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The synergy effect between gamma and beta phase of bismuth molybdate catalysts: Is there any relation between conductivity and catalytic activity?

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Abstract

This work aims to clarify the postulate that the catalytic activity of bismuth molybdates (β-$Bi_2Mo_2O_9$ and γ-Bi_2MoO_6) and their mixtures is related to their conductivity. Mixtures of these pure bismuth molybdate phases have been recognized to possess high catalytic activities owing to the synergy effect. Pure bismuth molybdate phases and their mixtures were synthesized using sol–gel method. This method has been considered as one of the best methods to result in stoichiometric bismuth molybdate products. Conductivities of these samples were recorded at the catalytic reaction temperature (300–450 °C). The comparison of the measured conductivities allows us to conclude that the high number of active sites to abstract the α-hydrogen is more important factor than the influence of conductivity in the mechanism of the selective oxidation of propylene.

Keywords: Bismuth molybdates; Synergy effect; Sol–gel; Selective oxidation; Propylene; Conductivity

1. Introduction

A synergy effect between phases of bismuth molybdate catalysts (α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$ and γ-Bi_2MoO_6) has been proposed in the literature by several authors [1–6]. The synergy effect is expressed as the enhancement of the catalytic activity when two or three phases are present in the catalyst. This synergy effect has been interpreted differently by different groups of authors. For example, El Jamal et al. [4] interpreted the origin of the synergy effect between gamma and alpha phases in terms of the elimination of excess Bi at the surface of the gamma phase or Mo at the surface of the alpha phase. Recently, it has been found by our group that the gamma phase is essential for the occurrence of a synergy effect [7]. Amongst three phases of bismuth molybdate, the gamma phase is known to be the best phase for oxygen transport due to its layered structure [6,8], therefore it possesses the highest conductivity [9–11]. In our previous publication [7], the synergy effect in several mixtures of beta or alpha phase with gamma phase was interpreted based on the previously proposed mechanism of the selective oxidation of hydrocarbon. The oxidation is a complex process including many steps: (1) chemisorption of propylene on the surface of the catalyst; (2) abstraction of an α-hydrogen to form an allylic intermediate; (3) insertion of lattice oxygen into the intermediate to form acrolein; and (4) replenishment of lattice oxygen removed from the surface of the catalyst during the third step in order to reconstitute the active site [3]. The second step has been agreed to be the rate-determining step at high temperatures, while there are indications that the re-oxidation of the catalyst is rate determining at low temperatures [12,13]. The alpha and beta phases are known as phases which possess a high ability to abstract the α-hydrogen and therefore a high catalytic activity. Based on our catalytic experimental data [7], we postulated that the synergy effect in several mixtures of beta or alpha phase with gamma phase resulted from the cooperation between the high ability to abstract the α-hydrogen

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of the beta or alpha phase and the high ability to replenish lattice oxygen of the gamma phase. Owing to this cooperation, both important steps during the selective oxidation process: the abstraction of an α-hydrogen to form an allylic intermediate (step 2) and the replenishment of lattice oxygen removed from the surface of the catalyst in order to reconstitute the active site (step 4) are enhanced. Therefore, the catalytic activity of the mixture is higher than the catalytic activity of each separate phase. It is also postulated that the replenishment of lattice oxygen which is stronger for the gamma phase may play an important role in the catalytic process.

In order to prove our previous postulate, in the present work, we aim to measure conductivities of several mixtures of gamma and beta bismuth molybdates and to find out the relation between the conductivities and the catalytic activities of these mixtures.

2. Experimental

Catalysts with different Bi/Mo ratios ranging from 1 to 2 were prepared by the sol–gel method described in our previous work [14]. The precursor solutions were prepared from aqueous solutions of 0.14 M $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (Merck, p.a.) (solution A) and 0.67 M $Bi(NO_3)_3{\cdot}5H_2O/HNO_3$ (Riedel-dehaen, p.a.) (solution B). Fifty milliliters of solution A was slowly added into an equivalent amount of solution B corresponding to the desired Bi/Mo molar atomic ratios, and concentrated HNO_3 was continuously added in order to preserve the high acidity of the medium and to prevent the precipitation of bismuth molybdates. Citric acid was added as a solution of 10%w citric acid monohydrate (Merk, p.a.) in order to result in a ratio of citric acid per bismuth ions of 2.5. The obtained solutions were gellyfied at 60–80 °C until the gels were completely formed. The transparent yellow gels were then dried at 110 °C for 2 h, and the spongy solid precursors obtained were crushed. Powders obtained after the gelation were directly calcined in an air flow at 580 °C for 2 h with the heating rate of 10 °C/min.

Obtained catalysts were characterized using XRD diffraction on a D8-ADVANCE-BRUKER diffractometer using Cu Kα radiation over a 2θ range between 10° and 60°. The morphologies of the bismuth molybdates were examined using a JEOL LSM 6360 LV and a FEI Quanta 200 scanning electron microscope. Specific surface area of powders was measured by the BET method using nitrogen gas with a Micromeritics Gemini device. XPS spectra were recorded using an ESCA Phi 600 spectrometer equipped with an Al anode ($h\nu$ = 187.850 eV). The powdered samples were pressed into pellets for the measurements. The binding energy of C1s (285 eV) was chosen as reference.

In order to measure conductivities, tablets of bismuth molybdates 1.3 cm in diameter and about 1 mm thick were prepared by a hydraulic press under a pressure of about 3 tonnes. Because as-prepared tablets were still easily breakable, they were immediately sintered at temperatures mentioned above for another 2 h. Contact electrodes on both surfaces of the tablets were made of gold by using vacuum evaporation technique. The conductivity measurements were performed by an impedance technique in air atmosphere. A HP4192A impedance analyzer was used. The impedance measurements were made in the frequency range 5 Hz to 13 MHz and in the temperature region from room temperature to 460 °C. The obtained data were analyzed by a Zview simulation program in order to calculate the resistance R. The conductivity σ was calculated from the resistance R using the following equation:

$$\sigma = \frac{d}{SR} \tag{1}$$

where σ is conductivity, d is the thickness of the tablets, S is the area of the contact electrode, and R is resistance.

The conductive activation energy E_a (eV) was estimated according to the general Arrhenius equation:

$$\sigma = \sigma_o \exp\left(\frac{-E_a}{kT}\right) \tag{2}$$

Or

$$\ln\sigma = \ln\sigma_o - \frac{E_e}{kT} \tag{3}$$

where σ_o is a constant and k is Boltzmann's constant (8.617×10^{-5} eV/K).

Thus, the activation energy E_a can be determined from the slope of the Arrhenius curve: $-E_a/k$.

Catalytic activities were measured in a conventional fixed-bed reactor with a stainless steel tube with an internal diameter of 0.4 cm. 0.2 g of catalyst (particle sizes are within the range 200–400 μm) was used with a total gas flow rate of 0.04 mmol/s at a pressure of 1 atm. The volume composition of the gas flow was $C_3H_6/O_2/N_2$ = 2.5/2.5/95 (%) and the reaction temperatures were maintained at 375, 400 and 425 °C. The reactor was operated as a differential reactor by keeping the conversion below 10%. Analysis of the propylene, oxygen and acrolein was performed using an on-line Trace GC Ultra-Thermo Electron Cooperation gas chromatograph with a column of 80/100 chromosorb and carbowax 20 M. The catalytic activity is expressed by the number of moles of acrolein formed per 1 g or 1 m^2 surface of the catalyst for 1 s.

3. Result and discussion

3.1. Composition and morphology of bismuth molybdates

In order to investigate the relationship between conductivity and catalytic activity and explore the origin of the synergy effect, pure gamma and beta phases and mixtures of beta and gamma phases were prepared as listed in Table 1. In Table 1, composition of each phase in the mixtures was determined from corresponding XRD data as shown in Fig. 1. The content of one phase is determined as:

$$A\,(\%) = \frac{I_A}{\sum(I_A + I_B + I_C + \cdots)} \times 100 \tag{4}$$

where A, B, C represent a given phase and I represents the intensity of the strongest XRD reflection. For mixtures of

Table 1
Composition of prepared bismuth molybdates

Bi/Mo ratio	Composition calculated from the used Bi/Mo ratio	Calculated composition from XRD data
2	100% γ	100% γ
1.5	67% γ + 33% β	72% γ + 28% β
1.3	46% γ + 54% β	46% γ + 54% β
1.1	18% γ + 82% β	29% γ + 71% β
1	100% β	≈100% β

gamma and beta, the strongest XRD reflection at, respectively, $2\theta = 28.08^\circ$ and 27.72° (Fig. 1) were used.

Table 1 shows that the compositions determined from XRD data compare quite well with the compositions calculated from stoichiometry.

The crystals of gamma and beta phases can be seen in SEM images in Fig. 2. These images show that crystals of beta phase

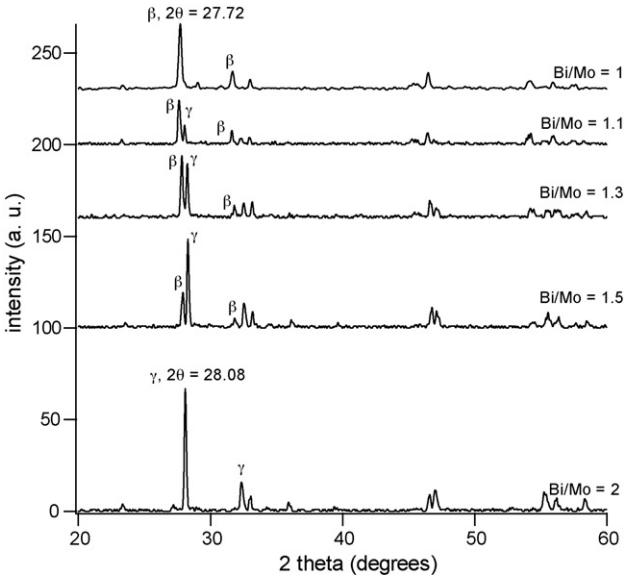

Fig. 1. XRD patterns of prepared bismuth molybdates.

(about 1 μm) are larger than the crystals of gamma phase (about 0.5 μm), which is in an agreement with our previous results [15]. The crystal sizes of bismuth molybdates prepared by sol–gel method are smaller than those synthesized by spray drying method as seen from our above-mentioned publication.

3.2. The dependence of conductivity of pure and mixed bismuth molybdates on the temperature

In order to investigate the dependence of conductivity of pure and mixed bismuth molybdates on the temperature and determine the activation energy, the samples were applied in the elevated temperature from room temperature to 460 °C in static air and their resistances were measured at a certain points. As a result, corresponding Arrhenius curves represented the relation between logarithm of conductivity σ and inverse temperatures were obtained (Fig. 3). Fig. 3 shows that at low temperatures, conductivities of all samples are low and approximately the same. Arrhenius curves have almost the same slopes, i.e. the same activation energies, at the low temperature ranges. It is of course due to the nature of bismuth molybdates which have low conductivity at low temperature but it might also be due to the poor compact or high porosity of the tablets of bismuth molybdates as seen in Fig. 4.

However, the slopes of the Arrhenius curves increase significantly at high temperature ranges. At the same time, conductivities increase remarkably and become different from sample to sample. Calculated activation energies of all samples at high temperatures (from 300 to 450 °C, the temperature where the catalytic reactions occur) are listed in Table 2.

It can be concluded from conductivity measurement that pure gamma bismuth molybdate (Bi/Mo = 2/1) has the highest conductivity while pure beta bismuth molybdate (Bi/Mo = 1/1) has the lowest conductivity. It is in an agreement with the literature and our previous data [9–11]. For the mixture of gamma and beta bismuth molybdate, the conductivities increase when the content of gamma phase increases. The dependence of conductivity of mixed samples at 425 °C (calculated from corresponding Arrhenius curves) on the ratio of Bi/Mo and the percentage of gamma or beta phase is shown

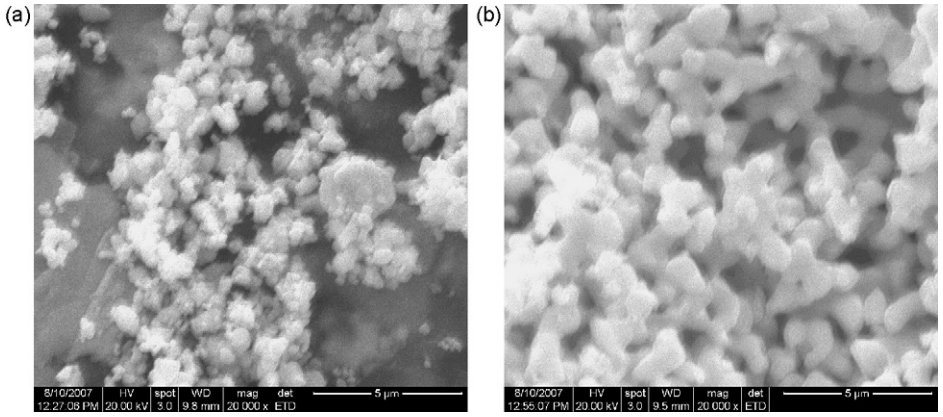

Fig. 2. SEM images of bismuth molybdate powder before conductivity and catalytic activity measurements: (a) pure gamma bismuth molybdate (Bi/Mo = 2), (b) pure beta bismuth molybdate (Bi/Mo = 1).

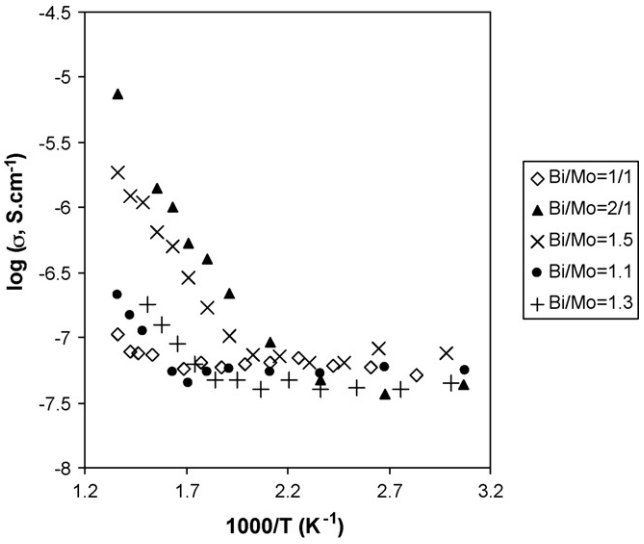

Fig. 3. Conductivities of bismuth molybdates as a function of temperature.

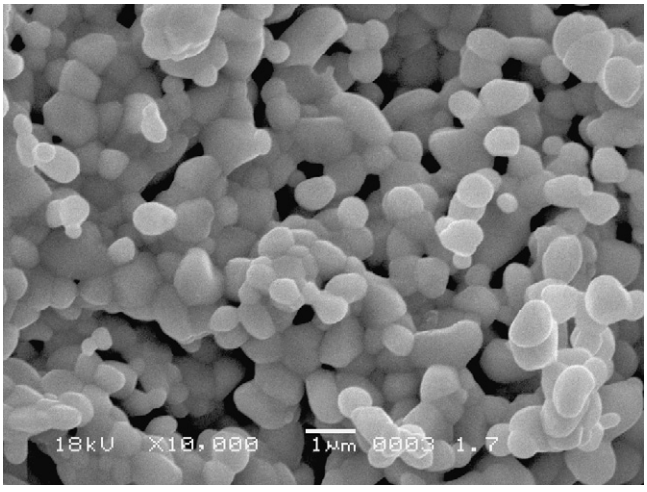

Fig. 4. SEM image of the tablet of gamma bismuth molybdate (Bi/Mo = 2/1) for the conductivity measurement.

in Fig. 5. It is noticed that the theory values of conductivities of mixed samples, which are calculated from the conductivities of each pure phase (gamma and beta) according to the rule of mixtures, locate at the line which connect the conductivity values of pure gamma phase (100% γ) and pure beta phase (100% β). However, the measured values of conductivities of mixed samples are lower than this line although they follow the

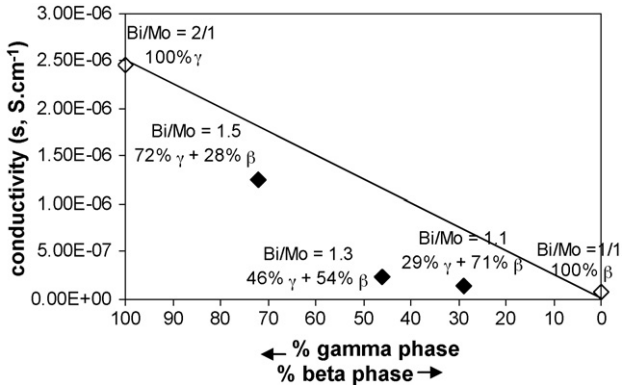

Fig. 5. Conductivities at 425 °C of bismuth molybdate samples with different percentage of gamma or beta phase as calculated from XRD data (white square: pure samples, black square: mixed samples).

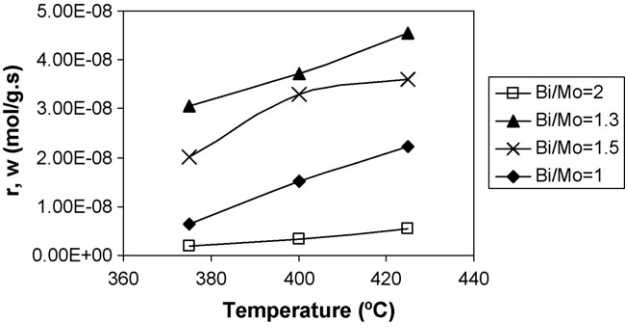

Fig. 6. Reaction rates for acrolein formation based on catalyst mass (r_w, mol/g s) at different temperatures (375–425 °C).

same trend: the conductivities increase when the content of gamma phase increases. Thus, the presence of the lower conductive phase – the beta phase – decreases remarkably the conductivity of the mixtures.

The observation of a (negative) deviation of the rule of mixtures is uncommon in ceramic composites and may require a deeper research in the way in which both components make contacts with each other and give rise to the overall value of the measured conductivities. In addition, our measurements do not differentiate between ionic and electronic contributions.

3.3. Catalytic activities of pure and mixed bismuth molybdates at different temperatures

Reaction rates for acrolein formation based on catalyst mass (r_w, mol/g s) at different temperatures (375–425 °C) are shown

Table 2
Conductive activation energy of bismuth molybdates at the temperature range of the catalytic reactions (300–450 °C)

Sample (Bi/Mo ratio)	E_a (300–450 °C) (eV)
2	0.43
1.5	0.43
1.3	0.34
1.1	0.40
1	0.12

Table 3
Surface areas (S_{BET}) and catalytic activation energy of bismuth molybdates at the temperature range of the catalytic reactions (375–425 °C)

Sample (Bi/Mo ratio)	S_{BET} (m^2/g)	E_a (375–425 °C) (kJ/mol)	E_a (375–425 °C) (eV)
2	1.5	76.17	0.79
1.5	1.7	43.75	0.45
1.3	1.8	29.97	0.31
1	1.3	92.77	0.96

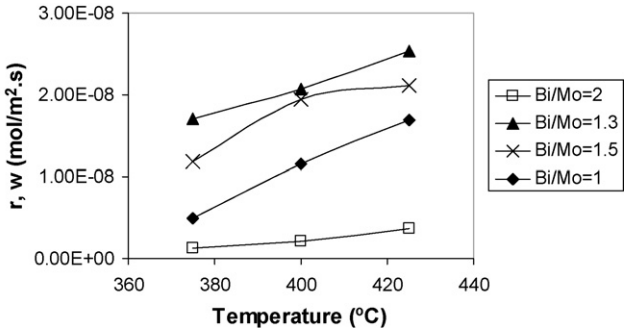

Fig. 7. Reaction rates for acrolein formation based on catalyst's surface areas (r_s, mol/m^2 s) at different temperatures (375–425 °C).

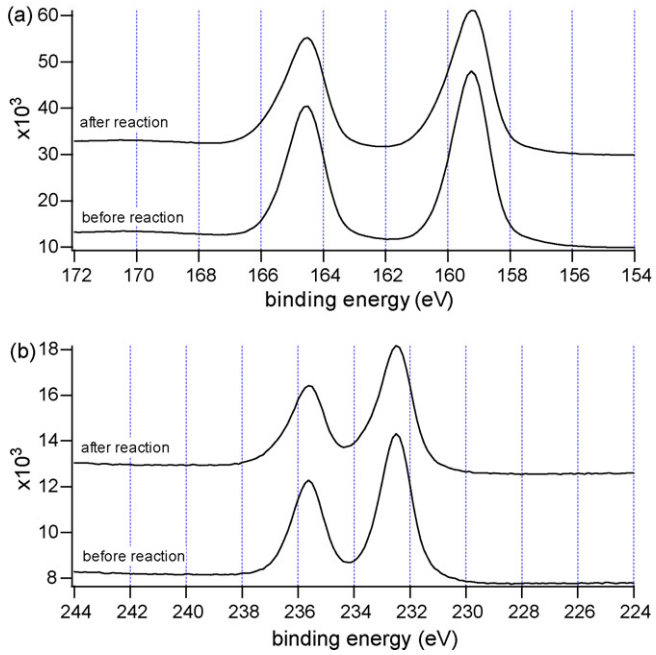

Fig. 8. Bi4f (a) and Mo3d (b) binding energy of gamma bismuth molybdate before and after a catalytic reaction.

in Fig. 6. Catalytic activation energies (E_a, kJ/mol) were determined from Arrhenius plots represented the dependence of ln(r_w) on 1/T. The data are shown in Table 3, here, value of E_a is also expressed using eV unit in order to make

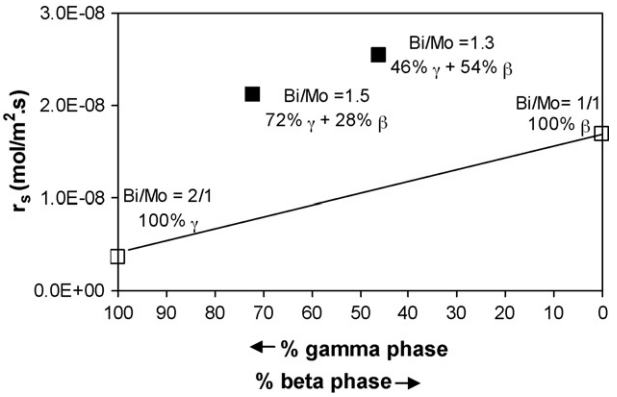

Fig. 10. Catalytic activities (reaction rate for propylene consumption) at 425 °C of bismuth molybdate samples with different percentage of gamma or beta phase as calculated from XRD data (white square: pure samples, black square: mixed samples).

it easily to compare with conductive activation energies (Table 2).

It is known that the catalytic activity is influenced by the surface area of the samples. Therefore, a more precise look on the catalytic activities of above-mentioned samples can be seen in Fig. 7—reaction rate for acrolein formation based on catalyst surface area (r_s, mol/m^2 s), where the surface areas of the catalysts (Table 3) have been taken into account.

The results clearly show that the catalytic activity of mixed samples (Bi/Mo = 1.3 and 1.5) are higher that those of pure samples (Bi/Mo = 2 and 1). This is due to the well-known synergy effect between gamma and beta phases both presented in these mixtures [7]. As seen from XPS measurements (Fig. 8), binding energy of bismuth molybdates before and after a catalytic reaction is completely the same. Thus, the origin of the observed synergy effect may not due to the formation of a new valency of bismuth or molybdenum atoms at the surface. The proposal about the assistance of a higher conductive phase in transportation of lattice oxygen during the catalytic reaction may, therefore, be sufficient in this case.

SEM images of samples before and after a catalytic measurement (Fig. 9) show no significant change in the crystal size. Thus, high temperatures (375–425 °C) of the catalytic reaction, which last for about 5 h, did not influence remarkably on the morphology of the catalysts.

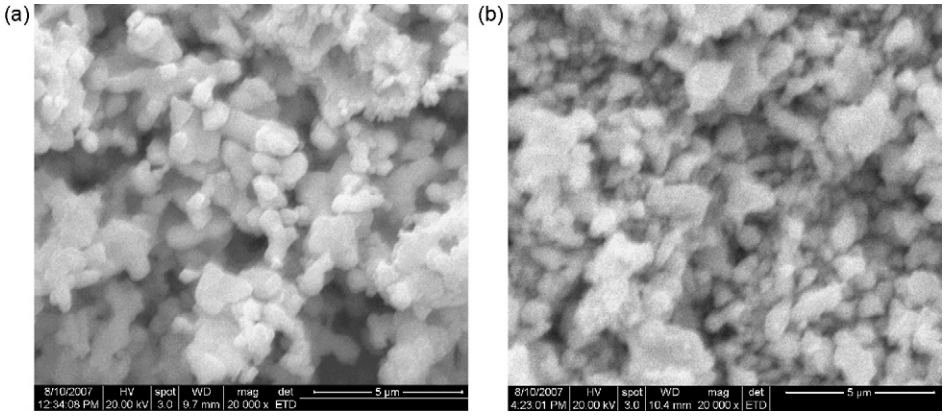

Fig. 9. SEM images of a mixed sample of bismuth molybdate (Bi/Mo = 1.3) before (a) and after (b) catalytic activity measurements.

3.4. The relation between conductivity and catalytic activity of bismuth molybdates

The relation between conductivity and catalytic activity of bismuth molybdates is explored by comparing the trend of conductivity and catalytic activity at the same temperature. The dependence of catalytic activity of mixed samples at 425 °C on the ratio of Bi/Mo and the percentage of gamma or beta phase is shown in Fig. 10. Oppositely to the conductivity, the catalytic activities of mixed samples are higher than the activities of both pure phases: gamma and beta. This is the synergy effect mentioned previously. Thus, the comparison on trends of conductivity and catalytic activity showed that the postulate that the sample with high conductivity will also have high catalytic activity is not true. For example, the mixed sample with Bi/Mo ratio of 1.3 possesses significant high catalytic activity although it has low conductivity. On the other hand, although the conductivity of the sample with Bi/Mo ratio of 1.3 does not increase remarkably compared to the conductivity of pure beta bismuth molybdate, its catalytic activity still increase significantly. When the content of gamma phase increases, the conductivity increases and the catalytic activity still reasonable high (the sample with Bi/Mo = 1.5) but when the beta phase is disappeared from the mixture, the catalytic activity became low even of the high conductivity (the pure gamma phase sample). Thus, the presence of beta phase is essential for resulting in a synergy effect. The reasonable content of gamma phase in the mixture is also an essential factor to result in a synergy effect even if its presence can increase significantly the conductivity of the mixture or not.

A look at the conductive activation energies (Table 2) and catalytic activation energies (Table 3) of these bismuth molybdate samples shows that the conductive activation energies and catalytic activation energies of the samples possess synergy effect (Bi/Mo = 1.3 and Bi/Mo = 1.5) are very close. These catalytic activation energies are lower than those of pure phases (Bi/Mo = 1 and Bi/Mo = 2), which correctly fit with their higher reaction rates. However, these conductive activation energies are not the lowest or highest ones compared to those of pure phases. That is probably another evidence proving that they possess synergy effect in catalytic properties but not in conductive properties.

4. Conclusions

It is turned out here that it is not easy to conclude on the relation between conductivity and catalytic activity of bismuth molybdates and the origin of the synergy effect. Probably, the high conductivity or the high ability to replenish lattice oxygen which is represented through the presence of the gamma phase does play a role during the selective oxidation process but the role of the high number of active sites to abstract the α-hydrogen which is represented through the presence of the beta phase is more important. Thus, only a very small increase in conductivity of the mixed bismuth molybdate samples is enough to result in a remarkable increase in their catalytic activity (the sample with Bi/Mo = 1.3). However, this effect is easily lost and overcompensated by decreasing the number of active sites to abstract the alpha hydrogen (the sample with Bi/Mo = 1.5). Therefore, it may be worth to continue the study on the improvement of conductivity by inducing defects inside the structure but the number of active sites to abstract the α-hydrogen is still maintained.

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References

[1] D. Carson, G. Coudurier, M. Forissier, J.C. Vedrine, J. Chem. Soc., Faraday Trans. 1 (79) (1983) 1921.
[2] D. Carson, M. Forissier, J.C. Vedrine, J. Chem. Soc., Faraday Trans. 1 (84) (1980) 1017.
[3] Z. Bing, S. Pei, S. Shishan, G. Xiexian, J. Chem. Soc., Faraday Trans. 86 (1990) 3145.
[4] M. El Jamal, M. Forissier, G. Coudurier, J.C. Vedrine, in: M.J. Phillipd, M. Ternan (Eds.), Proceedings of Ninth International Congress on Catalysis, The Chemical Institute of Canada, Ottawa, (1988), p. 1617.
[5] E. Godard, E.M. Gaigneaux, P. Ruiz, B. Delmon, Catal. Today 61 (2000) 279.
[6] A.P.V. Soares, L.D. Dimitrov, M.C-R.A. de Oliveira, L. Hilaire, M.F. Portela, R.K. Grasselli, Appl. Catal. A-Gen. 253 (2003) 191.
[7] M.T. Le, W.J.M. Van Well, P. Stoltze, I. Van Driessche, S. Hoste, Appl. Catal. A-Gen. 282 (2005) 189–194.
[8] R.K. Grasselli, Topics Catal. 21 (2002) 79.
[9] L. Boon, R. Metselaar, J. Solid State Inorg. Chem. 27 (1990) 381.
[10] L. Boon, R. Metselaar, Solid State Ionics 16 (1985) 201.
[11] M. Hartmanova, M.T. Le, I. Van Driessche, S. Hoste, F. Kundracik, Russ. J. Electrochem. 41 (5) (2005) 455–460.
[12] Y. Moro-Oka, W. Ueda, Adv. Catal. 40 (1994) 233.
[13] R.K. Grasselli, J.D. Burrington, Adv. Catal. 30 (1981) 133.
[14] M.T. Le, W.J.M. Van Well, I. Van Driessche, S. Hoste, Appl. Catal. A-Gen. 267 (2004) 227–234.
[15] M.T. Le, J. Van Craenenbroeck, I. Van Driessche, S. Hoste, Appl. Catal. A-Gen. 249 (2003) 355–364.