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Oxidation of *n*-butane over vanadyl pyrophosphates prepared from lamellar vanadyl alkylphosphates

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Abstract

Vanadyl pyrophosphates ($(VO)_2P_2O_7$) having different microstructures were prepared by calcination of vanadyl alkylphosphates ($V = V^{4+}$ and $P = P^{5+}$), which were synthesized with methanol, 1-butanol, and benzyl alcohol. XRD, SEM, and IR measurements revealed that these alkylphosphates were lamellar compounds and exhibited different morphologies retaining the lattice V–O–P bondings. It was found that among these precursors, vanadyl methylphosphate was superior to the others as the precursor for $(VO)_2P_2O_7$ with the high surface area, catalytic activity, and selectivity to maleic anhydride. The catalyst obtained from methylphosphate possessed $42\,m^2\,g^{-1}$ of the surface area after the reaction and exhibited 67% of the selectivity at the conversion of 52% in the oxidation of *n*-butane at 703 K. This high catalytic performance would be brought about by the formation of single phase of $(VO)_2P_2O_7$ consisting of smaller crystallites. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Vanadyl pyrophosphate; Vanadyl methylphosphate; Lamellar compound; Selective oxidation; *n*-Butane

1. Introduction

Selective oxidation of *n*-butane to maleic anhydride (abbreviated as MA) is an important commercial process, because the product MA is a useful raw material for agricultural chemicals, food additives, and unsaturated polymer resins. Furthermore, at present, this reaction has only a few commercialized applications in the gas–solid reaction of alkane with oxygen. Vanadyl pyrophosphate, $(VO)_2P_2O_7$, is the main component of the commercial catalyst for this reaction [1]. One of the present critical problem in this catalytic system is insufficient yield of MA. It is thus desirable to improve the yield by the development of the catalytic performance.

There are many reports about the synthesis of vanadyl pyrophosphate (VP) oxides with unique nanostructured materials, i.e., intercalation compounds [2–4], lamellar compounds [5–8], large crystallites [9], mesostructured materials [10,11], and thin-layered compounds [12,13]. The lamellar compounds are represented by vanadyl alkylphosphonates and vanadyl alkylphosphates. These compounds can also be recognized as intercalation compounds of the layered VP oxides by alkyl groups. Vanadyl alkylphosphonates are given by the formula $VO(RPO_3){\cdot}nH_2O$, in which the oxidation numbers of V and P are +4 and +3, respectively, and R is the alkyl group. These compounds contain O=P–C bonds. On the other hand, vanadyl alkylphosphates are given by the formula $(VO)((R)_x(H)_{1-x}OPO_3)\cdot nH_2O$, where the oxidation

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numbers of V and P are +4 and +5, respectively. The ester bonds of O=P–O–C are included in these materials.

Johnson et al. [14] synthesized a variety of alkylphosphonates from V_2O_5 and alkylphosphonic acid (R–OPO_2). In addition, Pinnick and Durham [15] reported the formation of vanadyl phenylphosphonates. Guliants et al. [5] claimed that a vanadyl methylphosphonate prepared from methanol was converted to $(VO)_2P_2O_7$ by the calcination. The obtained $(VO)_2P_2O_7$ showed an activity for selective oxidation of *n*-butane, while the selectivity to MA was less than 60%.

On the other hand, there is no academic report about the systematic preparation of vanadyl alkylphosphates. The researchers of Du Pont [16] have described the synthesis of vanadyl alkylphosphates using V_2O_5 and P_2O_5 in alcohol. However, the synthesized vanadyl alkylphosphates are limited only to those from primary alcohol. Furthermore, the above patent described that the calcination of vanadyl *n*-propylphosphate at 723 K brought about $(VO)_2P_2O_7$ exhibiting the selectivity to about 70%, while the detailed catalytic performance was not shown.

Recently, we found that a variety of vanadyl alkylphosphates from alcohol including secondary aliphatic and alicyclic alcohols through partial reduction of V_2O_5 with a mixture of isobutyl alcohol and benzyl alcohol, followed by the additions of alcohol and P_2O_5 in toluene [17]. In the present study, the microstructures of these alkylphosphates were characterized systematically by elemental analysis, XRD, IR, and SEM. Furthermore, the catalytic property for the selective oxidation of *n*-butane was examined.

2. Experimental

2.1. Materials

Vanadyl alkylphosphates were prepared as follows. V_2O_5 (0.16 mol, Koso Chemical) was added to a mixture of 180 cm^3 of isobutyl alcohol (Koso Chemical) and 120 cm^3 of benzyl alcohol (Koso Chemical) at room temperature. The suspension was refluxed at 378 K for 3 h, and then was cooled to room temperature. The resulting solid was separated, washed with acetone, and dried at room temperature for 16 h. XRD revealed that the solid was a mixture of V_2O_5 and V_4O_9. The average oxidation number of V of the solid determined by a redox titration method using $KMnO_4$, $FeSO_4(NH_4)_2SO_4\cdot 6H_2O$, and $(NH_4)_2S_2O_8$ [18] was 4.7, showing that the molar ratio of V_2O_5 to V_4O_9 was about 2/3. To the suspension (300 cm^3) of alcohol containing the solid, a suspension of toluene (75 cm^3) with P_2O_5 (29.6 g) was slowly added with stirring at room temperature. This suspension was refluxed until the color of the suspension changed to light blue. The resulting light blue solid was separated by filtration, washed with acetone, and dried at room temperature for 16 h. The catalysts obtained by the calcination at 773 K of these precursors from methanol, 1-butanol, and benzyl alcohol in 9.1% O_2 (He balance) are denoted as VP(MeOH), VP(1-Bu), and VP(BeOH), respectively. As reference, the precursor $VOHPO_4\cdot 0.5H_2O$ (denoted as P-3) was prepared using isobutyl alcohol and benzyl alcohol by organic solvent method [1], and the corresponding $(VO)_2P_2O_7$ (denoted as C-3) was obtained by the calcination at 773 K in 9.1% O_2 (He balance).

2.2. Characterization

Powder XRD patterns were obtained on an X-ray diffractometer (Rigaku MiniFlex) with Cu Kα radiation ($\lambda = 0.154$ nm). Infrared spectra were recorded with an IR spectrometer (Bio-rad FTS-7) by a KBr method. Elemental analysis of the samples was performed with a Microanalytisch Labor Pascher (Germany) for V, P, C, O, and H after the samples were evacuated at 323 K for 24 h. SEM micrographs were measured with a Hitachi S-2100A. The surface area was measured by a BET method with automatic adsorption system (BEL 28SA, BEL Japan).

2.3. Catalytic oxidation of n-butane

Catalytic oxidation of *n*-butane was carried out in a flow reactor (Pyrex tube, 10 mm inside diameter) under an atmospheric pressure at 703 K. The reactant mixture consists of *n*-butane (1.5%), O_2 (17%), and He (balance). The vanadyl alkylphosphates (about 1.0 g) were pretreated with a gas flow (110 $cm^3\,min^{-1}$) consisting of O_2 (9.1%) and He (balance) for 8 h at 773 K. Then the reactant gas was fed to the catalysts at 703 K. The products were analyzed with gas chromatographs (a high speed GC (TCD), Area Japan M-200 and an

FID GC, Shimadzu 8A) equipped with columns of Molecular Sieve 5A and Porapak QS.

3. Results and discussion

Table 1 summarizes the compositions of methylphosphate and *n*-butylphosphate. From Table 1, the chemical formulae of these vanadyl alkylphosphates are deduced to be $(VO)(R_{1-x}H_xOPO_3)(ROH)_y{\cdot}nH_2O$ ($x + y = 1$, R = CH_3 or *n*-C_4H_9). The data of TG suggest that x is about 0.5 for methylphosphate [19]. The oxidation titration method [18] showed that the oxidation numbers of V are very close to 4 for these three alkylphosphates.

Fig. 1 shows the XRD patterns of these vanadyl alkylphosphates. All these materials gave intense peaks at less than 10° of 2θ, indicating lamellar compounds. Assuming that these intense peaks correspond to the diffraction from (0 0 1) plane, the distances of layer (d(0 0 1)) are estimated to be 0.89, 1.40, and 1.53 nm for methylphosphate, *n*-butylphosphate, and benzylphosphate, respectively. Since the d(0 0 1) values increased linearly as the length of alcohol increased for a variety of alcohols [17], it is considered that the alkyl groups are inserted in the interlayer space with the bonding of O=P–O–R. The peak at about $2\theta = 30°$ corresponds to the diffraction from (1 3 0) plane [1]. This peak was relatively intense for these layered materials especially for P-3 (Fig. 1), which is probably due to the thinner crystallites.

Infrared spectra of these alkylphosphates are given in Fig. 2. These compounds displayed similar peaks in the lattice vibration region (less than 1500 cm^{-1}). The peaks of $VOHPO_4{\cdot}0.5H_2O$ (Fig. 2d) were assigned to $\nu_{as}(PO_3)$ for 1197 cm^{-1}, δ(P–OH) for 1131 cm^{-1}, $\nu(PO_3)$ for 1102 cm^{-1}, $\nu(PO_3)$ for 1050 cm^{-1}, ν(V=O) for 976 cm^{-1}, and ν(P–OH) for 931 cm^{-1} [20]. For all these alkylphosphates, the peaks at 1193, 1092 and 1052 cm^{-1} are assigned to $\nu(PO_3)$. In addition, the peak at 980 cm^{-1} is assignable to ν(V=O). The vibrations of P–O–C bond were detected at around 1161 cm^{-1} as shoulder peaks [21].

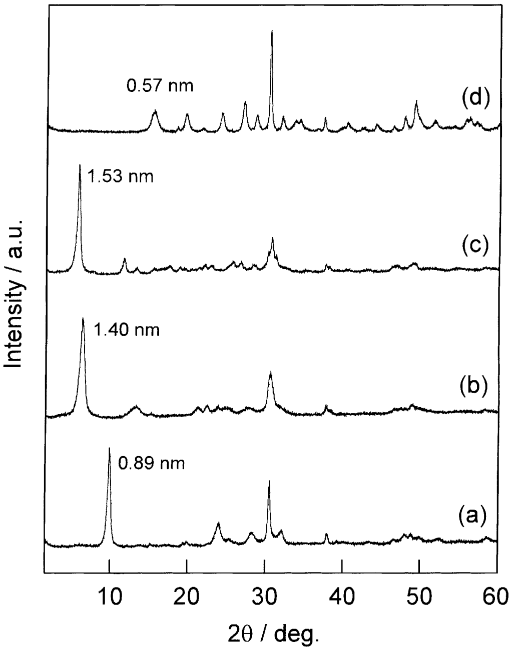

Fig. 1. XRD patterns of vanadyl alkylphosphates and $VOHPO_4{\cdot}0.5H_2O$: (a) methylphosphate; (b) *n*-butylphosphate; (c) benzylphosphate; (d) $VOHPO_4{\cdot}0.5H_2O$ (P-3).

SEM micrographs are given in Fig. 3. It was found that the morphology of the alkylphosphates changed significantly depending on the alkyl group. Vanadyl methylphosphate and vanadyl *n*-butylphosphate displayed sponge-like and grape-bunch shapes, respectively. On the other hand, the shape of vanadyl benzylphosphate resembles that of P-3, rose-petal.

Table 1
Composition of vanadyl alkylphosphates

R[a]	Weight percentage[b]				
	V	P	C	H	O
Methyl	28.1 (1.00)	17.4 (1.02)	6.5 (0.98)	2.0 (3.62)	46.06 (5.22)
n-Butyl	23.3 (1.00)	14.3 (1.02)	21.1 (3.91)	4.2 (9.33)	37.15 (5.16)

[a] Alkyl group in vanadyl alkylphosphate.

[b] The figures in parentheses are relative atomic ratios.

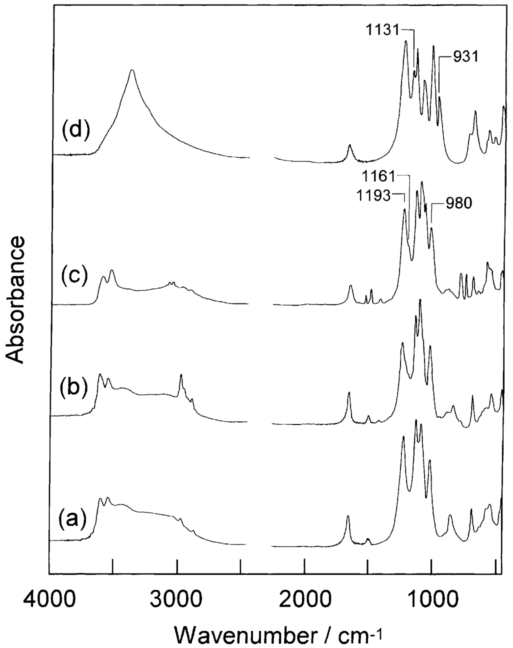

Fig. 2. Infrared spectra of vanadyl alkylphosphates and $VOHPO_4 \cdot 0.5H_2O$: (a) methylphosphate; (b) *n*-butylphosphate; (c) benzylphosphate; (d) $VOHPO_4 \cdot 0.5H_2O$ (P-3).

As was not shown here, the SEM micrographs of the catalysts derived from these precursors were essential, the same as each precursor, indicating that the morphology almost remained unchanged during the transformation to the catalyst and catalytic reaction.

3.1. Catalytic oxidation of n-butane

Figs. 4 and 5 show the time courses of the selective oxidation of *n*-butane over VP oxide catalysts. As shown in Fig. 4, changes in the conversion at the initial stage of the reaction differed depending on the kind of catalysts. In the case of VP(MeOH), the conversion increased once with time, and then decreased gradually.

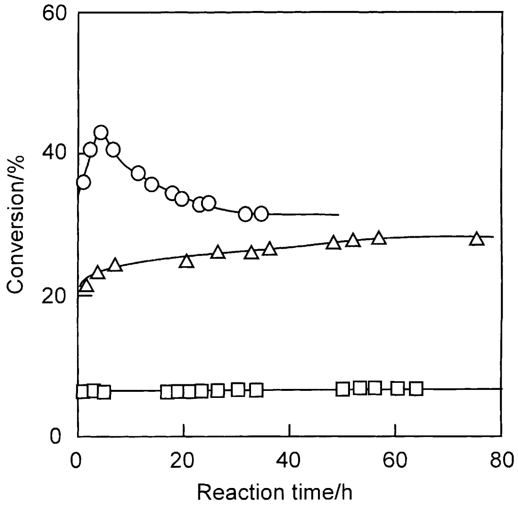

Fig. 4. Changes of the conversion in the oxidation of *n*-butane over various VP oxide catalysts: (○) VP(MeOH); (△) VP(1-Bu); (□) VP(BeOH). The reaction was performed at 703 K with *n*-butane (1.5%) and O_2 (17%). $W/F = 109\,\mathrm{g\,h\,mol^{-1}}$ for VP(MeOH) and $272\,\mathrm{g\,h\,mol^{-1}}$ for VP(1-Bu) and VP(BeOH).

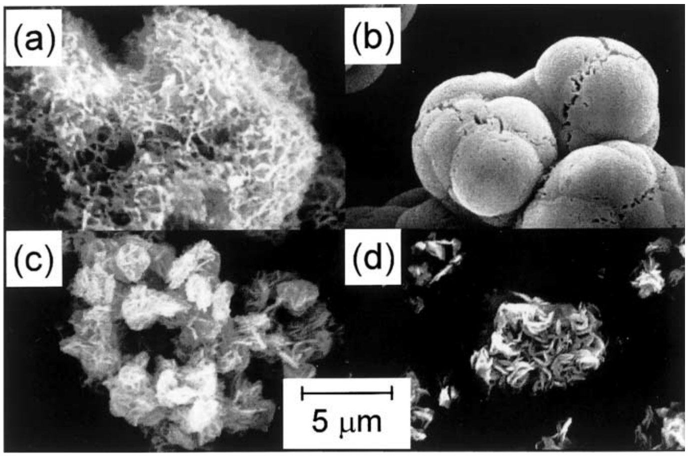

Fig. 3. SEM micrographs of vanadyl alkylphosphates and $VOHPO_4 \cdot 0.5H_2O$: (a) methylphosphate; (b) *n*-butylphosphate; (c) benzylphosphate; (d) $VOHPO_4 \cdot 0.5H_2O$ (P-3).

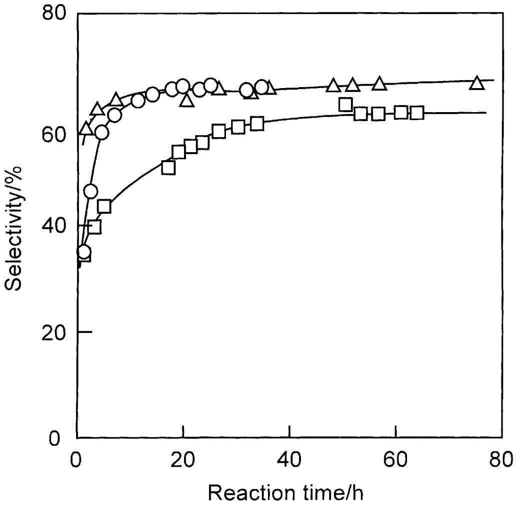

Fig. 5. Changes of the selectivity in the oxidation of *n*-butane over various VP oxide catalysts: (○) VP(MeOH); (△) VP(1-Bu); (□) VP(BeOH). The reaction was performed at 703 K with *n*-butane (1.5%) and O_2 (17%).

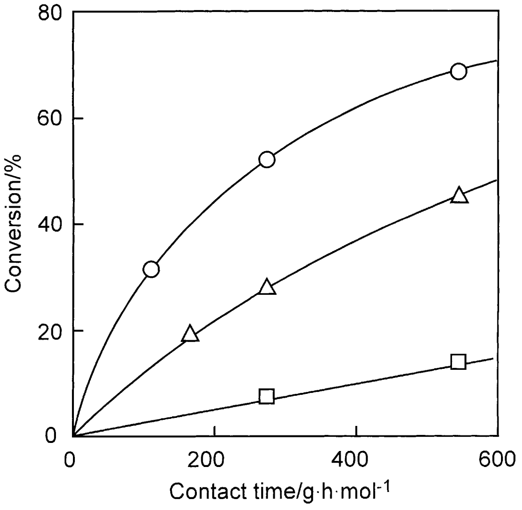

Fig. 6. Dependence of the conversion of *n*-butane on the contact time: (○) VP(MeOH); (△) VP(1-Bu); (□) VP(BeOH). The reaction was performed at 703 K with *n*-butane (1.5%) and O_2 (17%).

For all cases, the stationary conversions were obtained after about 40 h of the reaction. Thus the reaction rates were determined from the data obtained at least after about 40 h.

As Fig. 5 shows, the selectivities to MA increased greatly with time at the initial period (∼10 h), and became nearly constant after 40–60 h. The selectivities were thus compared at these stationary states.

In order to evaluate the catalytic activity, the dependence of conversion on contact time was measured. In Fig. 6, the conversion is plotted against *W*/*F*, where *W* is the catalyst weight (g) and *F* the flow rate of *n*-butane ($\mathrm{mol\,h^{-1}}$). From the slope of curve at the initial stage, the catalytic activity was estimated. The catalytic activity was significantly influenced by the kind of alkyl group of the vanadyl alkylphosphates. The order of the catalytic activity was VP(MeOH) > VP(1-Bu) > VP(BeOH).

Fig. 7 presents the change in the selectivity to MA as a function of the conversion of *n*-butane. It was observed that the selectivities to MA reached about 70% over VP(MeOH) and VP(1-Bu) at the low conversions and those decreased slightly as the conversion increased. On the other hand, the selectivity over VP(BeOH) was lower than the other two.

In Table 2, the catalytic data are summarized, together with the surface area. The great difference in the catalytic activity among these catalysts is attributed to the difference in the surface area. The specific activity defined as the activity per surface area was comparable with each other. It should be noted that VP(MeOH)

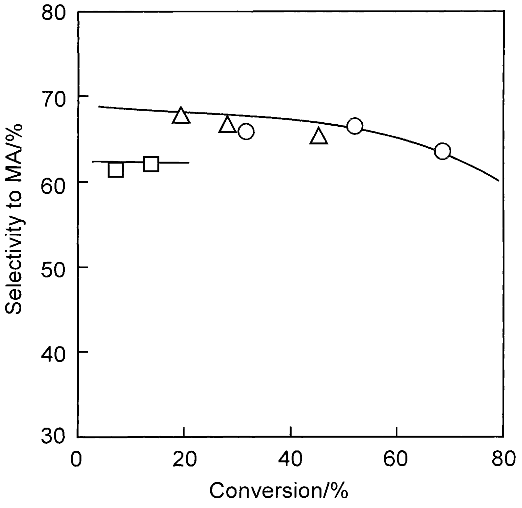

Fig. 7. Selectivity to MA as a function of the conversion: (○) VP(MeOH); (△) VP(1-Bu); (□) VP(BeOH). The reaction was performed at 703 K with *n*-butane (1.5%) and O_2 (17%).

Table 2
Activity and selectivity of VP oxide catalysts for oxidation of *n*-butane[a]

Catalyst	Rate[b]	Surface area ($m^2\,g^{-1}$)	Selectivity[c] (%)			
			MA	CO	CO_2	
VP(MeOH)	54.9	42.0	66.7	21.0	12.3	(51.8)
VP(1-BuOH)	14.3	9.0	65.0	22.3	12.8	(45.0)
VP(BeOH)	2.5	1.5	62.0	26.8	11.2	(13.5)
C-3[d]	24.0	33.9	72.1	18.1	9.7	(56.3)

[a] The reaction was performed at 703 K with a mixture of *n*-butane (1.5%), O_2 (17%), and He (balance).
[b] In the unit of $10^{-4}\,mol\,g^{-1}\,h^{-1}$.
[c] At the conversion shown in the parenthesis.
[d] $(VO)_2P_2O_7$ prepared by organic solvent method.

was most selective (about 67% at 52% conversion) among these vanadyl alkylphosphates, while C-3, which was prepared by so-called organic solvent method [1], was slightly more selective under these conditions. Considering the activities, VP(MeOH) was superior to C-3 in the productivity of MA.

In order to elucidate the difference in the selectivity, the catalyst was characterized by XRD. Powder XRD patterns of the catalyst after the reaction are given in Fig. 8. Basically all these samples show the patterns of the phase of $(VO)_2P_2O_7$. VP(MeOH) and VP(1-Bu) gave only the peaks due to $(VO)_2P_2O_7$, and the peak intensities of VP(MeOH) were far strong as compared with those of VP(1-Bu). On the other hand, the XRD patterns of VP(BeOH) contain δ-$VOPO_4$ phase [22], which is one of the V^{5+} phases, together with the phase of $(VO)_2P_2O_7$. Since it is well known that the phases of $VOPO_4$ were less selective for the *n*-butane oxidation, the presence of these phases would cause decrease in the selectivity. Therefore, the highest selectivity of VP(MeOH) among these catalysts is probably due to the presence of single phase of $(VO)_2P_2O_7$. Keily et al. [23] pointed out that the V^{5+} phases tend to be readily formed as the crystalline size of the precursor increased. Since the length and thickness of primary crystallites of VP(MeOH) were smaller, the non-selective V^{5+} phases would not be formed during the reaction.

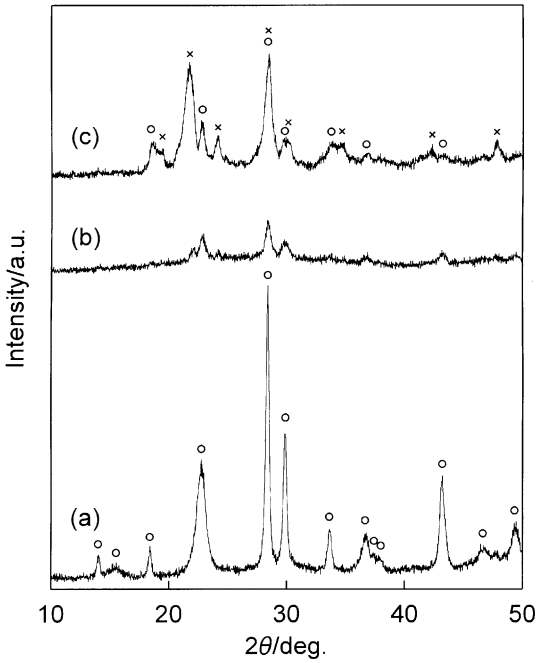

Fig. 8. XRD patterns of VP oxide catalysts: (a) VP(MeOH); (b) VP(1-Bu); (c) VP(BeOH). (○) $(VO)_2P_2O_7$; (×) δ-$VOPO_4$.

4. Conclusion

New lamellar compounds, vanadyl alkylphosphates, were prepared through the partial reduction of V_2O_5, followed by the reaction with P_2O_5 and alcohol such as methanol, 1-butanol, and benzyl alcohol. The layered structure was confirmed by XRD, and the lattice bonding was admitted by infrared spectroscopy. The shape of the crystallites of the $(VO)_2P_2O_7$ catalysts derived from the alkylphosphates was depending to a great extent on the kind of alkyl group of the precursors. The catalyst with the high catalytic performance was obtained by the calcination of vanadyl methyphosphate.

Acknowledgements

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