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Liquid phase catalytic oxidation of benzyl alcohol to benzaldehyde over vanadium phosphate catalyst

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1. Introduction

Vanadium phosphate materials continue to attract attention of researchers as a well studied heterogeneous catalyst. Recent interest in VPO solid materials stems from their structural diversity and potential application in catalysis and material science. An astonishing variety of novel phases of this material arises due to versatility of vanadium in terms of its variable oxidation states (III, IV, V) and co-ordination geometry (tetrahedral, square pyramidal and octahedral). There are many well characterized, crystalline VPO phases were identified whose structure and catalytic properties have been well documented. Some of the most widely studied are the V⁵⁺ vanadyl ortho phosphate (α -, β -, γ -, δ -, ε - and ω -VOPO₄) and VOPO₄·2H₂O), and the V⁴⁺ vanadyl hydrogen phosphates (VOHPO₄·4H₂O, VOHPO₄·0.5H₂O, VO(H₂PO₄)₂), vanadyl pyrophosphate ((VO)₂P₂O₇) and vanadyl metaphosphate (VO(PO₃)₂).

The (VO)₂P₂O₇ catalyst and its precursor VOHPO₄·0.5H₂O phase have been extensively studied, including preparation procedures, activation conditions, crystal structures, activity and catalytic kinetics [1–9]. On the other hand, the crystalline VO(PO₃)₂ catalyst is mostly a combination of amorphous VO(PO₃)₂, monoclinic α -VO(PO₃)₂ [10] and tetragonal β -VO(PO₃)₂ phases [11]. The crystalline VO(PO₃)₂ was obtained from calcination of VO(H₂PO₄)₂ phase under air flow conditions. The catalytic performance of both VO(PO₃)₂ and (VO)₂P₂O₇ have been evaluated in gas phase

ABSTRACT

Vanadium phosphate (VPO) is well known as a heterogeneous catalyst in gas phase oxidation reactions. Till date, this material has not drawn much attention for its application in liquid phase reactions. This paper briefly highlights our recent research on vanadyl metaphosphate concerning its fabrication, characterization and application towards liquid phase oxidation of benzyl alcohol to benzaldehyde using tert-butyl hydroperoxide (TBHP) as the oxidant. In our preliminary catalytic studies, we find that the $VO(PO_3)_2$ exhibits extraordinarily high activity and selectivity in oxidation of benzyl alcohol under mild conditions. The benzyl alcohol conversion is largely increased but the selectivity for benzaldehyde is slightly decreased with the increase in reaction period or temperature. The present catalyst $VO(PO_3)_2$ showed remarkable catalytic activity with respect to other catalytic system; conversion and selectivity with respect to aldehyde is 97 and 99%, respectively.

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reactions such as oxidations, oxidative dehydrogenations and ammoxidations [12–19]. However, VO(PO₃)₂ catalyst has shown poor catalytic performance in gas phase oxidation of *n*-butane to maleic anhydride when compared to high catalytic performance of (VO)₂P₂O₇ catalyst. The poor catalytic performance of VO(PO₃)₂ catalyst in *n*-butane oxidation has made to test its application in other reactions.

Liquid phase oxidation of benzyl alcohol is a hot topic in modern organic synthesis. The design and development of a catalyst with high conversion and selectivity for partial oxidation must also be carried out with regard to the preservation of oil related resources. For selective oxidation reactions, there is tremendous challenge to prevent over oxidation of the products, which are often more sensitive to be oxidized than the reactants. The direct oxidation of benzyl alcohol to benzaldehyde is such type of reaction. Benzaldehyde is a chief raw material in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives. It is also an important intermediate for the processing of perfume and flavoring compounds and in the preparation of certain aniline dyes.

Several methods are available for alcohol oxidations using metal salts in the form of homogeneous catalysis [20–26] or supported metal ions as heterogeneous catalysts [27–31]. However the common methods of alcohol oxidation may use toxic, corrosive, expensive oxidants such as chromium (VI), and setting up a severe condition, like high pressure or temperature, using strong mineral acids.

Structural stability, heterogeneity, deactivation rates and recyclability of the solid acid catalysts are still critical impending to the liquid phase reaction's impact on solid catalyst [32]. Although

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Fig. 1. XRD patterns of the (a) $VO(H_2PO_4)_2$ and (b) $VO(PO_3)_2$.

VPO catalyst system has been studied extensively in gas phase oxidations, including the catalyst structure stability, morphology, crystalline structure, surface composition after hundreds hours of testing, these type of studies are very limited in liquid phase reactions. It is well known that VPO catalysts are structural sensitive to its catalytic activation and reaction conditions [33–35].

Herein, we investigated the impact of *benzyl alcohol* oxidation reaction on VO(PO₃)₂ catalysts structures, micro structural properties and their recyclability performance. The main purpose of our investigation is to prove the catalytic activity of VO(PO₃)₂ in liquid phase reaction. The catalysts were characterized by powder XRD, XPS, SEM, FTIR and BET surface area techniques.

2. Experimental

2.1. Materials and methods

2.1.1. Preparation of catalyst

The vanadyl hydrogen phosphate precursor was prepared according to the procedure as follows: V_2O_5 (5.0 g, Strem, 99%) and o-H₃PO₄ (30 ml, 85% Aldrich) was refluxed with isobutanol for 24 h. The solid was recovered by vacuum filtration, washed with cold water (100 ml) and acetone (100 ml) and dried in air (110 °C, 24 h). The VO(H₂PO₄)₂ precursors thus obtained was calcined in air at 500 °C for 5 h.

2.1.2. Characterization of catalyst

Phase analysis of the material was performed by X-ray diffraction (XRD, P ANAlytical) using Mo K_{α} radiation of 0.7093 Å.

The FE-SEM was performed with a ZEISS 55 microscope. Magnification in the range 15.83–44.90 K has been used to get a better micrograph.

The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multilab ESCA 3000 spectrometer with a non-monochromatized with Mg K_{α} X-ray source. Energy resolution of the spectrometer was set at 0.8 eV with Mg K α radiation at pass energy of 50 eV. The binding energy correction was performed using the C 1s peak of carbon at 284.9 eV as a reference.

2.2. Catalytic tests

In a typical reaction procedure, a mixture of 0.05 g catalyst, acetonitrile (15 ml, S.d. fine, 99.0%) and benzyl alcohol (30 mmol, S.d. fine, 99.5%) was stirred in a three-necked glass batch reactor equipped with a double walled air condenser and magnetic stirrer. The reaction was carried out under atmospheric N₂ at 50 °C for 30 min. Then the oxidant tert-butyl hydroperoxide (TBHP) (30 mmol, Merck, 70%) was added and the mixture was refluxed at 80 °C for 6 h. The reaction mixture was altered and the products were isolated by column chromatography and then analyzed by offline GC (Shimadzu, GC-17A) equipped with capillary column (ZB-1, 30 m length, 0.5 nm ID and 3.0 µm film thickness) using flame ionization detector (FID). The main products were then quantified by HPLC (equipped with a C18 column) with UV-vis detector. The conversion, selectivity and yield were calculated by using Eqs. (1)–(3).

Conversation (%) = $\frac{\text{moles of benzyl alcohol reacted}}{\text{total moles of benzyl alcohol}} \times 100$ (1)

Selectivity (%) =
$$\frac{\text{moles of product formed}}{\text{moles of benzyl alcohol reacted}} \times 100$$
 (2)

Yield (%) =
$$\frac{\text{mole amount of product}}{\text{initial mole amount of benzyl alcohol}} \times 100$$
 (3)

3. Results and discussion

3.1. X-ray diffraction

Fig. 1 shows the XRD patterns of VPO materials. For the precursor, all major diffraction peaks can be attributed to VO(H₂PO₄)₂. The highly intense (001) peak at $2\theta = 13.9^{\circ}$ corresponds to the reflectance patterns of VO(PO₃)₂. Besides this, additional peaks are present with most intense line at d = 2.94 Å. The most intense peak at $2\theta = 15.5^{\circ}$ corresponds to the reflectance patterns of VO(H₂PO₄)₂ with *d* value = 3.11 Å. The XRD patterns reveal that the (001) peak for VO(H₂PO₄)₂ is shifted to lower end after activation i.e. in the VO(PO₃)₂ phase. This is in accordance with JCPDS file 4-880. After activation, the intensity of the peak at $2\theta = 13.9^{\circ}$ increases while the peak at $2\theta = 15.5^{\circ}$ gets decreased. The peaks at $2\theta = 11.09^{\circ}$ and 12.3° can be attributed to the presence of V⁵⁺ species (δ -VOPO₄), which suggest the well crystallinity of the material. The crystallite size (*D*) of VPO catalyst was determined from (001) plane of VO(PO₃)₂ by employing Scherer's formula:

$$D = \frac{k\lambda}{\beta\,\cos\,\theta}$$

For which λ is the wave length of the X-ray (Mo K α), β is the full width at half maximum of the diffraction peak, k is a shape factor (0.94) and θ is the angle of diffraction. The intensity of the XRD peaks, as well as the sharpness indicates high crystallinity and also large crystallite size. The crystallite size of the catalyst was found to be 24.3 nm.

3.2. Scanning electron microscope studies

Fig. 2 shows the FE-SEM micrograph of $VO(PO_3)_2$. The SEM picture of the material revealed that the samples possess slate like morphology. Further, aggregates without regular shapes are observed in $VO(PO_3)_2$. This is the reason for the low surface area of the $VO(PO_3)_2$ catalyst.



Fig. 2. Scanning electron micrograph of VPO.

3.3. X-ray photoelectron spectroscopy (XPS) studies

The XPS-investigations reported herein were aimed towards the determination of the vanadium oxidation state present in the catalyst sample. The representative photoelectron peaks of O 1s, V $2p_{3/2}$, P 2p are depicted in Fig. 3(a), (b) and (c) respectively. Since controversial interpretations of the right broad V 2p_{3/2} photoelectron peak as well as somewhat contradictory values for the binding energies for the V^{n+} contributions is found in the literature, VOPO₄ with phase structure found by UV-vis spectra was used to calibrate the binding energy of the reference V $2p_{3/2}$ (V⁵⁺) peak. The measured value of 517.3 eV and the independently obtained value of 516 eV for V⁴⁺ state [36] are in a good agreement with the literature [37–39], and were used for the V 2p_{3/2} peak deconvolution for VO(PO₃)₂ catalyst studied herein. The high resolution P 2p with binding energy 134 eV corresponding to a formal effective oxidation state of +5 was depicted in Fig. 3(c). Binding energy value 531.8 eV of the O 1s peak indicated that the oxygen species was O²⁻ in oxides, and therefore the increase of O/V ratio supports the fact that a measurable fraction of V⁴⁺ at the equilibrated surface is oxidized to V5+.

The calcined VPO catalysts showed vanadyl metaphosphate $VO(PO_3)_2$ as the predominant phase present in addition to some $VOPO_4$ phase. P/V ratios in the precursor higher than stoichiometric stabilize the $VO(PO_3)_2$ phase from re-oxidation in the reactant atmosphere as well as during calcination in air at high temperatures [40]. It has been suggested that VPO catalysts may be terminated by a distorted vanadyl pyrophosphate structure [41], which may result in the generation of more Lewis (V⁴⁺⁾ and Bronsted (P–OH) acid sites on the catalyst surface. It is also reported that maximum catalytic performance requires a certain degree of disorder in the VPO lattice [42,43]. XPS studies have shown that catalysts calcined at lower temperatures (<750 °C) contain superficial V⁵⁺ species [44].

From the above physical properties it has been found that the material contains V⁴⁺ phase along with a little V⁵⁺ phase. We have studied from the literature that the oxygen associated with V⁴⁺ activates the substrate while the oxygen associated with V⁵⁺ is



Fig. 3. XPS spectra of (a) O 1s, (b) V 2p and (c) P 2p.

incorporated latter. Hence the presence of couple V⁴⁺/V⁵⁺ on the surface of our material facilitates the reaction. This is in good agreement with the literature [45]. Experimental results on pure vanadium phosphate phases and active catalysts suggest that the active catalyst is vanadyl metaphosphate with domains of V⁵⁺ on the (100) face. Thus V⁴⁺/V⁵⁺ couple is the active site, which is present on the surface of a range of vanadyl meta-phosphate phases.

Table 1

Benzyl alcohol conversion using various heterogeneous catalysts^a.

Catalyst	Oxidant	Time (h)	Benzyl alcohol conversion (%)	Aldehyde selectivity (%)	Yield (%)	Reference
Without catalyst	TBHP	6	10	30	3	-
VO(PO ₃) ₂	TBHP	6	97	99	96	Our catalyst
VO(PO ₃) ₂	-	6	53	48	25	Our catalyst
VO(PO ₃) ₂	O ₂	6	66	78	51	Our catalyst
Ru 1.9/TiO ₂	TBHP	1	30	82	24	[54]
$H_5PV_2Mo_{10}O_{40}$	O ₂	6	8	100	8	[47]
Mn-Cr-LDH	TBHP	5	50	84	42	[49]
RuO ₂	O ₂	1.5	16	99	15	[48]
CuCl	O ₂	48	1	50	0.5	[46]
Co-Cr-LDH	TBHP	5	60	70	42	[53]
CuCl ₂	TBHP	17	20	-	-	[51]
PdO·CuO·3H ₂ O	O ₂	1	45	98	44	[50]
[Co(bpy)2]/bentonite	TBHP	8	53	100	53	[55]
Au/U ₃ O ₈	TBHP	2	100	85	85	[56]
Au/TiO ₂	TBHP	2	63	79	50	[57]

^a Conditions: catalyst: 0.05 g, temp.: 80 °C, molar ratio: (1:1) (substrate:oxidant).

Table 2

Conversion of TBHP with and without benzyl alcohol.

Entry	Substrate	Oxidant	Benzyl alcohol conversion (%)	TBHP conversion (%)
1	Benzyl alcohol	TBHP	97	99
2	-	TBHP	-	96
3	Benzyl alcohol	-	53	-

Conditions: catalyst: 0.05 g, substrate: oxidant molar ratio(1:1), temp.: 80 $^\circ \rm C$, time: 6 h.

3.4. Catalytic reaction

The oxidation of benzyl alcohol over VO(PO₃)₂ using TBHP was carried out and the result was illustrated in Table 1 along with the various catalytic systems. The present catalyst VO(PO₃)₂ showed remarkable catalytic activity with respect to other catalytic system [46–57]. For our catalytic system, the conversion and selectivity with respect to aldehyde is 97 and 99%, respectively. Therefore this catalytic system is suitable for the oxidation of alcohols. A typical reaction involving TBHP without benzyl alcohol was carried out and the results were given in Table 2.

3.4.1. Effect of reaction period

Fig. 4 shows the influence of reaction time on benzyl alcohol oxidation. When the reaction time was increased from 1 to 10 h, the benzyl alcohol conversion continuously increases and then remains



Fig. 4. Effect of time period on benzyl alcohol conversion and benzaldehyde selectivity. *Conditions*: catalyst: $0.05 \,g$, temp.: $80 \,^{\circ}$ C, molar ratio: (1:1).

constant. But the yield for benzaldehyde was increased up to 6 h and then slightly decreased. The decrease in benzaldehyde yield was due to the increase in benzyl benzoate formation. With the progress of the reaction time benzaldehyde gets oxidized to benzoic acid. From Fig. 4, it was concluded that 6 h was the optimum reaction period to achieve high degree of benzaldehyde product. It is interesting to note that benzyl benzoate was the only other product formed apart from benzaldehyde and the formation of benzoic acid was not at all detected in GC analysis. This is expected because of the fact that the benzyl alcohol, thereby increasing the benzyl alcohol conversion, forming benzyl benzoate (Scheme 1).

3.4.2. Effect of reaction temperature

Oxidation of benzyl alcohol was carried out at 40, 60, 80 and 100 °C in the same reaction conditions. The results were illustrated in Fig. 5. Although VPO material uses its lattice oxygen at higher temperature in gas phase oxidation, the use of oxidant in liquid phase made it easy to carry out the reaction at lower temperature. As expected the influence of reaction temperature on benzyl alcohol conversion is very strong. However the yield for benzaldehyde is influenced appreciably only when the temperature is increased from 80 to 100 °C. The catalyst showed promising results at 80 °C that means 80 °C is the optimum temperature for this reaction. The decrease in yield with amplifying temperature is due to over



Fig. 5. Effect of temperature on benzyl alcohol conversion and benzaldehyde selectivity. *Conditions*: catalyst: 0.05 g, time: 6 h, molar ratio: (1:1).



Scheme 1. Catalytic oxidation reaction.

oxidation of benzaldehyde to benzoic acid which subsequently reacted with benzyl alcohol to form benzyl benzoate.

3.4.3. Effects of solvents

The results of oxidation of benzyl alcohol in different solvents were depicted in Table 2. It is evident from the fact that the behavior of benzyl alcohol oxidation in various solvents is conspicuously different. Acetonitrile showed the best conversion results followed by toluene. The observed lower benzyl alcohol conversion utility of the catalyst in the presence of different solvents is mostly attributed to the competitive adsorption between the solvents and benzyl alcohol on the catalyst and thereby occupying part of the active sites of the catalyst by the adsorbed solvent molecules. However the lower conversion value for chloroform is due to the presence of lone pair of electrons on chlorine that attach to the strong Lewis acid sites of the VO(PO₃)₂. In case of toluene the decrease in conversion value is due to the low solubility of TBHP in a nonpolar solvent as a result of which the reaction could not proceed. Acetonitrile readily dissolved TBHP along with the benzyl alcohol as it is polar and having a very high dielectric constant. This facilitates the adsorption of reactions on the catalyst surface and increases the efficiency of the conversion. The catalytic evaluation of VO(PO₃)₂ with different substrates was also performed and the results are depicted in Table 3.

3.4.4. Effect of catalyst loadings

Fig. 6 shows the effect of catalyst loadings on benzyl alcohol oxidation. Note that the variation was studied at 6 h of reaction time since it was the optimum time period for this reaction. It has been found that with the increase of catalyst amount the conversion and yield increases. This may presumably due to the availability of more active sites of the catalyst. Increasing the catalyst amount to 0.05 g

Table 3

Effect of solvents on oxidation of benzyl alcohola.

Solvent	Dipole moment (D)	Conversion (%)	Selectivity ^b (%)	Yield (%)
Acetonitrile	3.92	97	99	96
Chloroform	1.04	48	90	43
Toluene	0.37	75	99	74

 $^{\rm a}$ Conditions: catalyst: 0.05 g, temp.: 80 $^\circ\text{C},$ molar ratio: (1:1) (substrate:oxidant), time: 6 h.

^b Benzaldehyde.



Fig. 6. Effect of catalyst loadings. *Conditions*: time: 6 h, temp.: 80 °C, molar ratio: (1:1) (substrate:oxidant).



Fig. 7. Effect of amount of catalyst on benzyl alcohol conversion with shorter time. Conditions: time: 2 h, temp.: 80 °C, molar ratio: (1:1) (substrate:oxidant).

improved the conversion to 97% within 6 h of time. However the conversion and yield remain nearly same upon further increasing the catalyst amount to 0.07 g, which suggests that large amount of catalyst is not needed to improve the reaction product. However when the effect of amount of catalyst (0.01–0.07 g) was studied verses the benzyl alcohol conversion for shorter reaction time, a linear relation was obtained from which indicates that there was no contribution of homogeneity in the reaction (Fig. 7). Again when it was plotted from 0 to 0.07 g a non-monotonous conversion change was obtained with shorter time.

3.4.5. Effect of molar ratio of substrate to oxidant

The activity of VO(PO₃)₂ catalyst in the oxidation of benzyl alcohol was also evaluated using three different molar ratios of substrate to oxidant. The effect of substrate oxidant molar ratio on the oxidation of benzyl alcohol is depicted in Fig. 8. Conversion of 97% was achieved at the substrate oxidant molar ratio 1:1 in 6 h when 30 mmol of benzyl alcohol reacted with 30 mmol of TBHP in acetonitrile medium at 80 °C. Increasing the ratio to 1:2 improved the conversion to 98%, while further increase of TBHP showed no such improvement in conversion.



Fig. 8. Effect of molar ratio of substrate to oxidant.

3.5. Heterogeneity test

To determine whether the catalyst is functioning in a heterogeneous manner, a hot filtration test was performed in the oxidation reaction. During the catalytic oxidation of benzyl alcohol, the solid catalyst was separated from the reaction mixture by filtration after 3 h of the reaction and the filtrate obtained was continuously stirred under same reaction conditions for further 3 h. GC analysis showed no increment in the conversion. ICP-OES (Optima 2100 DV, PerkinElmer) using a microwave pressure digestion (MDS 200; CEM) with hydrofluoric acid and aqua regia at 9 bar was used to analyze the chemical composition of fresh and used catalyst. The sample was analyzed thrice and the results presented here are the average values. The results are given in the Table 4. This fact suggests that there is no loss of catalyst components during the course of reaction which confirmed the heterogeneity of the catalyst. The P/V ratio detected here indicates the presence of V⁴⁺ species in the materials. From the literature it has been found that a P/V ratio > 1 is necessary for high catalytic performance [58]. It has also been studied that at P/V ratios of less than 1.0, a number of vanadium sites remain inactive but at the higher P/V ratios all surface sites are active [59]. This is in good agreement with our results. Elemental analysis of liquid after the reaction was also performed. Vanadium leaching was very negligible during the reaction. The vanadium concentration in the filtrate is less than 1 ppb as found by ICP and also by AAS (Table 5).

3.6. Recapability of the catalyst

The recapability performance of VO(PO₃)₂ for 4 cycles batch oxidation reaction is illustrated in Fig. 9. After the reaction with benzyl alcohol VPO was separated from the reaction mixture by centrifugation, thoroughly washed with acetone and then reused as catalyst for the next run under the same conditions. The catalyst did not show any significant change in the activity after 24 h. The conversion showed to stabilize in a range of between 95 and 97% with benzaldehyde selectivity remaining fairly constant between 98 and 99%. The slight deactivation of the catalyst may presumably due to the adsorption of large polar molecules that resulted from the by-product reactions on the surface of the catalyst. The adsorption of polar molecules on the catalyst surface is usually temporary and can be resolved by calcination of the catalyst at high temperature to recover its activity.

Table 4

Catalytic activity evaluation of VPO with various alcohols^a.

Entry	Time (h)	Substrate	Product	Conversion (%)	Yield (%)	Yield (%) of byproduct
1	6	СІ	ci	84	83	1
2	6	ОН	0	89	86	2
3	6	s	s	92	88	3
4	6	м		87	78	8
5	6	ОШ		93	92	1
6	6			91	89	2
7	6	он	ο	95	94	1
8	4	ОН	 o	86	85	1
9	4	ОН	~0	90	89	1
10	6	Вг	Br	85	84	1
11	4	он		96	94	2
12	3	он	o	95	94	1
13	5	О		95	94	1
14	6	О2N	O ₂ N O	94	94	0
15	5	ОН		88	88	0
16	5	ОН	o	96	95	1

252

Entry	Time (h)	Substrate	Product	Conversion (%)	Yield (%)	Yield (%) of byproduct
17	10	М ОН	N	90	90	0
18	6	он	~o	84	83	1

^a Conditions: catalyst: 0.05 g, temp.: 80 °C, molar ratio: (1:2) (substrate:oxidant).

Table 5

Estimation of component of catalyst by ICP-OES.

Catalyst	V	V		Р		
	Fresh	Used	Fresh	Used		
VO(PO ₃) ₂	18.7	18.69	28.91	28.90	1.54	



Fig. 9. Recapability performance of VO(PO₃)₂.

4. Conclusions

In summary, we have successfully synthesized vanadyl metaphosphate with a beautiful plate like morphology and proved that this material can be used in liquid phase reaction. The catalytic activity of the material was investigated by examining its use in the selective oxidation of benzyl alcohol to benzaldehyde using TBHP as oxidant. Excellent conversion and selectivity of this catalyst towards the oxidation of benzyl alcohol was observed. The material is also effective for the oxidation of other organic substrates. The catalyst can be recycled several times without any loss in conversion and selectivity. This suggests its reusability and stability. Easy product recovery and recycling efficiency along with high selectivity of this material may be useful for the synthesis of different chemicals under eco-friendly conditions. This cheap process could be of great interest for selective oxidation of primary alcohol. We anticipate that our findings will initiate attempts to understand the detailed mechanism of oxygen activation at catalyst surfaces, which might lead to commercial exploitation of the high catalytic activity of VO(PO₃)₂. Further research will emphasize additional catalytic application.

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