Mechanochemically Assisted Synthesis of $Bi_2Mo_3O_{12}$ Catalysts

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Abstract

The solid phase synthesis of $Bi_2Mo_3O_{12}$ is investigated. The mechanochemical activation is used in order to reduce the synthesis times and temperatures. A 5 h mechanical treatment leads to a drastic decrease in the temperature of classical solid state synthesis of $Bi_2Mo_3O_{12}$ (from 600 to 350 °C). The product obtained is single-phase, consisting of even size distributed submicronic particles. The synthesis of $Bi_2Mo_3O_{12}$ was monitored by X-ray diffraction (XRD) and infrared spectroscopy (IR). Shape and size changes of reagent particles after mechanical treatment and morphological peculiarities of the products were studied by SEM.

INTRODUCTION

Bismuth molybdates have been the subject of extraordinary high and permanent interest due to their wide use as highly efficient catalysts for selective oxidation/oxidative dehydrogenation or ammoxidation of lower olefins [1]. Among bismuth molybdates, those having the general formula $Bi_2O_3 \cdot nMoO_3$ (where $n = 3$, 2, 1 for α-, β- and γ-molybdates, respectively) are the most catalytically active ones.

The traditional synthesis method for obtaining these compounds is solid state interaction between Bi_2O_3 and MoO_3. Using the same method, synthesis of γ-Bi_2MoO_6 was performed by solid state interaction between Bi_2O_3 and MoO_3 with 2 days heating at 500 °C, 6 days at 580 °C and 8 days at 580 °C. Meanwhile the samples were reground and pressed into pellets [2].

M. Le and co-workers [3] recommended a spray drying synthesis process as the best route to produce fine-grained bismuth molybdate catalysts, grinding being needed.

Our research has focused on developing a rational route for synthesis of ultra fine bismuth molybdate powder which is a precondition for its high catalytic activity. For that purpose we investigated the two step process of mechanically assisted synthesis involving mechanical treatment of reagents and synthesis of the product at relatively lower temperature. Some properties of the product are also studied.

EXPERIMENTAL

Stoichiometric mixtures of MoO_3 (Merck) and Bi_2O_3 (Merck) in a 1 : 3 molar ratio were subjected to intense mechanical treatment in a Fritsch planetary mill for different periods of time. Stainless steel vessels and balls (Ø 10) were used and a small amount of reagents was removed periodically from the reactor for XRD and SEM analyses. The mechanically treated samples were heated in an air atmosphere at temperatures below the eutectic point (618 °C) [4]. The synthesis of $Bi_2Mo_3O_{12}$ was monitored by X-ray phase analysis using a Philips APD-15 apparatus with CuK_α radiation and infrared spectroscopy using KBr pellets and a Nicolet 320 FTIR spectrometer. Shape and size changes of reagent particles after mechanical treatment and morphological peculiarities of the products were studied by SEM (Jeol-357).

RESULTS AND DISCUSSION

Figure 1 presents a SEM image of homogenized reagents for synthesis of $Bi_2Mo_3O_{12}$ before mechanical treatment. The particles have

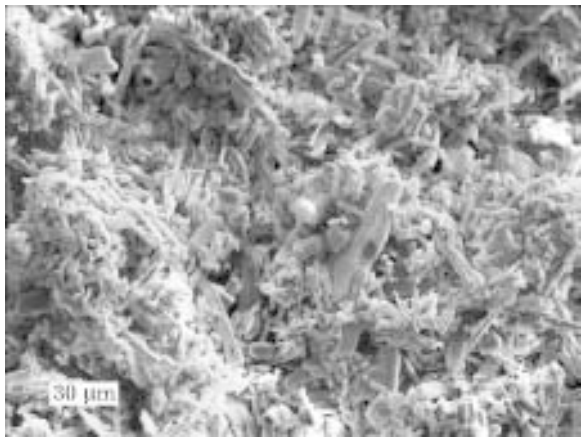

Fig. 1. SEM image of the initial reagent mixture Bi_2O_3 : MoO_3 in a molar ratio 1 : 3. ×600.

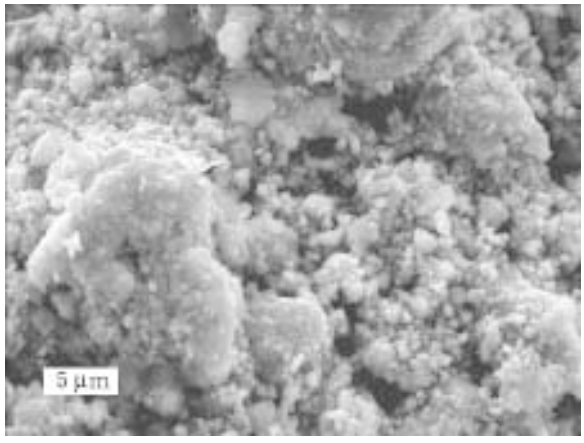

Fig. 2. SEM image of reagents after 5 h mechanical activation. × 4000.

a lengthened needle-like (MoO_3) and globular (Bi_2O_3) shape with a mean size of about 30 mm. The processes of milling and enhancing the contact area among the reagent particles, as well as the appearance and accumulation of different types of defects in the course of mechanical treatment, led to a higher activity of Bi_2O_3 and MoO_3 and made the synthesis of the final product under milder conditions possible.

A SEM image of a reagent mixture of Bi_2O_3 and MoO_3 (1 : 3) after 5 h intense mechanical treatment in a planetary ball mill is shown in Fig. 2. After the milling process, the particles acquire a submicronic size and closer contacts. The planetary mills are especially suitable for mechanical activation due to the high acceleration values and the complicated trajectory of milling bodies.

Figure 3, *a* and *b* shows the diffraction patterns of mixtures of initial reagents before and

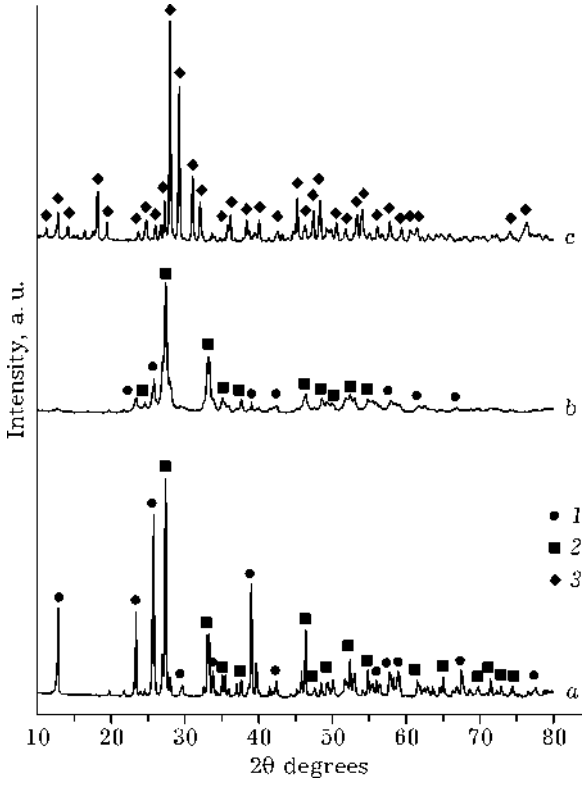

Fig. 3. X-ray diffractograms of reagent mixture before mechanical treatment (*a*), after 5 h mechanical treatment (*b*), and mechanochemically activated for 5 h and calcinated for 3 h at 350 °C (*c*): *1* – MoO_3, *2* – Bi_2O_3, *3* – $Bi_2Mo_3O_{12}$.

after mechanical treatment. X-ray phase analysis shows no phase changes after mechanical activation of the initial oxide mixture. The broadening and intensity decrease of the characteristic peaks after the mechanical treatment indicate formation of structural defects, which are the main reason for the temperature decrease of the $Bi_2Mo_3O_{12}$ synthesis. After a 5 h

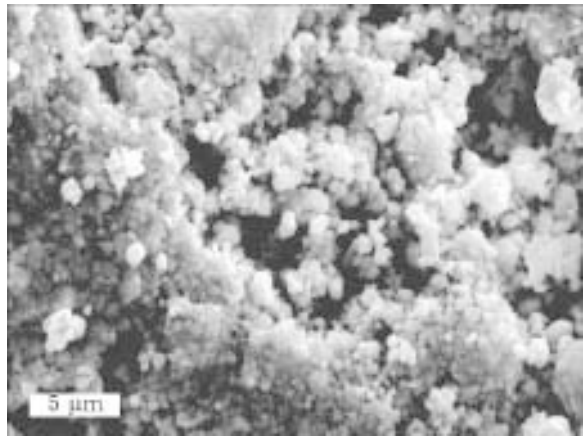

Fig. 4. SEM image of $Bi_2Mo_3O_{12}$, obtained by mechanically assisted synthesis. × 4800.

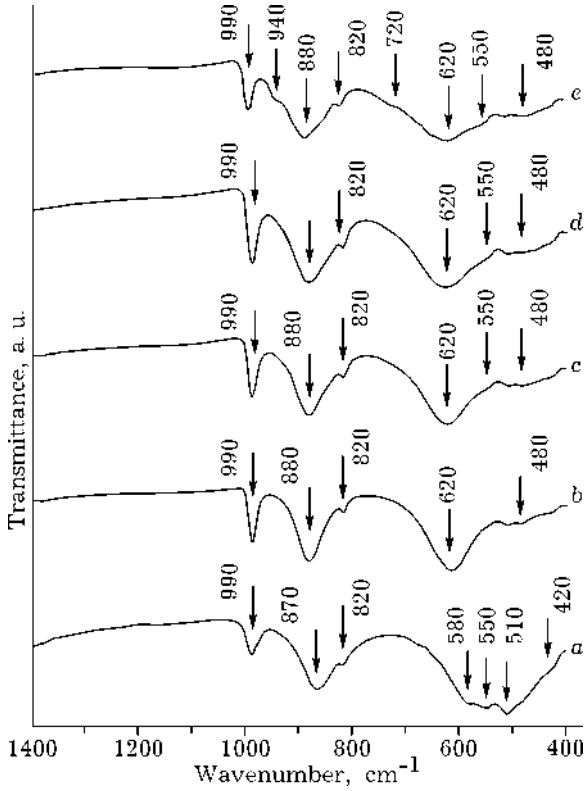

Fig. 5. Infrared spectra of reagent mixture before mechanical treatment (*a*), after 1 (*b*), 2 (*c*), 3 (*d*) and 5 h (*e*) mechanical treatment.

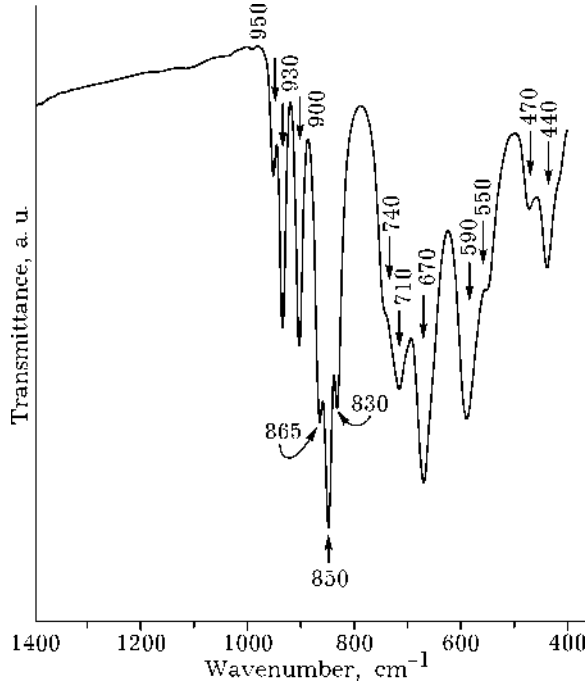

Fig. 6. Infrared spectrum of $Bi_2Mo_3O_{12}$.

activation of the initial mixture followed by 3 h calcination at 350 °C, single phase $Bi_{12}Mo_3O_{12}$ was obtained [5] (see Fig. 3, *c*). Figure 4 presents a SEM image of the product obtained by mechanically assisted synthesis at 350 °C. The particles possess uniform morphology and a mean size of about 0.5 μm.

Figure 5 presents the infrared spectra of a mixture of the initial reagents before and after mechanical treatment for different periods of time. The vibration spectrum of the nonactivated sample (see Fig. 3, *a*) shows the characteristic absorption bands of MoO_6 and BiO_6 polyhedra building the structure of MoO_3 and Bi_2O_3. The band at 990 cm^{-1} corresponds to the stretching modes of the short Mo=O band. The absorption bands at 870 and 820 cm^{-1} are due to the vibrations of Mo–O–Mo bridge bonds (Mo_2O entity) of corner-bound MoO_6 polyhedra whereas the band at 580 cm^{-1} is ascribed to stretching modes of Mo_3O entity of edge-bonded MoO_6 groups in the structure of MoO_3 [6, 7]. The bands at 550 and 510 cm^{-1} are associated with the vibrations of Bi–O bonds of strongly distorted BiO_6 groups in the crystal structure of Bi_2O_3 [8].

In the spectra of the mechanically activated initial mixtures there are visible changes in the low-frequency region (below 600 cm^{-1}). The shift of the 580 cm^{-1} band to 620 cm^{-1} and its broadening with the activation time is an indication of the distortion of the MoO_6 units forming the short range order of MoO_3. The appearance of shoulders at 940 and 720 cm^{-1} evidences that part of the MoO_6 octahedra were transformed into MoO_4 units [9, 10]. Figure 6 shows the IR spectrum of $Bi_2Mo_3O_{12}$ prepared by mechanically activated synthesis. All characteristic absorption bands of $Bi_2Mo_3O_{12}$ are present [11, 12].

CONCLUSIONS

This study demonstrates the advantages of the method of mechanically assisted synthesis of $Bi_2Mo_3O_{12}$. The product obtained is single-phase, consisting of even size distributed submicronic particles.

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