ROLE OF MECHANICAL TREATMENT IN PREPARATION OF MULTICOMPONENT BISMUTH MOLYBDATE CATALYST FOR PROPYLENE AMMOXIDATION

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Received March 4, 1991
Accepted August 8, 1991

The multicomponent catalyst $Mo_{12}Bi_1Fe_3Co_{4.5}Ni_{2.5}K_{0.1}P_{0.5}O_x/SiO_2$ (50% w/w) for propylene ammoxidation was prepared by mechanical treatment of the initial components and compared with the catalyst obtained by co-precipitation. Data on its catalytic activity, selectivity and texture (surface area and porosity) are reported. X-Ray study of the samples subjected to mechanical treatment for different times (from 0·5 to 12 h) showed that the treatment leads to changes in phase composition of the catalyst which become more pronounced on prolonged grinding time. The increase of grinding time results also in reduction of the surface area and porosity of the catalysts. Notwithstanding, data obtained demonstrate that mechanical treatment exerts favourable effect on the activity of Fe–Bi–Mo oxide catalysts.

Mechanical activation of multicomponent catalysts was studied by several authors[1-12]. Such a treatment was shown to result in the decreased temperature of reaction initiation and the lower activation energy as well as in the increased conversion and reaction rate. However, the nature of the activated state of crystal lattice atoms in these catalysts has so far been little understood.

The present work reports on the effect of mechanical activation in the synthesis of multicomponent Bi–Mo catalysts for propylene ammoxidation, having the composition $Mo_{12}Bi_1Fe_3Co_{4.5}K_{0.1}P_{0.5}O_x/SiO_2$ (50% w/w). The above compound is a traditional industrial catalyst for acrylonitrile production and is synthesized by co-precipitation. The application of mechanical treatment was thought to be useful for formation of multicomponent catalysts since it results in increasing crystal dispersiveness and formation of defects, leading thus to homogeneous phase composition.

EXPERIMENTAL

Catalyst samples were prepared in a ball mill by mixing and grinding the following reactants — ammonium paramolybdate $[(NH_4)_6Mo_7O_{24}.4\,H_2O]$, the corresponding metal nitrates $[Fe(NO_3)_3.9\,H_2O$, $Bi(NO_3)_3.5\,H_2O$, $Co(NO_3)_2.6\,H_2O, KNO_3]$, H_3PO_4 and silica (40%

aqueous solution of SiO_2). Grinding time varied from 0·5 to 12 h. The obtained slurry was dried at 120°C and calcined at 600°C for 5 h.

For comparative purposes, one sample was prepared by co-precipitation, by adding the solution containing Fe(III), Bi(III), Co(II) and Ni(II) nitrates warmed up to 80°C to an aqueous solution of ammonium paramolybdate, H_3PO_4, KOH and SiO_2 maintained at 50°C. The yellow precipitate obtained at pH 1 – 1·5 and 60°C was isolated by evaporation of the solvent. The slurry so formed was then dried at 120°C and calcined at 600°C for 5 h.

The activity tests of the catalysts were preformed in a flow reactor, using catalyst volume 9 cm^3, the flow composition 8·2 mole % propene, 10·8 mole % ammonia, 17·0 mole % oxygen at 64·0 mole % nitrogen and the reaction temperature 430°C.

X-Ray measurements were made with DRON diffractometer, using CuK_α radiation. IR spectra were recorded with UR 20 spectrometer (Zeiss Jena, F.R.G.). Surface area was determined chromatographically from nitrogen adsorption. Porosity was evaluated from the degree of water soaking to catalyst particles.

RESULTS AND DISCUSSION

Based on IR measurements, Si–Mo heteropoly compounds are the constituent of the slurry composition, bands at 960, 910 and 790 cm^{-1} corresponding to Si and Mo

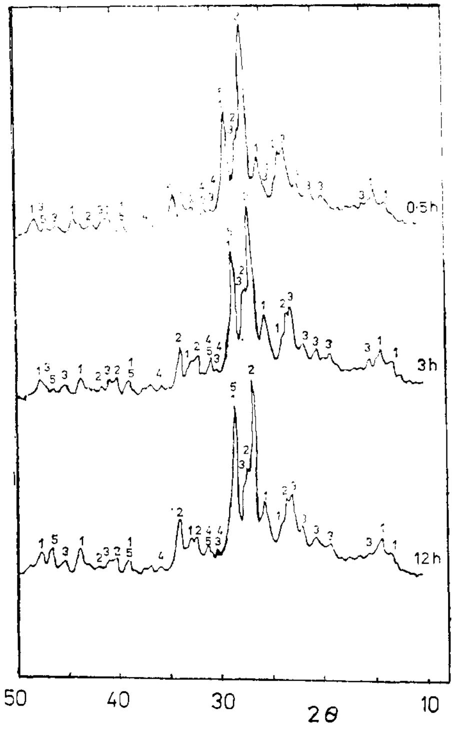

FIG. 1

X-Ray patterns of the multicomponent catalyst prepared by mechanical treatment for different grinding times. Designation: 1 α-$CoMoO_4$, 2 β-$CoMoO_4$, 3 $Fe_2Mo_3O_{12}$, 4 $Bi_2Mo_3O_{12}$, 5 Fe–Bi–Mo oxide components. Similar data were obtained both for the samples prepared by co-precipitation and for those obtained by mechanical treatment.

TABLE I

Activity of molybdenum catalysts in ammoxidation of propene (for conditions see Experimental)

Catalyst	Surface area, m^2/g	Total propene conversion, mole %	Propene conversion (mole %) to		Selectivity to $CH_2{=}CHCN$, mole %
			$CH_2{=}CHCN$	CO_2	
Co–Mo oxide	29·8	5·0	trace	3·0	0
Ni–Mo oxide	22·8	5·0	trace	4·0	0
$Fe_2(MoO_4)_3$	20·6	5·0	trace	4·0	0
$Bi_2(MoO_4)_3$	10·7	50·7	4·0	6·3	78·8
Fe–Bi–Mo (1 : 1 : 1)[a]	10·6	70·3	52·3	8·0	74·4

[a] Catalyst volume 3 cm^3, contact time 3 s.

TABLE II

The effect of grinding time on the catalytic activity of the molybdenum catalyst in propylene ammoxidation and texture changes (for synthesis of the catalyst see Experimental)

Time of grinding, h	Propene conversion (mole %) to			Total conversion, mole %	Selectivity	Surface area, m^2/g	Porosity, cm^2/g
	$CH_2{=}CHCN$	CO_2	CO				
0·5	69·5	12·8	5·3	94·8	73·3	25·0	0·39
1	71·5	11·5	4·5	95·2	75·1	23·5	0·37
2	76·3	8·8	3·5	96·3	79·2	21·0	0
3	78·0	7·9	3·1	96·7	80·7	—	0·36
4	77·2	8·7	3·6	98·2	78·6	—	—
5	75·9	12·2	4·9	99·0	76·7	—	—
6	75·4	10·7	4·2	98·5	76·6	—	—
8	72·9	11·5	4·7	96·3	75·7	19·0	0·34
10	67·0	13·1	5·3	93·7	71·5	—	—
12	66·9	12·8	5·1	93·3	71·1	17·0	0·30
Reference[a]	78·9	8·9	3·6	98·4	80·2	—	—

[a] The sample prepared by co-precipitation (see Experimental).

According to X-ray analysis, the multicomponent catalyst consists of the α-Co(Ni)MoO_4 and β-Co(Ni)MoO_4, ferric molybdate $Fe_2(MoO_4)_3$, the admixture of the α-phase $Bi_2(MoO_4)_3$ and of Fe–Bi–Mo oxide[4,5]. Comparison of X-ray diffractograms of the samples treated mechanically for different times (from 0·5 to 12 h) shows changes in the catalyst phase composition which become more pronounced on prolonged grinding (Fig. 1). The diffraction maximum 314 pm, which increases on increasing grinding time, can be ascribed either to the Fe–Bi–Mo oxide or to the α-$CoMoO_4$. For resolving this line, the samples were further calcined at 600°C for 5 h. This resulted in the occurence of the α → β-phase $CoMoO_4$ transition that was accompanied with the corresponding decrease of the intensities of characteristic maxima at 632, 345, 312, 274, 230, and 208 pm. Accordingly, the 314 pm line became thus more distinct. Therefore, data show that the Fe–Bi–Mo oxide content depends on grinding time.

To determine which of the components is more active, their activity was tested in propene ammoxidation. Data presented in Table I show that the Fe–Bi–Mo oxide exhibits the highest activity. The catalyst activity is affected also by grinding time (Table II). The selectivity toward acrylonitrile formation passes through maximum at grinding time 2 – 4 h while preserving high propylene conversion. The activity and selectivity data are very similar to those obtained with the sample prepared by co-precipitation. The grinding time of 0·5 to 1 h does not seem to be sufficient for producing the active and selective catalyst.

Because of the incomplete interaction of the components and of the inhomogeneity of sample composition, the prolonged grinding time does not lead to increased selectivity. Texture data show that the increase of grinding time decreases the surface area and porosity of the samples likely due to formation of high-dispersed particles.

Summarizing, mechanical treatment provides the procedure which is useful alternative to the more frequent co-precipitation method.

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Translation revised by J. Hetflejš.