Short Communication

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Oxidation of Ethanol to Ethylacetate on Sb-Mo Oxide Catalysts

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One of the interesting trends in conversion of ethanol to ethyl acetate along with metal and metal-zeolite catalysts also molybdenum oxide-containing systems has been applied for this purpose [1-3]. The present work concerns with the oxidation of ethanol to ethyl acetate on Sb-Mo oxide catalysts.

The catalytic activity of three types of Snb-Mo-O catalyst in the title reaction has been investigated. The catalyst $Sb_2Mo_{10}O_{31}$ showed the highest and the catalyst $Sb_2Mo\ O_6$ the lowest activity. The distances between the surface and the intensities for the three forms of Sb-Mo-O catalysts $Sb_4Mo_{10}O_{31}$, $Sb_2Mo_{10}O_{31}$, and $Sb_2Mo\ O_6$ were obtained by diffractometric measurements.

The catalysts were prepared from $Sb_2\ O_3$ (reactive) and MoO_3 (obtained by heating ammonium paramolybdate at 500° for 5 hrs). The activity of individual and mixed oxides was measured at 200-350°, flow rate of the mixture (ethanol, oxygen, water stream) being 3000 h^{-1}, using a fixed bed flow reactor at normal pressure. The reaction products were analyzed in chromatograph LXM-80 instrument. Diffraction measurements were made with difractometer Dron-1.

It was found that the oxidation of ethanol of Sb-Mo oxide catalysts leads to the following products: ethanoic acid (CH_3 COOH), ethanol (CH_3CHO), Co, CO and H_2O. The presence of the product of oxidation-esterification process, ethyl acetate, has not been detected. However, after the catalyst had been regenerated in flow of ethanol, ethyl acetate formation does proceed. Figure 1 demonstrates the dependence of ethylacetate output on reaction temperature for the Sb-Mo-O catalysts of different compositions. The pure MoO_3 does not catalyze ethanol esterification. The addition of a small amount of Sb_2O_3 to MoO_3 increases ethanol conversion.

The highest activity in ethanol esterification was observed for the Sb-Mo-O catalysts with the Sb:Mo molar ratio = 4:1. The increase of reaction temperature above 300° reduces ethyl acetate output, likely due to the re-oxidation of both ethanol and reaction products to CO_2.

The true dependance of catalyst activity for the above mentioned Sb-Mo-O catalyst (Sb:Mo = 4:1) at a temperature of 300° is shown in Fig. 2.

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The increase in the selectively for ethyl acetate for mation explained by the reformation of the catalyst during the oxidation process, in favour of the compounds which produce ethyl acetate. Furthermore, one cannot exclude the possibility that during the contact of the catalysts with the reaction mixture some unfavourable products possessing catalytic activity in this reaction are being accumulated.

It was shown in another work [4] based on equilibrium phase diagrams of Sb-Mo-O catalysts, there exist three forms $Sb_4Mo_{10}O_{31}$, $Sb_2Mo_{10}O_{31}$ and $Sb_2Mo\ O_6$. Apparently, phase data are formed in the regeneration process of catalysts.

Diffraction study of the mechanical mixture of MoO_3 and Sb_2O_3 and the three phases of Sb-Mo-O catalysts yielded the distances between the surfaces and the appropriate intensities(Table 1).

As follows from the table, new lines of high intensities (dÅ = 4.69, 3.76, 3.03 and 2.60) along with the lines of

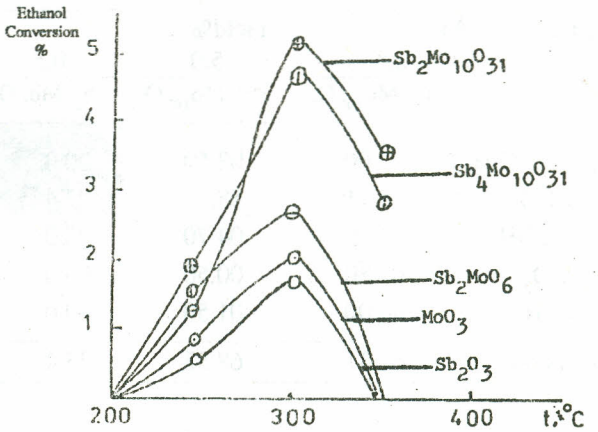

Fig. 1. The activity of Sb-Mo-O catalysts of different composition in the ethanol oxidation.

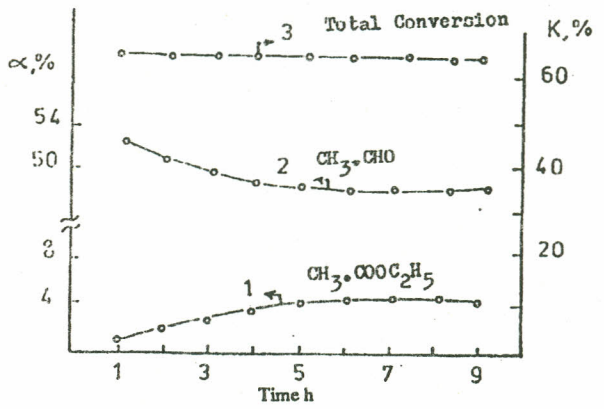

Fig. 2. Catalyst activity changes for the Sb-Mo-O catalyst with Sb: Mo mol. ratio = 4.1 independence on time.

TABLE 1. THE DISTANCES BETWEEN THE SURFACE dÅ AND THE INTENSITY OF I_o PEAKS OF Sb - Mo - O CATALYSTS.

dÅ	I%	dÅ	I%	dÅ	I%	dÅ	I%
6.91	100.0	6.91	99.3	6.91	100.0	6.91	46.5
0.00	00.0	4.69	47.1	4.67	21.8	4.67	40.7
0.00	00.0	3.76	92.0	3.76	62.2	3.76	17.4
3.42	89.7	3.42	98.6	3.42	95.6	3.42	27.3
3.25	76.5	3.25	100.0	3.25	80.0	3.25	36.1
0.00	00.0	3.03	89.1	3.03	32.9	0.00	00.0
0.00	00.0	2.60	34.1	0.03	00.0	2.60	24.4
2.69	13.2	2.69	30.3	2.69	16.9	0.00	00.0
2.30	48.4	0.00	44.2	2.30	48.9	2.30	9.9
2.28	47.9	2.28	47.1	2.28	48.8	2.28	9.9
1.56	21.6	1.56	29.0	1.56	22.2	1.56	10.5
0.00	00.0	1.24	8.7	1.24	04.0	1.24	10.5
0.00	00.0	1.19	5.8	0.00	00.0	1.19	4.7

TABLE 2. THE ACTIVITY OF Sb-Mo-O CATALYSTS AT 300°.

Product	Mo/Sb	2.5	5.0	0.5
		$Sb_4.Mo_{10}.O_{31}$	$Sb_2.Mo_{10}.O_{31}$	$Sb_2.Mo.O_6$
		Yield%		
CH_3-COO C_3H_5		02.00	03.50	00.0
CH_3 -CHO		51.01	58.32	23.4
CH_3 -COOH		03.50	04.70	00.0
$CO + CO_2$		04.80	00.50	00.0
$CH_2 = CH_2$		00.00	01.50	00.0
Conversion		61.31	68.52	23.4

dÅ - 1.24 and 1.99 are observed on diffractograms of the Sb-Mo-O catalysts which are absent in the case of the mechanical mixture of MoO_3 and Sb_2O_3. This fact provides to the interaction of these oxides resulting in the formation of a phase which was active in ethanol oxidation.

Therefore, it was of interest to study catalytic activity of these forms in ethanol esterification. For this purpose the Sb-Mo-O catalysts of three types were synthesized by heating the mixtures of the known amounts of MoO_3 and Sb_2O_3 in flow of air at 500° for 5 hrs. The obtained white powder was tableted and crushed. Prior to measurements, samples were regenerated during in flow of ethanol for 4 hrs (ethanol-nitrogen volum ratio was 1:4) under reduced pressure. Then the ethanol oxidation by O_2 was carried out. Table 2 shows data on the catalytic activity of the three phases of the Sb-Mo-O catalysts.

It follows that the $Sb_2Mo_{10}O_{31}$ catalyst shows the highest efficiency while the Sb_2MoO_6 catalyst the lowest activity. The formation of a small amount of ethanol (CH_3CHO) has been observed on the latter catalyst. Thus the Sb-Mo-O catalysts are active in the studied esterification reaction, the selectivity of which increases during the reaction.

Key words: Oxidation, Ethanol, Sb-Mo-Oxide.

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