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Location and Functions of Zn as a Promoter Element in the V–P–O Catalysts for *n*-Butane Oxidation to Maleic Anhydride

YUSAKU TAKITA,*,[1] KATSUYOSHI TANAKA,* SHIRO ICHIMARU,* TATSUMI ISHIHARA,*
TAKANORI INOUE,† AND HIROMICHI ARAI†

**Department of Environmental Chemistry and Engineering, Faculty of Engineering, Oita University, Oita 870-11, Japan; and †Graduate School of Engineering Sciences, Department of Materials Science and Technology, Kyushu University, Fukuoka 816, Japan*

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Location of zinc in the V–P–O catalysts containing zinc was examined along the preparation process. The mixture of $H_4(VO)_2P_2O_9$, $(NH_4)_2ZnCl_4$, and NH_4ZnPO_4 was formed, when an aqueous solution containing VO^{2+}, Zn^{2-}, and NH_3OHCl was evaporated to dryness. TG–DTA results of the mixture revealed that $(NH_4)_2$ $ZnCl_4$ decomposed to ZnO at 470–570 K and water molecules were eliminated from $H_4(VO)_2P_2O_9$ to give $(VO)_2P_2O_7$ at 670–700 K, then the solid phase reaction between $(VO)_2P_2O_7$ and ZnO took place at 790–810 K without any loss of the weight. Addition of 10 at.% of ZnO addition to $(VO)_2P_2O_7$ by mechanical mixing brought about drastic increase in the oxidation rate of the catalyst to $VOPO_4$. This may be responsible for the increase in the rate of catalytic *n*-butane oxidation without significant changes in the product distribution observed over the Zn-promoted V–P–O catalysts.

INTRODUCTION

V–P–O catalysts were used exclusively for the partial oxidation of butane to maleic anhydride (MA) (*1–9*). Since all the catalysts that have been claimed to be effective for the oxidation contain $(VO)_2P_2O_7$ and MA was obtained in high selectivity over pure $(VO)_2P_2O_7$, it has been considered that $(VO)_2P_2O_7$ is one of the active phase for the oxidation (*10*). To improve MA selectivity and/or catalytic activity, one or more of elements are added into practical catalysts among so many elements such as Te, Zr, Ni, Ce, W, Pd, Cu, Ag, Mn, Cr, Zn, Mo, Re, Sm, La, Hf, Ta, Th, Co, U, Sn, alkali metals, and alkaline earth metals (*11, 12*). The preparation method of the catalyst can be classified into two categories. One method of preparation is that V_2O_5 dispersed in water is reduced to VO^{2+} typically by HCl or NH_2OH HCl, then H_3PO_4 is added into it. Another method is that of a source material of vanadium dispersed in organic medium such as iso-butanol and benzylalcohol, is reduced by the organic medium then reacted with H_3PO_4 to obtain the catalyst. Activity of the catalyst prepared by the former method is generally lower than that of the latter method; conversely MA selectivity of the former is rather high.

Brutovsky and Gerev studied the promotion effect of various metal ions on the catalytic properties of the catalysts prepared in aqueous media (*13*). They evaluated the selectivity, yield, and the reaction temperature of *n*-butane oxidation over the catalyst containing 20 at.% of metal ions, and found the order of the promotion effect,

$$\text{Mn} > \text{Co} > \text{Fe} > \text{Cu} > \text{Zn, Li, Ce, Cd} > \text{none, Ba} > \text{Ni, Pd} > \text{Sn}.$$

It is noteworthy that the order was dependent of the amount of additives. They concluded from the observed decrease in inten-

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[1] To whom correspondence should be addressed.

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sity of XRD reflections that the additives except Pd were incorporated into the lattice of the basic catalysts (*14*).

Hodnett and Delmon studied the role of Co addition into the β-$VOPO_4$ catalysts prepared from V_2O_5, $Co(NO_3)_2 \cdot 6H_2O$, and H_3PO_4 in the water–lactic acid medium (*15*). The X-ray diffractograms revealed that no new phases containing cobalt were present in the catalysts with Co/V ratio up to 0.05 after calcination at 773 K for 16 h in the air. They observed segregation of cobalt (Co/V = 0.15) on the surface, and also found that the addition of a small amount of cobalt brought about a large change in the surface area of catalysts. They concluded from these results that the dopant was incorporated partly into the lattice of β-$VOPO_4$ phase. However, there is no direct evidence for the incorporation of the promoter element into the lattice of a crystalline phase effective for *n*-Butane oxidation. It will be essential for understanding the catalysis to know the location of the promoter element in V–P–O catalysts.

This paper deals with the structure of compounds containing promoter elements in catalysts formed in an aqueous media and its effect on the oxidation rate of catalysts themselves.

EXPERIMENTAL

V–P–O catalysts were prepared as follows. V_2O_5 was dissolved into an aqueous solution of hydroxylamine hydrochloride and phosphoric acid. The clean blue-color solution formed was evaporated to dryness over a hot plate then the powder obtained was dried at 403 K for 15 h then pressed into cylindrical form. It was broken and 0.9 g of granules of 14–32 mesh were used for the catalytic reaction. Mechanical mixing catalysts were prepared from $H_4(VO)_2P_2O_9$ powder and ZnO of commercial origin. These compounds were physically well mixed in a mortar using a small amount of water. Crystalline phases of the samples were analyzed by Rigaku CN2013 X-ray diffractometer. A Shimadzu ESCA 850 spectrometer with Mg$K\alpha$ excitation was used.

Catalytic oxidation of *n*-butane was carried out using an ordinary flow type reaction system using a 12-mm-i.d. Pyrex glass tubelar reactor with a fixed catalyst bed inside. MA in the effluent gas was collected into a trap kept at 273 K for 1 h then it was analyzed by both GC and titration with an aqueous solution of sodium hydroxide. Butane, CO, and CO_2, were analyzed by GC.

Catalyst sample, 100.0 mg, was dissolved in 16 ml of perchloric acid (Wako pure chem. 60%). One-half of the solution was subjected to the determination of Zn and V content by atomic absorption spectroscopy, using a Hitachi Model Z-8100 spectrometer. Prescribed amounts of aqueous solutions of ammoniummetavanadate and ammoniumparamolybdate were added into another half of the solution, then P content was determined spectrophotometrically, using a Shimadzu Model MPS-5000. Thermogravimetric analysis was carried out using a Seiko Model TG-2000.

RESULTS AND DISCUSSION

Zinc in the Catalyst Precursor

In the course of preparation of the catalyst precursor in aqueous media, location of zinc atoms as a promoter element in the catalyst was examined. The preparation procedure of the catalyst precursor and its successive treatments are shown in Fig. 1. An aqueous solution of $ZnCl_2$ was added into the blue solution containing $(VO)^{2+}$ then the solution was evaporated to dryness on a hot plate. The powder formed was then subjected to heat treatment at various temperatures. The Zn/V ratios of the samples determined by chemical analysis are also shown in Fig. 1. The ratio of sample A, the sample without washing, was 0.107 which agreed well with the designed value of $\frac{1}{9}$. After the washing process, which consisted of washing 15 g of sample A three times with 400 cm^3 each of boiling water for 20 min, the Zn/V ratio of sample B decreased drastically to 0.0024.

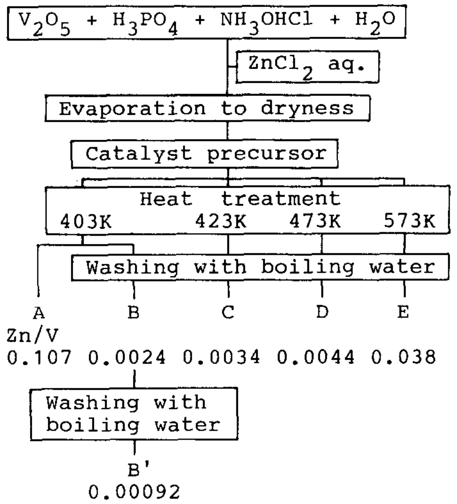

FIG. 1. Preparation procedure of catalyst precursor and Zn/V ratios.

Further washing reduced the ratio to 0.00092 which was only 0.86% of the initial value. This strongly suggests that most of the Zn atoms are present on the surface of crystalline $H_4(VO)_2P_2O_9$ in the form of a water soluble compound. A small amount of Zn atoms in the inner grain boundaries may explain the final value.

Figure 2 showed the XRD pattern of sample A. There are four small diffraction lines in addition to the lines attributable to $H_4(VO)_2P_2O_9$. If crystalline $H_4(VO)_2P_2O_9$ was first deposited during evaporation of the solution in the preparation of the catalyst precursor, the concentrations of Zn^{2+}, NH_4Cl, and phosphoric acid in the remaining solution should be increased with time. The XRD patterns of the powder obtained from equimolar mixture of H_3PO_4, NH_3OHCl, and $ZnCl_2$ by the same preparation procedure as sample A is shown in Fig. 2(b). $(NH_4)_2ZnCl_4$ and NH_4ZnPO_4 were formed as the major products. Figure 2b revealed that the four small lines other than the lines of $H_4(VO)_2P_2O_9$ in the spectrum (2a) can be assigned to the peaks of these compounds which contain zinc.

Figure 3 shows the depth profiles of the concentrations of component elements of catalysts measured by means of ESCA. For the catalyst prepared using $ZnCl_2$ without washing, after the N_2 pretreatment, the concentration of Zn was high at the surface, but it became small at the bulk of the catalyst. On the other hand, during 14 min of Ar ion bombardment, no Zn was detected from the catalyst which was washed with hot water and then treated in a N_2 stream at 773 K. Similar results were obtained in the case of copper.

It can be concluded that no zinc atoms were incorporated into the crystalline $H_4(VO)_2P_2O_9$.

Zinc in the Activation Process

The catalyst precursor formed in the manner described in the previous section is subjected to the heat treatment for the activation. This treatment is usually carried out in the stream of N_2, air, or a mixture of butane and air. Can $(NH_4)_2ZnCl_4$ and NH_4ZnPO_4 be reacted with $H_4(VO)_2P_2O_9$ during the heat

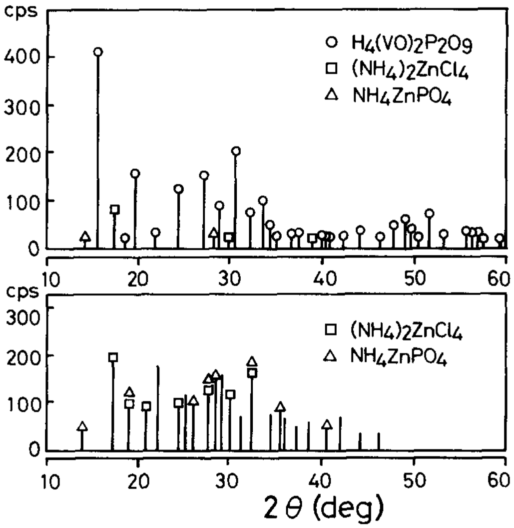

FIG. 2. XRD patterns of catalyst precursors. (a) precursor prepared from V_2O_5, NH_3OHCl, H_3PO_4, and $ZnCl_2$ (0.9 : 2.0 : 1.1 : 0.1, mol ratio). (b) powders obtained from the solution of NH_3OHCl, H_3PO_4, and $ZnCl_2$ (1 : 1 : 1).

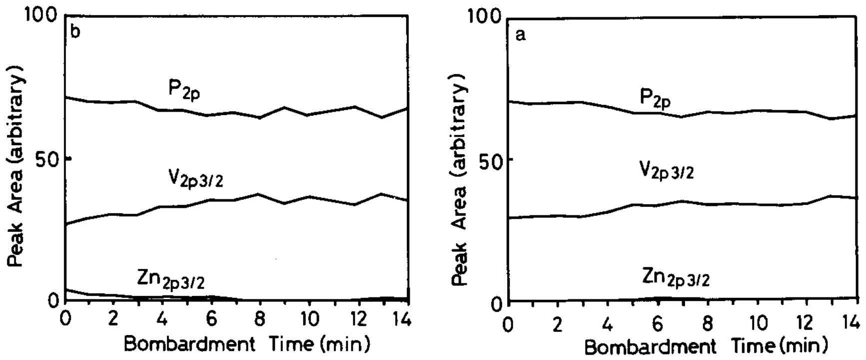

FIG. 3. ESCA depth profile of component elements. (a) Catalyst A in Fig. 1. (b) Catalyst B in Fig. 1.

treatment? TG–DTA analysis of separately prepared $(NH_4)_2ZnCl_4$ revealed that it eliminated NH_4Cl to give $ZnCl_2$ at around 570 K, then holding the temperature at 773 K more than 80% of $ZnCl_2$ was sublimated in the stream of N_2 or air. Figure 4 shows the TG–DTA curves of the sample prepared by physical mixing of $H_4(VO)_2P_2O_9$ and $(NH_4)_2ZnCl_4$. Weight loss at around 500–570 K agreed with the weight change assuming that all of $(NH_4)_2ZnCl_4$ changed into ZnO, and the loss at 670–700 K corresponded to the change of $H_4(VO)_2P_2O_9$ to $(VO)_2P_2O_7$ + $2H_2O$. After heating at 773 K for 5 h, the sample gave broad peaks attributable to $(VO)_2P_2O_7$ and ZnO in XRD as shown in Fig. 5, so most of the $(NH_4)_2ZnCl_4$ existed in the catalyst precursor is believed to be transformed into ZnO during the pretreatment at the temperatures up to 773 K.

An exothermic peak was observed in the DTA spectrum in Fig. 4 at 790–815 K, which suggested the solid phase reaction. The sample which has 10 at.% of Zn composition (based on Zn + V) and was treated in a N_2 stream at 823 K for 2 h gave no XRD peaks other than $(VO)_2P_2O_7$. Some new peaks, however, appeared in the XRD spectrum of the sample which has 20% of Zn composition (Fig. 6a). Although assignment of the peaks remained obscure, it was confirmed that these peaks could not be assigned to phosphates, chlorides, or oxide of zinc.

Reactivity between $H_4(VO)_2P_2O_9$ and ZnO was examined by TG–DTA and the results are shown in Fig. 7. Pure $H_4(VO)_2P_2O_9$ liberated two molecules of water to give $(VO)_2P_2O_7$ at 650–720 K. Exothermic peaks

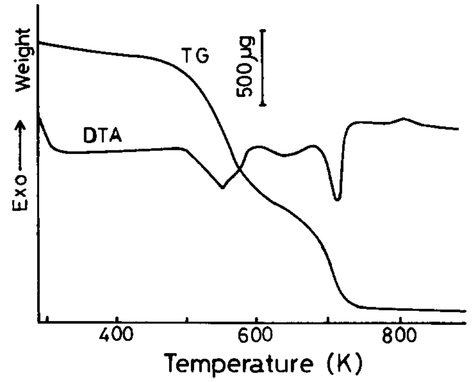

FIG. 4. TG–DTA of a mixture of $H_4(VO)_2P_2O_9$ and $(NH_4)_2ZnCl_4$ (V : Zn = 9 : 1). N_2 flow rate: 150 cm^3/min, heating rate: 5 K/min.

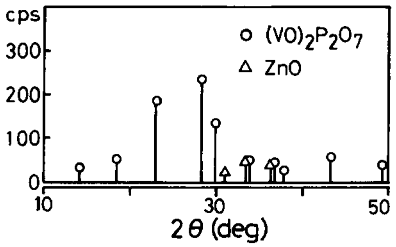

FIG. 5. XRD pattern of the sample after heat treatment in N_2. $H_4(VO)_2P_2O_9$ + ZnO (V : Zn = 9 : 1), N_2 treatment at 773 K for 2 h.

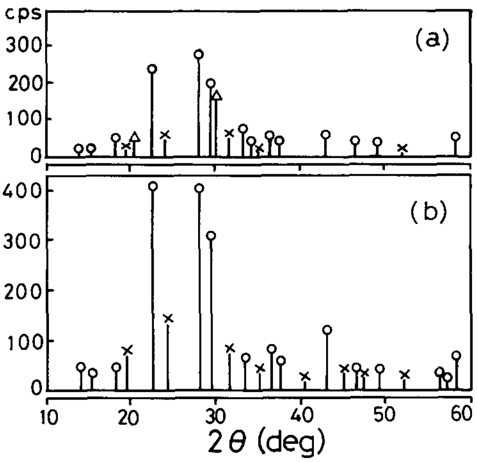

FIG. 6. XRD patterns of the samples after heat treatment in N_2. (a) $H_4(VO)_2P_2O_9$ + $(NH_4)_2ZnCl_4$ (V : Zn = 8 : 2), N_2 treatment at 873 K for 2 h. (b) $H_4(VO)_2P_2O_9$ + ZnO(V : Zn = 8 : 2), N_2 treatment at 823 K for 2 h. ○: $(VO)_2P_2O_7$, △, ×: unknown.

without weight change were observed at 790 K for the sample of 10% Zn and at 800 K for that of 20% Zn in addition to the endothermic peaks at 700 K due to the elimination of water corresponding to the weight loss at 650–720 K. It is noteworthy that these temperatures are well coincided with that of the mixture of $H_4(VO)_2P_2O_9$ and $(NH_4)_2ZnCl_4$ as seen in Fig. 4.

The samples composed of $H_4(VO)_2P_2O_9$ and ZnO gave the XRD peaks due to component compounds. After the heat treatment at 723 K in N_2 stream, weak peaks due to ZnO and the peaks due to $(VO)_2P_2O_7$ appeared. The sample after the treatment in N_2 at 823 K, which is the temperature higher than the exothermic peak in TG–DTA spectrum, gave the new peaks in XRD spectrum in addition to the peaks due to $(VO)_2P_2O_7$ as shown in Fig. 6b. These peaks cannot be identified but most are well coincided with the peaks in the spectrum of the sample which was obtained by heat treatment of $H_4(VO)_2P_2O_9$ and $(NH_4)_2ZnCl_4$ at 873 K in N_2 (Fig. 6a). This suggests that $(NH_4)_2ZnCl_4$ in the catalyst precursor converted to ZnO without reacting with both $H_4(VO)_2P_2O_9$ and $(VO)_2P_2O_7$ during the heat treatment at the temperatures up to 773 K.

Catalytic Properties of the ZnO-Containing Catalysts

The results of *n*-butane oxidation over several catalysts were shown in Table 1. Catalytic activity of ZnO was very low at 773 K and was practically inactive for the oxidation of butane. The pure $(VO)_2P_2O_7$ catalyst attained high MA selectivity, more than 70%, although the conversion was slightly declined with reaction time. MA was formed with 60% selectivity over the catalyst containing 10% ZnO pretreated at 773 K; the conversion, however, was about two times of that over pure $(VO)_2P_2O_7$. After the operation for 27 h, the conversion decreased slightly while the MA selectivity increased compared with the initial value by ca. 10%. Centi *et al.* (*16*) reported that V–P–O catalyst associated with ZnO were active and selective in the oxidation of butane. The catalytic performance of the catalyst pretreated at 823 K was close to that of pure $(VO)_2P_2O_7$. Over the catalyst containing 20% of ZnO, conversion was close to that of pure $(VO)_2P_2O_7$ but MA selectivity was rather low. Decrease in surface area will compensate for the promotion effect by the addition of ZnO.

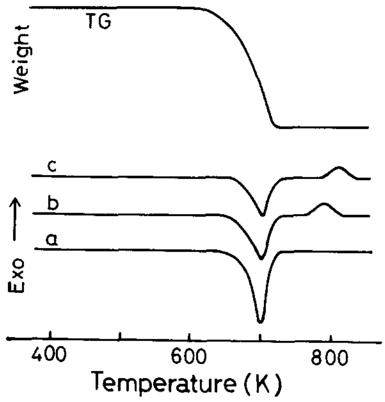

FIG. 7. TG–DTA of catalyst precursors. N_2 flow rate, 150 cm^3/min; heating rate: 5 K/min. (a) $H_4(VO)_2P_2O_9$, (b) $H_4(VO)_2P_2O_9$ + ZnO (V : Zn = 9 : 1), (c) $H_4(VO)_2P_2O_9$ + ZnO (V : Zn = 8 : 2).

TABLE 1

Oxidation of *n*-Butane over ZnO-Promoted V–P–O Catalysts

Catalyst	$(VO)_2P_2O_7$		ZnO	$H_4(VO)_2P_2O_9$ + ZnO (V : Zn = 9 : 1)				$H_4(VO)_2P_2O_9$ + ZnO (V : Zn = 8 : 2)	
Temp. of N_2 treatment (K)	773		773	773		823		773	
Reaction time (h)	6	24	5	5	27	5	27	5	27
Conversion (%)	22.2	18.9	0.4	50.8	46.4	20.2	19.0	19.5	22.4
Selectivity (%)									
MA	71.8	73.5	—	60.0	67.2	62.8	70.5	43.8	58.8
CO	20.8	18.0	—	26.4	21.1	23.0	18.3	38.6	29.7
CO_2	7.0	7.2	100	13.6	11.1	14.0	10.9	15.5	11.4
MA Yield (%)	15.9	13.9	—	30.5	31.2	12.7	13.4	8.9	13.2
SSA[a] (m^2/g)									
After N_2 treatment		12.7	5.2		13.4		11.5		6.9
After oxidation		14.1	5.2		12.3		12.5		4.3

[a] Specific surface area; reactant gas composition, butane 1.5 mol%; O_2 19.7 mol%; N_2 78.8 mol%; reaction temperature, 673 K; W/F = 0.80 g s/cm^3.

Taking into account the XRD results, the catalyst, pretreated at temperatures below 773 K and composed of no homogeneous compounds, is preferable to selective MA formation.

Effect of Added ZnO on the Rate of $(VO)_2P_2O_7$ Oxidation

Rates of oxidation of catalysts were examined by TG and the results are shown in Fig. 8. After keeping at a designated temperature in N_2 stream, the atmosphere of the sample was changed to air and change in weight was observed by TG. The pure $(VO)_2P_2O_7$ was oxidized very slowly as shown in Fig. 8 and the weight of the sample reached steady value which corresponded to $VOPO_4$ after 12 h from introduction of air at 873 K, while the catalyst containing ZnO was oxidized very rapidly. Since specific surface area of the catalysts were almost the same and Zn atoms were present on the surface of $(VO)_2P_2O_7$, the rate coefficient of the oxidation of catalysts may reflect the rate of incorporation of gaseous oxygen into catalyst. The rate coefficient of Zn-containing catalyst which was evaluated from initial weight increase under first-order rate equation was about 100 times larger than that of pure $(VO)_2P_2O_7$. The MA selectivity of the ZnO-containing catalysts was not higher than that of pure $(VO)_2P_2O_7$ and only the conversion was increased. This can be accounted for by the increase in the rate of oxidation of catalyst.

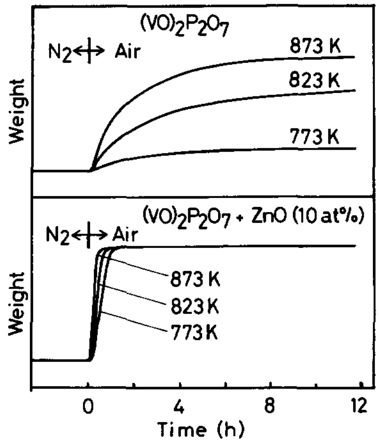

FIG. 8. Effect of ZnO addition on the rate of oxidation of $(VO)_2P_2O_7$. (a) $(VO)_2P_2O_7$, 12.7 m^2/g, (b) $(VO)_2P_2O_7$ + ZnO (V : Zn = 9 : 1), 13.4 m^2/g.

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