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Promotional effect of niobium phosphate for vanadyl pyrophosphate catalyst on selective oxidation of butane to maleic anhydride

Ikuya Mastuura *, Tomohiro Ishimura, Satoko Hayakawa, Naomasa Kimura

Faculty of Science, Toyama University, Toyama 930, Japan

Abstract

$NbOPO_4$ and α-$VOPO_4$ can easily form a solid solution such as $V_{1-x}Nb_xOPO_4$, because $NbOPO_4$ is isostructural to α-$VOPO_4$ with a tetragonal structure. The VNbPO catalysts prepared by the reduction of $V_{1-x}Nb_xOPO_4$ with benzyl alcohol form compounds of the type $(V_{1-x}Nb_xO)_2(P_2O_7)_{1-x}(PO_4)_{2x}$. The catalyst keeps the oxidizing ability of $(VO)_2P_2O_7$ and gives strong Lewis acid sites. As a result, VNbPO catalysts have high catalytic activity in the oxidation of butane to maleic anhydride.

Keywords: Vanadyl pyrophosphate; Niobium phosphate; Maleic anhydride; Butane oxidation; Butene oxidation

1. Introduction

Butane oxidation to maleic anhydride is known to be catalyzed by $(VO)_2P_2O_7$. The reaction starts with the step of the dehydrogenation of butane to butene and is followed by the same sequence as the butene oxidation, i.e., $C_4H_{10} \rightarrow C_4H_8 \rightarrow C_4H_6 \rightarrow C_4H_4O \rightarrow C_4H_2O_3$ (MA). Trifiro et al. [1] reported that butane can be activated firstly by the coordinated–unsaturated V-ion which is acidic situated in the (100) surface plane of $(VO)_2P_2O_7$ and then oxidized to maleic anhydride by the oxygen double-bonded with the other paired V-ion. A number of promoters, e.g., Co, Ni, Fe, Mo and Nb, have been shown to be effective and those promoters may form solid solutions with $(VO)_2P_2O_7$ to form compounds of the type $((VO)_xM_{1-x})_2P_2O_7$, where M is the promoter [2]. It is interesting to note that the promotion effect of $NbOPO_4$ is isostructual to vanadium phosphate and this probably aids to the solution formation. In this work, the preparation of VNbPO solid solution catalyst was studied. The catalyst was tested for the oxidation of butane and butene into maleic anhydride.

2. Experimental

The VNbPO catalyst used in this work was prepared by the following process. V_2O_5 and $Nb_2O_5(H_2O)_{3.3}$ are added into orthophosphoric acid aqueous solution and reflux of the solution was carried out at 80°C for 16 h. A yellow–green precipitate $V_{1-x}Nb_xOPO_4 \cdot 2H_2O$ $(x = 0\text{–}0.3)$

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* Corresponding author.

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was obtained. The solid product was put into benzyl alcohol and a 24 h reflux at 80°C in the solution produced green precipitate. Then it was washed thoroughly with distilled water and dried at 100°C and $V_{1-x}Nb_x(HPO_4)\cdot 0.5H_2O$ was obtained. The solid product was treated at 480°C for 8 h with artificial air containing 2% butane and the final product, VNbPO catalyst, was obtained.

Powder X-ray diffraction of each solid product at each catalyst preparation stage was measured with a SHIMAZU XD-3A X-ray diffractometer. The specific surface area of the catalyst was measured by the conventional BET method of Kr adsorption. The acidity of each catalyst was determined by the TGA of the pyridine adsorption–desorption and also by examining the dehydration of 2-propanol. The dehydration of 2-propanol was carried out in a conventional fixed-bed reactor. The feed gas consisting of 5 vol.-% 2-propanol and He gas was allowed to flow at a space velocity of 2400 ml/h g catalyst. The oxidation of butane and butene into maleic anhydride was measured using a normal pressure flow reactor. Catalyst with a uniform size, 24–35 mesh, was packed in a tubular reactor and artificial air containing 2 vol.-% butane or butene was flowed through the reactor. The space velocity was 2400 ml/h g catalyst.

3. Results

The results of XRD measurements of solid solutions at VNbPO catalyst preparation stages, are shown in Fig. 1a, Fig. 1b and Fig. 1c. Fig. 1a shows the XRD pattern of the phosphate produced in the reaction between V_2O_5 and $Nb_2O_5(H_2O)_{3.3}$ in orthophosphoric acid aqueous solution. The XRD pattern in Fig. 1a was the same as that of $VOPO_4\cdot 2H_2O$ reported by Leonowicz et al. [3] which proves that the solid solution $V_{1-x}Nb_xOPO_4\cdot 2H_2O$ was produced by this method. As the Nb cation dissolves into $VOPO_4\cdot 2H_2O$, the (001) peak shifted from $2\theta = 11.49$ to 12.4°. Accordingly, it was found out that the c axis length of $VOPO_4\cdot 2H_2O$

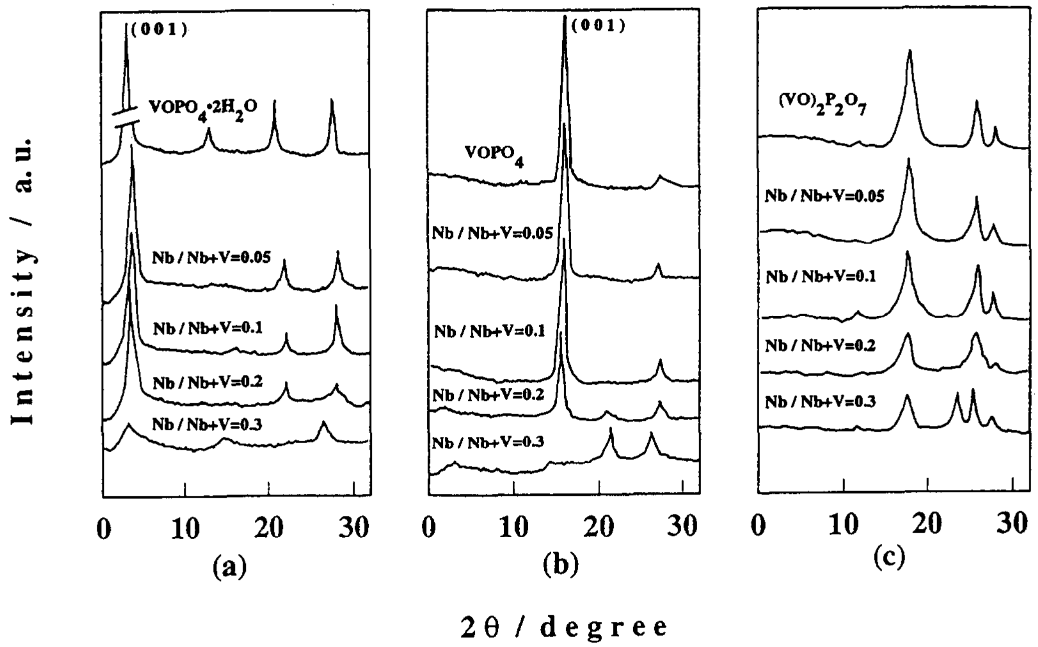

Fig. 1. XRD pattern of VNbPO catalyst preparation stages. (a) $V_{1-x}Nb_xOPO_4\cdot 2H_2O$, (b) $V_{1-x}Nb_xOPO_4$, (c) VNbPO catalyst.

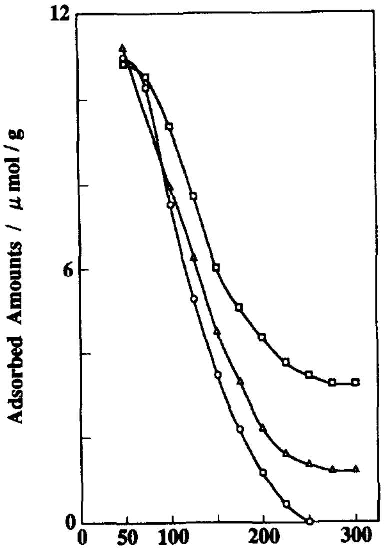

Fig. 2. Thermal programmed desorption of pyridine on VNbPO catalysts. (○) $(VO)_2P_2O_7$; (△) Nb/Nb + V = 0.05; (□) Nb/Nb + V = 0.2.

shortened from 7.41 to 7.13 Å. For reference, the XRD pattern of $V_{1-x}Nb_xOPO_4$ produced in the calcinating of $V_{1-x}Nb_xOPO_4 \cdot 2H_2O$ at 600°C is shown in Fig. 1b. The formed $V_{1-x}Nb_xOPO_4$ had an α_I-$VOPO_4$ type structure reported by Centi et al. [4]. However, as dissolution of the Nb cation increased, the (001) peak intensity became weaker and the very weak (200) peak became stronger. This finding shows that as Nb cation dissolution into $V_{1-x}Nb_xOPO_4$ increases, its structure changes from α_I-type to α_{II}-type, which was reported by Jordan and Calvo [5]. Precursor $V_{1-x}Nb_x(HPO_4) \cdot 0.5H_2O$ was produced in the reduction of $V_{1-x}Nb_xOPO_4 \cdot 2H_2O$ with benzyl alcohol and made into catalysts by activation treatment. The XRD patterns of the catalysts are shown in Fig. 1c. All catalysts gave the XRD pattern of $(VO)_2P_2O_7$. However, as the Nb cation dissolution increased, the relative intensity $I(001)/I(042)$ became lower. And the catalyst, with Nb/Nb + V = 0.3, gave a peak ($\theta = 26.8°$) which was not observed in $(VO)_2P_2O_7$. Accordingly, it was found out that the VNbPO solid solution with the composition of Nb/Nb + V > 0.2 is not formed.

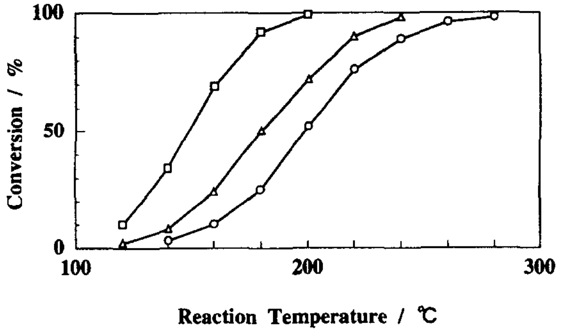

Fig. 3. Dehydration of 2-propanol on VNbPO catalysts. (○) $(VO)_2P_2O_7$; (△) Nb/Nb + V = 0.05; (□) Nb/Nb + V = 0.2.

Argon gas saturated with pyridine was flowed over the VNbPO catalyst set in a TGA equipment at room temperature for 8 h, after that argon gas was flowed at 50°C and the physically adsorbed pyridine was removed. The thermal programmed desorption of pyridine was measured. The temperature programming rate was 10°C/min. The result is given in Fig. 2. In rising the temperature up to 250°C, all the adsorbed pyridine of $(VO)_2P_2O_7$ was desorbed. It was found, however, that as for the catalyst with Nb cation dissolution, strongly adsorbed pyri-

Table 1
Acidic property of the VNbPO catalysts

Catalyst (Nb/Nb + V)	Surface Area ($m^2 g^{-1}$)	Acidic amount (μmol/g)			Dehydration of 2-C_3H_7OH (T_{50}, °C)
		Weak	Strong	Total	
$(VO)_2P_2O_7$	24.7	10.85	–	10.85	200
0.05	25.6	9.85	1.35	11.20	180
0.10	23.6	8.60	2.70	11.30	160
0.20	22.6	6.80	4.00	10.80	150
0.30	10.4	5.25	5.20	10.45	160

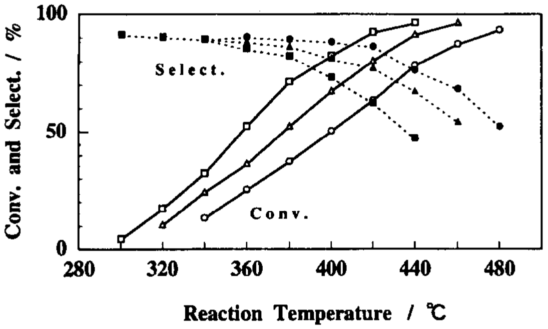

Fig. 4. Butane oxidation on VNbPO catalysts. (○,●) $(VO)_2P_2O_7$; (△,▲) Nb/Nb+V = 0.05; (□,■) Nb/Nb+V = 0.2.

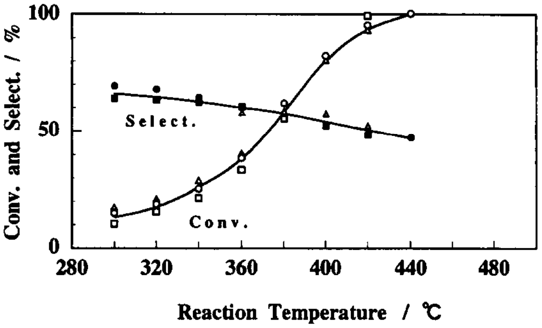

Fig. 5. Butene oxidation on VNbPO catalysts. (○,●) $(VO)_2P_2O_7$; (△,▲) Nb/Nb+V = 0.05; (□,■) Nb/Nb+V = 0.2.

dine remained even at a temperature over 250°C. The amount of adsorbed pyridine at 50°C is considered to be the total amount of acid sites of the catalyst, assuming that the amount of the remaining pyridine over 250°C is equivalent to a strong acidic site. The results are shown in Table 1. The specific surface area of the catalyst determined by the BET method is also shown in Table 1.

Acidic property of the VNbPO catalyst was measured by the dehydration of 2-propanol (Fig. 3). It shows that as the Nb cation in the VNbPO catalyst increases, the activity for dehydration was increased. The reaction temperature, T_{50}, at which 50% 2-propanol was dehydrated, is given in Table 1. The dehydration temperature (T_{50}) goes down as strong acid sites of the VNbPO catalyst increased.

The results of the butane oxidation with the VNbPO catalysts are shown in Fig. 4. With the $(VO)_2P_2O_7$ catalyst, the butane oxidation started to take place around 320°C and finishes at 500°C. With the VNbPO solid solution catalyst, however, the initiation temperature of the butane oxidation went down as the amount of Nb cation dissolution increased. With the VNbPO catalyst composed of Nb/Nb + V = 0.2, which showed the highest activity, oxidation started around 260°C and finished at 440°C. Table 2 shows the result of the butane oxidation with

Table 2
Activity of butane oxidation at the optimum yield for maleic anhydride on the VNbPO catalysts

Catalyst (Nb/Nb + V)	React. temp. (°C)	Butane conv. (%)	MA select. (%)	MA yield (%)
$(VO)_2P_2O_7$	460	85	72	61.2
0.05	440	86	72	61.9
0.10	420	83	74	61.4
0.20	400	81	78	63.2
0.30	420	82	74	60.7

Table 3
Activity of the butene oxidation at the optimum yield for maleic anhydride on the VNbPO catalysts

Catalyst (Nb/Nb + V)	React. temp. (°C)	Butene conv. (%)	MA select. (%)	MA yield (%)
$(VO)_2P_2O_7$	400	88	53	46.4
0.05	400	86	56	48.2
0.10	400	84	51	42.8
0.20	400	86	51	43.9
0.30	400	84	50	42.0

each catalyst at the reaction temperature at which the optimum yield of maleic anhydride was obtained. Fig. 5 shows the result of the butene oxidation with the VNbPO catalysts. Unlike the butane oxidation, the butene oxidation with the VNbPO catalysts did not show the activity difference between $(VO)_2P_2O_7$ and Nb cation dissolved VNbPO catalysts. Table 3 shows the result of the butene oxidation with each catalyst at the reaction temperature at which the optimum yield of maleic anhydride was obtained.

4. Discussion

Misono et al. [6] have reported that in the butane oxidation into maleic anhydride over $(VO)_2P_2O_7$, the oxidative dehydrogenation and the oxygen addition reaction take place consecutively. From that point of view, the abstraction of hydrogen anion from butane by Lewis acid sites of the catalyst seems an important step. To clarify the relationship between the acidity of the VNbPO catalysts and the activity of butane oxidation, the relationship between the dehydration temperature (T_{50}) of 50% 2-propanol conversion — a factor of the acidity of the catalyst — and the oxidation temperature (T_{80}) of the 80% butane conversion, is shown in Fig. 6. As the acidity of the catalysts become higher, the butane oxidation temperature goes down. It suggests that the acidity of the VNbPO catalysts plays an important role in the butane oxidation into maleic anhydride.

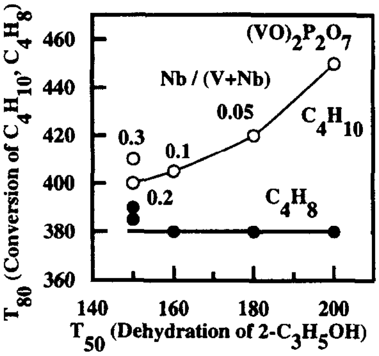

Fig. 6. Reaction between catalytic activities and acidic properties of VNbPO catalysts. (●) Butane conversion; (○) butene conversion.

Trifiro et al. [1] suggested that the Lewis acid site of $(VO)_2P_2O_7$ is the coordinated-unsaturated V cation in the surface layer of the (100) plane. They have reported that the Lewis acid strength depends on the distortion of $(P_2O_7)^{4-}$ ion which is bound to a pair of $(VO)^{2+}$ ions. During the preparation of the VNbPO catalyst, $V_{1-x}Nb_xOPO_4 \cdot 2H_2O$ is reduced with benzyl alcohol to get the precursor of the catalyst. In general, the V^{5+} ion is reduced to the V^{4+} ion with ease, but the Nb^{5+} ion is not easily reduced to the Nb^{4+} ion. Therefore, the produced precursor becomes $V_{1-x}^{4+}Nb_x^{5+}(H_{1-x}PO_4) \cdot 0.5H_2O$. The VNbPO solid solution catalyst produced from the precursor by heat-dehydration is $(V_{1-x}^{4+}Nb_x^{5+}O)_2(P_2O_7)_{1-x}(PO_4)_{2x}$. Linde and Gorbunova [7] determined the crystal structure of $(VO)_2P_2O_7$, in which the five-coordinated pair of V-ions, having oxygen atoms double-bonded to them in *trans* position, are situated parallel and form (100) crystal plane, supported by pyrophosphate $(P_2O_7)^{4-}$ ions from both sides of the (100) plane. When part of the V^{4+} ions in the (100) layer are replaced by Nb^{5+} ions, part of the pyrophosphate $(P_2O_7)^{4-}$ ions, which are bound to $(VO)_2^{2+}$ ions, take in oxygen ions and form each two orthophosphate $(PO_4)^{3-}$ ions. In other words, when Nb^{5+} ion is introduced in $(VO)_2P_2O_7$, orthophosphate ion is formed between the (100) layers of the catalyst as follows; $P_2O_7^{4-} + O^{2-} \rightarrow 2PO_4^{3-}$. The weak acid sites of $(VO)_2P_2O_7$ change into strong acid sites, as shown in Table 1. It is certain that since the Nb^{5+} ion has a higher electronegativity than the V^{4+} ion, coordinated-unsaturated Nb^{5+} ion in the (100) surface layer of the VNbPO catalyst becomes a stronger Lewis acid site than the V^{4+} ion. VNbPO catalyst — $(VO)_2P_2O_7$ partially replaced with $NbOPO_4$ — still keeps the oxidizing ability of $(VO)_2P_2O_7$ and gives strong Lewis acid sites, which promotes $C_4H_9^+$ carbenium ion formation from butane through the abstraction of a hydrogen anion. In conclusion, VNbPO catalysts have high catalytic activity in the oxidation reaction of butane into maleic anhydride.

References

[1] G. Busca, G. Centi and F. Trifiro, Appl. Catal., 25 (1986) 265.
[2] G.J. Hutchings, Appl. Catal., 72 (1991) 1.
[3] M.E. Leonowicz, J.W. Johnson, J.F. Brody, F. Shannon, Jr. and J.M. Newsam, J. Solid State Chem., 56 (1985) 370.
[4] G. Centi, F. Trifiro, J.R. Ebner and V. Franchetti, Chem. Rev., 88 (1988) 55.
[5] B.D. Jordan and C. Calvo, Acta Crystallogr. Sect., B32 (1976) 2899.
[6] T. Shimoda, T. Okuhara and M. Misono, Bull. Chem. Soc. Jpn., 58 (1985) 2163.
[7] S.A. Linde, Yu.E. Gorbunova, A.V. Lavrov and V.G. Kuznetsov, Dokl. Akad. Nauk SSSR., 245 (1979) 584.