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Selective oxidation of isobutane to methacrolein over Mo–V–Te–Sb mixed oxide catalysts with different antimony contents

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A series of $MoV_{0.3}Te_{0.23}Sb_x$ ($x = 0$–0.6) mixed oxides were prepared and investigated for the selective oxidation of isobutane. Among them, $MoV_{0.3}Te_{0.23}Sb_{0.5}$ showed the best methacrolein selectivity (as high as 39%), and the yield to methacrolein reached 7.8% at 20.0% isobutane conversion at 470 °C.

KEY WORDS: isobutane; isobutylene; selective oxidative; methacrolein.

1. Introduction

The direct oxidation of isobutane by molecular oxygen to valuable oxygenated products has attracted much attention in both academia and industry. Various catalyst systems, including heteropoly compounds [1–5], mixed oxide catalysts (such as Mo–V–Sb, Pt/SbO_x, etc) [6–10] and mesoporous materials [11, 12], have been studied for the selective oxidation of isobutane to isobutylene, methacrolein and methacrylic acid. Among them, heteropolyacid (HPA) catalysts have been the most extensively studied system. A sample of $P_{1.1}Mo_{12}V_{1.1}Cu_{0.11}Cs_{1.1}O_y$, which is one of the best heteropolyacid catalysts ever reported, was able to convert isobutane directly into the aldehyde and acid with a respective selectivity of 16.3 and 55.7% at an isobutane conversion of 10.3% at 320 °C [13]. However, a major drawback of these HPA catalysts is the poor thermal stability, e.g. they begin to decompose at elevated temperature around 320 °C, thus considerably decreasing the activity [14].

Mo–V–Te mixed oxides have recently been proposed as active and selective catalysts in the oxidation of propane to acrylic acid [15, 16]. Generally, it has been known that activation of propane is more difficult than isobutane. Recently, Jacobs *et al.* [6, 17] reported that the addition of antimony to Mo–V-based catalysts favors the formation of methacrolein from isobutane. In these cases, isobutane could be selective oxidized to methacrolein and isobutylene with a selectivity of 30 and 43%, respectively, at a relatively low isobutane conversion of 1.9% at 400 °C. This progress, though limited, clearly demonstrated that multi-ingredient mixed oxides catalysts might also be potential catalysts for the selective oxidation of isobutane.

In this work, we attempt to introduce different contents of antimony into the $MoV_{0.3}Te_{0.23}$ catalyst for the selective oxide of isobutane. We found that the addition of appropriate amounts of antimony into the mixed metal oxides can considerably change the redox capability of the catalysts, and hence improve the catalytic performance for the selective oxidation of isobutane to MAL.

2. Experimental

2.1. Catalysts preparation

The Mo–V–Te–Sb catalyst was prepared by a slurry method as described in a literature procedure for the preparation of Mo–V–Te–Nb [18]. Initially, ammonium metavanadate was dissolved in water by heating under stirring, and then ammonium molybdate and different amounts of antimony trioxide were added into the metavanadate solution. The suspension was refluxed at 90 °C for 12 h. After cooling to room temperature, an aqueous solution of telluric acid was added. The slurry was stirred vigorously for 30 min, then concentrated and dried at 120 °C to obtain the catalyst precursor. The catalyst precursor was calcined at 600 °C under a flow of nitrogen for 2 h. The final catalysts had a composition of $MoV_{0.3}Te_{0.23}Sb_x$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6$).

2.2. Catalysts characterization

Surface areas of catalysts were measured from the adsorption isotherms of N_2 at 77 K using the BET method (Micromeritics ASAP2010N). X-ray diffraction patterns (XRD) were collected using a Shimadzu XRD-6000 by the continuous scanning (4°/min) with Cu Kα

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radiation (40 kV, 30 mA). The infrared spectra (IR) of various samples were recorded at room temperature on a NICOLET Impact 410.

2.3. *Catalytic tests*

The reaction was performed in a tubular fixed bed stainless-steel reactor (i.d. 16 mm, length 400 mm) under atmospheric pressure. Each catalytic test was carried out using 1.0 g catalyst, which was granulated into particles of 0.3–0.5 mm size and diluted with 0.5 g SiC particles to prevent temperature gradients and hot spots in the reactor. Under our reaction temperature, the homogeneous reaction can be neglected. Carbon balance was always more than 95%.

The feed was controlled by mass flow controller, and water was fed with mini-pump. The catalytic reaction condition was as follows: feed gas molar ratio O_2: i-C_4H_{10}: $H_2O = 1:1:1$, gas hourly space velocity (GHSV) = 2550 mL h^{-1} $g_{cat}{}^{-1}$. Experiments were carried out in the range of 360 to 480 °C. Gaseous products were analyzed by on-line gas chromatography with a GDX-501 column using FID detection (Shimadzu GC-8A). Other products were absorbed in water and analyzed by a gas chromatograph with an 8% polyethylene glycol sebacate 2% sebacic acid on GDX-501 column using FID detection (Shimadzu GC–8A). Isobutylene (i-$C_4^=$), methacrolein (MAL), methacrylic acid (MAA), CO_x (CO, CO_2), propylene ($C_3^=$) were the main products. Besides, small amounts of methane, propane, acetone, acrolein, acrylic acid, acetic acid were also detected. Generally, conversion and selectivities were measured after 3 h of reaction at each reaction temperature.

3. Result and discussion

3.1. *XRD study*

XRD patterns of various $MoV_{0.3}Te_{0.23}Sb_x$ mixed oxide catalysts are shown in figure 1. In the case of the Sb-free sample, it shows the presence of MoO_3 [JCPDS 5-508], $TeMo_5O_{16}$ [JCPDS 31-874], $(V_{0.07}Mo_{0.93})_5O_{14}$ [JCPDS 31-1437] and Te*M*O (TeVMoO) [15, 19] phases (figure 1a). In the XRD pattern of the $MoV_{0.3}Te_{0.23}Sb_x$ mixed oxide catalyst with antimony below the ratio of Sb/Mo = 0.2, the peaks due to MoO_3 are very weak (figure 1a, b). The incorporation of Sb provokes an increase in the intensities of the peaks corresponding to MoO_3 and the appearance of peaks at $2\theta = 22.1$, 28.2, 36.2, 45.2, and 50.0°, corresponding to Te*M*O (TeVSb-MoO) crystalline phase [15, 19]. With further increasing Sb content ($x \geq 0.2$) in the $MoV_{0.3}Te_{0.23}Sb_x$ catalysts, the intensity of the peaks corresponding to MoO_3 gradually decrease, and the peaks corresponding to $TeMo_5O_{16}$ completely disappear. Notably, when the Sb/Mo ratio reaches 0.6, only Te*M*O phases (might be composed of TeVMoO and/or TeVSbMoO) can be observed in the catalyst, and no peaks due to MoO_3, $(V_{0.07}Mo_{0.93})_5O_{14}$, or $TeMo_5O_{16}$ can be detected, indicating that these crystallites are either absent or present in a highly dispersed state in the catalyst.

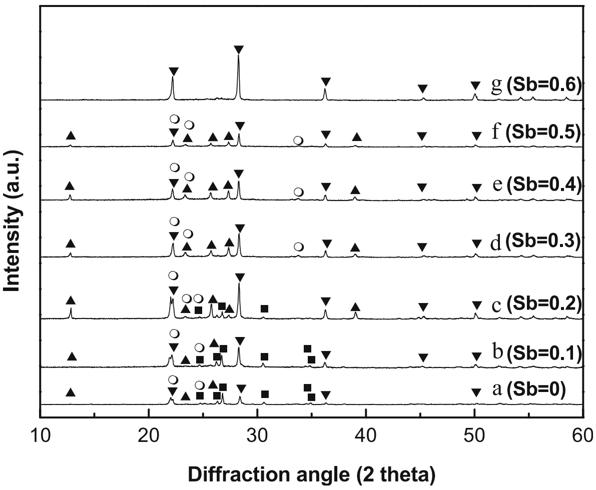

Figure 1. The XRD patterns of $MoV_{0.3}Te_{0.23}Sb_x$ mixed metal oxides catalysts with different antimony contents (from a to g $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 respectively) calcined and activated under the same condition before catalytic testing: (▲) MoO_3; (○) $(V_{0.07}Mo_{0.93})_5O_{14}$; (■) $TeMo_5O_{16}$; (▼) Te*M*O (TeVMoO and/or TeVSbMoO) crystalline phase.

3.2. *FT-IR results*

Figure 2 shows the FT-IR spectra of samples with different antimony contents. The band at 993 cm^{-1}

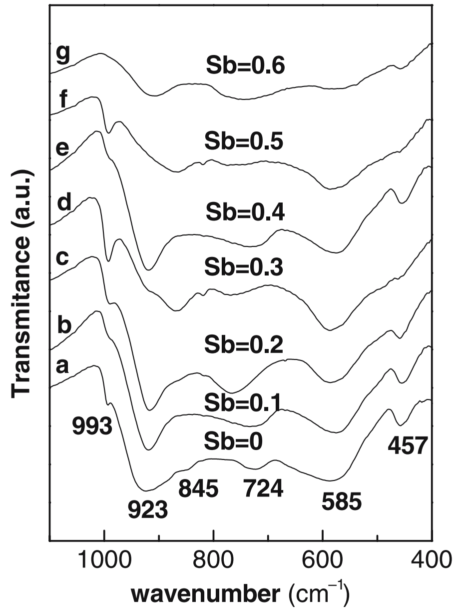

Figure 2. The FT-IR spectra of $MoV_{0.3}Te_{0.23}Sb_x$ mixed oxides catalysts with different antimony contents (from a to g $x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 respectively).

correspond to symmetric stretching vibrations of Mo = O groups in MoO_3, while the bands detected at 845 and 724 cm^{-1} are due to antisymmetric vibrations of Mo–O–M (M = Mo, Sb) bridging bonds [15, 19, 20]. Moreover, bands at ca. 923, 585, and 457 cm^{-1} are probably related to V = O groups and V–O–M bonds [19]. All of these bands shift slightly from their original positions due to the incorporation of Sb atoms to the system. For the sample of $MoV_{0.3}Te_{0.23}Sb_{0.6}$, the peak at 993 cm^{-1} disappears, which is related to MoO_3. Combined with the XRD results, it can be concluded that there is no MoO_3 crystallite in the catalyst.

3.3. Catalytic results

Table 1 shows the catalytic data against reaction temperature for isobutane oxidation of $MoV_{0.3}Te_{0.23}Sb_{0.5}$. Partial oxidation products, i.e., isobutylene, methacrolein, methacrylic acid, propylene, acetone, acetic acid and carbon oxides, have been observed. The conversions of isobutane and oxygen increase with increasing reaction temperature. In the meanwhile, the selectivity to MAL dramatically increases from 12 to 39%, when the temperature changes from 360 to 470 °C. On the other hand, the selectivity to isobutylene simultaneously decreases with the increase of temperature. By increasing the reaction temperature, the selectivity toward CO_x ($= CO + CO_2$) always increases.

The effect of time on stream of the $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst on the product distribution in the oxidation of isobutane at 470 °C is presented in figure 3. Isobutane conversion almost keeps constant during the period of 500 min. Initially, a small decrease in MAL selectivity can be observed during a period of 90 min, after which the selectivity toward the aldehyde increases slightly, and then keeps stable. Isobutylene selectivity increases all along and reaches maximum at 180 min, then keeps steady. On the other hand, the selectivity to CO_x simultaneously decreases at that time, and then keeps steady. This slight decrease of CO_x selectivity is compensated by a small increase in isobutylene formation.

Table 2 shows the BET specific surface area and reaction data of various $MoV_{0.3}Te_{0.23}Sb_x$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6 respectively) catalysts in the selective oxidation of isobutane at 470 °C. As it can be seen, all the samples possess very low specific surface areas whatever the Sb/Mo ratio changed. The Sb-free sample presents a very high isobutane conversion but a relatively low selectivity to MAL. The conversion of isobutane on the $MoV_{0.3}Te_{0.23}Sb_x$ catalysts descends with the addition of antimony content. The MAL selectivity of the catalysts is considerably improved by the addition of small amount of antimony, e.g. the MAL selectivity has reaches to 16% when the Sb/Mo is as low as 0.1. The MAL selectivity increases continuous with the increase of Sb content, and reaches a maximum of 39% MAL selectivity when the Sb/Mo ratio is 0.5. Then the MAL selectivity decreases with further increasing Sb content. It should be pointed out that the product yields ($i\text{-}C_4^= + MAL + MAA$) are not significantly affected by the addition of Sb content, despite the variations in chemical and phase composition. However, the isobutane conversion and the yield of CO_x decrease after the incorporation of Sb. This indicates that the incorporation of Sb can modify the active sites for the transformation of isobutane to MAL. The most remarkable result is the relatively high yield to MAL, a yield of 7.8% can be obtained over $MoV_{0.3}Te_{0.23}Sb_{0.5}$, which is to our knowledge the highest ever reported for the direct oxidation of isobutane.

For comparative purposes, figure 4 shows the variation in selectivities to the main reaction products with the isobutane conversion for both catalysts ($MoV_{0.3}Te_{0.23}Sb_{0.5}$ and $MoV_{0.3}Te_{0.23}$). It could be noticed that at a similar isobutane conversion, $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst shows lower selectivities to CO_x, but higher selectivities toward the partial oxidation products (methacrolein and MAL/MAA) than the Sb-free sample. Therefore, the role of Sb ions, in this case, should be related to the formation of active sites for the selective oxidation, or decrease the amount of complete oxidation sites.

It is generally accepted that the oxidative dehydrogenation of isobutane to isobutylene is the first step in the selective oxidation of isobutane to MAL on

Table 1
Catalytic data of selective oxidation of isobutane at different temperature over $MoV_{0.3}Te_{0.23}Sb_{0.5}$ mixed oxide catalyst[a]

RT (°C)	Conversion (%)		Selectivity (%)						Yield (%)		
	iC_4H_{10}	O_2	$i\text{-}C_4^=$	MAL	MAA	CO_x	$C_3^=$	Others[b]	$i\text{-}C_4^=$	MAL	MAA
360	14.9	22.1	50	12	10	13	6	9	7.5	1.8	1.5
380	17.4	29.0	44	15	12	16	6	7	7.7	2.6	2.1
400	18.2	33.3	38	16	17	18	6	5	6.9	2.9	3.1
420	18.5	36.2	31	24	14	20	6	5	5.7	4.4	2.6
450	19.0	41.0	25	30	12	24	6	3	4.8	5.7	2.3
470	20.0	45.1	19	39	5	26	7	4	3.8	7.8	1.0
480	22.8	64.0	15	32	3	40	8	2	3.4	7.3	0.7

[a] Operating condition: isobutane/oxygen/steam molar ratio of 1/1/1, GHSV = 2550 ml. h^{-1}. g_{cat}^{-1}, $P = 101$ kPa.

[b] Others include acetone, acrolein, acrylic acid, and acetic acid, etc.

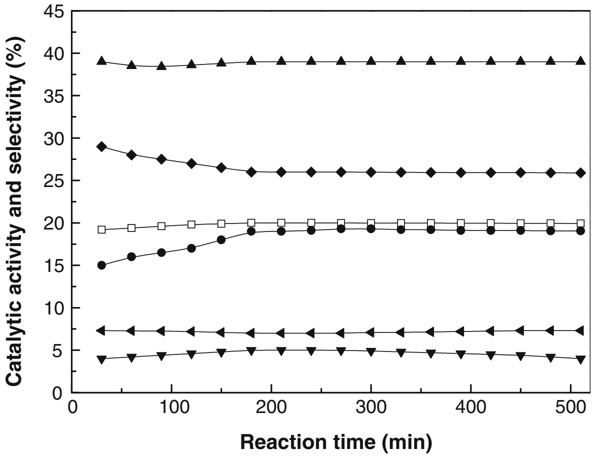

Figure 3. Conversion/selectivity vs. time on stream for isobutane oxidation with $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst. Experimental conditions as in Table 1. Symbols: (□) isobutane conversion; (●)$i\text{-}C_4^=$; (▲) MAL; (▼) MAA, (◆) CO_x; (◀)$C_3^=$.

Table 2
Catalytic data of $MoV_{0.3}Te_{0.23}Sb_x$ catalysts for isobutane oxidation at 470°C[a]

Value of x	$S_{BET}(m^2/g^{-1})$	Conversion (%)		Selectivity (%)						Yield (%)		
		iC_4H_{10}	O_2	$i\text{-}C_4^=$	MAL	MAA	CO_x	$C_3^=$	Others	$i\text{-}C_4^=$	MAL	MAA
0	3.0	31.7	93.4	11	11	9	46	10	13	3.5	3.5	2.9
0.1	1.5	28.3	80.0	15	16	12	40	9	8	4.2	4.5	3.4
0.2	1.8	26.2	70.7	18	18	13	38	8	5	4.7	4.7	3.4
0.3	2.2	25.8	66.0	19	21	11	35	9	5	4.9	5.4	2.8
0.4	2.5	22.3	55.5	20	26	6	34	9	5	4.5	5.8	1.3
0.5	2.9	20.0	45.1	19	39	5	26	7	4	3.8	7.8	1.0
0.6	2.6	18.8	47.2	29	22	4	34	7	4	5.5	4.1	0.7

[a]Experimental conditions and symbols as in Table 1.x

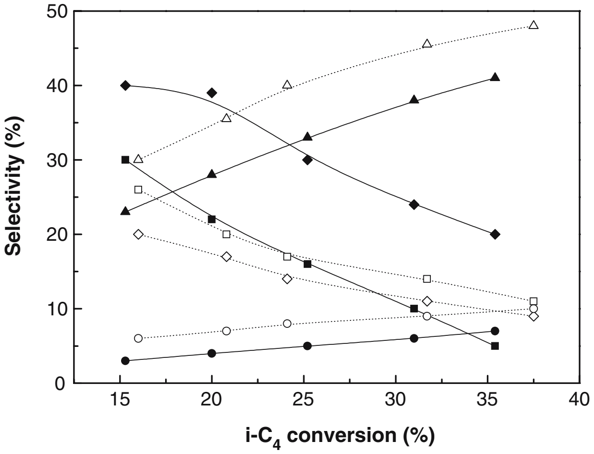

Figure 4. Comparison of the relation between isobutane conversion and selectivity towards the main partial oxidation products for the $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst (filled symbols) and the $MoV_{0.3}Te_{0.23}$ catalyst (open symbols) at 470 °C (◆, ◇: methacrolein; ●, ○: methacrylic acid; ■, □: isobutylene; ▲, △: CO_x).

Mo–V–Sb-based catalysts [17, 21]. Then the isobutylene intermediate is oxidized to MAL. T. Shishido and coworkers [21] report that the oxidative dehydrogenation of isobutane to isobutylene mainly proceeds over $VSb_{10}O_x$ containing $VSbO_4$ and $\alpha\text{-}Sb_2O_4$ phases, and the addition of molybdenum species to $VSbO_4$ and/or $\alpha\text{-}Sb_2O_4$ increases the selectivity to MAL. Jacobs *et al.* [6, 17, 22] also reports that the addition of antimony to Mo–V-based catalysts remarkably increases the selectivity to MAL. Besides, Botella *et al.* [15] proposes that the activation of propane proceeds over V-sites (e.g. MoOVOMo) and the oxidation of propene proceeds over Mo sites (e.g. TeOMoOTe) by the study of Mo–V–Te–Nb-based catalysts.

According to our results, the addition of a small amount of Sb to $MoV_{0.3}Te_{0.23}$ could observably increase the MAL selectivity and yield. In addition, the performance of $MoV_{0.3}Te_{0.23}Sb_{0.6}$ catalyst, which contains only pure Te*M*O (TeVMoO and/or TeVSbMoO) crystalline phase, is worse than that of $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst in the selective oxidation of isobutane (Table 2). Thus, it seems that the active sites for the transformation of isobutane to MAL should be a mixture of binary or multitudinous phases. In another words, the oxidative dehydrogenation of isobutane to isobutylene should mainly proceed over V-containing and/or V-Sb-containing phases (e.g. $(V_{0.07}Mo_{0.93})_5O_{14}$ crystalline phase), and the oxidation of isobutylene to MAL should mainly proceed over Mo-containing phases (e.g. Te*M*O crystalline phase).

Nevertheless, concerning the complexity of multi-ingredient mixed oxides, a further effort should be made to study the nature of the active sites and the reaction mechanism for the selective oxidation of isobutane over these multicomponent catalysts.

4. Conclusions

The reactivity of antimony doping in the $MoV_{0.3}Te_{0.23}$ mixed metal oxide catalysts were investigated for the selective oxidation of isobutane. These catalysts showed a definite activity for the selective oxidation isobutane. It has been found that the incorporation of a certain amount of Sb has a positive effect in MAL selectivity. Under our test conditions, the sample of $MoV_{0.3}Te_{0.23}Sb_{0.5}$ catalyst achieved the best MAL selectivity (39%) and the highest yield (7.8%) for MAL.

Acknowledgments

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