde appeared from 340 K and showed two peaks at 460 and 530 K. Ethylene appeared at a higher temperature than that of acetaldehyde and had a peak at 520 K. It is remarkable that in fig. 3B the peak temperature of acetaldehyde depended strongly on the nature of the samples. The V_2O_5 thin films (a in fig. 3B; 16.9 wt% V_2O_5/SiO_2(CVD)) produced acetaldehyde at low temperature ranges, as compared with V_2O_5 crystallites (b in fig. 3B; 14.8 wt% V_2O_5/SiO_2(Imp)) and isolated V species (d in fig. 3B; 3.2 wt% V_2O_5/SiO_2(Imp)). Whereas the isolated species was active for photo-oxidation reactions [3,4,15], it was less active for the thermal dehydrogenation. For cleavage of O–H and C–H bonds of adsorbed ethanol, sites more complicated than the isolated site are probably necessary.

When catalytic oxidative dehydrogenation of ethanol was performed at 493 K in the presence of ethanol (22 Torr) and O_2 (22 Torr) over these V_2O_5/SiO_2 and V_2O_5/Al_2O_3 samples, acetaldehyde was produced with selectivities of more than 90%. As will be described in detail elsewhere [18], the catalytic activity declined in the order 7.4 wt% V_2O_5/Al_2O_3(CVD) (12.0×10^{-4}) > 9.1 wt% V_2O_5/Al_2O_3(Imp) (7.0×10^{-4}) > 7.4 wt% V_2O_5/SiO_2(CVD) (4.1×10^{-4}) > 9.1 wt% V_2O_5/SiO_2(Imp) (1.3×10^{-4}) > 3.2 wt% V_2O_5/SiO_2(Imp) (0.1×10^{-4}), where the figures in the parentheses are the rates of acetaldehyde formation per unit weight of V_2O_5 (mol $\min^{-1}$ $(g\text{-}V_2O_5)^{-1}$). The dispersion of V_2O_5 declined in the order 3.2 wt% V_2O_5/SiO_2 (Imp) (1.0) > 7.4 wt% V_2O_5/SiO_2(CVD) (0.6) > 9.1 wt% V_2O_5/SiO_2 (Imp) (0.3), where the figures in parentheses are the number of ethanol molecules adsorbed divided by the number of V atoms in the catalyst. Therefore, it is concluded that activities are strongly affected by the structure; the activity of thin films is greater than that of crystallites, which is much greater than that of isolated species.

4. Conclusions

EXAFS spectra revealed that the structure of V_2O_5 is very sensitive to the supports and the preparation method (impregnation or CVD). The Al_2O_3 surface stabilized the V_2O_5 overlayers as thin films, independent of the preparation method. V_2O_5/SiO_2 ($V_2O_5 > 5$ wt%) prepared by the impregnation method consisted of small crystallites. Preparation by CVD brought about thin films which had high thermal stabilities and catalytic activities for dehydrogenation.

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