CHEMISTRY LETTERS, pp. 1513-1516, 1990.

Amorphous V-P Mixed Oxide with P/V=2.0 as Active Phase for Butane Oxidation

Hidetaka MORISHIGE, Jun TAMAKI, Norio MIURA,
and Noboru YAMAZOE
Department of Materials Science and Technology, Graduate School of Engineering Sciences,
Kyushu University, Kasuga, Fukuoka 816

V-P mixed oxide catalysts prepared by evaporation method was made up of a mixture of an amorphous phase with P/V=2.0 and a crystalline phase of $(VO)_2P_2O_7$. The amorphous phase, separated from the $(VO)_2P_2O_7$ particles by dissolving the precursor in boiled water, was found to show essentially the same selectivity and activity per unit surface area for the maleic anhydride formation from butane as the unseparated catalyst.

V-P mixed oxide system has so far provided sole industrial catalysts for the synthesis of maleic anhydride (MA) from butane. Among the several identified phases of the system, a crystalline phase $(VO)_2P_2O_7$ having four valent vanadium has been ascribed to be responsible for the activity and selectivity to MA.[1] The industrial catalysts, however, are prepared to contain phosphorus in a little excess of the $(VO)_2P_2O_7$ composition, i.e., to a composition of P/V=1.05-1.20, and show the butane conversion of 80-100% and the selectivity to MA of 50-60% at 350-500 °C.[2] Thus the role of excess phosphorus is a matter of interest. Our recent investigation on the system by using XPS showed that even when the P/V ratio of the catalyst bulk was set to be close to unity, the surface P/V ratio of the resulting catalyst was considerably larger than unity, although $(VO)_2P_2O_7$ was detected as a single crystalline phase from X-ray

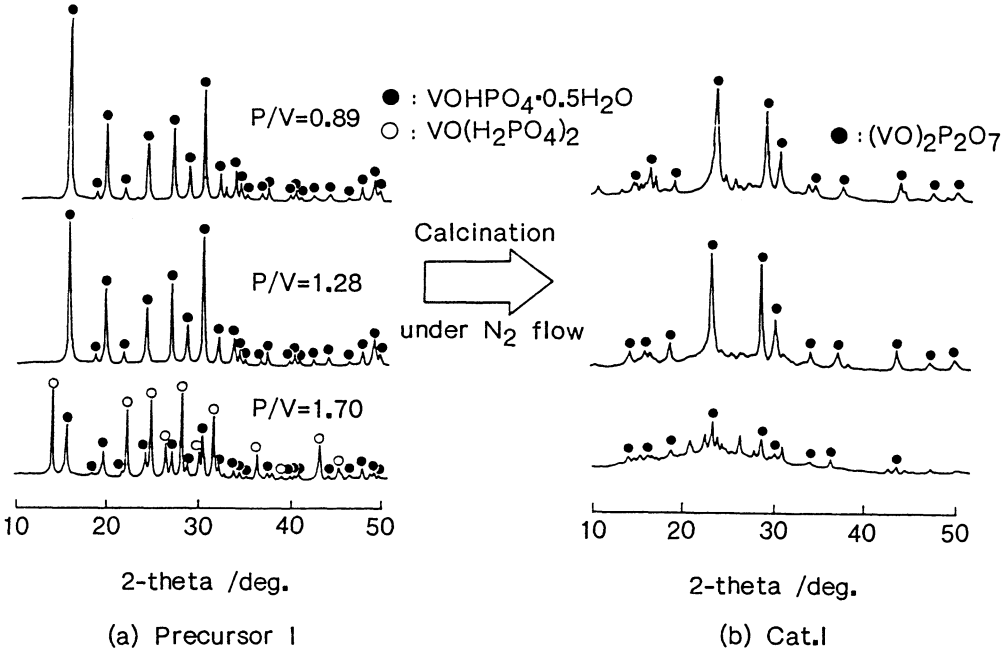

Fig. 1. XRD patterns of Precursor I and Cat.I with various P/V compositions.

diffraction (XRD) analysis.[3,4] In fact, the surface P/V ratio exhibited a plateau of 1.6-1.8 when the bulk P/V ratio varied from 0.95-1.20. This suggests that a phosphorus rich layer on the $(VO)_2P_2O_7$ phase is effective to the selective oxidation of butane to MA. All these results indicate that the prepared catalysts are the mixtures of $(VO)_2P_2O_7$ and amorphous phase, the latter being associated with the excess phosphorus. This prompted us to investigate the role of the amorphous phase in the butane oxidation catalysis. In this paper, we attempted to separate the amorphous part from the catalysts and the resulting amorphous phase was subjected to catalytic investigations.

Catalysts were prepared from aqueous solution dissolving V_2O_5, H_3PO_4 and $NH_2OH{\cdot}HCl$ (reducing agent) at desired compositions.[1] Each solution was evaporated to dryness to obtain solid powder, denoted here as Precursor I. Precursor I (5 g) was mixed with water (150 ml) and the whole mixture was boiled for 15 min. The mixture was then filtrated to separate the residue (Precursor II) from the filtrate. The filtrate was further evaporated to dryness to obtain Precursor III. The three precursors thus prepared were calcined under N_2 flow at 500 °C for 2 h, the resulting V-P mixed oxide catalysts being denoted Cat.I, II, and III, respectively.

The characterization of each precursor and catalyst was carried out by means of XRD, X-ray fluorescence (XRF) analysis and the measurement of specific surface area by BET method (N_2 adsorption). The oxidation of butane was performed in a conventional fixed bed flow reactor at an atmospheric pressure. 1.5% butane diluted with artificial air was fed at SV=2400 $ml{\cdot}h^{-1}{\cdot}g^{-1}$-cat. The gaseous components in the effluent (butane, CO and CO_2) were analyzed quantitatively by gas chromatography, while produced MA was trapped in water to be titrated with an aqueous NaOH solution.

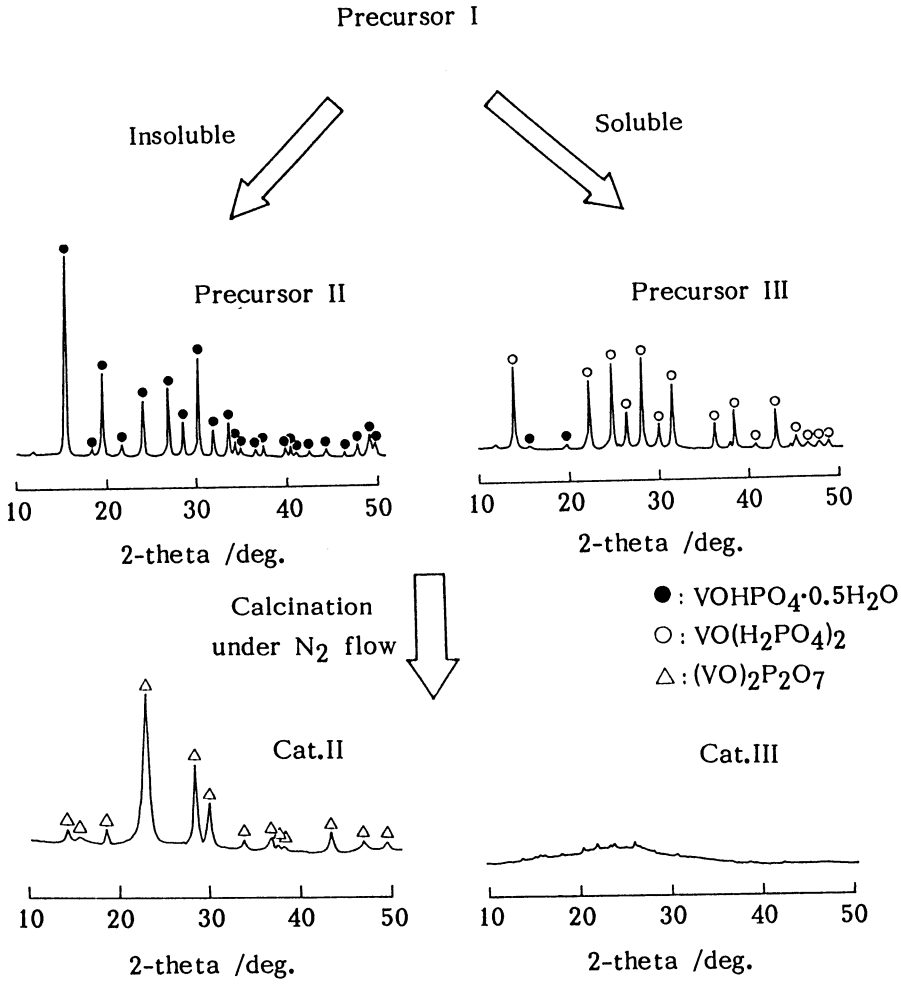

Fig. 2. XRD patterns of precursors and catalysts obtained with the starting P/V ratio of 1.70.

Figure 1 shows the XRD patterns of a series of

Precursor I and Cat.I with various starting P/V ratios. They were identified as $VOHPO_4 \cdot 0.5H_2O$ phase at P/V=0.89 and 1.28, while $VO(H_2PO_4)_2$ phase was also visible at P/V=1.70. After the calcination of these precursors, only $(VO)_2P_2O_7$ phase was indicated by XRD, but particularly weak XRD intensities of $(VO)_2P_2O_7$ at P/V=1.70 suggested the co-presence of an amorphous phase resulting from $VO(H_2PO_4)_2$.

This suggestion was verified by the XRD patterns of Precursors II and III and their calcination products (Cat.II and III). As shown in Fig.2, with the starting P/V ratio of 1.70, the two phases of $VOHPO_4 \cdot 0.5H_2O$ and $VO(H_2PO_4)_2$ contained in Precursor I were separated almost completely into Precursors II and III, respectively. On calcination, these phases were converted into $(VO)_2P_2O_7$ and an amorphous phase, respectively. These results suggest that $VO(H_2PO_4)_2$ phase is soluble in water, while $VOHPO_4 \cdot 0.5H_2O$ phase is almost insoluble, and that the former phase can be separated from the latter by the dissolution-filtration treatment.

Figure 3 shows the bulk P/V compositions of Precursors I, II, and III as measured by XRF, as a function of the starting P/V ratio. Quite naturally, the P/V compositions of Precursor I agreed very closely with the starting P/V ratio. On the other hand, those of Precursors II and III took values rather close to 1 and 2, respectively, when the starting P/V exceeded 1.0. These results again confirm that Precursors II and III consist of $VOHPO_4 \cdot 0.5H_2O$ and $VO(H_2PO_4)_2$, respectively, when the catalyst preparation started with P-excess compositions. It follows that the catalyst prepared by the evaporation method, Cat.I, is made up of an amorphous phase with P/V=2.0 and $(VO)_2P_2O_7$.

In order to evaluate the importance of the amorphous phase, the oxidation reaction of butane was carried out at 450 °C over Cat.III prepared from a starting P/V ratio of 1.70. Table 1 indicates the catalytic performance of Cat.III together with those of Cat.I and II. Although the butane conversion over Cat.III was low (11.1%), the selectivity to MA (64.5%) was comparable to the other catalysts. XRD and XRF analyses for Cat.III showed no changes in the amorphous state or in the bulk P/V composition (P/V=2.0) before and after the butane oxidation reaction. It is quite important that the amorphous catalyst (Cat.III) exhibits almost the same selectivity as Cat.I in which crystalline $(VO)_2P_2O_7$ phase dominates. The low conversion level seems to be simply due to a small specific surface area (2.0 $m^2 \cdot g^{-1}$). The rates of butane oxidation per unit surface area, denoted here as r_b, are again almost the same for Cat.I and Cat.III. These results strongly suggest that the amorphous phase is responsible for the catalytic activity of the V-P-O catalysts in the selective oxidation of butane to MA. In the case of Cat.II, the selectivities to MA are also very close to

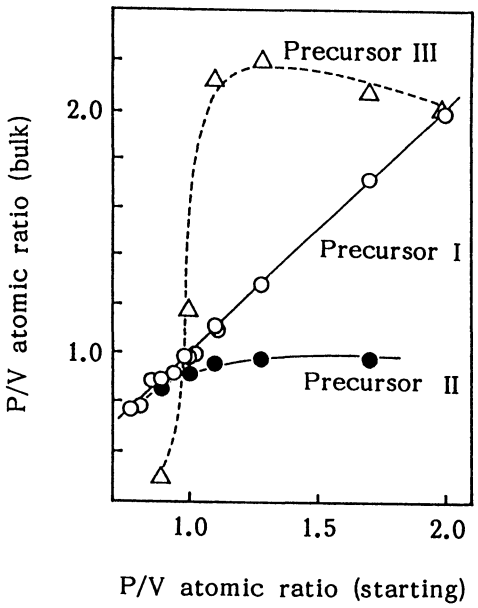

Fig. 3. The P/V compositions of Precursors I, II, and III with various starting P/V compositions.

those of Cat.I and III. We assume that part of the amorphous phase still remains sticking on the surface of $(VO)_2P_2O_7$ particles after the treatment, although the activity have decreased considerably probably because of a change in the surface. We reported previously that crystalline $(VO)_2P_2O_7$ phase in the actual catalysts (P/V=0.95-1.20) appeared to be covered with a P-rich amorphous layer.[3] The present finding of the catalytically active amorphous phase with P/V=2.0 is quite consistent with our previous report. It seems that $(VO)_2P_2O_7$ phase in V-P-O catalysts acts as a sort of support to increase the surface area of the amorphous phase which actually provides the catalytic activity.

In conclusion, the V-P-O catalyst prepared by the evaporation method is made up of an amorphous phase with P/V=2.0 and a crystalline phase of $(VO)_2P_2O_7$ when the starting P/V ratios exceed unity. The amorphous phase, separated from these mixtures, shows almost the same MA selectivity and activity as the original mixtures. Therefore the amorphous V-P mixed oxide is possibly an active phase responsible for the selective oxidation of butane to MA.

Table 1. Butane oxidation over Cat.I, II, and III with various P/V composition.

Catalyst	P/V[a]	Conv.	Selectivity /%			r_b[b]	S.S.A[c]
		%	CO	CO_2	MA		$m^2 \cdot g^{-1}$
Cat. I	1.02	86.1	25.2	14.9	59.9	8.82	15.7
	1.13	62.8	25.6	12.1	62.3	8.70	10.3
	1.28	21.3	30.6	10.0	59.4	9.97	3.2
Cat. II	1.02	53.1	25.2	12.1	62.7	4.95	15.9
	1.13	53.2	25.1	12.9	62.0	5.02	16.6
	1.28	32.4	27.4	10.8	61.8	3.97	12.2
Cat.III	1.70	11.1	21.1	14.4	64.5	8.64	2.0

Reaction temperature : 450 °C, SV=2400 $ml \cdot h^{-1} \cdot g^{-1}$-cat.
a) starting P/V compositions, b) the rate of butane oxidation per unit surface area ($10^{-5} mol \cdot m^{-2} \cdot h^{-1}$), c) specific surface area

References

1) T. Shimoda, T. Okuhara, and M. Misono, Bull. Chem. Soc. Jpn., 58, 2163(1985).
2) B. K. Hodnett, Catal. Rev., 27, 373(1985).
3) N. Yamazoe, H. Morishige, and Y. Teraoka, "Successful Design of Catalysis," Elsevier, Amsterdam (1988), p.15.
4) H. Morishige, J. Tamaki, Y. Teraoka, N. Miura, and N. Yamazoe, Nippon Kagaku Kaishi, 1989, 1983.

(Received May 28, 1990)