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Vanadium phosphorus oxide catalyst modified by silver doping for mild oxidation of styrene to benzaldehyde

Junhua Liu[a,*], Fang Wang[b], Zhenggui Gu[a], Xianlun Xu[b]

[a] College of Chemistry and Environmental Science, Nanjing Normal University, 122# Ninghai Road, Nanjing 210097, China
[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China

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ABSTRACT

A series of silver-doped vanadium phosphorus oxides (Ag-VPO) catalysts were prepared by in situ synthesis, the catalytic tests showed that silver component significantly increased the overall activity for the oxidation of styrene by *tert*-butyl hydroperoxide (TBHP). It is interesting that Ag-VPO catalysts show no epoxidation selectivity but good selectivity for benzaldehyde in this study. To investigate the origin of the silver effect, the solids were characterized using X-ray diffraction (XRD), Fourier transformed-infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS) and other instruments, the $(VO)_2P_2O_7$, β-$VOPO_4$, $Ag(V_2P_2O_{10})$ and $Ag_2(VO_2)(PO_4)$ phases were detected in all the Ag-VPO catalysts. This study also confirms that ratios of P/V play a crucial role in the activity and the selectivity of the catalyst, meanwhile, the other factors, such as solvent, oxidant concentration, reaction time, also have been investigated and reaction conditions are optimized.

1. Introduction

The oxidation of styrene at side chains is of considerable interest for academic research and utilization in the industry; consequently, there is a growing interest in the synthesis of fine chemicals via this versatile reaction, such as oxidative conversion of styrene to benzaldehyde. Due to the ease in separation, recovery and recycling for continuous processing, heterogeneous catalytic oxidation is a more acceptable pathway compared to homogeneous counterparts. So there has been an increasing interest in the development of heterogeneous catalysts for this reaction in the liquid phase with eco-friendly oxidants, such as molecular oxygen, aqueous hydrogen peroxide or organic peroxides. The catalysts which they used have fallen into two broad categories: (1) development of new transition metal immobilized/constituted molecular sieves, such as NbCo-MCM-41 [1], VSB-5 [2], Co-ZSM-5 [3]; (2) application of metal oxides/complexes, such as $Mg_xFe_{3-x}O_4$ [4], TiO_2/SiO_2 [5], rhodium carbonyl complexes [6]. However, the research in this area still is not enough and it is necessary to develop a better solid catalyst to improve both the catalytic activity and selectivity for benzaldehyde.

Vanadium phosphorus oxides catalysts (VPO) are known to catalyze the mild oxidation of *n*-butane to maleic anhydride (MA), very good and promising results have been obtained on bulk VPO or supported VPO catalysts so far [7–9]. Catalytic performance may be improved by adding specific doping agents to the VPO composition [10], but their effects on conversion and selectivity may be different, the nature, the location, and the role of these dopants have been previously reviewed in the open literature [11]. However, there are few literatures on the oxidations of other hydrocarbons, such as alcohols, alkenes, using metal-doped VPO catalysts. Herein we report an efficient oxidation of styrene over silver doped VPO catalyst in an environmentally benign oxidation protocol involving aqueous *tert*-butyl hydroperoxide in argon atmosphere; meanwhile, we investigated the active sites of the vanadium phosphorus oxides during the oxidations of styrene.

2. Experimental

2.1. Materials

TBHP (70% in water) and other chemicals were all purchased from commercial sources and were of analytical grade, unless otherwise noted. All the chemicals were used without any further purification.

2.2. Catalyst preparation

Silver doped vanadium phosphorus oxides (Ag-VPO) catalysts with different P/V ratios were prepared by refluxing an appropriate quantity of V_2O_5 (2.5 g) and a mount of $AgNO_3$ (0.467 g, n Ag/n V = 0.1) in a mixture of isobutanol (30 mL) and benzyl alcohol (15 mL) for 12 h (120 °C), followed by addition of 85% H_3PO_4

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[*] Corresponding author. Tel.: +86 25 83598233; fax: +86 25 83598233.
E-mail address: liujh2010@yahoo.cn (J. Liu).

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(*P*/*V* = 0.75, 1, 1.5), coprecipitation-refluxing for further 6 h to give a light green precipitate (110 °C). The precipitate was filtered off, dried at 110 °C overnight and then calcined in air at 400 °C for 4 h. The Ag-VPO (*P*/*V* = 1) catalysts with different silver content (n Ag/n V = 0.05, n Ag/n V = 0.15) were prepared by the same procedure and the VPO parent also was prepared as above except no addition of $AgNO_3$.

2.3. Catalyst characterization

The morphologies of obtained VPO and Ag-VPO particles were examined by transmission electron microscope (TEM) (JEM-1200EX) and scanning electron microscope (SEM) (JSM-5600 LV). The crystals of the catalysts were studied by X-ray diffraction (XRD), the XRD data were collected on X'Pert PRO X-ray diffraction, patterns were recorded using a X'Celerator Discover, with Cu Kα radiation (λ = 0.154 nm) and a graphite monochromator in the range 10–80°. Surface composition was determined by X-ray photoelectron spectroscopy (XPS), using an ESCALAB 210 XPS system with a Mg Kα source. The Fourier transformed-infrared spectroscopy (FT-IR) spectra of samples were obtained on a Bruker IFS 120 HR FT-IR spectrometer. Nitrogen adsorption–desorption isothermals were collected at 77 K using Brunauer–Emmett–Teller (BET, ASAP2010 Micromeritics, for specific surface area), all the samples were degassed at 100 °C and 10^{-6} Pa. Elemental analysis was determined by X-ray fluorescence spectrometry (XRF) (Magix PW 2403 XRF), using PAN analytical X radial tube with a Rh Kα source.

2.4. Styrene oxidation

Catalytic reactions were carried out according to the following procedure: a mixture of catalyst (0.1 g, 0.05 mmol silver), substrate (10 mmol) and acetonitrile (5 ml) was stirred under Ar atmosphere in a 50-ml round-bottom flask equipped with a condenser at room temperature for 30 min. After the addition of *tert*-butyl hydroperoxide (3 ml), the reaction was started by immersing the flask in the oil bath kept at the reaction temperature (82 °C), then carried out with vigorous stirring under argon atmosphere for 3 h. After filtration and extraction with solvent, the filtrate was concentrated by rotary evaporator then analyzed by gas chromatography (GC 201) with a SE-54 capillary column; the nature of the products was also determined by GC–MS.

3. Results and discussion

3.1. Catalyst characterization

BET surface areas of the bulk VPO and metal-doped catalysts are in the range of 15–20 m^2/g.

Fig. 1 shows the XRD patterns of Ag-VPO catalysts with different *P*/*V* ratios (n Ag/n V = 0.1) and different Ag/V ratios (*P*/*V* = 1). As seen from Fig. 1, β-$VOPO_4$ phase (JCPDS: 27-948) was the main crystalline phase in these solids, meanwhile, $(VO)_2P_2O_7$ phase (JCPDS: 41-698) was also observed in all these solids. Compared with the VPO parent, the peaks corresponding to β-$VOPO_4$ phase were decreased and two new phases were formed after adding the silver, the X-ray lines corresponding to $Ag_2(VO_2)(PO_4)$ (JCPDS:81-2149) and $Ag(V_2P_2O_{10})$ (JCPDS:81-2364) phases have been observed in these Ag-VPO solids, respectively. The *P*/*V* ratios had an important effects on the formations of various crystalline phases, XRD signals of $Ag_2(VO_2)(PO_4)$ and $Ag(V_2P_2O_{10})$ phases and their ratios decreased with increasing *P*/*V* ratios, also, the X-ray lines due to the β-$VOPO_4$ phase decreased firstly then increased with the increasing silver content. During these Ag-VPO (*P*/*V* = 1) catalysts with different silver content, the Ag-VPO catalyst (n Ag/n V = 0.1) had the best crystalline, excessive silver content inhibited the formation of silver vanadyl pyrophosphates and gave little effect on the translation of β-$VOPO_4$ phase.

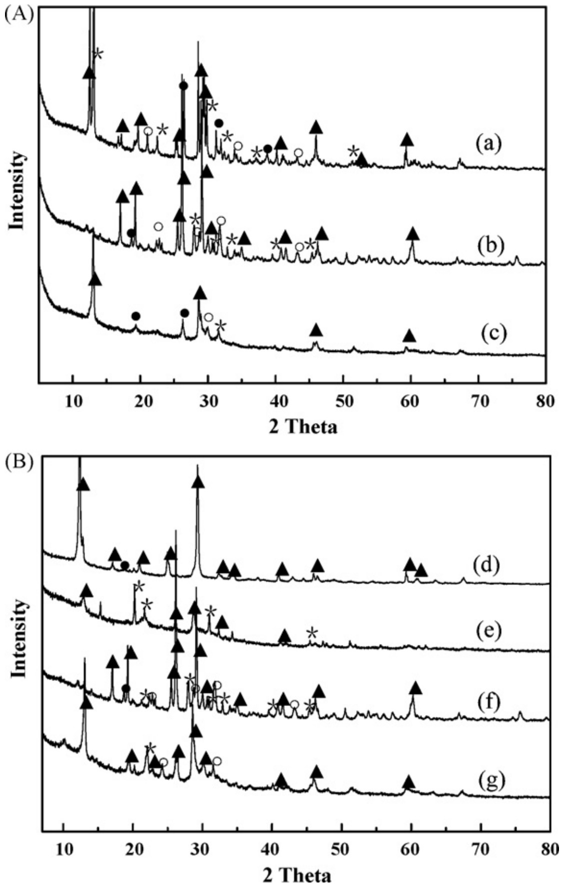


Fig. 1. XRD patterns of Ag-doped catalysts (A) with different *P*/*V* ratios (n Ag/n V = 0.1): (a) Ag-VPO (*P*/*V* = 0.75); (b) Ag-VPO (*P*/*V* = 1); (c) Ag-VPO (*P*/*V* = 1.5); (B) with different Ag/V ratios (*P*/*V* = 1): (d) without silver; (e) n Ag/n V = 0.05; (f) n Ag/n V = 0.1; (g) n Ag/n V = 0.15. Symbols: $(VO)_2P_2O_7$ (●); β-$VOPO_4$ (▲); $Ag_2(VO_2)(PO_4)$ (○); $Ag(V_2P_2O_{10})$ (*).

In the Ag-VPO catalysts with different *P*/*V* ratios or different Ag/V ratios, there appears a strong band at 970 cm^{-1} [$\nu\ V^{4+}{=}O$], the band at 947 cm^{-1} pertaining to V^{5+} species is visible but not obvious in all cases [12]. Other characteristic bands corresponding to vanadyl pyrophosphate phases are: 742–765 cm^{-1} (symmetric stretching of P–O–P bond), 1085, 1025 cm^{-1} (P–O stretching). Examination of the infrared spectrum suggests that the peaks of characteristic bands of VPO are weaker than silver-doped ones, meanwhile, the significant differences observed in the spectra are for vibrations of the linkages between the layers of the vanadyl pyrophosphates and this region is shown in Table 1. The V=O absorption bands of the catalysts containing silver are significantly shifted to lower wave number, while the P–O–P absorption bands of them shifted to higher wave number. According to the previous literatures, the introduction of promoter into the crystal lattice, in other words, the substitution

Table 1
IR absorption bands due to $V^{4+}{=}O$ and P–O–P of different catalysts.

Catalyst	$V^{4+}{=}O$ wave number (cm^{-1})	P–O–P wave number (cm^{-1})
VPO (*P*/*V* = 1)	986	742
Ag-VPO (*P*/*V* = 0.75, Ag/V = 0.1)	976	746
Ag-VPO (*P*/*V* = 1, Ag/V = 0.1)	972	763
Ag-VPO (*P*/*V* = 1.5, Ag/V = 0.1)	969	765
Ag-VPO (*P*/*V* = 1, Ag/V = 0.05)	969	755
Ag-VPO (*P*/*V* = 1, Ag/V = 0.15)	964	765

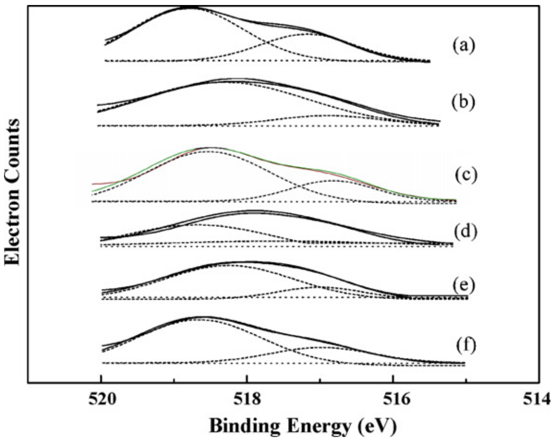


Fig. 2. XPS of V2p region of Ag-VPO (n Ag/n V = 0.1) catalysts (a) $P/V = 0.75$ (b) $P/V = 1$ (c) $P/V = 1.5$ and Ag-VPO ($P/V = 1$) catalysts (d) without silver (e) n Ag/n V = 0.05 (f) n Ag/n V = 0.15.

of vanadium by metal bring about a shift of V=O wave number to lower frequencies [13], and the higher shift in P–O–P wave number indicates the promoter atoms affect the layer linkages [14]. So these above results strongly suggest that promoter element silver is located in the crystal lattice of vanadyl pyrophosphate.

Fig. 2 shows a high-resolution XPS spectrum containing the V $2p_{1/2}$ and V $2p_{3/2}$ photoelectron peaks for VPO parent and a series of Ag-VPO catalysts. We used the peak deconvolution procedure where β-$VOPO_4$ or $Ag_2(VO_2)(PO_4)$ (oxidation, +5) phases confirmed by XRD provided the reference value for the binding energy of the V $2p_{3/2}$ peak, the measured V $2p_{3/2}$ peak could be well fitted with a single Gaussian with a maximum at 518.4 eV, the position of the V^{4+} component obtained independently lies at 516.7 eV, well separated from the V^{5+} contribution (Fig. 2). It is in a good agreement with the previously reported binding energies of 516.5–517.1 eV for V^{4+}, and values between 517.5 and 518.6 eV were given in the literature for V^{5+} [15]. Because the curve fitting and the deconvolution are performed in the same way for all the Ag-VPO samples and VPO parent under study, this technique allows to monitor the changes in the relative ratio of V^{5+} and V^{4+}, as shown in Fig. 2, the Ag-VPO catalysts with different P/V ratios ($P/V = 0.75$, 1, 1.5), the ratios of these oxidation states V^{5+}/V^{4+} were 62/38, 84/16, 72/28, respectively [15], also, the Ag-VPO ($P/V = 1$) catalysts with different silver content (n Ag/n V = 0, 0.05, 0.1, 0.15), the ratios of oxidation states V^{5+}/V^{4+} were 92/8, 88/12, 84/16, 76/24, respectively. McCormick et al. found that the average surface oxidation state of vanadium was increased in the Cr-promoted catalysts and caused oxidation of a small fraction of the pyrophosphate to form $VOPO_4$ [14], while in our catalysts, compared with the VPO parent, XRD and XPS all testified that the addition of silver by the method outlined in Section 2 decreased the average surface oxidation state of vanadium, part of V^{5+} species were deoxidized to V^{4+} ones, this case showed that the various promoters had different function mechanism. Also, the Ag $3d_{5/2}$ line appears at 368.1 eV for the synthesized Ag-VPO samples.

An additional method to find out the vanadium oxidation state is based on the difference in the BEs of O 1s and V $2p_{3/2}$ signals [Δ (O 1s–V $2p_{3/2}$)]. Coulston et al. elaborate a criterion independent of particular lineshapes [16]. This criterion for the average vanadium oxidation state (Vox) is based on the difference of the first momenta of the O 1s and V $2p_{3/2}$ peaks, and is independent of peak broadening since this does not change the position of the centroids, the equation for the definition of vanadium oxidation states as follows:

$$\text{Vox} = 13.82 - 0.68\,[\text{BE (O 1s)} - \text{BE (V}\,2p_{3/2})] \qquad (1)$$

where BE (O 1s) and BE (V $2p_{3/2}$) are an average BE of the O 1 s and V $2p_{3/2}$ lines, the XPS data and the calculated results are listed in Table 2, the results show that all silver doped catalysts give Δ values of 13.3 ± 0.3 eV and the Vox values of 4.6–4.9. Both methods support the overwhelming presence of V (V) on the surface of the VPO parent and silver doped ones. In previous reports, cobalt addition leads to phosphorus surface enrichment, produces an increase of surface P/V ratios [17,18], in our case, the addition of silver leads to its decrease, this effect could be due to a phosphorus diffusion into the bulk by forming $Ag(V_2P_2O_{10})$ or $Ag_2(VO_2)(PO_4)$ phase.

Fig. 3a and b shows SEM images of VPO and Ag-VPO solids ($P/V = 1$) respectively, parent VPO and other Ag-doped VPO solids are different slightly in the shape of crystallites, the addition of silver increase the sizes of crystallites. The particles of VPO are composed of lamellar crystallites, the size of them is 1–2 μm in diameter and 50–100 nm in thickness, while the Ag-VPO sample is composed of the fastener-like crystallites and size of them is larger than the former (3–5 μm in diameter and 100–250 nm in thickness).

3.2. *Catalytic activity*

The oxidations of styrene to benzaldehyde (BZ) on series of silver-doped VPO catalysts were investigated, phenylacetaldehyde (PA), styrene oxide (SO) and benzoic acid (BA) have been the main by-products during the oxidation of styrene on undoped and metal-doped VPO solids. The conversion, product selectivity were calculated as follows: conversion (%) = [(moles of reactant converted) × 100]/[moles of reactant in feed], product selectivity (%) = [(moles of product formed) × 100]/[moles of reactant converted], and the reaction procedure is given in Scheme 1.

3.2.1. *Effect of P/V ratios*

In this study, experiments on Ag-VPO (n Ag/n V = 0.1) catalysts with different P/V ratios were performed, the comparisons with respect to conversion and product selectivity are represented in Table 3. It was observed that P/V ratios had a notable effect on the catalytic activity and selectivity, when the ratio of P/V was 0.75, the catalytic activity of Ag-VPO was very low (56.2% conversion),

Table 2
XPS characteristics of the oxidation states vanadium.

Solid[a]	V $2p_{3/2}$	BE (eV) Ag $3d_{5/2}$	O 1s	Δ(O 1s – V $2p_{3/2}$) (eV)	Vox[b]	Energy reference[c] (eV)	P/V	Ag/V
VPO (1)	517.9	–	531.5	13.6	4.6	285.0	1.1	–
Ag-VPO (0.75)	518.3	368.1	531.6	13.3	4.8	285.0	0.7	0.09
Ag-VPO (1)	517.9	368.1	531.4	13.5	4.6	285.0	0.6	0.07
Ag-VPO (1.5)	518.5	368.1	531.5	13	4.9	285.0	0.9	0.05
Ag-VPO(1)[d]	517.9	368.3	531.3	13.4	4.7	285.0	0.7	0.02
Ag-VPO(1)[e]	518.6	368.4	531.6	13	4.9	285.0	0.6	0.07

[a] With different bulk P/V ratios (n Ag/n V = 0.1).
[b] The average oxidation state was calculated by using Eq. (1).
[c] The position of the C 1s peak.
[d] n Ag/n V = 0.05.
[e] n Ag/n V = 0.15.

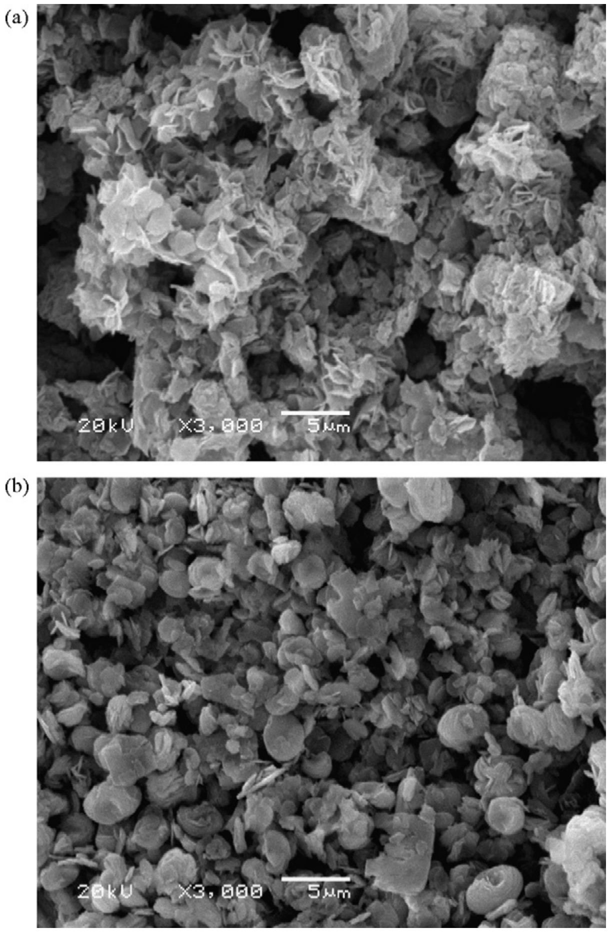
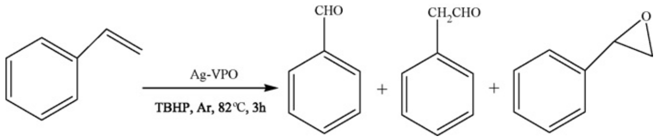


Fig. 3. SEM images of (a) VPO (*P*/*V* = 1) (b) Ag-VPO (*P*/*V* = 1, n Ag/n V = 0.1) catalysts.



Scheme 1.

meanwhile, the selectivity of benzaldehyde (BZ) was only 39.4%, but the conversion of styrene was achieved 98.4% and selectivity of benzaldehyde was got 89.2% at *P*/*V* = 1. Also, a comparative reaction was performed under air atmosphere (hydrous TBHP as oxidant) and gave only 19.6% conversion, similar results and discussion can be seen in previous literature [19].

So much effort has been spent to study the nature of the "active sites" in the oxidation of butane to maleic anhydride (MA), it is generally accepted that well crystallized $(VO)_2P_2O_7$ (which is a V^{4+}) is the major phase that is present in an industrial VPO catalyst [20], leading to the proposal that the active site for *n*-butane activation and oxyfunctionalisation resides on this plane. Some argue that the V^{5+}/V^{4+} species in the topmost oxidized layer of vanadyl pyrophosphate are the active sites [21], while others believe that the active sites lie within the microdomains of crystalline vanadyl (V^{5+}) orthophosphates [22]. In our case, the conversion of styrene over Ag-VPO catalyst (*P*/*V* = 1) was higher than the other ones (*P*/*V* = 0.75 and 1.5), meanwhile, XPS indicated when the *P*/*V* ratios were 0.75, 1 and 1.5, the ratios of these oxidation states V^{5+}/V^{4+} were 62/38, 84/16, 72/28, respectively (Fig. 2). Based on the above, we speculated that the ratios of V^{5+}/V^{4+} species in the topmost oxidized layer of vanadyl pyrophosphate play a key role in the oxidation of styrene.

Table 3
Oxidations of styrene on the Ag-VPO (n Ag/n V = 0.1) catalysts with different *P*/*V* ratios.

Catalyst[a]	Conversion (%)	Product selectivity (%)			
		BZ	PA	SO	BA
Ag-VPO (0.75)	56.2	39.4	57.4	Trace	3.2
Ag-VPO (1)	98.4	89.2	3.9	0.9	6.0
Ag-VPO (1.5)	91.4	81.1	4.5	9.6	4.8
Ag-VPO (1)[b]	19.6	87.5	Trace	9.5	3.0

[a] With different bulk *P*/*V* ratios.

[b] Air atmosphere instead of argon one.

3.2.2. The role of silver

In our experiments, the results of characterization reveal that the added silver exhibits a significant influence on the nature of VPO and, on the catalytic behavior, as shown in Fig. 4, when the ratios of Ag/V varied 0 from 0.15, the use of silver component notably increased the catalytic activity and intensified the C=C bond cleavage. But the content of silver had a optimal value, the styrene conversion increased firstly with the increasing silver content then almost remained constant when the ratio of Ag/V exceeded 0.1, the maximal conversion was 45.2% at Ag/V = 0.1. The selectivity for benzaldehyde increased from 70.4 to 85.8% after adding silver (Ag/V = 0.05), then they were decreased slightly when silver content further increased.

During the oxidation of *n*-butane to MA on the VPO catalyst, promoter always was added to improve the both catalytic activity and selectivity of MA. Many studies have tried to determine the role of the promoter in VPO matrix. Some suggested that promoter elements might partially form a solid solution [23], others showed that the promoter might be incorporated in the crystal lattice of vanadyl pyrophosphate and affected the layer linkages, then brought about the shift in the IR absorption bands of V=O [13,14], and the specific activity was dependent on the V=O wave number, and had a linear relevancy [13]. Similarly, in our catalysts, the V=O vibration was modified slightly by the presence of silver in FT-IR studies (Table 1), and catalytic activity seemed to be relative to the decrease in V=O wave number but no linear relevancy was found in our reaction system, meanwhile, XPS testified when the silver content varied as Ag/V = 0, 0.05, 0.1, 0.15, the ratios of these oxidation states V^{5+}/V^{4+} were 92/8, 88/12, 84/16, 76/24, respectively, which meant that the addition of sil-

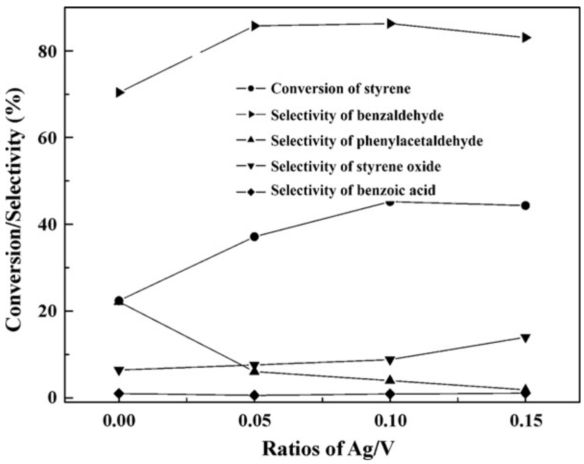


Fig. 4. Oxidations of styrene on Ag-VPO (*P*/*V* = 1) catalysts with different silver content. Reaction conditions: Ag-VPO (*P*/*V* = 1) catalyst 0.05 g, CH_3CN 5 ml, styrene 2 ml, TBHP 3 ml, 3 h, Ar.

Table 4
Oxidations of styrene on Ag-VPO (*P*/*V* = 1, n Ag/n V = 0.1) using different solvents.

Solvents	Conversion (%)	Product selectivity (%)			
		BZ	PA	SO	BA
Acetonitrile	98.4	89.2	3.9	0.9	6.0
Toluene	7.7	78.9	9.1	11.3	0.7
Dichloromethane	32.3	83.4	11.5	Trace	5.1
Methanol	91.2	57.1	34.3	2.4	6.2

ver decreased the average surface oxidation state of vanadium and the ratios of V^{5+}/V^{4+} were decreased with the increasing silver content. The results proved that the addition of silver could optimize the balance of V^{5+}/V^{4+}. Similar results were reported by Volta and their colleagues, using in situ Raman spectroscopy, they found that the incorporation of cobalt could change the V^{5+}/V^{4+} balance during the activation period, and therefore changed the catalytic performance in the steady state [18]. Moreover, on the basis of XRD and XPS data, we have know that silver atoms are incorporated between the layers rather than substituting for vanadium in the phosphate lattice, the presence of silver cations increases the degree of coordinative unsaturation of the surface vanadium as V^{5+}. Alternatively, promoters might activate oxygen more readily than VPO and catalyze oxidation of V^{5+} to form V^{4+} [14]. On the other hand, the formation of silver vanadyl pyrophosphates played a key role in the oxidation of styrene. According to Lii and co-workers [24], the structure of $Ag_2(VO_2)(PO_4)$, contains layers of dioxovanadium phosphate with Ag^+ ions between the layers. Each layer is composed of distorted VO_6 octahedra and PO_4 tetrahedra. There are two types of windows within a layer. One is formed by the edges of two octahedra and two tetrahedra and the other by the edges of four octahedra and two tetrahedra. Straight tunnels with tetragonal and hexagonal windows are formed which are vertical to the layers. The Ag^+ ions, which occupy sites in the walls of the tunnels, provide competitive advantages for the oxidation of styrene.

3.2.3. *Effect of solvent*

The oxidation of styrene to benzaldehyde, in the present of Ag-VPO (*P*/*V* = 1, n Ag/n V = 0.1) catalyst, was carried out in different solvents, the results are shown in Table 4. The results showed that the catalytic activity was relative to the polarity of the solvents, the conversion of styrene increased gradually with the increasing polarity of solvents ($CH_3CN > CH_3OH > CH_2Cl_2 > PhCH_3$), the oxidation of styrene in high-polar solvents such as methanol and acetonitrile gave 91.2 and 98.4% conversions, respectively, but gave relatively low selectivity for benzaldehyde (BZ) in CH_3OH (57.1%). The catalytic activity was found to decrease when oxidation reactions were performed in low-polar solvents, for example, reactions in dichloromethane and toluene gave, respectively, 32.3 and 7.7% of styrene conversion with selectivity of 83.4 and 78.9% towards benzaldehyde, so an appropriate solvent should be acetonitrile.

3.2.4. *Effect of reaction time*

The change in conversion of styrene in the presence of TBHP oxidant and Ag-VPO (*P*/*V* = 1, n Ag/n V = 0.1) catalyst was monitored and plotted with respect to time, the results are shown in Fig. 5, it was seen that the conversion of styrene increased continuously until 98.4% as time increased and then remained constant after 3 h, the selectivity of benzaldehyde decreased at all times, which was relative to the over-oxidation of benzaldehyde, however, it dropped sharply to 86.0% at 5 h, therefore duration about 3 h was the proper reaction time.

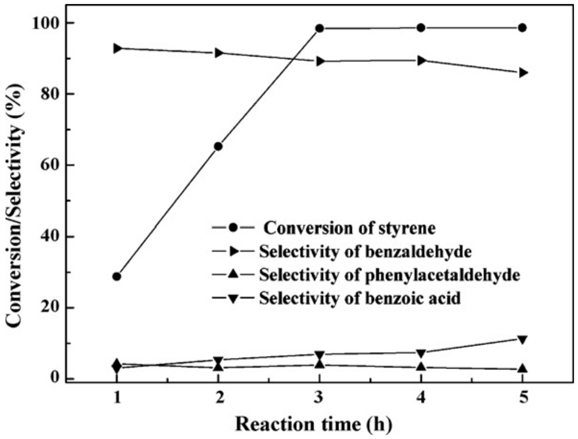


Fig. 5. Oxidations of styrene on Ag-VPO (*P*/*V* = 1, n Ag/n V = 0.1) catalyst at different time.

4. Conclusions

A series of Ag doped vanadium phosphorus oxides catalysts, were synthesized in situ and studied with TBHP as an oxidant for the oxidation of styrene to benzaldehyde. This study confirms that the silver promoted VPO catalysts can increase the activity and the selectivity than undoped ones, so, the key factors governing the activity and benzaldehyde selectivity of the Ag-VPO should be the ratios of oxidation states V^{5+}/V^{4+}, the addition of silver and the nature of solvent. A maximum conversion and selectivity (98.4% and 89.2%) were observed for a Ag-VPO (*P*/*V* = 1)/TBHP/acetonitrile system after 3 h of reaction when concentrations of catalyst and substrate were 0.1 g (0.05 mmol Ag) and 10 mmol, respectively.

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