Novel modifications in preparing vanadium phosphorus oxides and their applications for partial oxidation of *n*-butane

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Abstract

One novel modification in preparing high surface area VPO catalyst was established by applying polyethylene glycols (PEGs) as the unique additives. The PEG-derived samples possessed considerably high surface areas of 41–54 m^2/g, with the average particle size of 100–200 nm and well crystallized $(VO)_2P_2O_7$ phase, showing notably improved performances for the partial oxidation of *n*-butane to maleic anhydride (MA) even at lower reaction temperature. The principle function of PEG in preparation chemistry and the possible origins of the enhanced performance were preliminarily discussed. Another modification in preparing high surface area VPO catalyst adopted in this study was the combination of synthesizing high surface area VPO precursor by well-controlled addition of phosphoric acid, thermal pre-treating the precursor at certain temperature and ball milling in cyclohexane. The so-obtained catalysts also showed pronounced catalytic performance. The applied milling process not only effectively increased the surface areas of the milled samples and consequently the available number of active sites, but also somehow changed other sample characteristics such as the local environment and the redox behavior; which may also be responsible for the overall performance enhancement.
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1. Introduction

Vanadium phosphorus oxides are widely used in partial oxidation of *n*-butane to maleic anhydride (MA). Although laboratory and industry efforts have been exerted on this catalyst system, lots of details are still not thoroughly elaborated, especially the active phase/sites, the surface vanadium oxidation states, the detailed catalytic mechanism and so on, which is may be ascribed to both the complicated interac-tion between the surface and bulk elements, and the difficulty in detecting intermediate products in cat-alytic reaction [1]. After years of work, it has been recognized that preparation chemistry plays an in-comparable role in determining the structure of VPO catalysts and, accordingly, the catalytic behavior. There is also consensus that $(VO)_2P_2O_7$ is the major component of active VPO catalysts [2], but different phase components were also announced in papers or patents [3,4]. In recent years, there is a worldwide trend that the selectivity is more emphasized than the overall conversion, in order to decrease the amount of undesired by-products, especially the harmful ones [5]. For partial oxidation of lower paraffins including *n*-butane, the challenge is how to further increase the

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selectivity of target product, otherwise costly reactor design and engineering would be required to minimize the inefficiency of the process. Currently used industrial VPO catalysts showed the butane conversion beyond 80%, with MA selectivity of around 65 mol%. Large portion of *n*-butane is burned to carbon oxides. It is known that MA selectivity is strongly associated with *n*-butane conversion and can be increased at the expense of conversion. Although a few attempts have been made to improve MA selectivity, it is hardly beyond 80% with adequate *n*-butane conversion. Dupont reported that a higher level of MA selectivity could be achieved using a rising reactor in which the oxidation of *n*-butane and the regeneration of the catalyst were operated in the separate zones [6]. This process is rather attractive for high MA selectivity, but has not yet been widely applied possibly due to its specialty in engineering requirement and in preparation of the exclusive catalyst. Alternatively, improving catalyst performance through the approach of preparation chemistry is still very helpful. In this study, two modifications in VPO catalyst preparation have been studied in order to generate more efficient VPO systems.

2. Experimental

2.1. Preparation of the VPO catalysts in the presence of polyethylene glycols (PEGs)

The details for synthesizing VPO catalyst in the presence of polyethylene glycols (PEGs) with different molecular weight can be referred in a Chinese patent [7]. Briefly, the catalyst precursor was prepared by refluxing of vanadium pentoxide in a mixture of iso-butanol/benzyl alcohol, then appropriate amount of PEGs (PEG2000–PEG20000) and phosphoric acid (85 wt.%) were added in for further refluxing, with the controlled vanadium/phosphorus atomic ratio of 1.0/1.2. The resulting suspension was cooled down to room temperature and filtered. The precipitate was washed with iso-butanol and acetone and dried at 393 K for 24 h. The derived precursor was activated in the mixture of 1.5% *n*-butane/air at a rate of 2 K/min from room temperature to 673 K and kept at this temperature for 15 h. The obtained samples are symbolized as P2–P5. For comparison, another VPO catalyst (symbolized as P1) was prepared similarly except that no PEG additive was introduced.

2.2. Preparation of the ball milled VPO catalysts

The VPO precursors were prepared in organic medium by employing the reaction of vanadium pentoxide (32.9 g) with isobutanol (120 ml) in benzyl alcohol (120 ml). After the reaction mixture was refluxed for 6 h, phosphoric acid (29.3 g, 85 wt.%) was added into the hot black mixture at a rate of 0.6 ml/min, with the V/P ratio being 1.0/1.2. After refluxed for another 6 h, the turbid reaction mixture was filtered and the obtained blue–green precipitate, which was typically defined as VPO catalyst precursor, was dried at 393 K in air. The dried precursor was then pre-conditioned in flowing nitrogen at 573 K for 2 h, after that the received material was subjected to ball milling in agate pots with the solvent of cyclohexane for 5–20 h. Once the milling procedure completed, the agate pots were dried at 393 K in air to remove the solvent, and the collected sample was activated in the mixture of 1.5% *n*-butane/air (gas space hour velocity, GSHV = 1200 h^{-1}) at 673 K for 6–24 h.

2.3. Sample characterization and evaluation

BET surface areas of the samples were measured by nitrogen adsorption at 77 K on a Micromeritics ASAP2000 adsorption apparatus. X-ray diffraction (XRD) was conducted on a Shimadzu XD-3A diffractometer with graphite-filtered Cu Kα radiation. The morphology and particle size of the samples were examined on a TEM-200CX transmission electron microscopy (TEM). XPS measurement was performed on an X-ray photoelectron spectrometer—VG ESCALAB MK II, with the X-ray energy of 1253.6 eV (Mg Kα). The high voltage and emission current are 12 kV and 20 mA, respectively. The binding energy (BE) for each element was referred to the C 1s signal (284.6 eV). Removal of O 1s satellite and curve-fitting of the V $2p_{3/2}$ peak were performed by using the SCAKAB software. The surface concentration of the elements was estimated on the basis of the corresponding peak area which was normalized by using the Wagner Factor database. Infrared spectra were collected on a Nicolet 170SX Fourier transform infrared spectrometer, with the resolution of 4 cm^{-1}.

Temperature-programmed reduction (TPR) was performed in the temperature range of 298–993 K. An amount of 0.2–0.5 g sample was charged in a quartz reactor and reduced in the mixture of 10% H_2 in the balanced N_2 at a rate of 10 K/min. The catalytic performance was evaluated in a quartz micro-reactor in the temperature range of 653–698 K. The reaction mixture consists of 1.5% n-butane, 17.0% oxygen and balanced nitrogen. The GSHV is 1200–1800 h^{-1}. Two on-line gas chromatography systems were adopted to analyze the outlet reaction mixture and the carbon balance was generally better than 95%.

3. Results and discussion

3.1. The effects of polyethylene glycols (PEGs) on preparing VPO catalysts

It is recognized that the efficient VPO catalysts are generally associated with the presence of vanadyl pyrophosphate, $(VO)_2P_2O_7$, and the catalyst performance strongly depends on the preparation history [3,8,9]. In one standard method, the catalyst can be prepared by using HCl as the reducing agent, and typically has low surface areas ($<10\,m^2/g$) [3]. In another preparation route, the catalyst with surface area of $\sim20\,m^2/g$ can be obtained by using alcohols as the solvent and reducing agent, and usually shows better catalytic performance [10]. Since the surface area is closely related to the active sites available for the reaction, it is desirable to prepare a high surface area VPO system while still to retain the essential active component/phase for the reaction. Different approaches have been studied in our laboratory to synthesizing small particle, high surface area VPO system, including application of the SCFD process [11] and mechanical milling the adopted VPO catalysts [12]. The sample subjected to the SCFD process could have a BET surface area beyond $50\,m^2/g$, but the main sample phase deviated from the vanadyl pyrophosphate [11]. In addition, the SCFD process cannot be easily operated, especially for large quantity production. Here, we reported a novel modification in preparing high surface area VPO by using PEGs (PEG2000–PEG20000) as the unique additives. It was found that this preparation method was quite promising and the PEG-derived VPO samples possessed significantly large surface

areas ($41–56\,m^2/g$), with rather small particles (ca. 100–200 nm) of the well-crystallized $(VO)_2P_2O_7$ phase. More importantly, the catalysts showed great performance for partial oxidation of n-butane to MA.

The samples prepared by applying PEG2000, PEG6000, PEG10000 and PEG20000 had their surface areas of 41, 56, 54 and $52\,m^2/g$, respectively. Except for the samples prepared by using the SCFD process [11], they are among the highest surface area VPO analogues. Note that the P1 sample derived in the absence of PEG only had considerably low surface area of $19\,m^2/g$. XRD results indicated that all the precursors prepared in both the presence and the absence of PEG showed the typical $VO(HPO_4)\cdot0.5H_2O$ structure. TGA measurement revealed that the PEG-derived sample showed additional ca. 4% weight loss, which could be attributed to the residual PEG on the precursor surface. In the following activation procedure (at a rate of 2 K/min from room temperature to 673 K in the reaction mixture and kept at this temperature for 15 h), it was observed that the residual PEG would be gradually removed from the sample. The finally activated catalysts were presented as the well-crystallized vanadyl pyrophosphate phase, seen in Fig. 1. Note that although the P1 and the P3–P5 samples have essentially identical phase composition, the relative diffraction intensity for the (2 0 0) and the (0 4 2) crystalline planes changed notably from the P1 sample to the P3–P5 ones, suggesting there might be
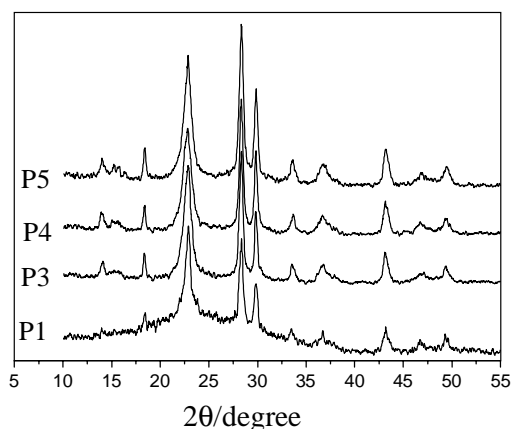

Fig. 1. The XRD patterns of the PEG-derived VPO catalysts, among them P1 was prepared in the absence of PEG while P3–P5 were prepared in the presence of PEG6000, PEG10000 and PEG20000, respectively.
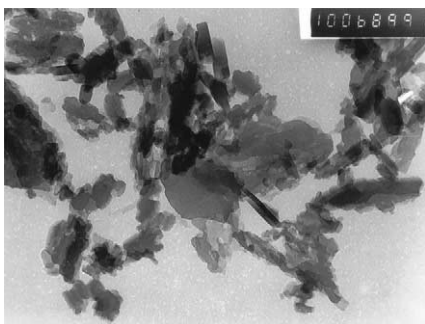
Fig. 2. The TEM photograph of the VPO sample prepared in the presence of PEG20000. The magnification is $100,000\times$.

Fig. 3. Temperature dependence of the performances on the P1 and P2 catalysts: P1 ($\triangle$), P2 ($\bigcirc$). The filled marks are for selectivity and the open ones are for conversion.

local structure/morphology deviation between these two kinds of the samples. TEM examination revealed that the PEG-derived samples exhibited small particle size (ca. 100–200 nm) and fairly even size distribution. The representative picture was shown in Fig. 2. Infrared measurement (not shown) indicated that all the activated VPO samples had the IR bands at 1244 cm^{-1} (νPO$_3$), 1060–1069 cm^{-1} (νPO$_3$) and 960 cm^{-1} (νV=O), which were the characteristic IR features for the (VO)$_2$P$_2$O$_7$ phase [13]. On the other hand, the PEG-derived samples (P2–P5) showed a much more intensive IR band at 1247 cm^{-1}, giving another indication of local structural deviation between the two kinds of samples. After a period of 15 h activation, no C–H and C–O bands can be ob-
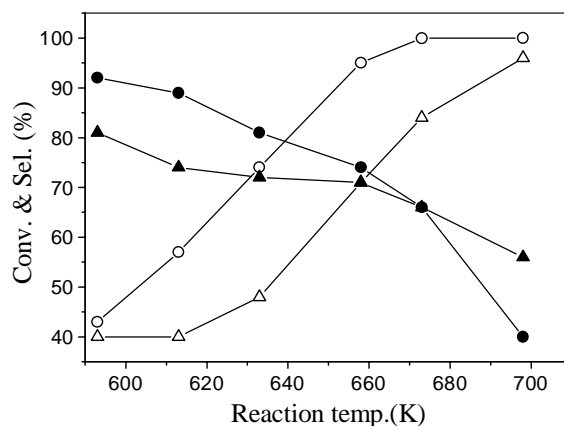
served in the IR spectra, suggesting that the residual PEG was entirely removed and the activated catalyst was PEG-free. XPS measurement demonstrated that the P element was slightly enriched on the catalyst surfaces, seen in Table 1, and this was in agreement with other observations made [14,18]. The binding energies of V 2p$_{3/2}$ and O 1s were also close to those of (VO)$_2$P$_2$O$_7$ reported [14].

The temperature dependence of the catalyst performance on the selected two samples was shown in Fig. 3. In the temperature range of 593–698 K, MA selectivity was decreased slowly while butane

Table 1
The XPS results and the catalytic performances of the four VPO catalysts prepared in the absence (P1) and presence (P3–P5) of PEGs

Catalyst	XPS results				Reaction data			
	P/V ratio	V 2p$_{3/2}$ (eV)	P 2p (eV)	O 1s (eV)	Temperature[a] (K)	C[b] (%)	S[c] (mol%)	Y[d] (mol%)
P1	1.6	517.0	133.9	531.4	658	71	71	51
					673	84	66	55
P3	1.5	516.9	133.8	531.2	658	87	78	68
					673	92	72	66
P4	1.5	517.2	134.0	531.5	658	85	75	64
					673	93	71	66
P5	1.5	517.2	134.0	531.6	658	94	72	68
					673	97	69	67

[a] Reaction temperature.
[b] n-Butane conversion.
[c] Selectivity for maleic anhydride.
[d] Yield for maleic anhydride.

conversion was increased drastically at elevating temperature on the P2 sample. Even at low reaction temperature of 593 K, catalyst P2 showed 43% conversion and ∼90 mol% selectivity. At 658 K, 90% butane conversion with 74 mol% MA selectivity can be achieved, resulting in 67 mol% MA yield. Comparatively, only 51 mol% MA yield was obtained on catalyst P1 under the same reaction conditions, with 71% conversion and 71 mol% selectivity, respectively. Note that the performance of catalyst P2 at 658 K is still noticeably better than that of P1 at 673 K.

The representative reaction data for the other PEG-derived samples (P3–P5) as well as the compared one (P1) were summarized in Table 1. The results clearly demonstrated that the samples prepared in the presence of PEGs showed considerably higher activity and selectivity than that derived in the absence of PEG, and the former catalysts also exhibited better low-temperature performance.

The application of PEGs seems to provide an effective and satisfactory medium to produce high surface area, good performance VPO catalyst. It is thought that the presence of PEG molecules can decrease the surface energy of nucleation of $VO(HPO_4)\cdot 0.5H_2O$ precursor and promotes the uniform precipitation of the fine $VO(HPO_4)\cdot 0.5H_2O$ particles. The PEG molecule adsorbed on the precursor surface may also effectively hinder the agglomeration of the precursor particles formed. The gradual removal of PEG covering on the precursor surface in the following activation procedure is likely beneficial in generating the high surface area $(VO)_2P_2O_7$. This kind of catalyst appears much more active on the basis of per unit mass sample due to much more active sites available, meanwhile it is also more selective possibly due to the unique structure feature/morphology formed in the PEG medium, which was partly revealed by XRD and IR investigations.

3.2. The effects of precursor preparation, pre-treatment and ball milling

Okuhara et al. first modified the morphology of a VPO catalyst by means of fracturing the plate form crystalline $(VO)_2P_2O_7$ in order to understand the origin of active sites [15]. They found that the fracture process did not notably alter the catalyst surface area and catalytic performance, which made them to conclude that the created new side faces were non-selective for MA formation. Zazhigalov et al. activated various promoted and non-promoted VPO catalysts by means of "mechano-chemistry" [16]. It was found that the applied process was beneficial for the promoted samples while almost ineffective for the non-promoted one. In another application of milling process [17], Hutchings and Higgins studied the effects of milling on the physico-chemical properties of VPO and observed positive effects in general. In their case, however, more than one special additive was usually used in the milling media, which introduced the complexity in both the milling process and the related chemistry. It is important to note that not only the milling process itself but also the nature of the precursor/sample for which the milling was applied determined the effectiveness of milling process. In this study, we did not directly fracture the crystalline $(VO)_2P_2O_7$, instead, ball-milled the $VOHPO_4\cdot 0.5H_2O$ precursor which was synthesized through a controlled preparation procedure in the organic media. Cyclohexane, with its non-polar character, would be a preferable choice as a milling solvent. Since the $VOHPO_4\cdot 0.5H_2O$ precursor derived through a common preparation route generally had low surface area ($<10\,m^2/g$), in order to enhance the effect of ball-milling, it is desirable to prepare a high surface area VPO precursor. It was found that careful controlling the speed of addition of phosphoric acid into the hot reaction mixture was quite helpful for this purpose. The as-synthesized precursor had a surface area of ca. $15\,m^2/g$ with the typical $VOHPO_4\cdot 0.5H_2O$ phase, notably larger than some values reported [17]. Interestingly, when the precursor was dried at 393 K in air and then directly applied for ball milling, the increment of surface area of the activated sample was quite limited. However, if the dried precursor was subjected to a short preconditioning in N_2 at 573 K prior to ball milling, the surface area of the activated sample, being in the range of 30–$38\,m^2/g$, was considerably larger than that of the VPO without such a pretreatment, seen in Table 2. Although XRD examination revealed that shortly treating the precursor in N_2 at 573 K did not change the phase composition of $VOHPO_4\cdot 0.5H_2O$, this thermal-treating process together with the following ball milling procedure apparently favored increment of surface area. Under the milling conditions applied, it was found that the surface area can be further enlarged by extending the

Table 2
The physical characteristics of the VPO precursors and the final VPO catalysts with or without milling

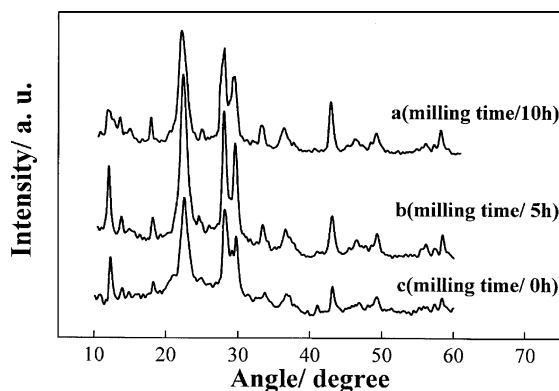| Sample	P-VPO (air/393 K)	P-VPO (N_2/573 K milling/10 h)	VPO (milling/0 h)	VPO (milling/5 h)	VPO (milling/10 h)
BET surface areas (m^2/g)	15	30	20	30	38
XRD principal phase	$VOHPO_4 \cdot 0.5H_2O$	$VOHPO_4 \cdot 0.5H_2O$	$(VO)_2P_2O_7$	$(VO)_2P_2O_7$	$(VO)_2P_2O_7$
XPS surface atomic P/V ratios	–	–	1.5	1.4	1.4
XPS surface atomic V^{5+}/V^{4+} ratios	–	–	26/74	15/85	15/85
XPS surface atomic O/V ratios	–	–	6.3	6.1	6.0

Fig. 4. The XRD patterns of the activated VPO samples milled for different period of time.

milling time to 10 h, but little increment was achieved as the milling was extended beyond 10 h. Therefore, the milling time for this study is generally 5–10 h. XRD results indicated that the milled samples after activation retained the typical phase composition of $(VO)_2P_2O_7$ [3], seen in Fig. 4, suggesting the ball milling process should not alter the essential phase structure. On the other hand, the ball milling indeed broadened the major diffraction peaks and also increased the intensity of some minor diffraction peaks, indicating both a reduction of particle size and a fine

variation in local structure could occur in the milled samples. The TEM results (seen in Fig. 5) demonstrated clearly the particle size/morphology changed with extended milling time. XPS examination revealed that the surface atomic P/V ratio of the milled sample was ca. 1.5, almost identical to that of the non-milled one. As mentioned above already, slight enrichment of the P element on catalyst surfaces was commonly observed on the VPO systems [14,18]. The binding energies of O 1s, V $2p_{3/2}$ and P 2p of the milled samples are around 531.6, 517.2 and 134.1 eV, respectively, and close to those reported for the $(VO)_2P_2O_7$ phase [14]. The XPS curve-fitting results for the surface V^{4+} and V^{5+} species (according to [19] the binding energies for V^{4+} and V^{5+} species are assumed to be 516.9 and 518.0 eV, respectively), however, indicated a notable difference in surface state between the milled and non-milled samples (see the data presented in Table 2). The surface V^{5+}/V^{4+} ratio was remarkably decreased after 5 h-milling, but essentially unchanged as the milling time was extended to 10 h, which was consistent with the trends in the surface areas and the reaction data of the milled samples.

The catalytic performances for the milled and non-milled samples were presented in Table 3. On the milled samples, even at lower reaction temperature
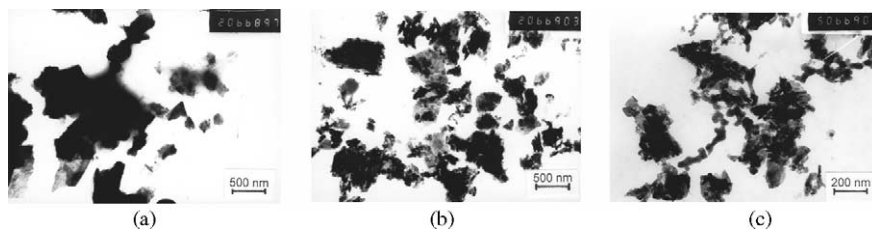

Fig. 5. The TEM photographs of the non-milled and milled VPO samples: (a) non-milled, (b) milled for 5 h, (c) milled for 10 h.

Table 3
The reaction performance of the milled and non-milled catalysts

Sample	VPO (0 h)			VPO (5 h)			VPO (10 h)		
Reaction temperature (K)	658	673	698	658	673	698	658	673	698
Conversion (%)	51	63	83	74	85	95	74	84	93
Selectivity (mol%)	70	67	59	77	75	64	79	78	59

(658 K), 77–79 mol% MA selectivity can be achieved with the butane conversion of ca. 74%. MA selectivity declined to ca. 62 mol% as the reaction temperature was raised to 693 K at which the butane conversion reached ca. 95%. The best performance, i.e. 78 mol% MA selectivity with 84% butane conversion, was achieved on the 10 h-milled sample at the optimal reaction temperature of 673 K. Since the non-milled sample only showed 67 mol% MA selectivity and 63% butane conversion under the same reaction conditions, it was clear that the combination of thermal pre-treating the precursor and ball-milling process did enhance the catalyst performance remarkably in the temperature range of 658–673 K. At the highest reaction temperature of 698 K, somewhat sintering of the fine VPO particles likely occurred, which in turn leaded to a slightly declined performance, seen on the 10 h-milled sample in Table 3.

In literature the P/V ratio of a VPO catalyst was thought to be one of the key factors determining the catalytic performance [1], therefore, three precursors with different bulk P/V ratio of 1.0, 1.2 and 1.5, respectively, were prepared, and then followed the same thermal treatment and 5 h ball milling. The typical reaction data derived on these milled samples were presented in Table 4. It was found that the best performance was again obtained on the milled sample with the bulk P/V ratio of 1.2, being consistent with the observations made on the other non-milled VPO catalysts [1]. It seems that the difference in bulk P/V ratio did not bring about a significant change in the

way of cleavage and accordingly, no unusually active and/or selective planes were generated.

The enhancement of the milled catalyst performance can be principally attributed to sliding of precursor platelets away from one another, exposing the certain surfaces that will further transfer into the active and selective faces. This transformation was known to be topotatic, and the morphology of the catalyst precursor will control the morphology of the final catalyst [20]. Besides the increment of surface areas and available reaction sites, other factors may be more or less relevant. Preliminary TPR investigation revealed that reduction of V^{5+} and V^{4+} species, corresponding to the shoulder at lower temperature and the main peak at higher temperature, respectively in the TPR profile, shifted to the lower temperature end as the milling time was extended (seen in Fig. 6). It seems that the milling treatment leads to a higher reactivity of the lattice oxygen associated with the V^{5+} and V^{4+} species. Moreover, the amount of reducible V^{5+} species also declines with extended milling, being in agreement with the XPS curve-fitting results mentioned above. Although a quantitative correlation
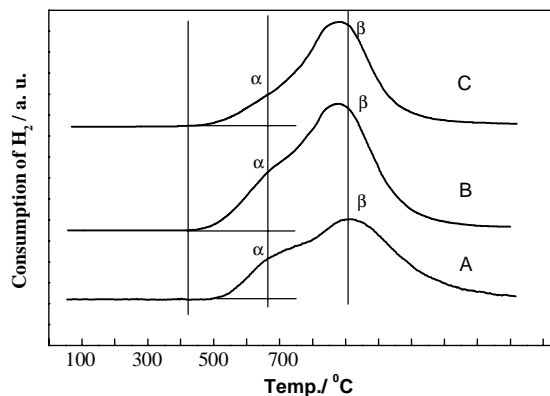
Table 4
The reaction performance of the milled samples with different bulk P/V ratios

Sample	VPO (1.0 h)	VPO (1.2 h)	VPO (1.5 h)
Reaction temperature (K)	673	673	673
Conversion (%)	77	86	83
Selectivity (mol%)	67	76	66

Fig. 6. The H_2-TPR profiles of the non-milled and milled VPO samples. Catalyst A: non-milled, catalysts B and C: milled for 5 and 10 h, respectively.

can hardly be established, it is clear that the applied milling process not only effectively increased the surface areas of the milled samples and consequently the available number of active sites, but also somehow changed the other characteristics such as the local environment and the redox behavior to a certain extent; and both of them may account for the overall enhancement of performance on the ball milled samples.

4. Concluding remarks

A successful approach to preparing large surface area VPO system by using PEGs as the unique additive has been established and the resulting materials showed notably enhanced performances. Another interesting feature of the PEG-derived sample was its better low-temperature performance. The principle function of PEG in preparation chemistry and the possible causes for the enhanced performance were briefly discussed. Another approach to preparing high surface area VPO system, namely, well-controlled addition of phosphoric acid to generate a high surface area VPO precursor, short preconditioning of the precursor in nitrogen at certain temperature and final ball milling the as-treated precursor, was also set up. The evaluation of target reaction confirmed its effectiveness. In addition to the increment of surface areas and available active sites, other factors induced by milling process may also be responsible for the overall enhancement.

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