

## THE INFLUENCE OF ACIDIC-BASIC PROPERTIES OF Sn-Mo-O CATALYSTS ON ITS ACTIVITY IN OXIDATION OF SOME ALCOHOLS

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The influence of acidic-basic properties of Sn-Mo-O catalysts on its activity in oxidation of ethanol, isopropanol and secondary butanol at 200 and 260° was investigated. The results show that the activity and selectivity of Sn-Mo-O catalysts in oxidation of alcohols depend on its surface acidic-basic properties. Carbon containing compounds form on basic sites. Acidic centres are responsible for alcohol dehydration. Preparation of Sn-Mo-O catalysts from KOH solution leads to an increase of their activity in alcohol oxidation reaction. By addition of KOH in small amounts, most acidic centres are blocked, while the less acidic centres, responsible for dehydration, are not effected. Increasing the amounts of added KOH lead to complete deactivations of acidic centres.

**Key words:** Acid basic properties, Sn-Mo-O Catalysts.

### Introduction

It is known that the oxide catalysts containing molybdenum have high activity in aliphatic alcohols oxidation reactions [1,2]. Satisfactory correlations between oxygen-catalyst surface bound-energy and selectivity of alcohol oxidation are absent [3] on title is known in the literature, especially the relation between acidic-basic properties of oxides catalysts and their catalytic activity in oxidation of alcohols.

The present study is deals with an investigation of the acid- basic properties of Sn-Mo-O catalysts, and the influence of its activity in oxidation of ethanol, isopropanol and secondary butanol.

### Experimental

The catalyst with atomic ratio of Sn: Mo = 9:1 was prepared by precipitation from an aqueous solution of ammonium paramolybdate on tin dioxide. The suspension formed was evaporated at 110°, the residue was dried at 140° and the calcined in air (300° for 3 hrs and 550° for 5 hrs).

In order to change acidic character into a basic one the Sn-Mo-O catalyst was prepared by adding a known amount of KOH; the catalysts was then dried at 110° and heated at 550° for 5 hrs. Specific surfaces of catalysts were measured by chromatographic method [2]. Their acidic-basic character was measured by NH<sub>3</sub> and SO<sub>2</sub> adsorption using the method described by Lucofokii [3]. X-Ray studies were done using a DRON-2 apparatus. Catalyst activity in alcohol oxidation process was determined in a flow-apparatus. Products were analyzed for their contents of alcohol, olefins (ethylene, propylene, butene isomers). Chromatographic analysis was used to determine the amount of carbon-containing compounds, i.e. acetaldehyde, acetone, methyl ethyl ketone and CO<sub>2</sub>. Acids in the reactions products were measured by titration method.

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### Results and Discussion

1. *Some physico-chemical features of the catalysts.* The X-ray analysis of the catalyst with Sn:Mo ratio = 9:1, did not show any line relating to MoO<sub>3</sub> but a strongly distorted profile relating to SnO<sub>2</sub> was observed. In diffractograms of mechanical mixture of SnO<sub>2</sub> and MoO<sub>3</sub> with the same ratio, a sharp lines relating to MoO<sub>3</sub> were detected.

Comparing the results of the X-ray analysis of the Sn-Mo-O catalyst (Sn:Mo = 9:1) with the catalysts prepared by adding known amounts of KOH showed no difference between them. In order to describe acidic-basic character, we compared adsorption abilities of NH<sub>3</sub> and SO<sub>2</sub> by the impulse method. Before filling the reactor with NH<sub>3</sub> or SO<sub>2</sub> we heated the catalyst in a helium stream inside reactor at 300°. The relation between peak area on chromatogram by using NH<sub>3</sub> or SO<sub>2</sub> from reactor with catalyst ( $S_{cat}$ ) and peak area in chromatogram after passing from quartz full reactor ( $S_{qu}$ ), illustrated the adsorption ability of molecule (Table 1. The data showed that, when  $S_{cat}/S_{qu}$  ratio was increased a weaker adsorption of reagent was observed. When the ratio  $S_{cat}/S_{qu} = 1$ , we could suggest that there is no adsorption of reagent on the catalyst.

As shown in Table 1, increasing the added amount of KOH leads to a reduction of specific surface area of the catalysts and the ratio  $S_{cat}/S_{qu}$  increased and that indicates a

TABLE 1. SPECIFIC SURFACE OF Sn-MO-O CATALYSTS WITH DIFFERENT ADDITIONS OF KOH.

KOH %	Surf. area m <sup>2</sup> /gm	$S_{cat}/S_{qu}$ for NH <sub>3</sub>			$S_{cat}/S_{qu}$ for SO <sub>2</sub>		
		25°	100°	200°	25°	100°	200°C
—	28.9	0.06	0.52	0.70	0.97	1.0	1.0
0.1	26.3	0.22	0.58	0.86	0.94	1.0	1.0
0.5	17.1	0.35	0.80	0.92	0.92	0.96	1.0
1.0	15.6	0.50	0.82	0.97	0.90	0.91	0.94



decrease of its adsorption, which may be due to decreasing acidity of Sn-Mo-O catalyst after its preparation with KOH. Also, number of acid centres is decreased. This fact is confirmed by adsorption of large amount of  $\text{NH}_3$  on alkali free catalyst even at  $200^\circ$  and ratio ( $S_{\text{cat}}/S_{\text{qu}} = 0.7$ ), while on catalysts with KOH, it is slightly adsorbed at ratio ( $S_{\text{cat}}/S_{\text{qu}} = 0.95 - 0.97$ ) Table 1 also showed that the increasing of  $\text{SO}_2$  adsorption in case of catalyst with KOH leads to strengthening of basic properties of Sn-Mo-O catalyst.

**2. Ethanol oxidation.** Figure 1 illustrated the products obtained in ethanol oxidation reaction at  $200$  and  $260^\circ$ . The reaction conditions are: Molar ratio of ethanol :  $\text{O}_2 = 1:2.4$ , and the volume of speed of reactive mixture =  $3450 \text{ h}^{-1}$ . Increasing amounts of KOH lead to decrease in the yield of acid, and increase in the yield of acetaldehyde  $\alpha_{\text{ald}}$ , and also it decrease the rates of complete oxidation and dehydration of ethanol. The data suggest that the oxidation of ethanol depends on the amount of KOH added to the Sn-Mo-O catalysts. Increasing temperature leads to increase of  $\alpha_{\text{acid}}$  value, and decrease of  $\alpha_{\text{ald}}$  value.

**3. Isopropanol oxidation.** Results shown in Fig. 2, present the isopropanol oxidation reaction at  $200$  and  $260^\circ$ . The reaction conditions are: Molar ratio of isopropanol :  $\text{O}_2 = 1:3.1$  and the volume of speed of reactive mixture =  $3420 \text{ h}^{-1}$ . By increasing amount of KOH, the  $\alpha_{\text{acid}}$  value decreases, but the  $\alpha_{\text{acet}}$  value increases. The effect of temperature is however inversely proportional to the amount of KOH. Also, a severe decrease of  $\text{CO}_2$  formation is observed with catalysts treated with KOH. At  $200^\circ$ , the yield of propylene  $\alpha_{\text{C}_3\text{H}_6}$  decreases, when the added amount of KOH to the catalyst is increased, but at  $260^\circ$  the obtained propylene reached a maximum value.

**4. Secondary butanol oxidation.** Figure 3 showed the dependence of the obtained acids, methyl ethyl ketone and  $\text{CO}_2$  on Sn-Mo-O catalyst treated with KOH at  $200$  and  $260^\circ$ . The reaction conditions are: Molar ratio of butanol :  $\text{O}_2 = 1:3.8$ , and the volume of speed of reactive mixture =  $3400 \text{ h}^{-1}$ . It is very clear that the behaviour is the same as in case ethanol of and isopropanol oxidation.

The obtained results were compared with previous ones [4,5] and comparison showed that decrease in the yield of acids is due to the formation of sites, while the increasing of aldehydes and ketones formed is due to their formation on the basic sites on the catalyst sample. The decrease of the obtained methyl ethyl ketone by increasing temperature, (Fig. 3) may be due to the increase of the rate of their further oxidation conversions. Also, the decrease of obtained  $\text{CO}_2$ , reveals responsibility of acid centres on catalyst surface for complete oxidation reaction. According to previous studies [6,7], we can propose that carbon containing compounds is strongly linked to these centres and converting into oxidative products.

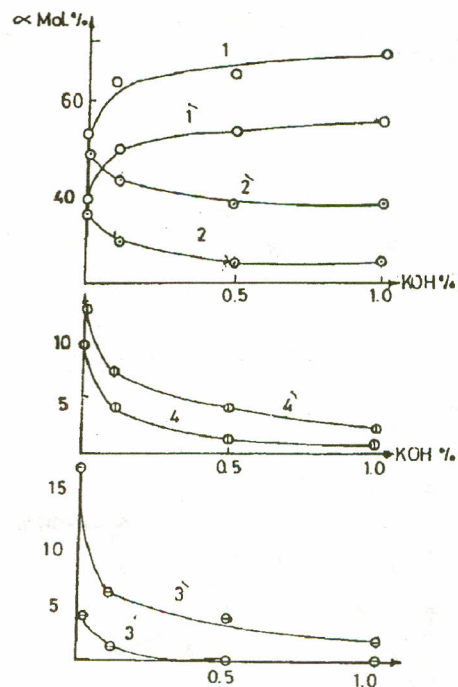


Fig. 1. Dependency of products outcome on KOH amount deposited on Sn-Mo-O catalysts in oxidation of ethanol.

1 - Aldehyde at  $200^\circ$ , 1' - Aldehyde at  $260^\circ$ ; 2 -  $\text{CO}_2$  at  $200^\circ$ , 2' -  $\text{CO}_2$  at  $260^\circ$ ; 3 - Acids at  $200^\circ$ , 3' - Acids at  $360^\circ$ ; 4 - Ethylene at  $200^\circ$ , 4' - Ethylene at  $260^\circ$

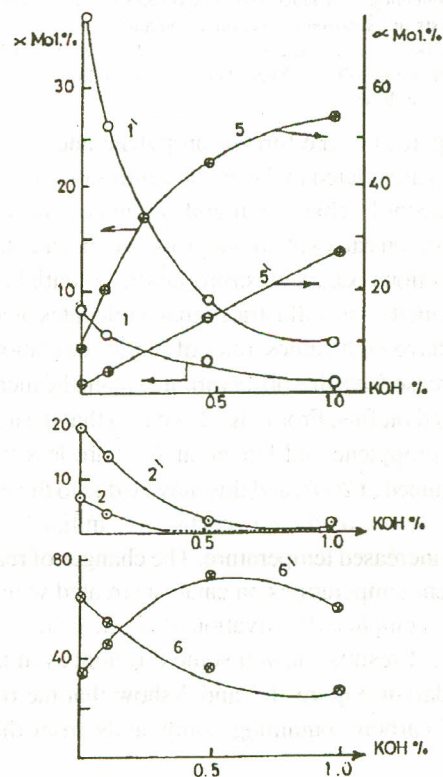


Fig. 2. Dependency of products outcome on KOH amount deposited on Sn-Mo-O catalysts in oxidation of isopropanol.

1 - Acids at  $200^\circ$ , 1' - Acids at  $260^\circ$ ; 2 -  $\text{CO}_2$  at  $200^\circ$ , 2' -  $\text{CO}_2$  at  $260^\circ$ ; 5 - Acetone at  $200^\circ$ , 5' - Acetone at  $260^\circ$ ; 6 - Propylene at  $200^\circ$ , 6' - Propylene at  $260^\circ$



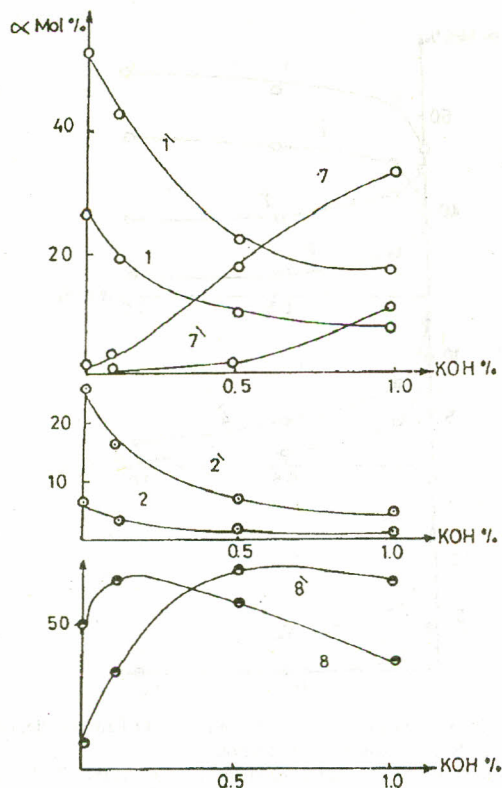


Fig. 3. Dependency of products outcome on KOH amount deposited on Sn-Mo-O catalysts in oxidation of secondary butanol.

1- Acids at 200°, 1' - Acid at 260°; 2-  $\text{CO}_2$  at 200°, 2' -  $\text{CO}_2$  at 260°; 7- Methyl ethyl ketone at 200°, 7' - Methyl ethyl ketone at 260°; 8- Butenes at 200°, 8' - Butenes at 260°

The properties of the formed propylene and butenes (at 200 and 260°) are related to the acidic centres of different potentials for alcohol dehydration and olefins oxidative reactions. This relation can explain our proposal, that alcohols dehydration reactions occurs on strong acidic potential centres.

The obtained results illustrated that while rates of alcohol dehydration have high values, rates of olefins oxidation reactions are decreased and this observation explain the increasing in the produced olefins. From Fig. 2, we find that the amounts of produced propylene and butene at 260° are less than the amounts produced at 200°, and this may be due to the increasing rates of olefins oxidation reaction on initial Sn-Mo-O catalyst with increased temperature. The changes of reactions rate at different temperatures on catalysts treated with KOH, are due to the complete deactivation of acidic centres.

Analysis of results showed some differences in laws of alcohols oxidation. Figure. 1, 2 and 3 show that the order of formation of carbon containing compounds from different

alcohols using Sn-Mo-O catalyst not treated with KOH, is as follow:

Ethanol > Isopropanol > Secondary butanol

while the order is reversed in case of  $\text{CO}_2$  formation:

Secondary butanol > Isopropanol > Ethanol

This discrepancy can be explained by the important inductive effects of alkyl groups in their molecules. It is well known that alkyl groups inductive effects are characterized by Taft constants ( $\delta$ -constant). Large negative value correspond to large electropositive substituents (Table 2).

TABLE 2. INDUCTIVE CONSTANTS OF SUBSTITUENTS IN SOME ALIPHATIC ALCOHOLS.

Alcohol	$\delta$ constant
$\text{CH}_3\text{CH}_2\text{OH}$	-0.01
$\text{CH}_3\text{CHOHCH}_3$	-0.19
$\text{CH}_3\text{CHOHCH}_2\text{CH}_3$	-0.21

We propose that alcohols are adsorped on acidic centres of catalyst which have electron accepting properties. It is clear that the increase of positive inductive effects values of alkyl groups leads to strengthening electron-donating properties of alcohol molecule bound to catalysts surface.

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