



Editor's choice paper

Promotive effect of Bi component on propane partial oxidation over MoBiTeO_x/SiO₂ catalystsYiming He^{a,*}, Ying Wu^c, Xiaodong Yi^b, Weizheng Weng^b, Huilin Wan^{b,**}^a Department of Materials Physics, Zhejiang Normal University, Jinhua 321004, China^b State Key Laboratory for Physical Chemistry of the Solid Surfaces, Xiamen University, Xiamen 361005, China^c Institute of Physical Chemistry, Zhejiang Key Laboratory for Reactive Chemistry on Solid Surfaces, Zhejiang Normal University, Jinhua 321004, China

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ABSTRACT

A series of MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts was prepared and catalytic performance of propane partial oxidation to acrolein was tested. The addition of low amount of Bi component to MoTeO_x/SiO₂ catalysts was found to significantly promote acrolein selectivity. The catalyst structure and redox properties were investigated by means of X-ray powder diffraction, Raman spectroscopy, *in situ* Raman spectroscopy, X-ray photoelectron spectroscopy, and H₂-TPR techniques. Results indicate that the Bi promotive effect can be attributed to two possible reasons. One is that the Bi component promotes the dispersal of MoO₃. The isolation effect results in acrolein selectivity increase. Another reason is that Bi doping enhances lattice oxygen diffusion and increases the amount of surface active oxygen, which is responsible for the oxidation of intermediate propylene to acrolein.

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1. Introduction

Selective oxidation of alkane to oxygenate or alkene for the utilization of hydrocarbons resources has been attracting much attention. A great deal of research has already been conducted to develop a catalyst system and understand catalytic properties [1–6]. Among the most frequently cited catalysts, vanadium and molybdenum-based catalysts deserve particular interest because of their high catalytic activity [1–6]. To improve the catalytic behavior of such catalysts and enhance the oxygenate or alkene productivity in terms of both yield and selectivity, a usual approach is incorporating well-chosen additional elements in the catalyst formulation [7–11]. Ueda and Oshihara [7] reported Mo–V–M–O (M = Al, Ca, Bi, Sb and Te) complex mixed oxide catalysts for partial propane and ethane oxidation. In ethane oxidation to ethene and to acetic acid, Mo–V–M–O (M = Al, Ca, Bi) catalyst is moderately active. On the other hand, Mo–V–M–O (M = Sb and Te) was found to be extremely active in the oxidative dehydrogenation and propane oxidation to acrylic acid. Fan et al. [8] reported Ce-doped BiVMoO mixed oxide catalyst for selective propane oxidation. Introducing the proper amount of cerium promotes selectivity to acrolein and can moderately enhance the oxidative ability. The above-mentioned cases show that the additive exhibits a great effect on catalyst activity and

product distribution. Understanding the role of additives in devising a catalyst that works well for the selective production of light alkane is very important.

In previous studies, MoBiTeO_x/SiO₂ catalyst was reported to be an effective catalyst for the selective oxidation of propane to acrolein [12,13]. Tellurium (Te) was considered as the α-H abstraction center for the intermediate propylene in addition to the isolation effect. Meanwhile, the bismuth (Bi) component is widely accepted as being responsible for the α-H abstraction of chemisorbed propylene in propane partial oxidation [14]. That the MoBiTeO_x/SiO₂ catalysts contain the two elements that play the same role in reaction is an interesting discovery. Is the Bi component necessary in the catalysts for propane partial oxidation? What is the role of the Bi component in MoBiTeO_x/SiO₂ catalysts? To resolve these questions, a series of MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts containing the same Mo/Te molar ratio was prepared and tested in partial oxidation of propane. A multi-technique approach including a variety of methods capable of providing insight into bulk and surface physicochemical properties, was applied to study Bi promotion effect in catalytic performance.

2. Experimental

2.1. Preparation of catalysts

Ammonium heptamolybdate (NH₄)₆Mo₇O₂₄·4H₂O (>99%), bismuth nitrate Bi(NO₃)₃·4H₂O (>99%), telluric acid H₂TeO₄·2H₂O (>99%), and silica SiO₂ used as the reference, were purchased

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commercially and used without further purification. SiO₂ supported MoBiO_x, MoTeO_x, TeO_x, and MoO_x catalysts, which had the same molar ratio (6 mol%) of the loading element to silicon (Si), were prepared via the impregnating method. Taking the MoBiO_x/SiO₂ ($[n_{\text{Mo}} + n_{\text{Bi}}]/n_{\text{Si}} = 6 \text{ mol\%}$) catalysts as an example, solutions of (NH₄)₆Mo₇O₂₄ and Bi(NO₃)₃ were first mixed. An appropriate amount of SiO₂ was then added, and the resulting mixture was allowed to impregnate at room temperature for 5 h. The water in the solution was evaporated at a temperature of 80 °C. After drying at 100 °C for 12 h, the sample was calcined at 600 °C for 4 h and then cooled to room temperature. The catalyst was obtained as the final product.

SiO₂ supported MoBiTeO_x mixed oxide catalysts were prepared via a two-step impregnating method. First, stoichiometric amounts of bismuth and molybdenum ($[n_{\text{Mo}} + n_{\text{Bi}} + n_{\text{Te}}]/n_{\text{Si}} = 6 \text{ mol\%}$) were loaded onto SiO₂. After calcination at 600 °C for 2 h in air, the SiO₂ mixture was then impregnated with stoichiometric amounts of Te, dried at 100 °C, and calcined at 600 °C for 4 h. The catalyst was obtained as the final product.

2.2. Catalytic testing

Catalytic testing was performed in a tubular fixed bed flow quartz reactor (inside diameter [i.d.] = 6 mm) with 100 mg catalyst under atmospheric pressure, gaseous hourly space velocity (GHSV) = 7200 mL (g-cat)⁻¹ h⁻¹, and C₃H₈/O₂/N₂ = 1.2:1:4. Propane oxidation reaction was performed at 550 °C. The reactants and products were analyzed using two on-line gas chromatography detectors with three columns. A TDX-601 column and an Al₂O₃ column impregnated with squalane (GC-950, TCD) were used for the separation of C₃H₈, C₃H₆, C₂H₄, CO, and CO₂. A GDX-103 column (GC-950, FID) was used for the acrolein, acetone, and propanal separation. Exit gases were heated to 120 °C to prevent product condensation. The catalysts were allowed to equilibrate under reaction conditions for at least 30 min.

The oxidation of propylene was performed with pulse method at 400 °C. Pulse of 100 μL propylene was introduced into a stream of N₂ carrier gas passing through the catalyst bed at a flow rate of 20 mL/min. The products were analyzed by gas chromatography.

2.3. Characterization of catalysts

N₂ adsorption and desorption isotherms were recorded on an automated Micromeritics Tri-Star3000 apparatus at LNT. X-ray diffraction (XRD) analysis of the catalysts was carried out on a PANalytical X'Pert Pro diffractometer using Cu Kα ($\lambda = 0.15406 \text{ nm}$) radiation (40 kV/40 mA).

Raman spectra were recorded on a Renishaw-UV-vis Raman System 1000 spectrometer with a CCD detector. Raman excitation at 325 nm provided by the He–Cd laser source was used for excitation, and the laser power applied on samples was 7 mW. *In situ* Raman experiments were also carried out on the same Raman system using a home built high temperature *in situ* Raman cell [15]. Powder samples were pressed into the sample holder equipped with a thermocouple placed underneath for temperature control. In order to avoid the temperature effect all *in situ* Raman spectra were collected after the cell temperature was cooled down to room temperature.

H₂-TPR experiment was carried out using a temperature-programmed reaction-TCD instrument. The sample (ca. 20 mg) was exposed to a 20 mL/min 5% H₂/Ar flow, and heated at a rate of 10 °C/min.

X-ray photoelectron spectroscopy (XPS) measurements were performed with a Quantum 2000 Scanning ESCA Microprobe instrument using AlKα. The C 1s signal was set to a position of 284.6 eV. The measurement error is ±0.2 eV.

3. Results and discussion

3.1. Catalytic performance

The catalytic performance of the catalysts in selective oxidation of propane to acrolein is shown in Table 1. No reaction occurred over quartz sand, indicating that the contribution of homogeneous reaction could be ignored. The MoO_x/SiO₂ catalyst showed the highest activity, but the propane was mainly converted to CO_x, and the selectivity toward acrolein was low. Bismuth and Te doping to MoO_x/SiO₂ catalyst promoted acrolein selectivity at the expense of propylene and CO_x selectivity. By two-step Bi and Te optimization, Mo₁Bi_{0.05}Te_{0.05}O_x/SiO₂ and Mo₁Bi_{0.05}Te_{0.1}O_x/SiO₂ catalysts were observed to show the highest catalytic performance. About 5.0% acrolein yield was obtained at 550 °C, C₃H₈/O₂/N₂ = 1.2/1/4. However, MoBiTeO_x/SiO₂ catalyst activity was not high, which might be due to the limited ability of molybdenum oxide to activate propane. To obtain high performance, propane homogeneous reaction is needed for the MoBiTeO_x/SiO₂ catalyst. Under optimum reaction conditions (530 °C, C₃H₈/O₂/N₂ = 1.2/1/4, and bigger quartz tube reactor [i.d. = 10 mm]), the Mo₁Bi_{0.05}Te_{0.05}O_x/SiO₂ and Mo₁Bi_{0.05}Te_{0.1}O_x/SiO₂ catalysts showed high catalytic performance. Moreover, about 14.0% acrolein yield (STY_{ACR} = 487 g kg_{cat}⁻¹ h⁻¹) was obtained with the help of homogeneous reaction. The catalytic performance of MoTeO_x/SiO₂ catalysts is also listed in Table 1. These catalysts were found to show lower acrolein selectivity and yield compared with MoBiTeO_x/SiO₂ catalyst. The Bi component is clearly needed to obtain higher catalytic performance, although Bi concentration in the MoBiTeO_x/SiO₂ catalyst is very low. Numerous researchers reported that Te plays the same role as Bi in propane partial oxidation [16]. However, in MoBiTeO_x/SiO₂ catalysts, Bi and Te appeared to play different roles. The role of the Bi component is thus worth studying.

3.2. Effect of Bi component on the catalyst specific surface area and structure

The BET surface areas of catalysts are shown in Table 2. The specific surface area of the amorphous silica sample equals 277 m² g⁻¹ as shown by N₂ adsorption. The loading of Mo, Bi and Te decreased the BET surface area. With the increase of Te content, the specific surface areas of MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts decreased, which might be one of the reasons for their decreased activities. The MoBiTeO_x/SiO₂ catalyst has larger specific surface areas than MoTeO_x/SiO₂ catalyst, indicating that Bi doping could increase catalyst surface area.

Table 2 also provides the XPS results of catalysts. The binding energy (BE) of the Mo 3d_{5/2} changed from 232.6 to 232.3 eV. The BE of MoO₃ was 232.6 eV, while Mo⁴⁺ cations were observed at 229.6 eV [17]. These changes in BE indicate that Mo⁶⁺ was present on the surface of these catalysts. In the same way, the Bi and Te valence state of the catalysts was determined to be +3 and +4, respectively, based on the literature reported [18,19]. By calculating the peak area of their core-level spectra, the molar ratios of Mo/Si, Bi/Si, and Te/Si can be obtained on the catalyst surface. Results indicate that MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts have similar Mo(Te)/Si ratios, and that bismuth concentration in the MoBiTeO_x/SiO₂ catalyst is very low. These results are consistent with their theoretical value.

The catalyst powder X-ray diffraction patterns are shown in Fig. 1. The wide hump between 15° and 35° could be assigned to amorphous SiO₂. In most of the catalysts, the presence of MoO₃ was characterized by reflections at $2\theta = 12.7^\circ$, 23.3° , 25.7° , 27.3° , and 38.9° (JCPDS 05-0508). With the increase of Te content, peaks of the MoO₃ phase weakened, indicating that the Te component

Table 1
Effect of active component on catalyst performance.

Catalysts	Conv. (%)	S _{ACR} (%)	S _{C⁻} (%)	S _{CO_x} (%)	S _{Others} (%)	Y _{ACR} (%)	STY _{ACR} (g kg _{Cat} ⁻¹ h ⁻¹)
^a Quartz sand	Trace	–	Trace	–	Trace	–	–
MoO _x /SiO ₂	19.7	9.8	20.8	56.4	13	1.9	66
Mo ₁ Bi _{0.05} O _x /SiO ₂	17.4	19.6	16.0	54.1	10.3	3.4	118
Mo ₁ Bi _{0.1} O _x /SiO ₂	16.0	19.8	18.4	53.5	8.3	3.1	108
Mo ₁ Bi _{0.2} O _x /SiO ₂	14.2	21.6	17.8	49.8	10.8	3.0	104
Mo ₁ Bi _{0.5} O _x /SiO ₂	10.8	27.2	12.3	45.9	14.6	2.9	101
Mo ₁ Bi ₁ O _x /SiO ₂	9.5	26.4	12.3	44.7	16.6	2.5	87
Mo ₁ Bi _{0.05} Te _{0.02} O _x /SiO ₂	13.1	32.9	13.7	42.4	11.0	4.2	146
Mo ₁ Bi _{0.05} Te _{0.05} O _x /SiO ₂	12.9	39.6	10.4	34.3	15.7	5.1	177
Mo ₁ Bi _{0.05} Te _{0.1} O _x /SiO ₂	12.3	40.1	9.3	36.0	14.6	4.9	171
Mo ₁ Bi _{0.05} Te _{0.2} O _x /SiO ₂	11.7	35.2	8.6	43.0	13.2	4.1	143
Mo ₁ Bi _{0.05} Te _{0.5} O _x /SiO ₂	10.2	34.5	4.6	46.8	14.1	3.5	122
Mo ₁ Bi _{0.05} Te _{1.0} O _x /SiO ₂	9.6	32.5	4.3	49.3	13.9	3.1	108
Mo ₁ Te _{0.05} O _x /SiO ₂	13.0	26.7	13.1	47.2	13.0	3.6	125
Mo ₁ Te _{0.1} O _x /SiO ₂	12.5	33.5	7.5	47.6	11.4	4.1	143
Mo ₁ Te _{0.2} O _x /SiO ₂	12.5	29.4	8.6	49.3	12.7	3.7	129
Mo ₁ Te _{0.5} O _x /SiO ₂	12.2	26.8	6.8	54.3	12.1	3.3	115
Mo ₁ Te ₁ O _x /SiO ₂	10.7	22.6	7.1	55.1	15.2	2.4	84

Notes: S: selectivity; ACR: acrolein; C⁻: propene; CO_x: CO + CO₂, Others: products CH₄, C₂H₆, C₂H₄, C₂H₄O, propanal, and acetone; STY: space time yield.

^a With the same volume of catalyst.

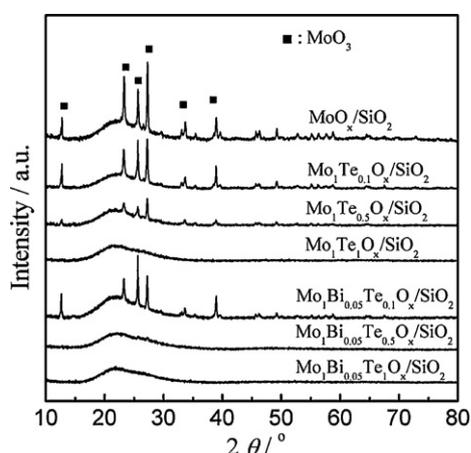


Fig. 1. XRD patterns of catalysts.

facilitated the dispersal of Mo oxides on SiO₂. In addition, MoO₃ phase was found to disappear on Mo₁Bi_{0.05}Te_{0.5}O_x/SiO₂ catalyst, but MoO₃ peaks on Mo₁Te_{0.5}O_x/SiO₂ could still be observed. The Bi component also appears to promote Mo oxide dispersal.

The Raman spectra of MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts are shown in Fig. 2. On the MoO_x/SiO₂ catalyst, MoO₃ was the only phase observed at 998, 821, 666, 342, and 288 cm⁻¹ [20]. After the Te component was doped into the MoO_x/SiO₂ catalyst, a weak band at 943 cm⁻¹ which could be assigned to surface polymolybdate species was observed [20]. With the increase in Te content, the polymolybdate species grew at the expense of MoO₃, indicating that chemical reactions existed between Mo oxide and Te oxides.

Table 2
BET and XPS results of catalysts.

Catalysts	BET (m ² g ⁻¹)	Binding energy (eV)			Surface atomic ratio (%)		
		Mo 3d _{5/2}	Bi 4f _{7/2}	Te 3d _{5/2}	Mo/Si	Bi/Si	Te/Si
MoO _x /SiO ₂	159	232.6	–	–	5.0	–	–
Mo ₁ Bi _{0.05} O _x /SiO ₂	130	232.3	159.5	–	4.0	0.3	–
Mo ₁ Te _{0.1} O _x /SiO ₂	73	232.4	–	576.3	3.8	–	0.5
Mo ₁ Te _{0.5} O _x /SiO ₂	33	232.5	–	576.4	3.2	–	1.2
Mo ₁ Te ₁ O _x /SiO ₂	28	232.5	–	576.4	2.6	–	2.1
Mo ₁ Bi _{0.05} Te _{0.1} /SiO ₂	158	232.5	159.4	576.4	3.5	0.12	0.7
Mo ₁ Bi _{0.05} Te _{0.5} /SiO ₂	76	232.6	159.6	576.2	3.0	0.08	1.5
Mo ₁ Bi _{0.05} Te ₁ /SiO ₂	64	232.5	159.5	576.1	3.0	0.05	2.1

Through this reaction, the polymolybdate species formed by the Mo–O–Te bonds and the growth of crystalline MoO₃ was prevented. Assigning the peaks to amorphous Te-polymolybdate-type species would thus be more logical. The same species was also found in the MoBiTeO_x/SiO₂ catalysts. No obvious signals associated with bismuth were observed. However, polymolybdate species was also found in the Mo₁Bi_{0.05}O_x/SiO₂ catalyst (Fig. 2B). Through certain chemical interactions, Mo and Bi oxide can also form the polymolybdate species. This result suggests that the low amount of Bi additive in the MoBiTeO_x/SiO₂ catalyst might be incorporated into the Te-polymolybdate species. Given that Bi³⁺ and Te⁴⁺ have similar outmost electronic structures and ion radii, some of the tellurium might possible be substituted with bismuth.

3.3. Effect of Bi component on catalyst redox property

In the section above, location of the Bi component in the MoBiTeO_x/SiO₂ catalyst was analyzed. The Bi component was found incorporated into the Te-polymolybdate species, wherein the substitution of Te⁴⁺ by Bi³⁺ might occur. The cation substitution was reported to enhance the rate of oxygen diffusion and alter redox properties [8,21]. Thus, redox properties of MoBiTeO_x/SiO₂ might change compared with the MoTeO_x/SiO₂ catalyst. To investigate these changes, *in situ* Raman and H₂-TPR experiments were carried out.

Since the changes induced by bismuth mainly lay on the Te-polymolybdate species, the Mo₁Te₁O_x/SiO₂ and Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalysts were chosen as the research objects. Fig. 3 shows the *in situ* Raman spectra of the Mo₁Te₁O_x/SiO₂ and Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalysts. As shown in Fig. 3A, significant structure changes were observed after the exposure of

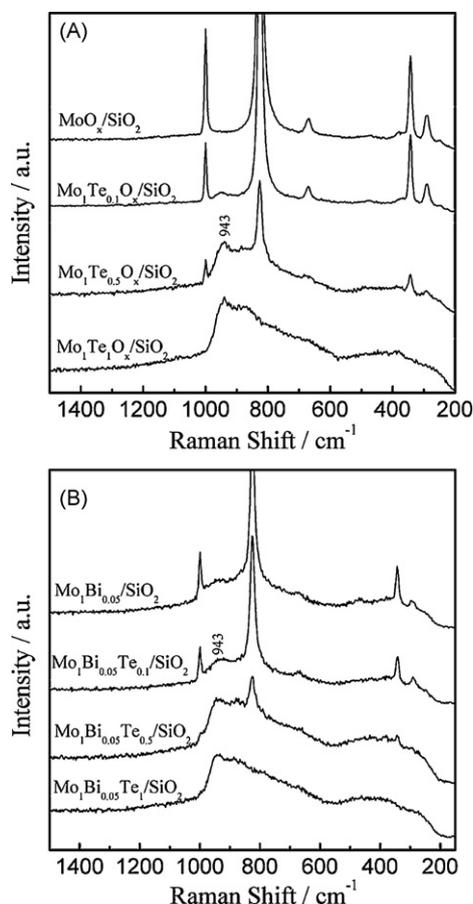


Fig. 2. Raman spectra of (A) MoTeO_x/SiO₂ and (B) MoBiTeO_x/SiO₂ catalysts.

Mo₁Te₁O_x/SiO₂ to 5% H₂/Ar flow for 20 min. The MoO₃ Raman bands appeared and the band intensity of Te-polymolybdate species significantly weakened. With calcination time increase, the MoO₃ bands (998, 821, and 666 cm⁻¹) became stronger, while the bands corresponding to Te-polymolybdate (943 and 880 cm⁻¹) disappeared. The analogous phenomenon was also observed on the Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalyst. As shown in Fig. 3B, after H₂/Ar-calcination, MoO₃ appeared accompanied by the declining Te-polymolybdate bands.

In general, MoO₃ is easily reduced by the reducing gas (such as H₂) at a high temperature [22]. Although the result in Fig. 3 appears strange, an explanation could be obtained from the H₂-TPR experiment. As shown in Fig. 4, several reduction peaks which appeared at near-identical temperatures were observed for the Mo₁Te₁O_x/SiO₂ and Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalysts. Based on literature assignments [23] and the H₂-TPR profiles of the MoO_x/SiO₂ and TeO_x/SiO₂ catalysts, the first peak may be assigned to the reduction of the Te–O species, while the others may be assigned to the Mo–O species. The Te–O species are clearly reduced much faster than the Mo–O species in the catalysts. Thus, when Mo₁Te₁O_x/SiO₂ or Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalyst is exposed to H₂/Ar atmosphere at 500 °C, the Te–O species would first be reduced to metal Te. As is already known, metal Te is volatilized easily at high temperatures [24]; hence, some Te components in the catalyst would be volatilized, causing the Mo–O–Te bonds to break and part of the Te-polymolybdate to subsequently collapse. Any Mo–O species that have not been reduced are apt to form part of the MoO₃ phase.

Aside from structure change, the different stability levels of Te-polymolybdate species in the Mo₁Te₁O_x/SiO₂ and Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalysts should be noted in Fig. 3. The Te-

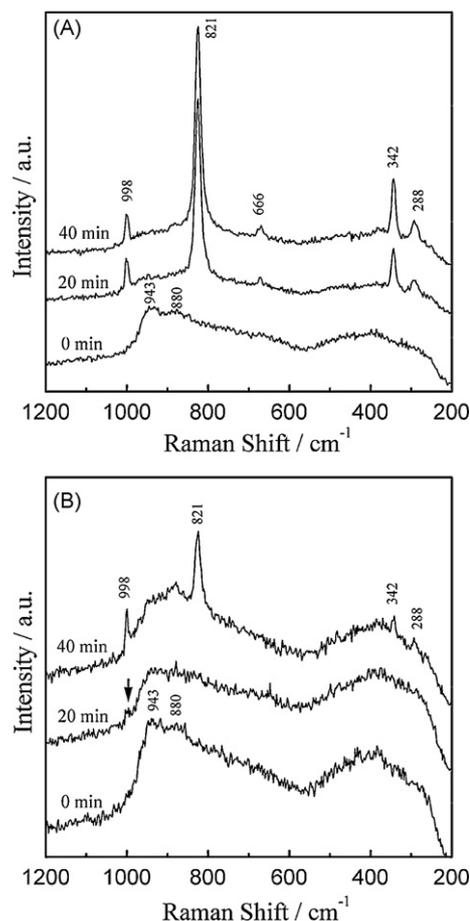


Fig. 3. *In situ* Raman spectra of (A) Mo₁Te₁O_x/SiO₂ and (B) Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalyst calcined in 5% H₂/Ar atmosphere at various times.

polymolybdate containing Bi³⁺ cation showed higher stability than that without a Bi component in the reducing atmosphere. Even after being calcined in 5% H₂/Ar flow for 40 min, the Raman bands of Te-polymolybdate species were still strong (Fig. 3B). Ueda et al. [25,26] studied the MoTeMO (M = Co, Mn, Fe) mixed oxide catalysts for propylene oxidation reaction. They found that Co, Mn and Fe could promote oxygen diffusion to the active site (Te–O species) aside from activating molecular oxygen. Thus, the Te could stay in a highly oxidized state and the vaporization of Te component is suppressed. In the case of MoBiTeO_x/SiO₂ catalyst, the

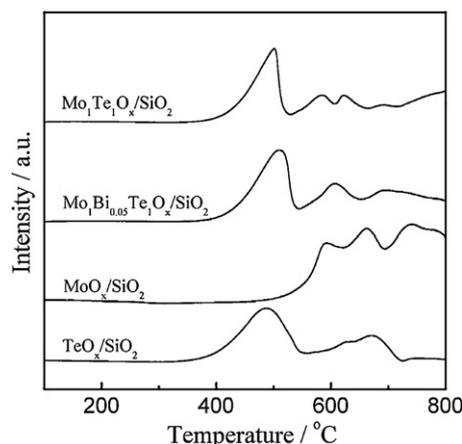


Fig. 4. H₂-TPR profiles of catalysts.

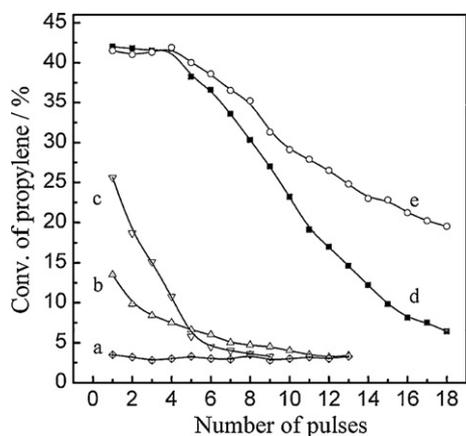


Fig. 5. Propylene conversion in the depletive oxidation over samples as a function of the number of pulses: (a) MoO_x/SiO₂; (b) Mo₁Bi_{0.05}O_x/SiO₂; (c) Mo₁Te_{0.05}O_x/SiO₂; (d) Mo₁Te₁O_x/SiO₂; (e) Mo₁Bi_{0.05}Te₁O_x/SiO₂.

doped Bi³⁺ seems to play a role similar to those of Co, Mn, and Fe. The cation substitution of Te⁴⁺ by Bi³⁺ might generate anion vacancy in the catalyst, which could promote lattice oxygen migration. The Te–O species could obtain the lattice oxygen supplement more easily during the reduction reaction. Therefore, the deep reduction of Te⁴⁺ to Te⁰ was partly suppressed and the stability of Te–polymolybdate species in the reduced atmosphere was improved.

3.4. Propylene pulse experiments

The pulse experiment is a useful technique to evaluate the amount of active oxygen species in catalysts [8,27]. It can also provide useful information about oxygen mobility. To prove the promotive effect of Bi cations on lattice oxygen migration, the propylene pulse experiment was carried out. Fig. 5 shows the effect of progressive reduction by repeatedly passing slugs of propylene over the samples under standard conditions at 400 °C. The propylene conversion and product distribution were differentiated vastly on the samples. As shown in Fig. 5, the MoO_x/SiO₂ catalyst (curve a) shows lower activity, which might be due to the lack of an α-H abstraction center in Mo oxide [28]. The α-H abstracting procedure is the rate determining step for the oxidation of propylene to acrolein, and both Bi and Te could abstract the α-H of propylene [16]. Thus, the addition of Bi or Te into MoO_x/SiO₂ catalyst improved propylene conversion. The Mo₁Te_{0.1}O_x/SiO₂ catalyst shows higher activity than Mo₁Bi_{0.05}O_x/SiO₂, which indicates that Te has stronger ability in α-H abstraction. These results are consistent with our previous work [12,13]. With pulse number increase, the propylene conversion of Mo₁Te_{0.1}O_x/SiO₂ decreased rapidly, which could be attributed to the low amount of Te. When the Te⁴⁺ was reduced by propylene after several pulses, the catalyst lost the ability to activate propylene.

The testing results of Mo₁Te₁O_x/SiO₂ and Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalysts are also listed in Fig. 5. They show higher activity than the other samples due to the large amount of active sites (Te–O species). With pulse number increase, the two catalysts lost their activity for propylene slowly, but the deactivation rate of Mo₁Bi_{0.05}Te₁O_x/SiO₂ catalyst was smaller than that of Mo₁Te₁O_x/SiO₂ catalyst. At the 18th pulse, the propylene conversion was 19.5% over Mo₁Bi_{0.05}Te₁O_x/SiO₂. However, over Mo₁Te₁O_x/SiO₂ catalyst, the value was 6.4%. Considering that the catalyst have nearly the same amount of active sites (Te–O species), we can conclude that the Te–O species in Mo₁Bi_{0.05}Te₁O_x/SiO₂ was more difficult to reduce. The addition of bismuth clearly promoted lattice oxygen migration in the catalyst. The oxygen could migrate

from the volume phase to the surface-reduced sites. Thus, Te reduction could be partly suppressed and the deactivation of the catalyst was retarded.

3.5. Discussion

Although both Bi and Te are widely accepted to be responsible for the α-H abstraction of chemisorbed propylene in propane partial oxidation, in the current case of MoBiTeO_x/SiO₂ catalyst, the Bi component was found to play a different role. The addition of a small amount of bismuth into MoTeO_x/SiO₂ further promotes selectivity to acrolein. To elucidate the Bi promotive effect, a multi-technique approach was applied. Characterization results indicate that increased acrolein selectivity of the MoBiTeO_x/SiO₂ catalyst might result from two factors.

The first factor could be ascribed to the isolation effect. Structure investigations have proven that the additive Bi promoted MoO₃ dispersal. Thus, the doping of Bi could geometrically break up Mo–O–Mo chains of the MoO₃ structure, thereby generating smaller and spatially isolated domains of Mo–O moieties (polymolybdate species) on the surface. These smaller oxygen groupings were postulated to be more selective than the base Mo–O–Mo chains because of the limited number of available surface oxygen within each given isolated domain [29]. Actually, previous studies have reported that MoO₃ was the suggested phase for propane activation and that the polymolybdate was responsible for the subsequent oxidation of propylene to acrolein [12,13].

The second factor is that Bi doping increases the amount of surface active oxygen of Te–polymolybdate species. Structure characterizations indicate that the bismuth was incorporated in the Te–polymolybdate and might be a substitute for the Te site. The cation substitution of Te⁴⁺ by Bi³⁺ could generate anion vacancy, promote lattice oxygen diffusion, and increase the amount of surface active oxygen. Thus, the selective oxidation of intermediate propylene to acrolein over Te–polymolybdate could be more efficient, and selectivity to acrolein could increase. In reality, because partial oxidation of propane to acrolein is a complex process which needs the cooperation of multi-centers, the catalyst with high performance usually contains several metal elements. Cation substitution is a common phenomenon in these composite oxide catalysts. The most representative case is the BiMoO based catalyst [29–34]. Taking the AgBiMoVO composite catalyst as an example, Moro-oka et al. [30–32] reported that the addition of Ag promoter into BiMoVO catalysts significantly enhances acrolein selectivity. They found that Bi³⁺ was substituted by Ag⁺. This substitution created anion vacancy in the catalyst and promoted the diffusion of lattice oxygen. The higher catalytic performance was then obtained. In this study using MoTeBiO_x/SiO₂ catalyst, the Bi promoter was believed to work in a similar manner to that reported by Moro-oka et al. The XRD result shows that the Te–polymolybdate species is an amorphous phase. Directly proving the cation substitution of Te⁴⁺ by Bi³⁺ is impossible. However, the *in situ* Raman and H₂-TPR experiments have proven that oxygen diffusion was enhanced in the Bi-doped Te–polymolybdate, which is usually induced by cation substitution [8,21]. The lattice oxygen could migrate to the active site (Te–O species) more easily in the Bi-doped Te–polymolybdate. In other words, enhanced oxygen diffusion promoted the amount of surface active oxygen species during the reaction. This result was also proven by the propylene pulse experiments (Fig. 5). Larger amounts of propylene were oxidized over Bi-doped Te–polymolybdate species (Mo₁Bi_{0.05}Te₁O_x/SiO₂) than those over Te–polymolybdate species (Mo₁Te₁O_x/SiO₂).

In addition, the Bi component is reported to activate molecular oxygen during reaction [29,34], which could facilitate the redox cycle and keep the tellurium element in a highly oxidized state.

The contribution in activating molecular oxygen might be another possible reason for the promotive effect.

4. Conclusions

The role of the Bi component in propane partial oxidation over MoBiTeO_x/SiO₂ catalysts was studied. The catalytic testing showed that the doping of low amounts of Bi to MoTeO_x/SiO₂ could significantly promote acrolein selectivity. To explain the promotive effect, MoTeO_x/SiO₂ and MoBiTeO_x/SiO₂ catalysts were characterized using different techniques. The isolation effect and the increased surface active oxygen species which is responsible for the oxidation of propylene to acrolein were considered as possible reasons for the promotive effect. Additionally, the contribution of α-H abstraction and activation of molecular oxygen, which are considered as the conventional role of Bi, could not be excluded.

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