The Mechanochemical Influence on the Physico-chemical Properties of CeO_2-MoO_3 System

Olena Sachuk, Valery Zazhigalov, Olena Diyuk

Department of Heterogeneous Catalytic Oxidation Processes, Institute for Sorption and Problems of Endoecology of NAS of Ukraine, Kyiv, General Naumov street, 13, E-mail: Lena951@i.ua

Abstract – Oxide system CeO_2-MoO_3 with atomic ratio Ce/Mo = 15:85, 25:75, 50:50 and 75:25 was modified by mechanochemical treatment (MChT) during 2, 4 and 8 hours in air. Obtained samples were studied by means of XRD, BET, TEM, sorption from the solution methods. It was shown, that mechanochemical modification leads to change of oxides crystalline structure, their surface morphology, porous structure and sorption ability to safranin-T dye.

Keywords – mechanochemistry, composition, cerium and molybdenum oxides.

I. Introduction

It is known that CeO_2-MoO_3 system is widely used in catalysis branch, namely is an effective selective reduction catalyst to remove nitrogen oxides (NO_x) [1], presentes high activity towards CO oxidation [2] and high photocatalytic ability in degrade process of organic dyes [3].

The preparation of oxide cerium-molybdenum system by traditional methods (solid phase synthesis, precipitation, hydrothermal synthesis etc.) is characterised have some drawbacks and the creation of new preparation methods of these compounds is very actual. It is found that mechanochemical treatment 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. In this communication the results of MChT on properties of CeO_2-MoO_3 system are reported.

II. Experimental

Cerium-molybdenum oxide system with a molar ratio of CeO_2/MoO_3 = 15:85, 25:75, 50:50 and 75:25 was prepared by mixing. Milling of samples was carried out in the planetary ball mill Pulverisette-6 (Fritsch) during 2, 4 and 8 hours in air. The rotation frequency was 550 rpm with the reverse after 30 min treatment. The vial (200 cm^3) and balls (5 mm in diameter) were made of ZrO_2. The ball-to-powder weight ratio (BPR) was 10:1.

The physico-chemical properties of investigated system before and after modification were studied by the following methods: XRD, BET, TEM and sorption from the solution.

III. Results

The X-ray data show that in initial mixture CeO_2-MoO_3= 50:50 all reflexes characteristic for simple oxides (Fig. 1, *1*) with significant domination reflex of α-MoO_3 from the plane (020). It is found, that MChT leads to decrease of intensity all reflexes that is caused by decrease of particle size of initial oxides.

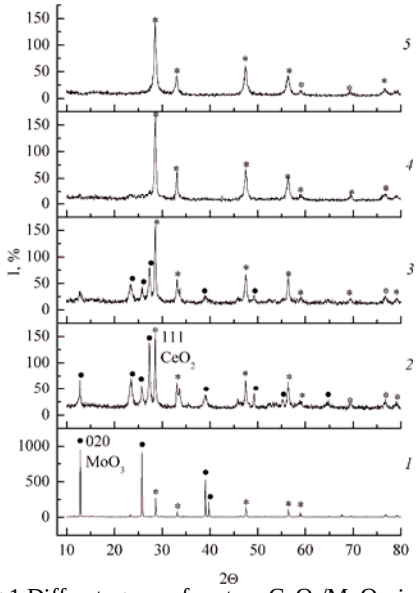

Fig.1 Diffractogram of system CeO_2/MoO_3: initial Ce/Mo=50:50 – *1*, after MChT of Ce/Mo=15:85 – 2, 25:75 – 3, 50:50 – 4, 75:25 – 5

It is shown, that in samples Ce/Mo= 50:50 and 75:25 after 2 hours treatment the reflexes α-MoO_3 are disappear that is connected with the amorphization process of this phase and simultaneously the dominance of phase CeO_2 from the plane (111) is observed.

The results of crystallite size (L) calculated by Scherer equation presented in Table I.

TABLE 1
XRD AND BET RESULTS OF SYSTEM CeO_2/MoO_3 SYSTEM

Atomic ratio Ce/Mo	Time processing, h	L, nm		S_{BET}, m^2/g	$V_\Sigma \times 10^{-2}$, cm^3/g
		MoO_3 (020)	CeO_2 (111)		
15:85	0	89	64	1,3	1,0
	2	47	36	11,6	11
	4	59	33	12,4	12
	8	50	28	13,0	12
25:75	0	96	55	1,1	2,0
	2	56	26	1,4	5,0
	4	44	25	4,6	5,0
	8	72	22	9,5	9,0
50:50	0	93	53	1,7	3,0
	2	-	21	2,7	3,0
	4	-	18	3,0	3,0
	8	-	15	4,7	6,0
75:25	0	-	48	6	4,0
	2	-	17	5,2	6,0
	4	-	16	6,4	6,0
	8	-	16	7,2	8,0

The studies of porous structure show that mechanochemical modification accompanied by increase of specific surface area and total pore volume (Table 1). Thus, the change of type isotherm from II to IV (IUPAC classification) for Ce/Mo=15:85 and 25:75 after treatment is observed that is connected with mesopores formation. The

modification of Ce/Mo=50:50 composition accompanied only increase of S_{BET} while the MChT of Ce/Mo=75:25 leads to formation of macropores from the the mesoporous structure as indicate the total pore volume (98-130 nm) and change type isotherm (from IV to II).

Results of transmission electron microscopy of mechanochemical treated samples of composition Ce/Mo=50:50 showed the formation of nanosized particles of cerium and molybdenum oxides. There are two types of initial oxide particles: big crystals 200-300 nm (MoO_3) and small crystals – 50-70 nm (CeO_2) (fig.2 *a*).

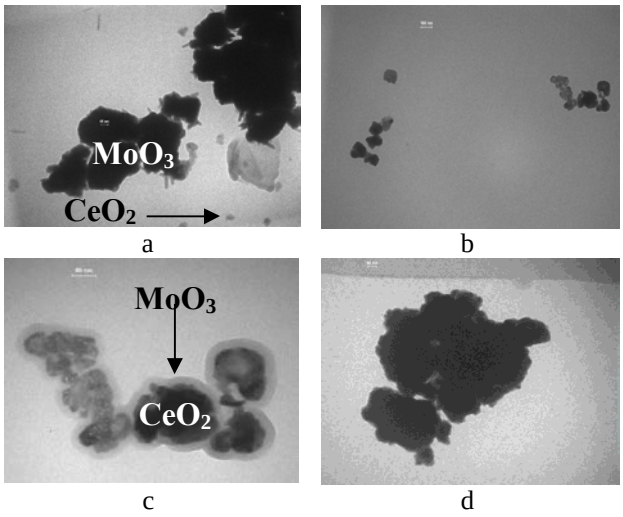

Fig.2 TEM microphotographies of initial composition Ce/Mo=50:50 – a and ater its treatment during 2h – b, 4h – c, 8h – d

The decrease of particles size to 20-40 nm after 2 hours treatment is shown from the fig.2 *b*. The modification of this sample during 4 hours accompanied by a formation of nanodispersed structure "core-shell" (fig.2 *c*), when after 8 hours this structure is destroyed with agglomerates formation (fig.2 *d*).

The studies of composition Ce/Mo=50:50 catalytic properties in ethanol selective oxidation reaction showed that the acetic aldehyde is major reaction product and the selective formation of ethen as collateral product is insignificant (3%).

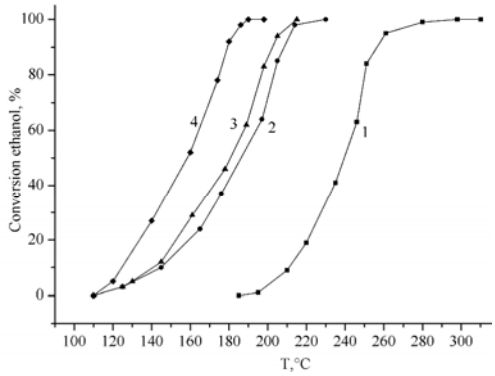

Fig.3 Depending ethanol conversion on the temperature for Ce/Mo=50:50 samples: 1- initial, after MChT during 2h – 2, 4h – 3, 8h – 4.

Such changes can be connected with icrease specific surface area for modified samples.

The comparative analysis of sorption properties of mechanochemical modified composition Ce/Mo=50:50 showed that type of kinetic curves changes from H2 to H1 (agree with classification to C.Giles). Efficiency of dye removal from water solution by materials modified during 2, 4 and 8 hours are 72, 78 and 87 % respectively, when this indicator for initial sample is only 50 %.

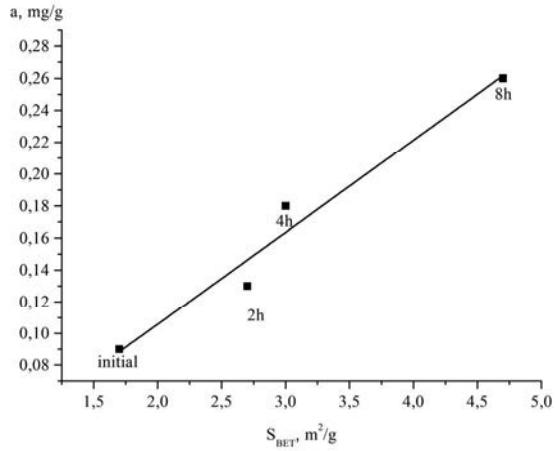

Fig.4 Graph of the adsorption dependence of safarin T on the specific surface of a mechanically activated composition Ce/Mo = 50:50

Obtained results testify about dependent of sorption ability from the specific surface area because with an increase in S_{BET} in 1,6-2,8 times the dye adsorption increases in 1,4-2,8 times (fig. 4).

Conclusion

This study has shown that mechanochemical treatment of CeO_2-MoO_3 system leads to decrease crystalline size, change of porous structure and direct dependence the sorption capacity from the specific surface area.

References

[1] Y. Jin, N. Li, H. Liu, X. Hua, Q. Zhang, M. Chen, F. Teng, "Heighly efficient degradation of dye pollution by Ce-doped MoO_3 catalyst at room temperature," Dalton Treans, vol. 43, pp.12860-12870, 2014.

[2] M. M. Mohamed, S. M. A. Katib, "Structural and catalytic characteristics of MoO_3/CeO_2 catalysts: CO oxidation activity, " Applied catalysis A: General, vol. 287, pp. 236-243, 2005.

[3] S. Zhao, J. Li, L.Wang, X. Wang, "Degradation of rhodamin B and safranin T by MoO_3:CeO_2 nanofibers and air using a continuous mode, " Clean-soil, air, water, vol. 38, pp.268-274, 2010.

Acknowledgments

The results were obtained with financial support of NASU Programme "New materials" (project 7-17).