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Super high selectivity of acrolein in oxidation of propene on molybdenum promoted hierarchical assembly of bismuth tungstate nanoflakes

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#### ABSTRACT

The catalytic properties of well-defined hierarchically assembled  $Bi_2WO_6$  nanoflakes with surface dispersed molybdena have been studied with selective oxidation of propene as probe reaction. The adsorption of oxygen causes the decrease in the conductivity of  $Bi_2WO_6$ , demonstrating its nation of n-type semiconductor. The adsorption of oxygen gains electrons from the conduction band of  $Bi_2WO_6$  to produce oxygen species active for propene reaction at low temperatures, which, however, gives mainly  $CO_x$  as products. The modification by surface molybdena significantly inhibited the total oxidation reaction of propene over the  $Bi_2WO_6$ , while dramatically increased the conversion of propene and selectivity to acrolein simultaneously, without the formation of acrylic acid. The characterization of conductivity measurements, H2-TPR, O2-TPD, XPS and TPSR indicated that the thermally excited electrons from the Bi<sub>2</sub>WO<sub>6</sub> were combined with surface dispersed molybdena and resulted in an extraordinary increase of selective oxidation performance. The unique effects of the hierarchically assembled  $Bi_2WO_6$  nanoflakes on the catalytic property of molybdena were discussed and the mechanism of the catalyst for the selectively catalytic oxidation was proposed. The results are useful to design novel catalysts for important reactions with nano concepts.

Keywords: selective oxidation; bismuth tungstate; molybdenum oxide; propene; acrolein.

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#### 1. Introduction

The selective oxidation of propene into useful functionalized chemicals is an extremely important reaction, since it produces a series of valued chemicals, including acrolein, acrylic acid, acetone and propene epoxide [1-4]. In 1957, Standard Oil of Ohio (Sohio) discovered the bismuth molybdate catalyst system, which yielded a fairly good selectivity but a low propene conversion [5]. It is now clear that with bismuth-molybdenum-based catalysts, heavy modifications, particularly with Bi<sub>2</sub>O<sub>3</sub> and transition metal oxides, are generally required to obtain moderate acrolein selectivity [6-7]. The selective oxidation reaction believed to occur through a classical Mars van Krevelen mechanism. The selectivity depending on the relative ease of desorption or further oxidation of the partially-oxidized chemisorbed species from propene [8]. During the past decades, traditional processes to produce acrolein by selective oxidation of propene are energy-intensive and inefficient since the processes involve multiple steps and create large quantities of by-products. The main byproducts are acrylic acid and carbon oxides in addition to minor products such as aldehyde, acetic acid and formaldehyde. Thus, one challenge of this route is suppressing of by-products and increasing the selectivities of target products in order to avoid trouble in the polymerization of the impurities.

The for partial conventional catalysts oxidation of propene, especially bismuth-molybdena-based oxides [9-10], are reported to improve the catalytic activities by finding the best combination of active components. Many studies concentrated on multicomponent bismuth molybdate catalysts, however, have failed to take into account the fact that specific structural interaction effects among the nano domains of a catalytic assembly significantly promote their catalytic performances. With the progress of materials science, the research on nanocatalysts has been widely spread, the catalysts with high activities and selectivities have been reported using modern technology for material synthesizing featured with the advantages of accurate control of catalytic structure [11-13]. Our previous studies have reported an important finding that the Bi-Mo-O catalyst with bismuth molybdate nanocrystals attached to molybdena nanobelts as oxidation catalyst showing high performance for propene oxidation with only two metallic elements of Bi and Mo [14], due to the interaction among them causes strong adjustment in structural as well as electronic properties of bismuth molybdate. Similarly,  $Bi_2WO_6$ , as a typical Aurivillius oxide, is a

unique photocatalytic material for solar-energy-conversion, which is ascribed to the excitation of  $Bi_2WO_6$  under visible-light irradiation to generate electron-hole pairs [15-16]. This property makes it useful under thermal excitation to shape and to enhance the property of the catalytic species it supported with the adjustment on the surface oxygen species, which are extremely important for catalytic oxidation reactions [8,17-19].

For this purpose, we have attempted to further develop our recent exploration that MoO<sub>3</sub> are immobilized on the surfaces of regular nanocrystals to obtain a model catalyst with clear structure and highly catalytic performance [17,20]. Briefly, the bismuth tungstate nanoflakes with loading of molybdena are highly active for propene conversion and especially selective to the formation of acrolein. Those by-products mentioned above such as acrylic acid could hardly be detected. The results are useful to design novel catalysts for important reactions with nano concepts.

#### 2. Experimental

#### 2.1 Catalysts preparation

All chemicals were analytical-grade reagents and were used without further purification. The hierarchical Bi<sub>2</sub>WO<sub>6</sub> hollow assembled nanoflakes were synthesized by a hydrothermal method. In a typical synthesis, 0.4548 g of Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O and 0.1546 g of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O were added into 15 mL of Polyethylene Glycol (MW $\approx$ 200) and 15 mL of deionized water, respectively. These two solutions were mixed together and stirred for 30 min and then were added into a 45 mL Teflon-lined autoclave up to 65 % of the total volume. The auto clave was sealed in a stainless steel tank and heated at 453 K for 24 h. Subsequently, the autoclave was cooled to room temperature naturally. The products were collected by filtration, washed with distilled water for several times, and then dried at 353 K in air and calcined in air at 623 K for 5 h.

The molybdenum catalysts were prepared by impregnating the bismuth tungstate with a appropriate amount of ammonium molybdate ( $(NH_4)_6Mo_6O_{24}\cdot 4H_2O$ ) solution for 5 h, then drying at 353 K, and calcining in air at 623 K for 5 h. Hereafter, the MoO<sub>3</sub>/Bi<sub>2</sub>WO<sub>6</sub> catalysts are denoted as xMo/BWO, where x indicated the loading of MoO<sub>3</sub> (mass fraction).

As reference catalysts, Mo-doped  $Bi_2WO_6$  hierarchical microspheres in similar compositions by a similar method using the mixture of aqueous solution of Bi-, Mo- and W-salts were synthesized. The catalysts were denoted as  $BMo_xW_{1-x}O$  in the context.

#### 2.2 Catalytic activity

The reactor was vertical and made of 6 mm. o.d. quartz glass tube. The catalyst was held in the middle of the tube between two layers of quartz wool. The catalyst was pretreated in the quartz reactor with air flow (15 mL min<sup>-1</sup>) at 373 K for 2 h, then the system was cooled down to the desired reaction temperature under the air flow to remove adsorbed moisture and any adsorbed impurities. The reaction was started by introducing a reactant gas flow containing propene and air. In kinetic measurement process, Helium was also used as a balance gas in the reactant mixture to regulate the partial pressures of propene and air. For the measurement of kinetics, the conversion of propene was kept between 3 and 15 % to enable calculation of reaction rates from the results. The temperature around the reactor was maintained by a furnace connected to a temperature controller. The catalytic performance was tested from 473 to 623 K. The products along with the unreacted propene were analyzed by on-line gas chromatography. All of the lines and valves between the exit of the reactor and the gas chromatographs were heated to 423 K, to prevent the condensation of organic products. Propene conversion was calculated on a carbon basis from the concentrations of the products detected, including aldehyde, propanal, acetone, acrolein, isopropanol, acrylic acid, CO, CO<sub>2</sub> and the residual propene.

#### 2.3 Characterization of the catalysts

XRD measurements were carried out on a Panalytical X'pert Pro Super X-ray diffractometer with Cu K $\alpha$  radiation (40 kV and 30 mA). The morphology and composition of the samples were analyzed by Hitachi S-4800 field-emission scanning electron microscope (FESEM) with an energy-dispersive X-ray (EDS) spectrometer. Transmission electron microscopy (TEM), high-resolution TEM (HRTEM), and selected area electron diffraction (SAED) of the hierarchical superstructures were performed on a JEOL JEM-2010UHR instrument at an acceleration voltage of 200 kV. N<sub>2</sub> physisorption experiments were performed at 77 K on a Micromeritics Tristar. The samples were outgassed overnight at 423 K under vacuum (2 Pa). The specific surface area was determined from the BET method in the 0.05~0.30 P/P<sub>0</sub> range. The pore size distribution was derived from the desorption branch using the BJH method. The average pore diameter is calculated as (4×pore volume/BET

specific surface area). Raman spectra were recorded with a Renishaw invia system equipped with a confocal microscope. A 514.5 nm exciting line was focused using a  $50 \times$  objective lens. The laser power at the sample was ~20 mW.

X-ray photoelectron spectroscopy (XPS) was recorded using a PHI 5000 Versa Probe system, using monochromatic Al K $\alpha$  radiation (1486.6 eV) operating at an accelerating power of 15 kW. Before the measurement, the sample was outgassed at room temperature in a UHV chamber ( $< 5 \times 10^{-7}$  Pa). The sample charging effects were calibrated with binding energy (BE) of the adventitious C 1s peak at 284.6 eV.

Temperature-programmed desorption of oxygen (O<sub>2</sub>-TPD) experiments were carried out in a quartz micro-reactor (i.d. 2 mm) which was connected to an on line multifunctional gas adsorption instrument PX200 (Tianjin golden eagle technology co., ltd.) equipped with a thermal conductivity detector (TCD). Typically, 1 g of the catalyst was pretreated at 623 K for 1 h under continuous He flow (30 mL min<sup>-1</sup>) to remove any adsorbed moisture, then cooled to 323 K and saturated with O<sub>2</sub> for 30 min. Subsequently, O<sub>2</sub> in physical adsorption and gas phase was purged in He flow (45 mL min<sup>-1</sup>) for a certain period at 323 K until a stable baseline was obtained. O<sub>2</sub>-TPD experiment was then carried out in the range of 323~673 K at a heating rate of 10 K min<sup>-1</sup>.

Temperature-programmed reduction of  $H_2$  ( $H_2$ -TPR) experiments (Tianjin Xianquan Industry and Trade Development Co., LTD) were carried out in a conventional setup similar to O<sub>2</sub>-TPD. Typically, the sample (0.1 g) was pretreated at 623 K for 1 h under Ar flow to remove water and other contaminants. Then the reduction step was carried out in a mixture flow of  $H_2/N_2$  (5 vol. %  $H_2$ ) from room temperature to 1073 K at a heating rate of 10 K min<sup>-1</sup>. The  $H_2$  signal was monitored on line by a TCD.

#### 2.4 Conductivity Measurements

The conductivities of the BWO and 5Mo/BWO catalysts were determined by measuring the specific resistance of the sample discs with the two-electrode DC method. The sample to be examined was compacted into a disc (2 mm thick and 13 mm diameter) containing two electrodes, each made from conductive silver paste on to which silver leads (0.1 mm diameter) were spot-welded. The final disc was further heated at 623 K for 5 h to remove impurities in

order to improve the electric conductance. The aim was to detect and measure the relative rates of reduction and oxidation of the samples, as preliminary experiments showed that extensive conductivity changes occurred and varied with the reaction condition. Its chief importance lies in the information it give about the net states of reduction of the catalyst surface during the early stages of the selective and nonselective oxidation of propene [21].

#### 2.5 C<sub>3</sub>H<sub>6</sub>-temperature programmed surface reaction (TPSR)

The C<sub>3</sub>H<sub>6</sub>-TPSR experiments were performed on a system equipped with an online quadrupole mass spectro-meter. The method similar to that of Zhao and co-workers [22], Typically,  $\sim 1.0$  g of the 5Mo/BWO catalyst was loaded into a U-type quartz tube and initially purged at 623 K with Air (30 mL min<sup>-1</sup>) for 1 h. The pretreated sample was cooled down in the flowing air to 473 K, then the gas stream was subsequently switched to a high purity He flow upon further cooling to 323 K maintained for 30 min. Propene adsorption was performed by flowing a 4.76 % C<sub>3</sub>H<sub>6</sub>/He gas mixture (42 mL min<sup>-1</sup>) for 30 min at 323 K and the sample was again purged with flowing helium for 30 min to remove residual physically adsorbed propene. The TPSR experiments were then performed with a heating rate of 10 K min<sup>-1</sup> in either flowing He or 5 vol. %  $O_2/He$ , and the desorbing products were monitored with the online quadrupole MS. The m/e values used to detect the different desorption products were m/e=41 for propene, m/e=56 for acrolein, m/e=43 for acetone, m/e=29 for aldehyde, m/e=44 for CO<sub>2</sub>. Unlike single crystal studies in vacuum, it is not possible to determine the kinetic parameters from the FWHM of the TPSR curve since the desorbing products signals become broadened due to dispersion of the gases as they pass through the thin catalyst bed. Consequently, only the  $T_p$  temperature during C<sub>3</sub>H<sub>6</sub>-TPSR can be accurately determined by use of the redhead equation [23].

#### 3. Results and Discussion

The morphology and structure of the product was examined by a scanning electron microscope and a transmission electron microscope (HRTEM). Fig. 1a shows a panoramic FESEM image of the as-synthesized hollow structured Bi<sub>2</sub>WO<sub>6</sub> microspheres. Low-magnification FESEM images show that the sample consists of a large quantity of

microspheres, indicating that  $Bi_2WO_6$  microspheres can be prepared on a large scale by this facile method. The sample mainly contains uniform spheres with diameters ranging in 3~5 µm. Higher magnification microscopy (Fig. 1c) provides the detailed surface structures of  $Bi_2WO_6$  microspheres. It can be clearly seen that the exterior surfaces of microspheres are rough and each microspheres actually were constructed by many crisscrossing nanoflakes with thickness of about 50 nm. Simultaneously, the small  $Bi_2WO_6$  nanocrystallines were connected to form the submicroscopical flake-like structure. (Fig. 1c).



Fig. 1. (a) and (b) FESEM and TEM images of as-prepared  $Bi_2WO_6$  hollow microspheres using polyethylene glycol (PEG 200) as the solvent; (c) Higher magnification microscopy FESEM images of the  $Bi_2WO_6$  hollow microspheres; (d) and (e) Higher magnification microscopy TEM images of the  $Bi_2WO_6$  nanoflakes. Inset of (d) shows the corresponding SAED image; (f) XRD pattern of the  $Bi_2WO_6$  sample.

A typical TEM image of the sample shows that the microspheres have a dimension of about

3  $\mu$ m, and the relatively pale center observed on the TEM images of a single microsphere further confirms that the as-prepared  $Bi_2WO_6$  microspheres have a hollow center (Fig. 1b). The shell thickness of the spheres is about 200 nm and the corresponding diffraction patterns of the selected area electron diffraction (SAED) indicate that Bi<sub>2</sub>WO<sub>6</sub> nanoflakes are single crystalline (Fig. 1d). From the high resolution transmission electron microscopy (HRTEM) image (Fig. 1e), the spacing between the adjacent fringes was measured to be 2.74 Å, which matches well with the (200) plane spacing of orthorhombic Bi<sub>2</sub>WO<sub>6</sub>. The phase structure is also characterized by X-ray powder diffraction (XRD, Fig. 1f) and the diffraction peaks of the  $Bi_2WO_6$  can be clearly indexed to the well-crystallized orthorhombic phase of  $Bi_2WO_6$  with lattice constants a=5.456, b=5.436, and c=16.426 Å (JPCDS 73-1126). Moreover, the strong and sharp diffraction peaks in the pattern show that the as-synthesized product is highly crystalline, which is in accordance with HRTEM results. These results indicate that as-prepared hollow Bi<sub>2</sub>WO<sub>6</sub> microspheres were composed of Bi<sub>2</sub>WO<sub>6</sub> nanoflakes with the orthorhombic structure. It is speculated that the small Bi<sub>2</sub>WO<sub>6</sub> nanocrystallines, connected each other to form the nanoflakes, mostly provide the (100) and (010) facets as the exposed surfaces in the view of crystalline model of the orthorhombic  $Bi_2WO_6$  structure [24]. The morphologies of the reference samples (not shown) are similar to the Bi<sub>2</sub>WO<sub>6</sub>.

In our previous study [25-27], the weak coordination among metallic species and PEG chains had been proved to aggregate  $M^{n+}$ -PEG into globules. The metallic species wrapped in the globules will preferentially hydrolyze to corresponding solid metallic compound nuclei, so the globules act as the soft templates for the formation of Bi<sub>2</sub>WO<sub>6</sub> microspheres. Studies have clarified that Ostwald ripening will occur during the hydrothermal process. Typically, the crystallites located in the central part of the spherical aggregates are smaller or less dense compared to those in the outer parts, and thus they will be dissolved and re-crystallized on the outer parts, resulting in hollow spheres [25,28-29]. Eventually, the core was dissolved and the shell gets rougher and more crystallized, and the solid primary spherical particles on the microsphere shell transfer into well-faceted Bi<sub>2</sub>WO<sub>6</sub> particles with the increase of the reaction time in synthesis.



**Fig. 2.** (a) FESEM images of 5Mo/BWO sample (scale bar is 1  $\mu$ m). (b) XRD patterns of the Bi<sub>2</sub>WO<sub>6</sub> and xMo/BWO samples with different MoO<sub>3</sub> contents. (c) and (d) Raman spectra and FTIR spectra of the catalysts with different MoO<sub>3</sub> loadings, respectively.

Fig. 2a shows the FESEM image of  $Bi_2WO_6$  sample supported with 5 wt % molybdena. Compared with pure  $Bi_2WO_6$  sample (Fig. 1a), both samples exhibit flake-like morphology, indicating that molybdena loading has no obvious influence on the morphology of  $Bi_2WO_6$ . The XRD diffraction patterns of the samples are shown in Fig. 2b. All of the diffraction peaks match the standard data for an orthorhombic  $Bi_2WO_6$  structure and no crystalline MoO<sub>3</sub> could be detected in the XRD spectra, suggesting that only thin layers or very small crystals of molybdena have been formed on the support. Moreover, neither possible impurities nor changes of the lattice parameters of  $Bi_2WO_6$  in all samples are found, which implies that the loading of MoO<sub>3</sub> does not result in the development of new phases. Raman and FTIR techniques are also applied to detect the state changes of the catalysts upon MoO<sub>3</sub> loading. In Raman spectroscopy (Fig. 2c), the sample  $Bi_2WO_6$  calcined at 623 K could be regarded as an appropriate standard sample for high-purity single-phase crystalline  $Bi_2WO_6$ . The Raman bands at the 996 and 291 cm<sup>-1</sup> are attributed to the symmetric stretching and the asymmetric bending modes of Mo=O bond, respectively. The bands at 821 cm<sup>-1</sup> are assigned to the

Mo-O-Mo symmetric stretch [30]. While, the intensity of the peak at 796 cm<sup>-1</sup> in the Raman spectra, assigned to one of the W-O stretches in the Bi<sub>2</sub>WO<sub>6</sub> lattice, decreased with an relative intensity of the increasing the MoO<sub>3</sub> loading [31], as well as the peak at 309 cm<sup>-1</sup>. These Raman band changes suggest the presence of tetrahedral coordinated Mo species on the Bi<sub>2</sub>WO<sub>6</sub> surface. Fig. 2d shows typical IR spectra of all samples. The high absorption in the  $800 \sim 650 \text{ cm}^{-1}$  spectral range can be related to the vibrations of W-O-W bridges between WO<sub>6</sub> octahedra. The shoulder at 827 cm<sup>-1</sup> is assigned to asymmetric stretching vibration modes of apical oxygen atoms connecting the WO<sub>6</sub> octahedra [32]. As it is seen, the characteristic vibrations of octahedral WO<sub>6</sub> and tetrahedral MoO<sub>4</sub> units are in the same spectral region, which makes difficulty to the precise assignment of the absorption bands [33]. According to the Raman spectra data, it could be deduced that the molybdenum oxide dispersed on  $Bi_2WO_6$ surface mainly as high dispersed or polymerized molybdenum oxide species. The dispersed nature of molybdena species on supports is consistent with the absence of crystalline structures in their X-ray diffraction patterns (Fig. 2b). X-ray photoelectron spectroscopy (XPS) is applied to detect the chemical states of Mo species and the surface composition of the catalysts and the results are listed in Table 1. Considering the Mo content in the 5Mo/BWO, the results imply that the molybdenum is mainly located on the surface of the catalyst. Two distinct peaks of binding energy corresponding to the Mo  $3d_{5/2}$  and  $3d_{3/2}$  (not shown), respectively at 232.5 and 235.7 eV, which are lower than Mo in bulk MoO<sub>3</sub> but similar to those of the molybdenum in bismuth molybdate. It appears the molybdenum is highly dispersed as surface bismuth molybdate-like species on the Bi<sub>2</sub>WO<sub>6</sub>, considering the results of Raman and XRD results listed in Fig. 2.

Table 1. The surface composition of the Bi<sub>2</sub>WO<sub>6</sub> and 5Mo/BWO catalysts.<sup>a</sup>

Samples	С	0	Mo	W	Bi
Bi <sub>2</sub> WO <sub>6</sub>	29.28	51.76	-	5.66	13.31
5Mo/BWO	20.83	53.97	5.58	5.75	13.86

<sup>a</sup> Determined by XPS analysis.

Catalysts	MoO <sub>3</sub> content	BET surface	Pore volume	Surface density of MoO <sub>3</sub>
	(wt %) <sup>a</sup>	area $(m^2 g^{-1})$	$(cm^3 g^{-1})$	on support (atoms/nm <sup>2</sup> )
Bi <sub>2</sub> WO <sub>6</sub>	0	14.3	0.069	0
1Mo/BWO	0.85	14.0	0.089	0.263
3Mo/BWO	2.54	13.4	0.064	0.823
5Mo/BWO	4.34	13.3	0.076	1.410
7Mo/BWO	5.32	11.8	0.077	1.956
BMo <sub>0.01</sub> W <sub>0.99</sub> O	0.85	17.5	0.063	-
BM0 <sub>0.03</sub> W <sub>0.97</sub> O	2.86	17.1	0.068	-
BM00.05W0.95O	4.26	16.8	0.071	
BM0 <sub>0.07</sub> W <sub>0.93</sub> O	6.07	14.5	0.076	

Table 2. The specific surface area of the xMo/BWO and  $BMo_xW_{1-x}O$  catalysts.

<sup>a</sup> Determined by XRF analysis.

The BET surface areas derived from N<sub>2</sub>-physisorption and the loading of MoO<sub>3</sub> evaluated from the XRF analysis are listed in Table 2. According to XRF results, the Mo contents in the four Mo-based catalysts were slightly less than the amount of MoO<sub>3</sub> added, just due to the loss in the synthetic process. As shown in Fig.1, the exterior surfaces of hollow microspheres are rough and each of microspheres actually is constructed by many crisscrossing nanoflakes with thickness of about 50 nm. Recently, Ryoo et al. have also reported a simple method to synthesize zeolites with crisscrossing nanoflakes structures [34]. Meanwhile, the large number of acid sites on the external surface of the zeolites nanoflakes renders them highly active for the catalytic conversion of large organic molecules, and the reduced crystal thickness facilitates diffusion and thereby dramatically suppresses catalyst deactivation through coke deposition during methanol-to-gasoline conversion. In current investigation, the catalytic properties of Bi<sub>2</sub>WO<sub>6</sub> nanoflakes supported with or without molybdena are tested with selective oxidation propene by air.

The catalytic properties of the samples for the selective oxidation of propene are carefully investigated and the results are shown in Fig. 3. As shown in Fig. 3a, with the

increase in loading of  $MoO_3$  from 0 to 5 wt %, the catalytic properties of the catalysts are significantly promoted. The selectivity to acrolein increases surprisingly from less than 5% to ~96% and the  $CO_2$  selectivity decreases to ~3%. Meanwhile, the production of aldehyde, propanal, acetone and isopropanol are greatly diminished with the MoO<sub>3</sub> amount increase. A further increase in MoO<sub>3</sub> loading has no obvious effect on catalytic property. The surface molybdena plays pivotal roles in enhancing acrolein selectivity. Fig. 3b shows that both propene conversion and acrolein selectivity over the 5Mo/BWO catalyst did not undergo significant changes with time on stream. The propene conversion is  $\sim 62.9$  % and is stable during the time on stream. The selectivity to acrolein as high as 96 % is also stable during the reaction. The catalytic performance of the model catalyst is better than many catalysts with multicomponent documented [6]. Only very small amounts of by-products are detected. Propene oxide and acrylic acid, however, are not formed in the oxidation of propene by gaseous molecular  $O_2$ . Introduction of  $MoO_3$  into the catalyst has a big promoting effect on the selective oxidation propene to acrolein. The catalytic performance of the reference catalysts was also investigated. In contrast, the reference catalysts are significantly less active and less selective for oxidation of propene to acrolein (Table 3). The MoO<sub>3</sub> promoted hierarchical assembly of Bi<sub>2</sub>WO<sub>6</sub> nanoflakes catalysts are specially active and selective for propene converted to acrolein in a moderate temperature range. Some industry catalysts patented in recent years with multi components are also listed for comparison.



Fig. 3. (a) Catalytic performance of the catalysts with different  $MoO_3$  contents. (b) Variation of propene conversion and acrolein selectivity with time on stream over the 5Mo/BWO catalyst. Reaction

Conditions: T=623 K, W= 0.45 g, F= 25.5 mL min<sup>-1</sup>, WHSV=3400 mL g<sup>-1</sup> h<sup>-1</sup>, P(C<sub>3</sub>H<sub>6</sub>)=1.99 kPa, P(Air)=99.31 kPa.

Catalysta		Temp. Conv. Selectivity of products					
Catalysis	(K)	(%)	Acrolien	$\rm CO_2$	Aldehyde	Others <sup>b</sup>	
BM0 <sub>0.01</sub> W <sub>0.99</sub> O	623	29.4	21.5	52.4	7.4	18.7	
BM0 <sub>0.03</sub> W <sub>0.97</sub> O	623	37.9	47.4	35.0	10.1	7.8	
BMo <sub>0.05</sub> W <sub>0.95</sub> O	623	23.3	63.6	24.9	6.7	4.9	
BM0 <sub>0.07</sub> W <sub>0.93</sub> O	623	21.2	64.8	20.7	5.6	8.9	
${}^{d}Mo_{12}Fe_{2}Bi_{1.5}Co_{4.4}K_{0.06}O_{x}$	593	99	90.50			1.62 <sup>c</sup>	
$^{e}Mo_{12}Fe_{2.94}Bi_{0.8}Co_{7}Si_{1.52}K_{0.08}O_{x}$	591	95	91.68			4.32 <sup>c</sup>	
${}^{f}\!Mo_{12}Fe_{2,4}Bi_{1.08}Co_{9.6}Al_{1.48}V_{0.056}Ag_{0.1764}Pd_{0.0019}K_{0.064}O_{x}$	615	97	98.56			-	
${}^{g}Mo_{12}Fe_{1.8}Bi_{1.7}Ni_{2.8}Co_{5.2}K_{0.1}O_{x}$	619	97	87.42			7.63 <sup>c</sup>	

Table 3. The catalytic performances of some reference catalysts.<sup>a</sup>

<sup>a</sup> Reaction conditions: T=623 K, W= 0.45 g, F= 25.5 mL min<sup>-1</sup>, WHSV=3400 mL g<sup>-1</sup> h<sup>-1</sup>, P(C<sub>3</sub>H<sub>6</sub>)=1.99 kPa, P(Air)=99.31 kPa. <sup>b</sup> Others products were acetone, propanal and isopropanol. <sup>c</sup> Acrylic acid. <sup>d</sup> LG Chem. Ltd, WO 079980 (2005). <sup>e</sup> BASF, EP 1005908 (1998). <sup>f</sup> Sabic, WO 2000009260, US 6143928. <sup>g</sup> Nippon Kayaku Co., Ltd., EP 807465 (1997).

The kinetic expression for the rate of propene oxidation to acrolein can be expressed as a power law:

$$\boldsymbol{r} = \boldsymbol{\kappa} \cdot \boldsymbol{P}_{C_3 H_6}^{\boldsymbol{x}} \cdot \boldsymbol{P}_{Q_2}^{\boldsymbol{y}} \tag{1}$$

where *r* represents the rate of reaction to propene [mmol·g<sup>-1</sup>·h<sup>-1</sup>], *k* is the apparent rate constant, x and y represent the reactant reaction orders. By respectively setting the pressures of the propene and  $O_2$  as a constant, the reactant reaction orders can be measured. The results are shown in Fig. 4a and Fig. 4b, with which the kinetic equation of the reaction for the catalyst can be expressed as:

$$\Gamma = \kappa \cdot P_{C_3 H_6}^{0.89} \cdot P_{Q_2}^{0.10}$$
(2)

Basically, the rate equation (2) reveals that the propene oxidation to acrolein reaction follows around first-order kinetics with respect to propene and around zero-order kinetics with respect to molecular  $O_2$  partial pressures. The partial reaction orders in both reactants observed, however, may indicate that the kinetics is a composite of the reoxidation and reduction kinetics. Similar results have been reported for the oxidation of propene over and

for the oxidation of propene over iron-antimony catalyst [35-36] and bismuth molybdate catalysts at low temperatures (<673 K) [37]. The apparent activation energy, Ea, for propene selective oxidation to acrolein over the 5Mo/BWO is determined from the plot of ln(*k*) versus 1/T in the temperature range of 608~628 K, as shown in Fig. 4c. In order to obtain reasonable results of the apparent activation energy, the catalytic conversion of propene is controlled less than 13 %, by using small amounts of catalysts. The apparent activation energy for the reaction is calculated as 32.8 kcal mol<sup>-1</sup> from the Arrhenius equation, which is less than and still in reasonable agreement with those recently reported for the selective oxidation of propene to acrolein over bismuth molybdate catalysts [38-39]. The similarities in kinetics and catalysts is similar, but the catalyst Mo/BWO shows higher activity with much simple structure and composition.



**Fig. 4.** (a) The plots of the logarithm of  $r(C_3H_6)$  against the logarithm of  $P(O_2)$ . Reaction Conditions: cat. 5Mo/BWO=0.05 g; Silica sand=0.40 g; T=623 K.  $P(C_3H_6)=4.51$  kPa, F=60 mL min<sup>-1</sup>. (b) The plots of the logarithm of  $r(C_3H_6)$  against the logarithm of  $P(O_2)$ . Reaction Conditions: cat. 5Mo/BWO=0.05 g; Silica sand=0.40 g; T=623 K.  $P(O_2)=12.80$  kPa, F=40 mL min<sup>-1</sup>. (c) The plots of the napierian logarithm of against the 1/T. Reaction Conditions: cat. 5Mo/BWO=0.05 g; Silica sand=0.40 g;  $P(C_3H_6)=1.99$  kPa, F=25.5 mL min<sup>-1</sup>.

In order to understand the structure of the  $Mo/Bi_2WO_6$  catalysts, Fig. 5 depicts the structural model of the orthorhombic  $Bi_2WO_6$  with the surface loading of molybdena. The

crystal lattice parameters calculated are as follows: a = 5.4326, b=16.4302 and c=5.4584 with a cell volume of 487.21 Å<sup>3</sup> for the orthorhombic Bi<sub>2</sub>WO<sub>6</sub> [40], which is a layered structure composed of WO<sub>6</sub> octahedral layers and Bi-O-Bi layers (Fig. 5b). Each Bi atom is coordinated with four O and four W atoms and, meanwhile, the WO<sub>6</sub> octahedral are connected to each other by corner-sharing O atom [40]. As mentioned above, the currently synthesized submicroscopical flake-like Bi<sub>2</sub>WO<sub>6</sub> are composed of small nanocrystals (Fig. 1c), which provide mainly (100) and (010) facets as the exposed surfaces.



Fig. 5. (a) The FESEM images of the as-prepared 5Mo/BWO catalyst. (b) The two-dimensional structure of the crystal planes: the (100) and (010) atomic planes of orthorhombic-phase  $Bi_2WO_6$ . (c) The schematic diagram of the formation of MoO<sub>3</sub> nanocrystal on the (100) and (010) atomic planes of  $Bi_2WO_6$  nanoflakes. Green bars mean the double bonds of Mo=O.

Molybdena loading has no obvious influence on the morphology and texture of  $Bi_2WO_6$ nanoflakes, owning to the structural similarity between the  $Bi_2MOO_6$  and  $Bi_2WO_6$ , which causes the easy epitaxial growth or highly dispersion of molybdena on the surface of  $Bi_2WO_6$ 

by attaching to the interface oxygen atoms, i.e., the two-dimensional cell structures of the (100) and (010) atomic planes of Bi<sub>2</sub>WO<sub>6</sub>, which are the two lateral facets of the Bi<sub>2</sub>WO<sub>6</sub> nanoflakes (Fig. 5b and 5c). The tetrahedral MoO<sub>4</sub> perfectly bonded to the surfaces can be modeled with two manners, as shown in Fig. 5c, in which the terminal Mo=O species of tetrahedral molybdate are exposed to the reaction atmosphere. For the selective oxidation of propene, the nature of active sites and the present state of oxygen species selective are still under debate, but it has been proposed that the Mo=O species is the selectively active oxygen species for inserting to form acrolein [7,39]. According to the Raman results, the bands around 996 and 291 cm<sup>-1</sup> from xMo/BWO samples are attributed to the symmetric stretching mode of Mo=O bonds of the tetrahedral molybdate (Fig. 2c). These results collectively suggest that lattice oxygen with molybdenum connected fitly with the regular surfaces of bismuth tungstate be important for the partial oxidation of propene (Fig. 5b and 5c).



**Fig. 6.** (a)  $H_2$ -TPR profiles of the catalysts with different MoO<sub>3</sub> loadings. (b)  $O_2$ -TPD profiles of the catalysts with and without MoO<sub>3</sub> loadings.

It is well accepted that the reducibility of the catalysts do have great influence on the catalytic activity. For the xMo/BWO samples, the main reduction processes take place at the temperatures higher than 700 K, as shown in Fig. 6a, which should be attributed to the reduction of tungstate. With increasing MoO<sub>3</sub> loadings, a shoulder peak at ~770 K appears gradually. As reported in the earlier literatures [41], the peak at ~770 K is related to the first step reduction of Mo(VI) $\rightarrow$ Mo(IV) of well dispersed octahedral Mo species. It is interesting

that the introduction of molybdenum causes the significant decrease in consumption of hydrogen during  $H_2$ -TPR of  $Bi_2WO_4$  at low temperatures of 500~650 K, implying that the overactive oxygen species of the  $Bi_2WO_4$  leading to unselective reaction are eliminated. It is well in agreement with the catalytic properties of the xMo/BWO, which is drastically modified by the molybdenum loading (Fig. 3).

That the selective oxidation of propene takes place with the chemisorbed allyl oxidized to acrolein by lattice oxygen or chemisorbed oxygen is a general consideration [8]. The activity or mobility of oxygen of the catalysts is very important. The results of temperature-programmed desorption of oxygen ( $O_2$ -TPD) are shown in Fig. 6b. The initial  $O_2$  evolution peak's summit appears at ~369 K for Bi<sub>2</sub>WO<sub>6</sub> catalyst. For 5Mo/BWO with molybdenum loading, the  $O_2$  evolution peak's summit shifts to a higher temperature (~389 K) and the amount of oxygen evolution increases markedly as compared with Bi<sub>2</sub>WO<sub>6</sub>. It is known that oxygen chemisorption depends strongly on the electrodonor properties [41]. According to the catalytic performance and the rate equation for the 5Mo/BWO catalyst, it involves much more active oxygen species selective for oxidation of propene than the Bi<sub>2</sub>WO<sub>6</sub>, also in consistent with the Raman results.

The measurement of conductivity is carried out to know the band information of the catalysts, which can be correlated to the selectivity for the propene oxidation [42]. Fig. 7a shows the variation in conductance of the 5Mo/BWO and Bi<sub>2</sub>WO<sub>6</sub> in different atmospheres. The conductance of the catalysts dropped immediately when the atmosphere is switched from argon to oxygen and the removal of oxygen restores the conductance of the catalysts. For both samples, the depleting adsorption of oxygen is deduced and indicates the n-type semiconductor of the two samples. The adsorbed oxygen species should gain electrons from the catalyst and turn to negative charged oxygen species. The higher conductance of 5Mo/BWO than Bi<sub>2</sub>WO<sub>6</sub> means more carrier concentration and also stronger adsorption for oxygen of the former. The Arrhenius plots of the dependence of conductance on temperature for Bi<sub>2</sub>WO<sub>6</sub> and 5Mo/BWO catalysts are shown in Fig. 7b. In comparison with Bi<sub>2</sub>WO<sub>6</sub>, the 5Mo/BWO catalyst possesses much less activation energy (0.22 eV versus 0.70 eV) for electron's moving. More electrons could be used for adsorption of oxygen on the Bi<sub>2</sub>WO<sub>6</sub> with the assistance of surface molybdenum deposition. The Mo/BWO is more active than





Fig. 7. (a) Variation in conductance of the catalysts in different atmosphere. Inset shows the conductivity cell. (b) Changes of the resistance with time on stream for the catalysts after different temperature. Inset shows arrhenius plots for the change of conductance over  $Bi_2WO_6$  and 5Mo/BWO catalysts.

 $C_3H_6$ -TPSR measurements are carried out with the 5Mo/BWO catalyst to investigate the catalytic surface reaction mechanism of propene selective oxidation to acrolein. The O<sub>2</sub>-free  $C_3H_6$ -TPSR spectra are shown in Fig. 8a and the main reaction products from propene oxidation by the lattice oxygen are acrolein, which appears in temperature ranges from 360~400 K. Chemisorbed propene desorbs at 425 K and the desorbing temperature makes it cannot be considered as physically adsorbed propene [22]. Interestingly, the formation of CO<sub>2</sub> at low temperature is suppressed under the O<sub>2</sub>-free condition and CO<sub>2</sub> production primarily occurs at the temperatures higher than 600 K. In the presence of gaseous oxygen, however, the C<sub>3</sub>H<sub>6</sub>-TPSR experiment yields carbon dioxide as the main reaction product, acrolein or aldehyde, are detected. These results reveal that the surface lattice oxygen from the catalysts could be effectively activate propene and selectively oxidize propene to acrolein. Introducing oxygen into propene stream, however, the C<sub>3</sub>H<sub>6</sub>-TPSR test yields CO<sub>2</sub> as the main reaction product. Thus, the oxygen atom of both acrolein and aldehyde should be originates

from the lattice oxygen of the catalyst rather than from the gaseous molecular oxygen directly. After the TPSR, the catalysts are checked by thermal gravity-mass spectrocopy measurement. It is found that the catalyst surface is clean after TPSR with presence of gaseous oxygen but small amount of carbon deposition is detected without the presence of gaseous oxygen. Similar results are also reported by Wachs et al. [22,43].



Fig. 8. The  $C_3H_6$ -TPSR spectroscopy of the 5Mo/BWO catalyst in a flow of (a) He ( $O_2$ -free) and (b)  $O_2$ /He.

Summing up the above results and discussions, the reaction routes of the selective oxidation of propene to acrolein over the molybdena loaded on bismuth tungstate catalysts is proposed and schematically illustrated in Fig. 9. With the temperature increasing, the electrons in the valence band of Bi<sub>2</sub>WO<sub>6</sub> are excited to its conduction band due to its intrinsic excitations as a semiconductor [44], this is also a process similar to photo-generated electrons and holes via visible-light irradiation. Then the conduction band electrons can interact with adsorbed O<sub>2</sub> to form chemisorbed oxygen species, O<sub>2</sub><sup>-</sup> and/or atomic O<sup>-</sup> [45-46], which are both strong oxidative species and play crucial roles in the oxidative of hydrocarbon. This kind of electrophilic addition of O<sub>2</sub><sup>-</sup> or O<sup>-</sup> results in the formation of peroxy- or epoxy-complexes, which are only transient products of the degradation of the carbon chain and the total oxidation under the conditions of catalytic oxidation. These reactions are so-called electrophilic oxidation [45-46]. Accordingly, the oxidation of propene with the bismuth tungstate catalyst also provided CO<sub>2</sub> as the main product (73 %, Fig. 3a). On the other hand,

according to Mars-van Krevelen mechanism [47], propene adsorbed on the surface of bismuth oxide with hydrogen abstraction forms a  $\pi$ -allyl radical, which then reacts with the nearby molybdenum oxo species to give rise to a C-O bond with the lattice oxygen. So, propene reactions follow an allylic C-H bond activation and undergo a nucleophilic addition of the lattice O<sup>2-</sup> ion, in which step causes the reduction of valence state of Mo(VI) and an oxygen vacancy is left on the surface. The gaseous oxygen then fills in the vacancy and causes the reoxidation of the Mo site for the next cycle of reaction. These reactions are classified as nucleophilic oxidations [41,48].

The suitable cooperation between the sites of molybdnaum and bismuth on the catalyst surface is extremely important, such the current catalyst with molybdena highly dispersed on the surface of well crystallized  $Bi_2WO_4$ , over which the selectivity of acrolein increases with temperature, while the selectivity of carbon dioxide decreases simultaneously. From the apparent rate equation, the observed kinetics would be a composite of both the reduction and reoxidation kinetics with partial dependencies on both propene and oxygen. In short, a synchronous redox mechanism is involved in the selective oxidation of propene over the current molybdena loaded bismuth tungstate catalysts.



Fig. 9. Schematic show of the reaction mechanism for the selective oxidation of propene by air over the supported Mo/BWO catalyst.

#### 4. Conclusions

Hierarchical Bi<sub>2</sub>WO<sub>6</sub> nanoflakes, assembled as hollow microspheres, are easily realized by solvenothermal synthesis using polyethylene glycol as the structure-directing agent. The

hollow architectures with a diameter of ca. 4  $\mu$ m are constructed by bismuth tungstate nanoflakes with a thickness of about 50 nm. Molybdenum oxide species are immobilized onto the nanoflakes surface in highly dispersed state via impregnation of ammonium molybdate. The Bi<sub>2</sub>WO<sub>6</sub> itself mainly catalyzes the formation of CO<sub>2</sub> for propene oxidation. The introduction of molybdena, however, dramatically increases the selectivity to acrolein and decreases the formation of CO<sub>2</sub> with significant promotion on propene conversion at the same time. There is no acrylic acid detected during the propene oxidation, which is especially interesting. The 5Mo/BWO catalyst exhibits the highest acrolein selectivity and propene conversion among a series of molybdena loaded catalysts. In addition, the catalyst is very stable and keeps an excellent catalytic performance in the selective oxidation of propene. In this process, the thermally excited electrons are proposed to be incorporated in the rapid regeneration of the active molybdenum sites, of which the lattice oxygen consumed in the nucleophilic oxidation of propene to acrolein. A reasonable mechanism of catalyst interactions and the routes of selective oxidation of propene are proposed to explain all the experimental data.

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Figure captions.

Fig. 1. (a) and (b) FESEM and TEM images of as-prepared  $Bi_2WO_6$  hollow microspheres using polyethylene glycol (PEG 200) as the solvent; (c) Higher magnification microscopy FESEM images of the  $Bi_2WO_6$  hollow microspheres; (d) and (e) Higher magnification microscopy TEM images of the  $Bi_2WO_6$  nanoflakes. Inset of (d) shows the corresponding SAED image; (f) XRD pattern of the  $Bi_2WO_6$ sample.

Fig. 2. (a) FESEM images of 5Mo/BWO sample (scale bar is 1  $\mu$ m). (b) XRD patterns of the Bi<sub>2</sub>WO<sub>6</sub> and xMo/BWO samples with different MoO<sub>3</sub> contents. (c) and (d) Raman spectra and FTIR spectra of the catalysts with different MoO<sub>3</sub> loadings, respectively.

Fig. 3. (a) Catalytic performance of the catalysts with different MoO<sub>3</sub> contents. (b) Variation of propene conversion and acrolein selectivity with time on stream over the 5Mo/BWO catalyst. Reaction Conditions: T=623 K, W= 0.45 g, F= 25.5 mL min<sup>-1</sup>, WHSV=3400 mL g<sup>-1</sup> h<sup>-1</sup>,  $P(C_3H_6)=1.99$  kPa, P(Air)=99.31 kPa.

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**Fig. 9.** Schematic show of the reaction mechanism for the selective oxidation of propene by air over the supported Mo/BWO catalyst.

#### **Graphical Abstract**

# Super high selectivity of acrolein in oxidation of propene on molybdenum promoted hierarchical assembly of bismuth tungstate nanoflakes

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#### Highlights

- Hierarchical Bi<sub>2</sub>WO<sub>6</sub> microspheres composed by well shaped nanoflakes are obtained.
- Surface modification of MoO<sub>3</sub> dramatically enhances the catalyst as selective one.
- Acrolein selectivity can surpass ~96% in oxidation of propene with high conversion.
- Cooperation between surface molybdena and n-type semiconductor Bi<sub>2</sub>WO<sub>6</sub> is important.

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