ELSEVIER

Catalysis Today 74 (2002) 101–110

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Effects of ball milling on the doped vanadium phosphorus oxide catalysts

Weijie Ji [a,*], Lijun Xu [a], Xiaoshu Wang [b], Zhen Hu [a], Qijie Yan [a], Yi Chen [a]

[a] *School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China*
[b] *Center of Materials Analysis, Nanjing University, Nanjing 210093, PR China*

Abstract

Vanadium phosphorus oxide (VPO) catalyst precursors were prepared in organic phase by using isobutanol as the reducing agent. They were doped by combined components—Zn + Zr + Mo, Zr + Zn and Zr + Mo—through impregnation. In order to increase the catalyst surface areas, the catalyst precursors were ball milled in different solvents for a certain period of time. X-ray diffraction (XRD), X-ray fluorescence spectrometer (XFS), DTA/TGA, X-ray photoelectron spectrometer (XPS) and BET were used to examine the bulk and surface properties of the final catalysts and their precursors. Catalytic performances were measured in the selective oxidation of *n*-butane into maleic anhydride (MA). The results revealed that ball milling could improve the performances of these VPO catalysts, without destroying the active physico-chemical structure and without exerting great influence on the surface characteristics of the catalysts. Interaction between the combined moderators was also preliminarily discussed. The Mo component was found to have some kind of stabilizing effect on the catalyst surface of this system. © 2002 Published by Elsevier Science B.V.

Keywords: VPO catalyst; Ball milling; Selective oxidation; Maleic anhydride

1. Introduction

Vanadium phosphorus oxide (VPO) catalysts are widely used in selective oxidation of *n*-butane into maleic anhydride (MA). Although laboratory and industry efforts have been exerted on this catalyst systems, lots of details are still not thoroughly elaborated, especially the aspects concerning active sites, surface vanadium oxidation states, catalytic mechanism and so on, which are maybe ascribed to both the complicated interaction between surface and bulk elements, and the difficulty in detecting the intermediate products in catalytic reactions [1]. After years of work, researchers have it in common that preparation methods play an important role in the structure of VPO catalysts and, accordingly, in the catalytic activity. There is also consensus that $(VO)_2P_2O_7$ is the active phase or major component of active VPO catalysts [2]. But different phase components are also announced in papers or patents [3,4]. Some catalysts achieved high conversion and fair selectivity at high temperature, which was attributed to the low surface areas of the catalysts [5]. In recent years the environmental aspect in catalysis becomes more and more important, which is typically represented by industrial production of MA using *n*-butane as a feedstock in place of benzene [6,7]. It will be desirable to improve the butane conversion while to maintain the MA selectivity at relatively low reaction temperature. As the surface area is tightly connected with the butane conversion and some definite phase composition is also essential for good MA selectivity [8], it will be interesting if some methods are adopted to increase the surface area with retaining active phase composition. Although standard

---

[*] Corresponding author.

0920-5861/02/$ – see front matter © 2002 Published by Elsevier Science B.V.
PII: S0920-5861(01)00535-1

preparations of VPO catalysts show no deliberate control of catalyst particle size, organic phase reduction in preparation, for example, using isobutanol as the reducing agent, can give smaller size of particles than other methods [5,9]. And ball milling is some kind of mechanical process that is able to increase surface area by reducing particle size without destructing or altering the chemical nature of phase composition. Some additives, including Zr, Zn or Mo, can increase the butane conversion and/or MA selectivity in the selective oxidation of *n*-butane to MA over the VPO catalysts [5,10]. In this work, the above beneficial aspects were integrated to prepare the VPO catalysts moderated by combined components, which was a special preparation routine by employing both the impregnation with combined moderators and the following ball milling procedure in the specific solvents. The characterization and evaluation results of these catalysts gave here some insights into the effects of the ball milling process on the physico-chemical properties and the catalytic performances of the resulting VPO systems.

2. Experimental

2.1. Preparation of the doped VPO catalyst precursors

The VPO precursors were prepared in organic phase by employing the reaction of vanadium pentoxide (32.9 g) with isobutanol (120 ml) in the solvent of benzyl alcohol (120 ml). After the reaction mixture was refluxed for 6 h, the phosphoric acid (29.3 g, 85 wt.%) was, with controlled phosphorus/vanadium (P/V) atomic ratio of 1.2/1.0, added into the hot black mixture at a rate of 0.6 ml per minute, and the mixture was further 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 (symbolized as “Y”), was dried in air at 120 °C. The precursor then was incipient wetness impregnated with a solution containing combined promoters such as Zr + Zn, Zr + Mo + Zn or Zr + Mo in the form of zirconium nitrate, zinc acetate and ammonium molybdate. The samples were symbolized as Yzmz, Yzz and Yzm for the precursors containing Zr + Mo + Zn, Zr + Zn and Zr + Mo, respectively. The controlled atomic ratio for the vanadium/promoter is 1:0.03. After that, the impregnated precursors were calcined in N_2 at 400 °C for 6 h. DTA/TGA techniques were used to help to determine the calcination temperatures for these precursors.

2.2. Ball milling process

The doped precursors were ball milled in the agate pots with the solvent of cyclohexane or alcohol for 5, 10 and 20 h, respectively. The controlled mass ratio of agate beads to sample was 8:1 and each pot contained 2.5 g sample and 10 ml solvent. Ball milling was performed in a rotated chassis at the speed of 175 rotations per minute. Once the ball milling was finished, the agate pots were dried in air at 120 °C to remove the solvent.

2.3. Activation and catalytic reaction

The ball milled catalyst precursors were activated in the reaction mixture of 1.5% *n*-butane/air (gas hour space velocity (GHSV), 1200 h^{-1}) at 400 °C for 6 h, at a rate of 2 K per minute from room temperature. The obtained catalysts were symbolized as Yzmz/6 h, Yzz/6 h and Yzm/6 h for the according precursors mentioned above. All of these VPO catalysts showed almost identical $(VO)_2P_2O_7$ or B-phase after activation. Served as the contrasting samples, several non-ball milled precursors were also activated under the same conditions. As for the catalytic activity measurements, a quartz micro-reactor was loaded with 0.5 g granulated catalyst; and 1.5% *n*-butane/air mixture was introduced at the GHSV of 1200 h^{-1}. On-line gas chromatography systems were used to analyze the outlet mixture, and the carbon balance was generally better than 95%.

2.4. Characterization

BET surface areas were measured by nitrogen adsorption at 77 K in a Micromeritics ASAP2000 adsorption apparatus. DTA/TGA was performed on a Rigaku-TG-DTA thermo-analyzer at a heating rate of 10 K per minute. XRD was conducted on a Shimadzu XD-3A diffraction meter with graphite-filtered Cu Kα radiation. The X-ray tube was operated at 35–40 kV and 100–120 mA. The X-ray fluorescence spectrometer (XFS) was measured through a home-assembled

XFS. X-ray photoelectron spectrometer (XPS) was performed on an XPS—VG ESCALAB MKII, with the X-ray (Mg Kα) energy of 1253.6 eV and the set vacuum less than 2×10^{-8} mbar. The binding energies were normalized according to the C1s value of 284.6 eV.

3. Results and discussion

3.1. Characterization of the catalyst precursors

The quantitative control in preparation was satisfactory because the XFS results proved that the ratio of P/V was, in a range of 1.2 ± 0.03, well controlled and so was the ratio of V/promoter. It is generally asserted that the active phase of VPO catalyst is transformed from the precursor of $VOHPO_4 \cdot 0.5H_2O$ [10,11]. Therefore, the DTA/TGA and XRD techniques were employed to examine all the obtained precursors in different preparation procedures, which showed that the obtained blue–green precipitate was a typical $VOHPO_4 \cdot 0.5H_2O$ phase. The detailed information was listed in Table 1and also showed in Figs. 1 and 2.

For the impregnated precursor, the DTA curve showed an endothermic peak centered at 400 °C while the TGA curve also presented the maximum weight loss at around 400 °C, indicating that the impregnated VPO precursor Yzmz experienced the phase transformation at about 400 °C. XRD also revealed that the impregnated precursor had a typical $VOHPO_4 \cdot 0.5H_2O$ phase and this phase can be almost completely transformed into a new phase by a 6 h of activation at 400 °C. It was found that two hours of calcination in N_2 at 400 °C only decomposed the additive precursors

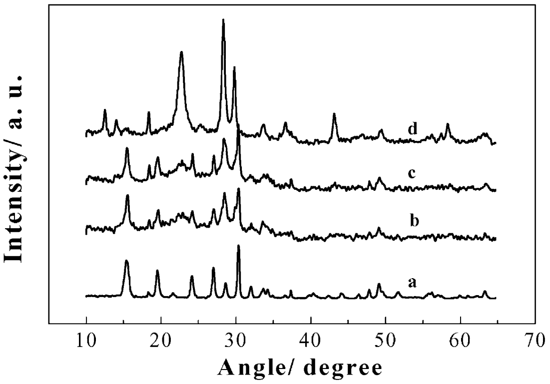

Fig. 1. XRD patterns of the precursors and the Yzmz final catalyst: (a) precursor Y; (b) precursor Yzmz; (c) ball milled precursor Yzmz; (d) catalyst Yzmz/6 h (activitated “c”). Ball milling solvent, cyclohexane; milling time, 5 h.

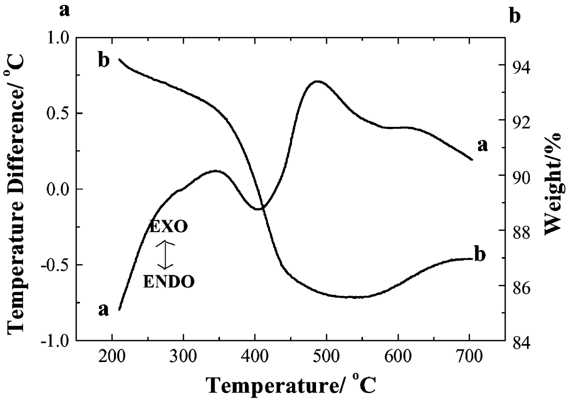

Fig. 2. DTA/TGA curves for the precursor Y: (a) DTA; (b) TGA.

Table 1
X-ray diffraction results of the various precursors

Precursors	Moderators	Principal XRD *d* values (Å)	Predominant phase
Y	None	2.94, 3.29, 4.53, 3.68	$VOHPO_4 \cdot 0.5H_2O$
Yzmz	Zr + Mo + Zn	2.94, 3.29, 4.52, 3.66	$VOHPO_4 \cdot 0.5H_2O$
Yzz	Zr + Zn	2.94, 3.30, 4.53, 3.66	$VOHPO_4 \cdot 0.5H_2O$
Yzm	Zr + Mo	2.94, 3.29, 4.53, 3.67	$VOHPO_4 \cdot 0.5H_2O$
Yzmz-ball milled[a]	Zr + Mo + Zn	2.94, 3.29, 4.51, 3.67	$VOHPO_4 \cdot 0.5H_2O$
Yzz-ball milled[a]	Zr + Zn	2.94, 3.29, 4.52, 3.69	$VOHPO_4 \cdot 0.5H_2O$
Yzm-ball milled[a]	Zr + Mo	2.94, 3.29, 4.53, 3.67	$VOHPO_4 \cdot 0.5H_2O$

[a] Ball milling conditions: ball milling time, 5 h; solvent, cyclohexane.

of nitrates but did not change the main phase of $VOHPO_4 \cdot 0.5H_2O$. Based on these observations, all the precursors prepared in this study were activated at 400 °C for 6 h or longer. By the XRD results, it seems that the introduced additives inflicted little influence on the major phase composition of the precursor. In fact, the impregnated precursors gave almost identical phases no matter what combination of moderators was adopted, and additionally, the ball milling process did not alter the phases of precursors, either. It was noted that, however, the ball milling changed the half width of the peaks in the XRD patterns, clearly indicating a decrease in the particle sizes. After activation, the moderated and ball milled precursors were transformed into a kind of phase which was essentially identical to the $(VO)_2P_2O_7$ or B phase, seen in Fig. 1.

3.2. Effects of ball milling on the surface area and the phase composition

The VPO catalyst precursor usually had a small surface area that will increase somewhat after calcination [12]. The obtained precursor Y in this study, however, had a BET surface area of 14.7 m^2/g, which was larger than some reported values [12], and the according catalyst Y/6 h had a larger surface area of 20 m^2/g. The controlled speed of adding phosphorus might have an effect on this increment. On the other hand, the ball milling procedure can enlarge the surface areas to a certain degree, and the effects were dependent on the characteristics of catalysts, such as the combination of moderators and the ball milling conditions, which were showed in Table 2.

Before ball milling, the doped precursors subjected their surface areas to the additive combinations. For instance, the doped precursor "Yzz" showed the largest surface area of 30 m^2/g, which was almost twice the surface area of "Yzm" sample. Different doped precursors also gave different responses to the length of ball milling time. If ball milled in cyclohexane for 5 h, only the precursor "Yzz" increased the surface area obviously. With ball milling up to 10 h, the "Yzmz" precursor enlarged its surface area by ca. 13% while the precursor "Yzm" had no enlargement in surface area until ball milled for 20 h (Fig. 3). When the alcohol was used as the solvent and a 5 h-milling was employed, the precursors showed a bit larger surface areas than those ball milled in cyclohexane under the same conditions. The differences became irregular if the samples were all milled for 20 h. The polar alcohol could have a stronger impact on the VPO precursors than the non-polar cyclohexane. Given the fact that the alcohol was even used as a reducing agent in the preparation, cyclohexane was likely more desirable as a solvent media. Since the ball milled precursors all retained the $VOHPO_4 \cdot 0.5H_2O$ phase composition, the ball milling process seems not to change the phase composition, but the particle size.

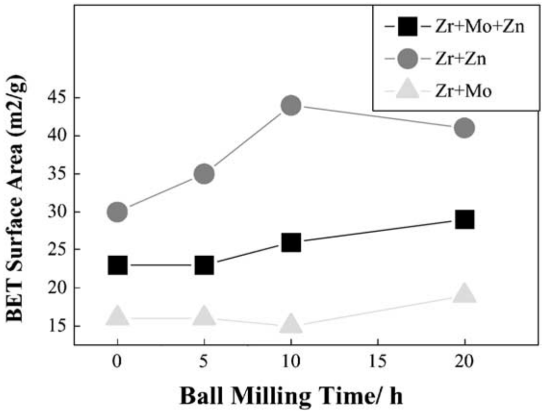

Fig. 3. Effects of the milling time on the surface areas of the moderated precursors (using cyclohexane as the solvent).

After ball milling the precursors were activated in a 1.5% *n*-butane/air mixture for 6 h. The surface areas all decreased to a certain extent except that the sample doped by Zr + Mo maintained or even enlarged the surface areas when the according precursor was ball milled in cyclohexane for 5 or 10 h (seen in Figs. 3 and 4). The time scale of ball milling exerted an interesting impact on the catalysts containing Zr + Mo and Zr + Zn additives. The final samples showed identical surface areas when their precursors were ball milled in cyclohexane for longer than 10 h. Considering the notable difference between the surface areas of their precursors and the changes in surface areas after activation, it was apparent that, when combined with the Zr, the Mo component had somewhat stabilizing the surface area of the catalysts and the Zn component had the reverse function. In the case of the catalyst containing Zr + Mo + Zn, the surface areas less changed after activation, which is possibly due to the offsetting effects of coexisting Mo and Zn components. The

Table 2
Effects of ball milling on the surface areas and phase compositions

Catalysts and precursors	Promoters[a]	Ball milling conditions[b]		BET surface area (m^2/g)	Predominant phase
		Solvents	Time (h)		
Yzmz	Zr + Mo + Zn	None	0	23	$VOHPO_4\cdot 0.5H_2O$
Yzz	Zr + Zn	None	0	30	$VOHPO_4\cdot 0.5H_2O$
Yzm	Zr + Mo	None	0	16	$VOHPO_4\cdot 0.5H_2O$
Yzmz (after ball milling &before activation)	Zr + Mo + Zn	Cyclohexane	5	23	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo + Zn	Cyclohexane	10	26	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo + Zn	Cyclohexane	20	29	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo + Zn	Alcohol	5	28	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo + Zn	Alcohol	20	30	$VOHPO_4\cdot 0.5H_2O$
Yzz (after ball milling & before activation)	Zr + Zn	Cyclohexane	5	35	$VOHPO_4\cdot 0.5H_2O$
	Zr + Zn	Cyclohexane	10	44	$VOHPO_4\cdot 0.5H_2O$
	Zr + Zn	Cyclohexane	20	40	$VOHPO_4\cdot 0.5H_2O$
	Zr + Zn	Alcohol	5	47	$VOHPO_4\cdot 0.5H_2O$
	Zr + Zn	Alcohol	20	38	$VOHPO_4\cdot 0.5H_2O$
Yzm (after ball milling & before activation)	Zr + Mo	Cyclohexane	5	16	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo	Cyclohexane	10	15	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo	Cyclohexane	20	19	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo	Alcohol	5	17	$VOHPO_4\cdot 0.5H_2O$
	Zr + Mo	Alcohol	20	18	$VOHPO_4\cdot 0.5H_2O$
Yzmz/6 h[c]	Zr + Mo + Zn	None	0	22	$(VO)_2P_2O_7$·or B-phase
Yzz/6 h	Zr + Zn	None	0	14	$(VO)_2P_2O_7$·or B-phase
Yzm/6 h	Zr + Mo	None	0	13	$(VO)_2P_2O_7$·or B-phase
Yzmz/6 h[d]	Zr + Mo + Zn	Cyclohexane	5	24	$(VO)_2P_2O_7$·or B-phase
Yzmz/6 h	Zr + Mo + Zn	Cyclohexane	10	23	$(VO)_2P_2O_7$·or B-phase
Yzmz/6 h	Zr + Mo + Zn	Cyclohexane	20	21	$(VO)_2P_2O_7$·or B-phase
Yzmz/6 h	Zr + Mo + Zn	Alcohol	5	23	$(VO)_2P_2O_7$·or B-phase
Yzz/6 h	Zr + Zn	Cyclohexane	5	17	$(VO)_2P_2O_7$·or B-phase
Yzz/6 h	Zr + Zn	Cyclohexane	10	18	$(VO)_2P_2O_7$·or B-phase
Yzz/6 h	Zr + Zn	Cyclohexane	20	18	$(VO)_2P_2O_7$·or B-phase
Yzz/6 h	Zr + Zn	Alcohol	5	17	$(VO)_2P_2O_7$·or B-phase
Yzm/6 h	Zr + Mo	Cyclohexane	5	16	$(VO)_2P_2O_7$·or B-phase
Yzm/6 h	Zr + Mo	Cyclohexane	10	18	$(VO)_2P_2O_7$·or B-phase
Yzm/6 h	Zr + Mo	Cyclohexane	20	18	$(VO)_2P_2O_7$·or B-phase
Yzm/6 h	Zr + Mo	Alcohol	5	19	$(VO)_2P_2O_7$·or B-phase

[a] The atomic ratio of V to Zn (or Zr, or Mo) is 1:0.03.

[b] Ball milling conditions referred to the ball milling process of the moderated precursors such as Yzmz.

[c] These catalysts were obtained by direct activation of the moderated but non-ball milled precursors.

[d] These catalysts were obtained by activating the moderated and ball milled precursors.

differences in the surface areas of the precursors were also reduced by the following activation step, seen in Fig. 4. It might be in part ascribed to the fact that the phase of $VOHPO_4\cdot 0.5\ H_2O$ was converted into the $(VO)_2P_2O_7$ or the B-phase or a combination of the two during the activation step. It was also found that either cyclohexane or alcohol was used, the catalysts containing the same additives showed the close BET surface areas and the identical phases, suggesting that the effect of solvent in the milling process could also be covered by the following activation procedure.

With a short period of milling (less than 10 h), it was clear that the surface areas were increased notably as compared to those without ball milling, especially for the samples containing Zr + Mo or Zr + Zn components, shown in Fig. 4. If the ball milling lasted for 20 h, however, the produced smaller particles could have some kind of constriction effect during the following activation procedure because of the very fine

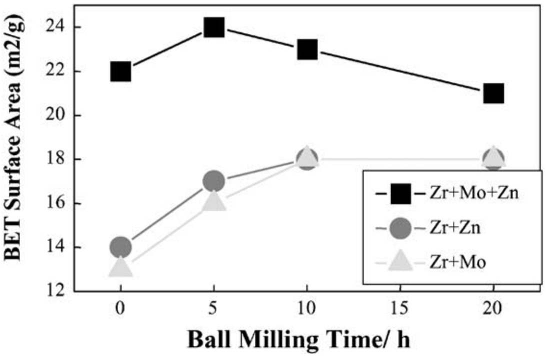

Fig. 4. Effects of the milling time on the surface areas of the final moderated catalysts (using cyclohexane as the solvent).

particle size and their relatively high surface free energies. This constriction effect could account for the decrease in the final surface areas of the catalysts as it was subjected to a longer period of milling. The optimal time scale for the ball milling apparently falls into the range of 5–10 h.

In terms of the XRD results, seen in Fig. 5, again it was found that the ball milling process inflicted little influence on the phase composition but the changes in the half width of the peaks of the final catalysts.

3.3. Effects of ball milling on the surface physico-chemical properties

The catalytic activity was directly related to surface properties of catalysts [13]. The valence state of surface vanadium, the ratio of phosphorus to vanadium and the contents of surface promoters were emphasized for their relations with the catalytic performance. XPS is a suitable approach to monitor the surface physico-chemical properties of these moderated and ball milled catalysts. Since the milling process might alter the surface state of the samples, it would be necessary to find out possible changes after the ball milling. And some data were presented in Table 3.

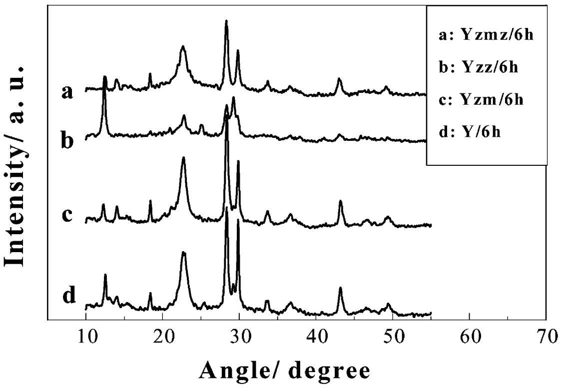

Fig. 5. The XRD patterns of the non-moderated, the moderated and ball milled VPO catalysts.

It is well known that the valence state of surface vanadium played an important role in the selective oxidation of *n*-butane to MA [14]. For the catalysts activated in the *n*-butane/air mixture, the binding energy of surface vanadium was ca. 517.2 eV, which was very close to that of fully characterized $(VO)_2P_2O_7$ [15]. Thus the surface vanadium in the moderated and ball milled samples may have its valence state of approximate +4. According to the data listed in Table 3, the surface vanadium in the final catalysts showed almost identical binding energies no matter whether their precursors were ball milled or not. Whereas, between the milled and the non-milled precursors, there were only slight differences in the binding energy of the surface vanadium. The small difference would disappear after the activation. It seems that the activation step in the *n*-butane/air mixture could level the surface vanadium valence state by smoothing the local structural changes caused by the milling process. Similar trends were observed for the other elements presented on the sample surfaces after ball milling and activation. Over all, the milling procedure exerted little influence on the valence state of elements on the surfaces of the moderated VPO catalysts. The first synthesis step should be more critical in determining the surface valence state of vanadium.

Surface P/V is another key point in catalytic reaction of butane oxidation [3]. XPS analysis has yielded surface P/V ratios ranging typically from 1.5 to 2.0, suggesting surface phosphorus enrichment, which is also in agreement with the other observations [16,17]. The introduced moderators did not lead to an unusual distribution of surface V and P components. The samples moderated by Zr + Mo + Zn and Zr + Zn combinations showed the P/V ratios were slightly increased after ball milling, but the values become almost identical after activation. Activation step showed little impact on the surface P/V ratios of the catalysts.

Table 3
Effects of ball milling on the surface physico-chemical characteristics

Catalysts and precursors	Vanadium/phosphorus/promoters (atomic)					Binding energy (eV)[a]				
	V_{2p}	P_{2p}	Mo_{3d}	Zr_{3d}	Zn_{3d}	V	P	Mo	Zr	Zn
Yzmz	1.0	1.8	0.073	0.15	0.030	517.2	134.0	233.0	183.5	1023.6
Yzz	1.0	1.5	–	0.11	0.042	517.0	133.7	–	183.3	1022.3
Yzm	1.0	1.7	0.078	0.11	–	517.2	134.0	233.0	183.3	–
Ball milled Yzmz[b]	1.0	2.1	0.10	0.14	0.042	516.9	133.7	232.7	183.2	1022.5
Ball milled Yzz[b]	1.0	2.0	–	0.14	0.030	516.8	133.7	–	183.1	1021.8
Ball milled Yzm[b]	1.0	1.7	0.086	0.10	–	517.0	133.8	233.0	183.3	–
Catalyst without ball milling[c]	1.0	1.7	0.057	0.15	0.002	517.3	133.8	232.9	183.0	1022.4
	1.0	1.6	–	0.13	0.008	517.2	133.7	–	183.2	1022.2
	1.0	1.7	0.085	0.13	–	517.3	134.0	233.2	183.1	–
Catalyst with ball milling[d]	1.0	1.4	0.071	0.10	0.008	517.2	133.9	233.0	183.0	1022.4
	1.0	2.0	–	0.16	0.074	517.1	133.8	–	183.0	1022.6
	1.0	1.7	0.083	0.10	–	517.2	134.1	233.3	183.4	–

[a] Binding energy was corrected according to C 1s at the peak of 284.6 eV.

[b] Precursors were ball milled in cyclohexane for 5 h before activation.

[c] These catalysts were obtained by direct activation of the precursors “Yzmz”, “Yzz” and “Yzm” without ball milling process.

[d] These catalysts were obtained by direct activation of the ball milled precursors “Yzmz”, “Yzz” and “Yzm”.

Note that, however, both Mo and Zr components segregated on the surfaces while the Zn component did not. For the Yzm sample, the P/V ratio keeps almost constant regardless of ball milling and activation procedures, which further supported a hypothesis that the co-existence of Zr and Mo may have a stabilizing effect on the catalyst surface. It was found that the ball milling process also caused some redistribution of the moderators over the catalyst surface, which may have an impact on the catalytic behavior.

3.4. Effects of ball milling on the catalytic performances

The promoted precursors, milled or not, were in situ activated for the selective oxidation of *n*-butane to MA. The relevant reaction conditions and catalytic performances were summarized in Table 4. Note that the data were collected at relatively lower reaction temperatures.

By comparing these data, it could be found that the milling process adopted in the preparation of VPO catalysts had an impact on the catalytic performances, especially the conversion of *n*-butane. This phenomenon was consistent with the increment of active surface areas, as a result of ball milling. Since the available number of active sites was closely related to surface area on a certain exposed surface planes. For some catalysts, the butane conversions were almost increased by 40% through the ball milling process. It was also noted that the MA selectivity was basically maintained. Given the fact that the ball milling process inflicted little influence on the phase composition and the surface physico-chemical properties of the final catalysts, it was not surprising since the selectivity was more correlated with these properties [18]. On the other hand, it implies that the fractured faces created by ball milling should have the similar structural features to those of original planes that were believed to be responsible for MA formation [19]. Compared to the SCFD method, although it generated the ultra fine particles, the phase composition had changed after the procedure [20], which explained the dramatic alteration of catalytic behavior after SCFD procedure. The solvents adopted in the ball milling process showed little effects on the catalytic activities. To summary, the milling process adopted in preparation can improve the catalytic performance, and different combinations of moderators also affected this sort of enhancement, seen in Figs. 6 and 7.

For the catalysts moderated by Zr + Zn or Zr + Mo, when milled in cyclohexane for longer than 5 h, the samples showed more notably increased *n*-butane conversion than the catalyst moderated by Zr + Mo + Zn.

Table 4
Effects of ball milling on the catalytic performances

Catalysts	Promoters[a]	Ball milling conditions		Catalytic activity (mol%)[b]			
		Solvents	Time (h)	Temp. (°C)	Conversion	Selectivity	Yield
Catalyst without ball milling the precursor [c]	Zr + Mo + Zn	None	0	385	60	53	32
	Zr + Mo + Zn	None	0	400	73	47	34
	Zr + Zn	None	0	385	22	70	15
	Zr + Zn	None	0	400	28	56	16
	Zr + Mo	None	0	385	36	66	24
	Zr + Mo	None	0	400	42	54	23
Catalyst with ball milling the precursor [d]	Zr + Mo + Zn	Cyclohexane	5	385	73	63	46
	Zr + Mo + Zn	Cyclohexane	10	385	74	65	48
	Zr + Mo + Zn	Cyclohexane	20	385	74	65	48
	Zr + Mo + Zn	Cyclohexane	5	400	85	54	46
	Zr + Mo + Zn	Cyclohexane	10	400	84	57	48
	Zr + Mo + Zn	Cyclohexane	20	400	84	56	47
	Zr + Mo + Zn	Alcohol	5	385	63	70	44
	Zr + Mo + Zn	Alcohol	5	400	78	59	46
Catalyst with ball milling the precursor	Zr + Zn	Cyclohexane	5	385	52	66	34
	Zr + Zn	Cyclohexane	10	385	54	64	34
	Zr + Zn	Cyclohexane	20	385	56	65	36
	Zr + Zn	Cyclohexane	5	400	65	57	37
	Zr + Zn	Cyclohexane	10	400	69	57	39
	Zr + Zn	Cyclohexane	20	400	68	58	39
	Zr + Zn	Alcohol	5	385	54	69	38
	Zr + Zn	Alcohol	5	400	67	62	41
Catalyst with ball milling the precursor	Zr + Mo	Cyclohexane	5	385	57	66	37
	Zr + Mo	Cyclohexane	10	385	60	68	41
	Zr + Mo	Cyclohexane	20	385	57	71	41
	Zr + Mo	Cyclohexane	5	400	67	56	38
	Zr + Mo	Cyclohexane	10	400	72	60	43
	Zr + Mo	Cyclohexane	20	400	69	61	42
	Zr + Mo	Alcohol	5	385	56	67	38
	Zr + Mo	Alcohol	5	400	68	64	43

[a] The atomic ratio of V to Zn (or Zr, or Mo) was 1:0.03.
[b] The GHSV was 1200 h^{-1}.
[c] These catalysts were obtained by direct activation of the precursors "Yzmz", "Yzz" and "Yzm" without ball milling process.
[d] These catalysts were obtained by direct activation of the ball milled precursor "Yzmz", "Yzz" and "Yzm".

Similar conversions will be obtained if their precursors were ball milled beyond 10 h, which accorded to the effects of ball milling on the surface areas of VPO catalysts discussed before. With regard to the catalyst containing Zr + Mo + Zn, although the surface content of Zn was rather low, it gave higher butane conversion than the catalyst moderated by Zr + Mo, which implies that the Zn component, though in small amount on the surface, could still be important for the butane conversion. Actually, the milling process could also change the selectivity of MA somewhat on this catalyst. On the Yzm sample, a constant MA selectivity was obtained with the milling time, seen in Fig. 7. As mentioned before, the phase composition and the surface features of this sample retained with respect to the milling process, so the observed unchanged MA selectivity was expectant. For the other two sets of the catalysts, if a long period of ball milling was employed, the selectivity becomes almost the same, and the milling time would exert less influence on the catalytic performances when it was beyond 5 h (Figs. 6 and 7). This trend could be explained by the fact that the longer period of milling resulted in the more similar surface features of the precursors and the following

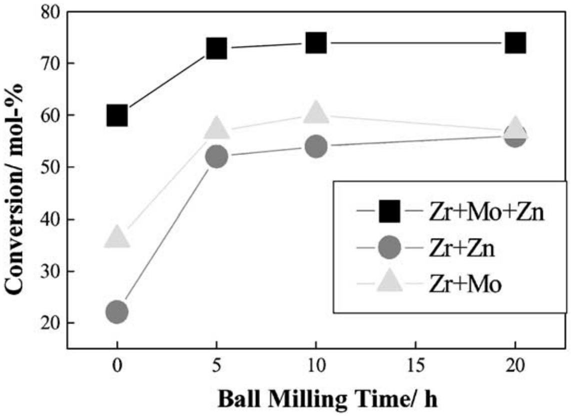

Fig. 6. Effects of the ball milling time on the n-butane conversion: GHSV, 1200 h^{-1}; reaction temperature, 385 °C; solvent for ball milling, cyclohexane.

activation step further smoothed the differences in the milled precursors. It can be concluded that 5 h of ball milling was generally enough to generate a sufficient improvement of the final catalyst—increasing the butane conversion notably while retaining the fairly good MA selectivity.

It seems as if the increased conversions of n-butane over those milled catalysts should be merely ascribed to the enlargement of the surface areas. When the specific activity (SA) was taken into account to deduct the influences of the enlargements in surface area, seen in Fig. 8, it was obvious that the ball milling process did improve not only the overall butane conversion on the basis of unit mass sample but also the specific activities, i.e. the conversion over the unit surface area, no matter what kind of combined moderators were introduced. It was also found that the prolonged milling process had different impact on the specific activities of the various moderated catalysts. For the catalyst moderated with Zr, Mo and Zn elements, although the SA was increased less notably as compared to that of the other moderated catalysts in the first 5 h milling, it can be continuously increased with extending the milling up to 20 h.

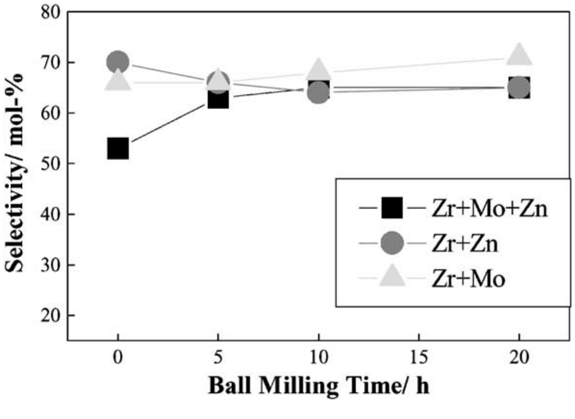

Fig. 7. Effects of the ball milling time on the MA selectivity: GHSV, 1200 h^{-1}; reaction temperature, 385 °C; solvent for ball milling, cyclohexane.

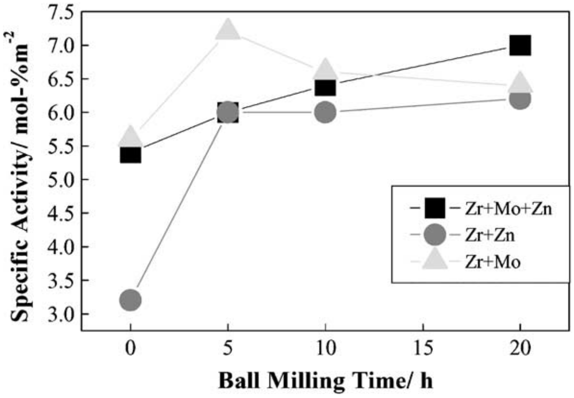

Fig. 8. Changes of specific activities with milling time over different moderated and ball milled catalysts: ball milling time, 5 h; milling solvent, cyclohexane; reaction temperature, 385 °C.

In Table 4, the catalytic data were collected either at 385 or 400 °C. Conversion of n-butane can be further increased at higher reaction temperatures. Although increasing the reaction temperature was an alternative way to achieve the same level conversion of n-butane over the non-ball milled catalysts, the MA selectivity would be sacrificed inevitably. It was rather difficult to retard the complete oxidation of n-butane or the product MA at higher reaction temperatures. By ball milling, however, a higher butane conversion can be achieved at relatively low temperatures, meanwhile the selectivity can also be maintained.

4. Conclusions

The introduction of moderators and the application of ball milling process adopted in this study to the VPO base did not change the principal phase composition, but decreased the particle sizes and accordingly the precursor surface areas that led to an increment of active faces in the final catalysts. The ball milling process also caused somewhat redistribution of the moderators over the catalyst surface, which apparently impacted on the formation of MA. The catalyst moderated with Zr, Mo and Zn elements and subjected to ball milling process showed a notable increase in the surface areas of both the precursor and the final catalyst. This catalyst can generate additional ca. 10 mol% MA yield at no expense of the MA selectivity than the corresponding VPO catalyst without moderators. Therefore, by means of ball milling the VPO precursors containing combined moderators, especially the three-moderator system, the catalytic performances (the butane conversion in particular) can be notably improved in the partial oxidation of *n*-butane to MA at relatively low temperatures. Although using high reaction temperature could be another way to get high conversion of *n*-butane, it can hardly avoid sacrificing the MA selectivity. Ball milling process, as an effective approach, is able to increase the conversion of butane without sacrificing the MA selectivity, because neither the active phase composition nor the main surface characteristics have been altered or disturbed.

Acknowledgements

The authors would like to acknowledge the financial support from the National Natural Science Foundation of China and SINOPEC (Grant: 29792073-1). We also appreciate the kind assistance of Professor Ding Weiping and Ms. Jiang Xiaohui in our experiments.

References

[1] J. Ebner, V. Franchetti, G. Centi, F. Trifiro, Chem. Rev. 88 (1988) 251.
[2] G. Centi, Catal. Today 16 (1993) 5.
[3] B.K. Hodnett, Catal. Rev.-Sci. Eng. 27 (1985) 373.
[4] G. Centi, I. Manenit, A. Riva, F. Trifiro, Appl. Catal. 9 (1984) 177.
[5] G.J. Hutchings, Appl. Catal. 72 (1991) 1.
[6] K. Wohlfahrt, G. Eming, Hydrocarbon process (1980) 83.
[7] D.A. De Maio, Chem. Eng. (1980) 104.
[8] G. Centi, Catal. Today 16 (1993) 1.
[9] G. Busca, G. Centi, F. Trifiro, V. Lorenzelli, J. Phys. Chem. 90 (1986) 1337.
[10] G.J. Hutchings, R. Higgins, J. Catal. 162 (1996) 153.
[11] J.W. Johnson, D.C. Johnston, A.J. Jacobson, J.F. Brody, J. Am. Chem. Soc. 106 (1984) 8213.
[12] G.J. Hutchings, R. Higgins, Appl. Catal. A: Gen. 154 (1997) 103.
[13] G. Centi, Catal. Today 16 (1993) 5.
[14] G.W. Coulston, S.R. Bare, H.H. Kung, K. Birkeland, G.K. Bethke, R. Harlow, N. Herron, P.L. Lee, Science 275 (1997) 191.
[15] H. Igarashi, K. Tsuji, T. Okuhara, M. Misono, J. Phys. Chem. 97 (1993) 7065.
[16] G. Centi, F. Trifiro, J.R. Ebner, V.M. Franchetti, Chem. Rev. 88 (1988) 55.
[17] L.M. Cornaglia, C. Caspani, E.A. Lombardo, Appl. Catal. 74 (1991) 15.
[18] I. Matsuura, Catal. Today 16 (1993) 123.
[19] B. Schiott, K.A. Jorgensen, Catal. Today 16 (1993) 79.
[20] L. Zeng, W. Ji, Y. Chen, Chem. J. Chin. Univ.-Chin. 20 (1999) 1595.