OXIDATION OF ETHANOL TO ETHYL ACETATE ON Sb–Mo OXIDE CATALYSTS

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Received April 4, 1991
Accepted June 20, 1991

The catalytic activity of three Sb–Mo oxide catalysts in the title reaction has been investigated. The catalyst $Sb_2Mo_{10}O_{31}$ showed the highest and the catalyst Sb_2MoO_6 the lowest activity. The distances between surfaces and intensities for the Sb–Mo–O catalysts $Sb_4Mo_{10}O_{31}$, $Sb_2Mo_{10}O_{31}$, and Sb_2MoO_6 were obtained by diffractometric measurements.

The development of a process for the synthesis of aliphatic alcohols, in particular of ethanol, from CO and H_2 (Fisher Tropsh synthesis) as well as the opportunity to obtain ethanol from vegetable raw materials, especially in the countires devoid of natural hydrocarbons, gives the basis for the wide utilization of ethanol in synthesis of various valuable products.

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

EXPERIMENTAL

The catalysts were prepared from Sb_2O_3 (reactive) and MoO_3 (obtained by heating ammonium paramolybdate at 500°C for 5 h). The activity of the individual and mixed oxides was measured at 200–350°C, flow rate of the mixture (ethanol, oxygen, water stream) being 3 000 h^{-1}; a fixed bed flow reactor at normal pressure was used for measurements. The reaction products were analyzed using chromatograph LXM-80. Diffraction measurements were made with Difractometer DRON-1.

RESULTS AND DISCUSSIONS

We have found that the oxidation of ethanol on Sb–Mo oxide catalysts leads to the following products: ethanoic acid (CH_3COOH), ethanal (CH_3CHO), CO, CO_2 and H_2O. The presence of the product of an oxidation-esterification process, ethy

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 ethyl acetate 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°C reduces ethyl acetate output, likely due to the oxidation of both ethanol and the reaction products to CO_2.

The true dependence of the catalyst activity for the above mentioned Sb–Mo–O catalyst (Sb : Mo = 4 : 1) at a temperature of 300°C is shown in Fig. 2. From the figure it follows that whereas the conversion does not depend essentially on time, the selectivity undergoes changes in the following way. In the initial stage, the main product is ethanal, ethyl acetate formation being negligible. Then, during further period, ethyl acetate production increases and becomes constant after 4 h, this being accompanied by gradual decrease of ethanol production.

The increase in the selectivity for ethyl acetate formation could be explained by the reformation of the catalyst during the oxidation process, in favour of the forms 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.

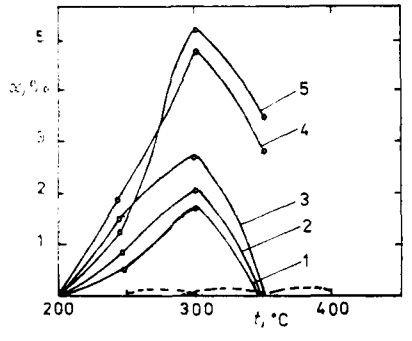

FIG. 1

The activity of Sb–Mo–O catalysts of different composition in ethanol oxidation (α, % (ethanol conversion)) 1 Sb_2O_3, 2 MoO_3, 3 Sb_2MoO_6, 4 $Sb_4Mo_{10}O_{31}$, 5 $Sb_2Mo_{10}O_{31}$

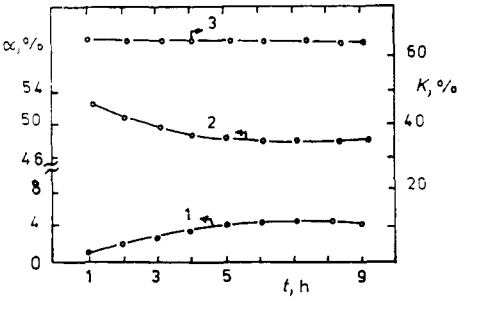

FIG. 2

Catalyst activity changes for the Sb–Mo–O catalyst with Sb : Mo molar ratio 4 : 1 in dependence on time (t). 1 $CH_3COOC_2H_5$, 2 CH_3CHO, 3 total conversion

It was shown in another paper[4] that, 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_2MoO_6. Apparently, these are formed in the regeneration process of the 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 I).

TABLE I

The distances between surfaces, dA^0, and the intensity of I_0 peaks of Sb–Mo–O catalysts

dA^0	I, %	dA^0	I, %	dA^0	I, %	dA^0	I, %
6·91	100	6·91	99·3	6·91	100	6·91	46·5
0	0	4·69	47·1	4·67	21·8	4·67	40·7
0	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	3·25	80·0	3·25	36·1
0	0	3·03	89·1	3·03	32·9	0	0
0	0	2·60	34·1	0·03	0	2·60	24·4
2·69	13·2	2·69	30·3	2·69	16·9	0	0
2·30	48·4	0	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	0	1·24	8·7	1·24	04·0	1·24	10·5
0	0	1·19	5·8	0	0	1·19	4·7

TABLE II

The activity of Sb–Mo–O catalysts at 300°C

Product	Yield, %, for the catalyst		
	$Sb_4Mo_{10}O_{31}$	$Sb_2Mo_{10}O_{31}$	Sb_2MoO_6
$CH_3COOC_2H_5$	2·0	3·5	0
CH_3CHO	51·0	58·3	23·4
CH_3COOH	3·5	4·7	0
$CO + CO_2$	4·8	0·5	0
$CH_2{=}CH_2$	0	1·5	0
Conversion, %	61·3	68·5	23·4

As follows from the table, new lines of high intensities (dA^0 = 4·69, 3·76, 3·03 and 2·60) along with the lines of dA^0 = 1·24 and 1·99 are observed on diffractograms of the Sb–Mo–O catalysts and these are absent in the case of the mechanical mixture of MoO_3 and Sb_2O_3. This fact indicates 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 the 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 known amounts of MoO_3 and Sb_2O_3 in a flow of air at 500°C for 5 h. The obtained white powder was tableted and crushed. Prior to measurements, samples were regenerated in flow of ethanol for 4 h (ethanol–nitrogen volume ratio 1 : 4) under reduced pressure. Then the ethanol oxidation by O_2 was carried out. Table II shows data on the catalytic activity of the three phases of the Sb–Mo–O catalysts.

From them 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 ethanal (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.

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