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Active Crystal Face of Vanadyl Pyrophosphate for Catalytic Oxidation of n-Butane to Maleic Anhydride

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$(VO)_2P_2O_7$ consisting of thin planar crystallites, which was selective for the butane oxidation, was first deactivated by the deposition of SiO_2 thin layer, and then fractured to create new side faces like (001) and (021). The side faces were non-selective for the reaction, indicating that (100) face, on which $V^{4+}(=O)-O-V^{4+}$ sites are located, is selective.

V-P oxides are known to be efficient for the selective oxidation of butane to maleic anhydride (abbreviated as MA).$^{1)}$ A single-phase of $(VO)_2P_2O_7$ has been inferred to be an active catalyst phase,$^{2)}$ while some claimed that the active phase is a combination of $(VO)_2P_2O_7$ and $VOPO_4$$^{3-5)}$ or is a phosphorus-rich phase.$^{6)}$ The active site of $(VO)_2P_2O_7$ for this reaction is thought to be $V^{4+}(=O)-O-V^{4+}$, which is located on the (100) face of $(VO)_2P_2O_7$,$^{1,7)}$ but has not been proved yet. We attempted to elucidate the active crystal face for the selective oxidation of butane.

After several trials and errors, large plate-like crystallites were obtained by the following method. Powder of V_2O_5 (Koso Chemicals Co.) was added to an aqueous solution of H_3PO_4 (40%) (P/V atomic ratio = 7). Then the solution was slowly stirred for several hours at room temperature. The formed precipitate (probably $VOPO_4 \cdot nH_2O$, $n > 2$) was refluxed at 393 K for 2 h in an aqueous solution of H_3PO_4 (85%). The obtained crystallites with sizes of 10 - 20 μm were confirmed to be $VOPO_4 \cdot 2H_2O$ by XRD. By the reduction with 2-butanol in 2-butanol solution at 358 K for 2 h,$^{8)}$ $VOHPO_4 \cdot 0.5H_2O$ crystallites having sizes of 3 - 10 μm were obtained. The $VOHPO_4 \cdot 0.5H_2O$ was treated in a flow of N_2 at 823 K for 5 h to transform it into $(VO)_2P_2O_7$. The average size of $(VO)_2P_2O_7$ was determined to be 5 μm in length by SEM. The thickness estimated was 20 nm from the line-width of XRD and 40 nm from the surface area and the density. SEM indicated about 150 nm in thickness (see below). Probably, the thickness measured by SEM corresponds to that of the plate formed by stacking of about 10 thin crystallites.

A part of $(VO)_2P_2O_7$ was treated with a mixture of $Si(CH_3)_4$ (200 Torr) and O_2 (70 Torr) at 773 K in a closed circulation system. The resulting sample will be denoted by $SiO_2/(VO)_2P_2O_7$. The samples were fractured by giving pressure (630 $Kg \cdot cm^{-2}$) by a tablet molding machine to create the side surfaces. Catalytic oxidation of butane was carried out in a flow reactor at 713 K as in the previous paper.9) The feed gas consisted of 1.5% butane, 17% O_2, and N_2 (balance).

The SEM micrographs of non-fractured and fractured $SiO_2/(VO)_2P_2O_7$ are shown in Fig. 1. The shape and size of $SiO_2/(VO)_2P_2O_7$ (Fig. 1a) were the same as those of the parent $(VO)_2P_2O_7$. By electron diffraction, the basal face of $(VO)_2P_2O_7$ crystallites was confirmed to be (100) as reported by Bordes and Courtine,10) where XRD lines for $(VO)_2P_2O_7$ were indexed following Gorbunova et al.11) After the sample was fractured once, the crystallites became smaller (average size; 3 µm) and new side faces were created as shown in Fig. 1b. When the crystallites were fractured 5 times, they became much smaller (about 1 µm).

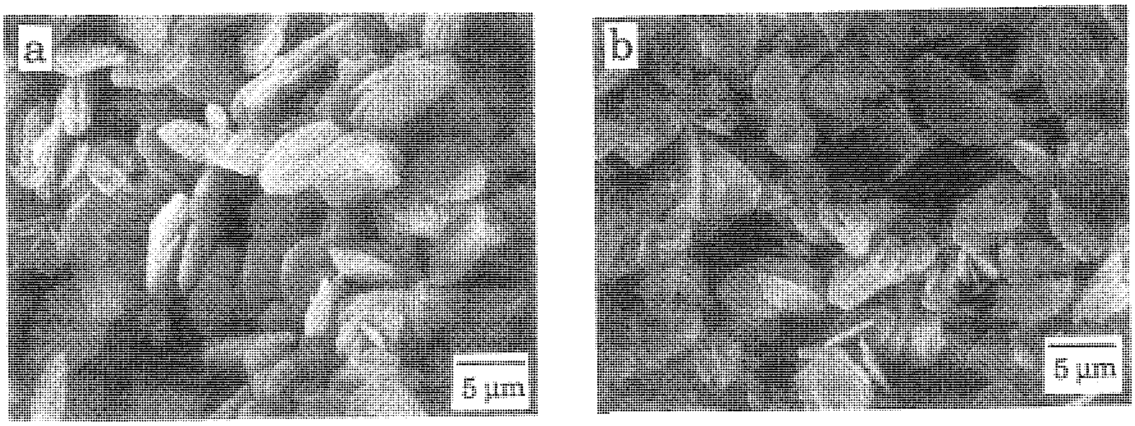

Fig. 1. SEM micrographs of $SiO_2/(VO)_2P_2O_7$ (a) and $SiO_2/(VO)_2P_2O_7$ fractured once (b).

In Table 1, the crystallite sizes, surface areas, and the results of the butane oxidation are summarized. Upon the fracture, the surface areas of $(VO)_2P_2O_7$ and $SiO_2/(VC)_2P_2O_7$ changed little, showing that the area newly created was small. This is reasonable because the fraction of the side faces is calculated to be 1.6 and 7.4% of the total surface area for the particles with the sizes of 5 and 1 µm, respectively, assuming the thickness of 40 nm. If the fracture brought about cleavage along (100) plane of the crystallites to change the average thickness to half (20 nm), the surface area would become about twice. Thus the little change of the surface area indicates that the cleavage along (100) plane upon the fracture is little.

TEM-EDX (JEM 2000 FXII, JEOL) measurement revealed that SiO_2 was deposited on both the basal and side faces and the density of SiO_2 was similar on both faces or slightly higher on the side faces.

As shown in Table 1, the parent $(VO)_2P_2O_7$ produced MA with the 60%-selectivity.[9] On the other hand, the conversion over $SiO_2/(VO)_2P_2O_7$ was very low and did not change for at least 8 h, showing that the surface of $(VO)_2P_2O_7$ was mostly covered by the SiO_2 layers and the SiO_2 layers were stable during the reaction.

It is noteworthy that the fractured $SiO_2/(VO)_2P_2O_7$ was active mainly for the formation of CO and CO_2. Therefore, it is concluded that the (100) face, on which $V^{4+}(=O)-O-V^{4+}$ sites are located, is selective for the formation of MA, while the side faces like (001) and (021) are non-selective. Changes in the crystallite size and shape measured by SEM were small during the reaction.

Table 1. Crystallite Size, Surface Area of Catalysts, and Results of Oxidation of Butane at 713 K

Catalysts	Size[a]	Surface area	Catalytic activity[b]	Selectivity to MA/%[c]
	μm	$m^2 \cdot g^{-1}$	10^{-5} $mol \cdot g^{-1} \cdot min^{-1}$	
$(VO)_2P_2O_7$	5	17	1.80 (0.11)	60 (46)
$SiO_2/(VO)_2P_2O_7$[d]	5	10	0.05 (0.005)	0 (2)
$SiO_2/(VO)_2P_2O_7$[d] fractured once	3	11	0.68 (0.062)	1 (20)[e]
$(VO)_2P_2O_7$ fractured once	3	17	1.91 (0.11)	56 (47)
Fractured 5 times	1	18	2.26 (0.13)	56 (52)

a) Average size measured by SEM. b) Stationary reaction rate: Butane; 1.5%, O_2; 17%. The figures in the parentheses are the rates divided by total surface area; 10^{-5} $mol \cdot m^{-2} \cdot min^{-1}$. c) The figures in parentheses are the %-conversions of butane. d) Atomic ratio of Si to V_{surf} was 6, where V_{surf} is the amount of surface vanadium atoms. e) Crotonaldehyde was formed with the selectivity of 10%.

The effect of the fracture of the parent $(VO)_2P_2O_7$ was also examined. The fractured $(VO)_2P_2O_7$ (without SiO_2-deposition) showed high initial activities as compared with the parent $(VO)_2P_2O_7$, and the conversion decreased appreciably and the selectivity increased with time at the initial stages of the reaction. This shows that the side faces created freshly tend to be deactivated under the reaction conditions. As given in Table 1, the stationary catalytic activities of the fractured $(VO)_2P_2O_7$ were slightly higher, and the selectivities were slightly lower than that of the parent $(VO)_2P_2O_7$. The differences between these catalysts are meaningful and support the conclusion as illustrated in Fig. 2.

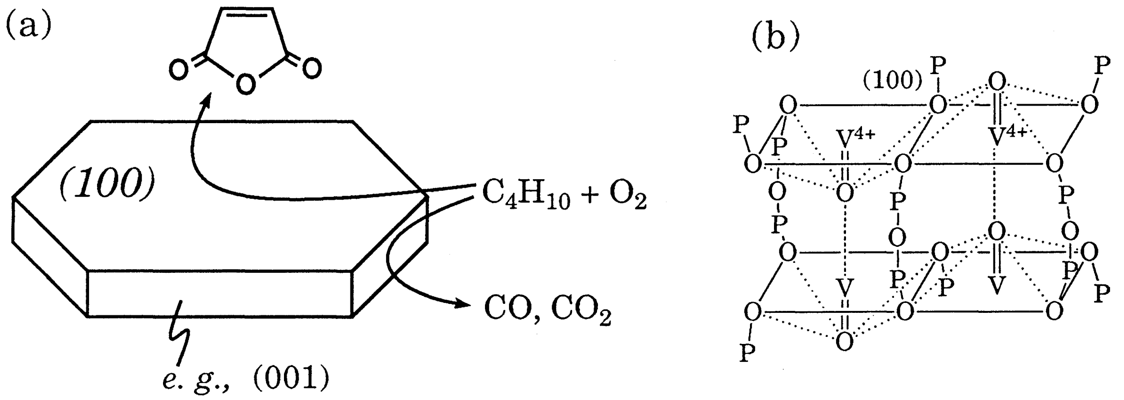

Fig. 2. Reaction model for oxidation of butane (a) and structure of $(VO)_2P_2O_7$ (b).

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