Influence of Mechanochemical and Ultrasonic Treatments on the Structure and Properties of ZnO-MoO_3 (1:1) Composition

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Abstract – Oxide mixture ZnO-MoO_3 (1:1) was modified by mechanochemical (during 2, 4 and 8 hours in air) and sonochemical (1 hr in water solution) treatments. The properties of obtained samples were studied by means of XRD, IR-spectroscopy, BET, DTA-TG, SEM methods. It was shown, that both kinds of treatments lead to the change of oxides crystalline structure, their surface morphology, porous structure and decrease particle size. The formation β-$ZnMoO_4$ in the milling process and β-Mo_8O_{23} at ultrasonic effect it was found.

Key words – mechanochemistry, sonochemistry, zinc oxide, molybdenum oxide, zinc molybdates.

I. Introduction

It is known that compositions on the base of zinc and molybdenum oxides (zinc molybdates) are widely use in electronic and as heterogeneous catalysts. In the last case the possibility of the use on the one hand, high catalytic activity of MoO_3 in the oxidation reactions of alcohols, amines, hydrocarbons [1], and, on the other hand, high photocatalytic activity of ZnO for removing of exhaust gases, hydrogen purification and methanol synthesis [2] exist. The traditional methods of zinc molybdates preparation (solid phase synthesis, precipitation, hydrothermal synthesis etc.) have some drawbacks and the creation of new methods preparation of these compounds is very actual.

It is found that mechanochemical treatment (MChT) permits to obtain the nanocompositions with larger specific surface area, the structure with specific planes and other properties, reduce the production stages, realize the energy consumption, and prepare the catalysts in metastable state. Ultrasonic treatment (UST) as a type of mechanochemistry but in solution allows to acceleration of the chemical reactions, obtaining the highdispersive, homogeneous and chemical pure mixtures of solid particles in solutions at room temperature. In this communication the results of MChT and UST treatment on ZnO-MoO_3 properties reported.

II. Experimental

Oxide zinc-molybdenum composition ZnO/MoO_3=50:50 was prepared by mixing of oxides zinc and molybdenum («p»). Mechanochemical treatment of samples was conducted in the planetary ball mill Pulverisette-6 (Fritsch) during 2, 4 and 8 hours in air. The rotation speed was 550 rpm. The vial (200 cm^3) and balls (5 mm in diameter) were made of ZrO_2. The BPR was 10:1. Ultrasonic treatment carried out in water solution during 1 hour to use apparatus UZDN which operate in the effect mode of acoustic cavitation at a frequency 22 kHz. The reaction medium temperature was supported at 80°C to circulation cold water around the reactor. Obtained suspensions were dried at 110°C in air.

The physico-chemical properties of investigated system before and after modification by both treatment methods were studied by means of XRD, IR-spectroscopy, BET, DTA-TG and SEM methods.

III. Results

X-ray data show that milling and ultrasonic effects lead to decrease of main reflexes of initial oxides intensity (Fig.1). The appearance of new reflexes which correspond to hydrated phase of molybdena $MoO_3 \times 0.5H_2O$ monoclinic modification with maximum reflex from the plane (-111), which formation can be connect with water, absorbed by initial oxides was fixed after 2 h MChT.

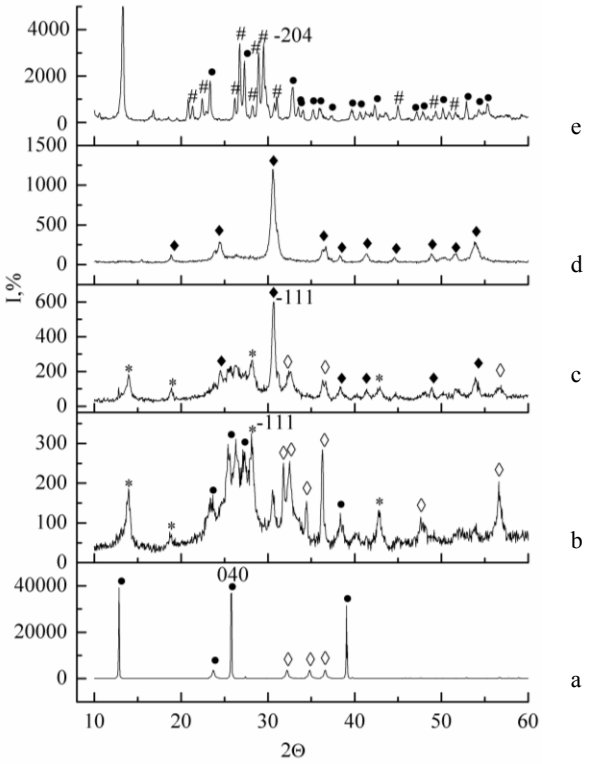

Fig. 1. Diffractogram of initial system Zn/Mo=50:50 - *a*, after MChT 2h - *b*, 4h - *c*, 8h - *d*, 1h UST- *e*
• α-MoO_3, ◊ ZnO, ♦ β-$ZnMoO_4$, * $MoO_3 \times 0.5H_2O$, # β-Mo_8O_{23}

Increase of processing time to 4 hours accompanied by subsequent decrease of reflexes intensity of initial oxides and $MoO_3 \times 0.5H_2O$ phase and the appearance of the reflexes of phase β-$ZnMoO_4$ with the most intense reflex from the plane (-111). After the further treatment (8h) the reflexes of β-$ZnMoO_4$ are observed on the diffractogram only that correspond to reaction:

$$ZnO + MoO_3 = ZnMoO_4 \quad (1)$$

The XRD analysis of the sample modified by ultrasound shows the crystallographic displace in MoO_3 occurs to formation of β-Mo_8O_{23} monoclinic modification with dominant reflex of this phase from the plane (-204) on the diffractogram.

The calculation of crystallite size (L) by Scherer equation shows their significant decrease after system modification by both treatment methods (Table I).

TABLE 1

XRD AND BET RESULTS OF SYSTEM ZnO/MoO_3=50:50

Parameter	MChT				UST
	0	2	4	8	1
L, nm	56	13	18	15	33
d, nm	0.34	0.32	0.29	0.29	0.33
S_{BET}, m^2/g	2	5	6	9	3
V_s, cm^3/g	0,015	0,021	0,027	0,036	0,056

The studies of the compositions by IR-spectroscopy confirm the changes of samples structure after ultrasonic and mechanical treatments. It is found, that the shifting of absorption bands of therminal bond Mo=O from 991 to 960 cm^{-1}, linear bridge Mo-O-Mo from 890 to 867 cm^{-1} and Zn–O bond from 473 to 450cm^{-1} are observed after mechanochemical modification. Presence of band at 955 cm^{-1}, which belongs to vibrations of Mo-OH bond confirms the formation of hydrated phase $MoO_3 \times 0.5H_2O$. IR-spectrum of sample treated by ultrasound shows the presence of absorption bands of edge bridge bond at 655, 746 cm^{-1} in Mo_8O_{23} and linear bridge Mo-O-Mo bond at 882 cm^{-1} in α -MoO_3.

According to results, obtained by BET and BJH methods the mechanochemical activation leads to increase of pore volume, specific surface area (Table I) and the change of sample porous structure – from macroporous to mesoporous, with the maximum values of pore volume equal to 5-22 nm, while the ultrasonic effect is not accompanied by porous structure change (main pore volume is 88 nm) and leads to an increase of macropores volume only.

The thermogram of initial mixture demonstrates the presence of two thermal effects: first endothermic effect is observed in temperature range 136-208°C, which corresponds to process of removal of strongly bounded water and second, exothermic effect at 510°C, associated with the process of crystallization wurtzite phase ZnO. Character thermo-analytical curves after 2 hours of MChT shows the weight loss (4%) on the TG-curve, which occurs at small endothermic effect (140-230°C). Endothermic effect in temperature range 660-740°C with maximum at 680° (without weight loss) associated with nanoparticles of α-MoO_3 melting, while for bulk MoO_3 the $T_{melt.}$ is 790-801°C.

The DTA data of sample after ultrasonic irradiation show the presence of endothermic effects series. In temperature range 150-280°C the composition loses the water by two steps every of which accompanied by weight loss 7%. The first dehydration of the sample (adsorbed water) occurs at 150-205°C with maximum at 175°C. Second dehydration step (constitutional water) is observed within 250-300°C, which causes the second endothermic peak with maximum at 277°C. At the increase of temperature up to 800°C on DTA-curve the insignificant endothermic effect at 740°C is observed which corresponds to melting process of MoO_3 and doesn't related with weight loss.

The studies of the samples surface morphology by SEM method show that the initial composition has the form of long plate formations while after mechanochemical and ultrasonic treatments the decrease of crystallite size occurs, that confirm the X-ray data. The significant amount of rod-like crystals are formed (Fig.2) also.

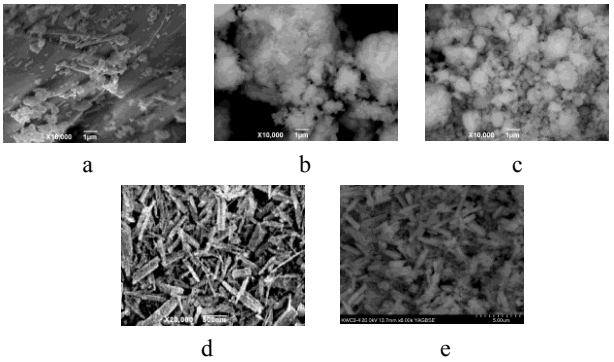

Fig. 2. Microphotographs surface of initial composition – *a,* after MChT 2h – *b,* 4h – *c,* 8h – *d,* UST 1h - *e*

Conclusion

This study has shown the prospect of the direct formation of β-$ZnMoO_4$ nano-rods by mechanochemical treatment and β-Mo_8O_{23} by ultrasonic irradiation of ZnO-MoO_3 mixture (1:1).

References

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