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STRUCTURAL CHARACTERISTICS AND OXIDATIVE ACTIVITY OF BISMUTH MOLYBDATE CATALYSTS

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SUMMARY

Bismuth molybdate materials with various phases were synthesized by spray drying method. Their structural characteristics were studied by XRD and SEM, and surface area was determined using BET method. Catalytic characteristics were investigated toward oxidation reaction of propylene to acrolein. The results obtained show that the material samples obtained correspond to three almost pure phases of bismuth molybdate, alpha, beta and gamma. The reaction rates over beta and alpha phases are higher however; activated energy is lower on gamma phase. These data are in agreement with reaction schema of propylene oxidation, in which the abstraction of the first hydrogen atom proceeds over Bi-O polyhedron, while oxygen inserted into carbon atom in reactant molecule is derived from lattice bound to Mo.

I - INTRODUCTION

Bismuth molybdate materials are known as good oxidative catalysts, especially in selective oxidation of olefins, and of industrially great interest [1]. The oxidation process over such oxide catalysts, for example, propylene oxidation, can begin with the abstraction of hydrogen atom from methyl group. The abstraction of the second hydrogen and transference of oxygen from bismuth molybdate lattice in order to bind to carbon of this group in forming aldehyde group can happen in different order. Thus, the lattice oxygen plays a key role in the process of selective oxidation over oxide catalysts. Bismuth molybdate have 8 different modifications, of this number, however, only three phases are catalytically active, these are alpha, beta and gamma, corresponding to chemical formulas $Bi_2O_3.3MoO_3$ (Bi/Mo = 2/3); $Bi_2O_3.2MoO_3$ (Bi/Mo = 2/2); and $Bi_2O_3.MoO_3$ (Bi/Mo = 2/1). The investigations on structure-catalytic activity relationship have attracted great interest for many years, however up to now one united viewpoint on this problem still cannot be achieved.

This work continues the previous studies [3] with the hope to contribute more knowledge about above mentioned relationship.

II - EXPERIMENT

Bismuth molybdate materials are prepared by spray drying (SD) method as described in detail in [4]. Briefly, the preparation of catalysts is carried out as follows: aqueous solution of $(NH_4)_6Mo_2O_{24}.4H_2O$ is mixtured with aqueous solution of $Bi(NO_3)_3.5H_2O$ with Bi/Mo ratios equal to 2/3, 2/2 and 2/1 aiming to form the phases alpha (Bi/Mo = 2/3), beta (Bi/Mo = 1/1) and gamma (Bi/Mo = 2/1) of bismuth molybdate. After mixture, obtained solutions are clear, homogeneous and stable for 24 hours. These solutions are spray dried on laboratory

equipment Büchi 190 with the rate of 5 ml/min at temperature 225°C.

X ray diffraction (XRD) experiments are performed on a Siemens D5000 Diffractometer, using CuKα radiation (λ = 1.5406 Å) with accelerating voltage of 35 kV and anode current of 30 mA. In all diffraction patterns scanning angle 2θ is changed from 5° to 75° and scanning rate is 0.2°/min.

Special surface area is determined using BET method on the apparatus Sorptomatic 1990 of company ThermpQuest.

Scanning electron microscopy (SEM) images are recorded on apparatus Philips 501. Before recording SEM images, the samples are washed carefully, carried on bracket and dried.

Oxidative catalytic activity is determined toward oxidation reaction of propylene to acrolein and carried out on microflow catalytic reaction system, inner diameter of reactor 0.4 cm. Catalyst particle sizes are 200 - 400 μm. The flow rate is 0.04 mmol/sec, pressure 1 atm and temperature changes in the range 375 - 400°C. Composition of gas flow $C_3H_6/O_2/N_2$ is equal to 2.5/2.5/95 (volume %). Reaction products are analyzed on chromatograph GC-17A Shimadzu connected directly to reactor, chromatographic column contains 80/100 chromosorb and carbowax 20M. Reaction rate is estimated as mol number of acrolein formed per 1 m^2 surface of catalyst in 1 second. Selectivity (%) is calculated as mol% of acrolein formed over mol number of reacted propylene.

III - RESULTS AND DISCUSSION

XRD spectra of bismuth molybdate samples are given on figure 1. The XRD spectra show that the samples obtained by spray drying correspond to the phases α (Bi/Mo = 2/3), β (Bi/Mo = 1/1) and γ (Bi/Mo = 2/1). From these results it can be asserted that the conditions used in this work for preparing bismuth molybdate materials allow to obtain almost pure phase's alpha, beta and gamma as intended for beginning.

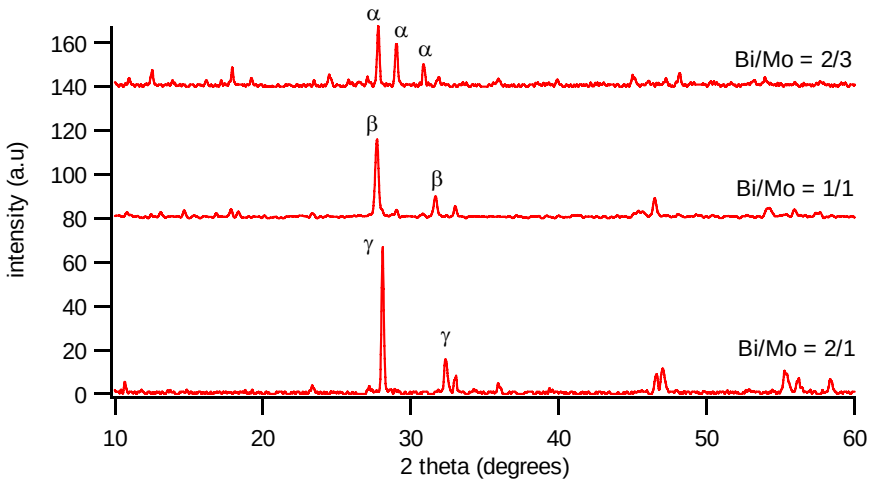


Figure 1: XRD spectra of bismuth molybdate samples

According to [5] the phases α and β have defective fluorite structure, while the phase γ belongs to Auruvillius structure. In [2] the crystalline structure of α-$Bi_2Mo_3O_{12}$ is described, in which all MoO_4 tetrahedrons are in the form of Mo_2O_8, while all Bi are linked with 8 neighbouring oxygen atoms; the crystalline structure of β-$Bi_2Mo_2O_9$ consists of Bi^{3+} cations coordinated octahedrally to oxygen anions with different distances, while Mo^{6+} have disorderly tetrahedral coordination. The crystalline structure of γ-Bi_2MoO_6 belongs to koechlinite

mineral structure, in which the layers of $(Bi_2O_2)_n^{2+}$ and $(MoO_2)_n^{2+}$ octahedrons are connected one another through O^{2-} in forming $(Bi_2O_2)_n^{2+}O_n^{2-}(MoO_2)_n^{2+}O_n^{2-}$ chains. Layer structure of γ-Bi_2MoO_6 is also considered in [1], according to that, the structure of γ-Bi_2MoO_6 consists of layers of MoO_6, separated by Bi_2O_3 layers. Such structures lead to their low surface area.

Our results obtained from measuring special surface area (S_{BET}) of bismuth molybdate catalysts are given in table 1. These results show that the special surface area of all samples is small. However, the special surface area of γ-Bi_2MoO_6 sample is higher. It may be due to the layer structure of γ-Bi_2MoO_6 material.

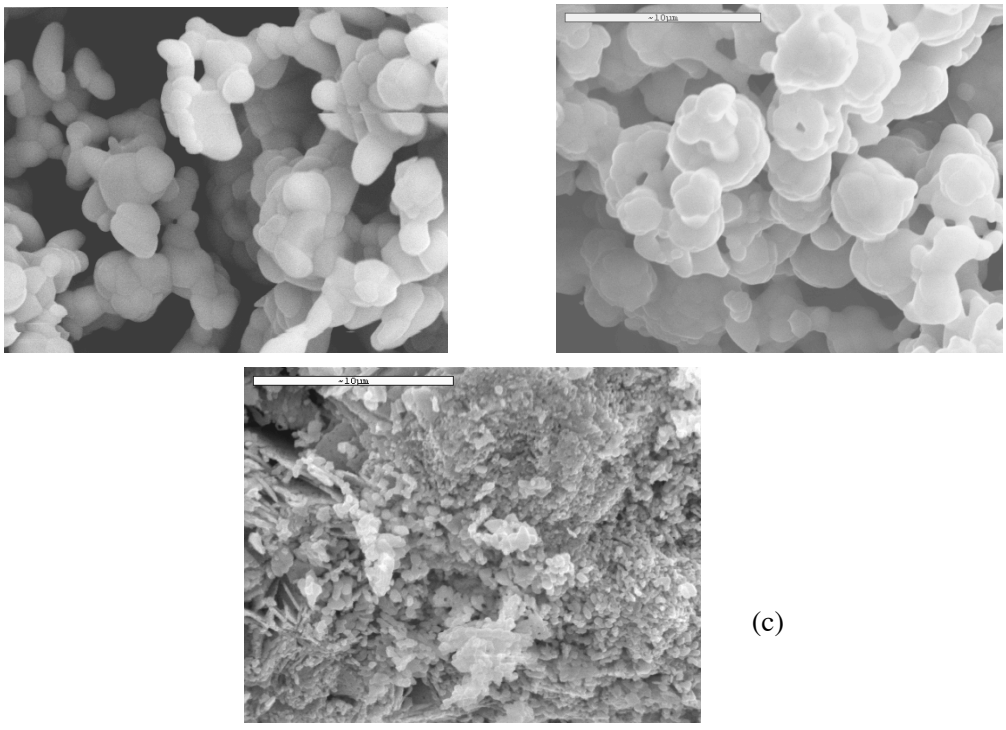
Figure 2 shows SEM images of bismuth molybdate materials. Fig. 2a gives SEM image of α-$Bi_2Mo_3O_{12}$, Fig.2b-β-$Bi_2Mo_2O_9$, and Fig.2c-γ-Bi_2MoO_6. From these images it can be seen the differences in surface states of bismuth molybdate phases, especially in comparison of the third sample with the first and the second ones. These differences certainly influence their catalytic activity, too.

Table 1: Special surface area of bismuth molybdate catalysts

Catalyst	S_{BET}, m^2/g
α-$Bi_2Mo_3O_{12}$ (2/3)	1.5
β-$Bi_2Mo_2O_9$ (1/1)	1.4
γ-Bi_2MoO_6 (2/1)	1.8

The results of investigating oxidative catalysis of bismuth molybdate phases towards oxidation reaction of propylene to acrolein are given in Fig. 3. From Fig. 3, the possibility of selective oxidation can be arranged in the following order: β-$Bi_2Mo_2O_9$ (1/1) > α-$Bi_2Mo_3O_{12}$ (2/3) > γ-Bi_2MoO_6 (2/1).

(a) (b)



(c)

Figure 2

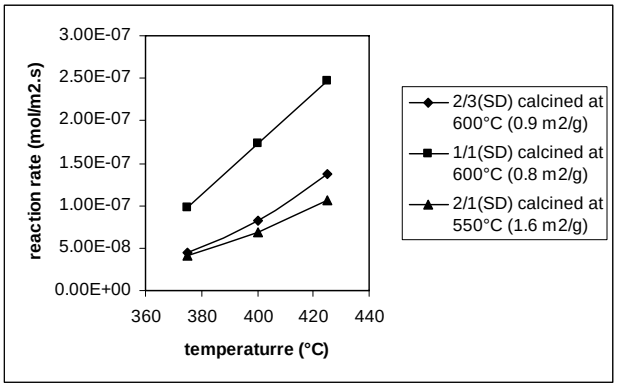


Figure 3: Rates of oxidation reaction of propylene to acrolein on bismuth molybdate catalysts.

The temperature dependences of reaction rates allow calculating approximately activated energies. The results of these calculations towards oxidation reaction of propylene to acrolein on bismuth molybdate catalysts are given in table 2.

Table 2: Activated energies (E_a) and selectivity's of oxidation reaction on bismuth molybdate catalysts

Catalyst	Ea (kJ/mol)	Selectivity, %		
		375□C	400□C	425□C
γ-Bi_2MoO_6 (2/1)	68.2	81	83	89
β-$Bi_2Mo_2O_9$ (1/1)	70.4	72	91	92
α-$Bi_2Mo_3O_{12}$ (2/3)	83.2	47	64	77

It can be more possible that the layer structure of γ-Bi_2MoO_6 (2/1) leads to easier transference of lattice oxygen [6]. The obtained data may be agreed to reaction schema for important role of lattice oxygen in oxidation reaction over bismuth molybdate catalysts [7] (Fig. 4).

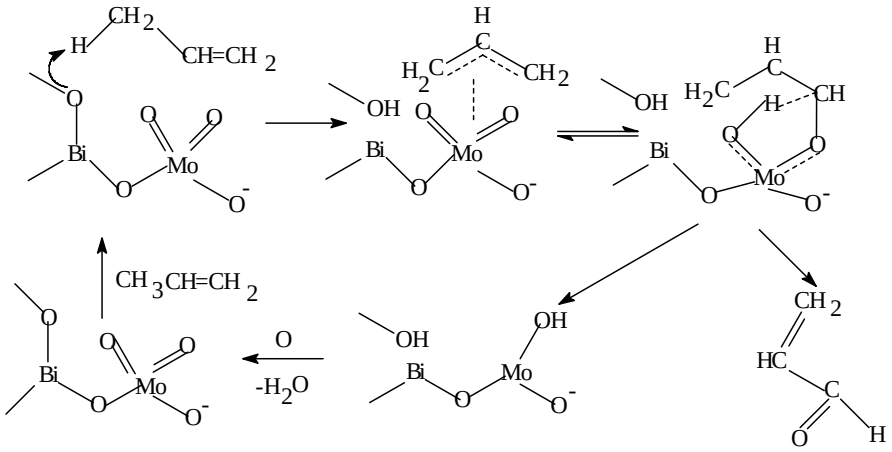


Figure 4: Schema for selective oxidation of propylene to acrolein over bismuth molybdate catalysts

According to above schema, the abstraction of hydrogen from methyl group happens over Bi-O polyhedrons, while oxygen atom inserted to carbon atom in forming aldehyde group is derived from the lattice bound to Mo [6]. It can be due to layer structure of gamma phase leading to either its higher special surface area or easier transference of oxygen.

IV - CONCLUSIONS

- By spray drying method are obtained bismuth molybdate samples, corresponding to almost pure alpha, beta and gamma phases;

- The results from investigations of XRD, SEM and determination of special surface area show the differences in structure of bismuth molybdate materials, in which two phase alpha and beta are not very greatly different, while gamma phase has layer structure;

- The reaction rate is higher over beta and alpha phases, but activated energy of reaction over gamma phase is lower. The results are agreed with the reaction schema, in which the abstraction of the first hydrogen happens over Bi-O polyhedron, and oxygen atom inserted into carbon atom of reactant is derived from lattice bound to Mo.

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