

Effects of Potassium Hydroxide on Catalytic Characters of Sn-Mo-O Catalyst in Isopropanol Oxidation Reaction

M. A. WASSEL* AND T. G. ALKHAZOV†

Chemistry, Department, Faculty of Science,
Al-Azhar University, Nasr City, Cairo, Egypt.

The influence of acidic-basic characters of Sn-Mo-O catalysts on its activity in isopropanol oxidation reaction at 170, 200, 230 and 260°C were studied. It was proved that acid formation occurs on acidic centres and acetone formation on basic centres of Sn-Mo-O catalysts. Preparation of catalysts with alkaline solution (0.1%, 0.5%, 1% KOH) leads to activity in acetone formation reaction.

INTRODUCTION

It is known that Sn-Mo-O catalyst have a high activity and selectivity in olefins oxidation into aldehydes and ketones^{1,2}. Experiments of Alkhazov³ proved that the catalytic characters in propylene oxidation reaction depend on acidic characters of the surface of Sn-Mo-O catalysts.

Wassel⁴ found similar results in the oxidation of ethanol with Sn-Mo-O catalyst in alkali solution. The specimens treated with concentrated KOH solution possess the main basic properties. The present study involves investigation of effects of Sn-Mo-O catalyst's acidic-basic characters on its activity in isopropanol oxidation.

EXPERIMENTAL

Tin-molybdenum oxides catalyst has been prepared by precipitation of aqueous solution of ammonium paramolybdate on tin dioxide, and was evaporated at 110°C and calcined at 550°C for 5 hrs.

The catalysts containing alkalis (0.1%, 0.5% and 1% KOH) were prepared by saturation of the above prepared Sn-Mo-O catalyst with potassium hydroxide of determined concentration and were evaporated at 110°C and heated at 550°C for 5 hrs.

Specific surfaces of catalysts were measured by chromatographic method. Acidic-basic characters of catalyst are determined by impulsing method by using adsorption of ammonia SO₂ by Lecohiskii⁵ method.

Catalytic activity of isopropanol oxidation process was determined in flow apparatus; at 170, 200, 230 and 260°C the amounts of reagents,

†Institute of Oil and Chemistry, Baku-370601, USSR

alcohol, oxygen and temperature of the reactor were automatically regulated. The products were analysed to determine their content of alcohol, olefins, ketones, CO₂ which was done chromatographically. Acid amount of reaction products was determined by titration with 0.1 M sodium hydroxide solution.

RESULTS AND DISCUSSION

The main acid characters of Sn-Mo-O catalysts with different potassium hydroxide containing amounts are presented in Table 1. (Vol. of catalyst = 0.1 ml; Vol. impulse NH₃ = 1 ml, impulse SO₂ = 1 ml). As is seen, if content of KOH in the catalyst increases, ammonium adsorption decreases because of lowering of catalysts acidity after alkali deposition on them. In this case, the total number of acidic centres is not only decreased, but their potency also is decreased. This explains why in the initial sample a large quantity of ammonia was adsorbed, even at 260°C, while in these same circumstances, ammonia was insignificantly absorbed by alkali-containing catalysts.

TABLE 1
MAIN ACIDIC CHARACTERS OF Sn-Mo-O CATALYSTS
WITH DIFFERENT CONTENTS OF KOH

Catalysts	Adsorption $\left(\frac{\text{mol}}{\text{m}^2}; 10^{-17}\right)$						
	NH ₃				SO ₂		
	25°C	100°C	200°C	280°C	25°C	100°C	200°C
Sn-Mo-O	28.9	34.9	20.1	17.1	1.29	0.00	0.00
Sn-Mo-O+0.1% KOH	25.6	31.1	16.9	04.5	3.87	0.00	0.00
Sn-Mo-O+0.5% KOH	17.1	23.3	13.2	00.7	5.93	2.67	0.00
Sn-Mo-O+1% KOH	15.6	12.0	04.6	0.00	7.45	6.80	4.63

Fig. 1 shows that KOH deposition leads to strengthening of catalyst's basic characters. This is confirmed by results of probing catalysts surface with SO₂. Catalyst containing KOH (1% of its mass) has the most highest basicity. Illustrations show dependency of reaction products accumulation speed at different temperatures on the content of KOH in the catalysts. It is shown that increasing the alkali content of the catalyst does not increase the acid accumulation rate, but increases acetone accumulation rate. The rate of these reactions depends on temperature in different ways. If temperature increases, acid accumulation speed also will increase, while acetone speed will decrease.

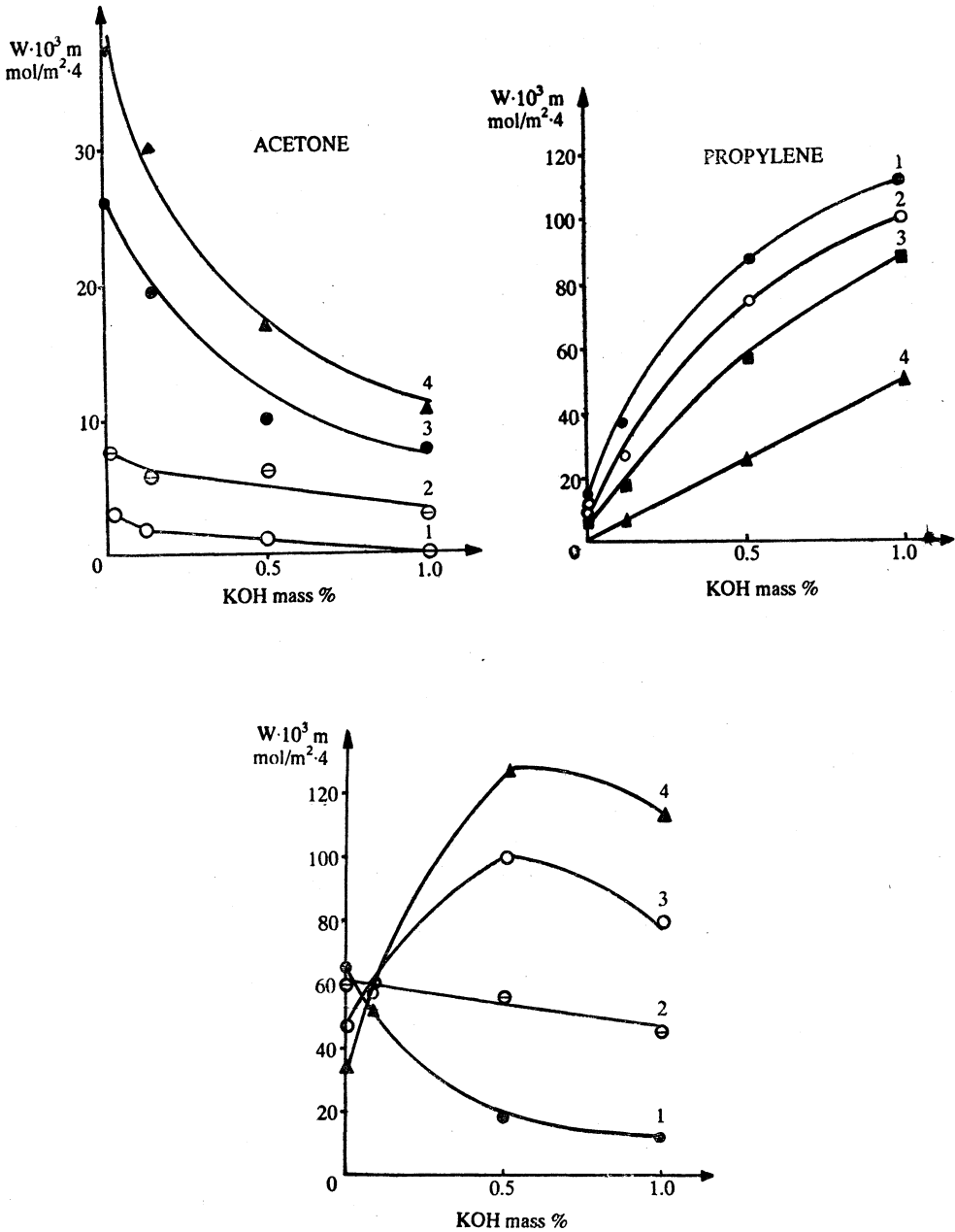


Fig. 1. Effect of KOH content in Sn-Mo-O catalyst on acidic accumulation speed.

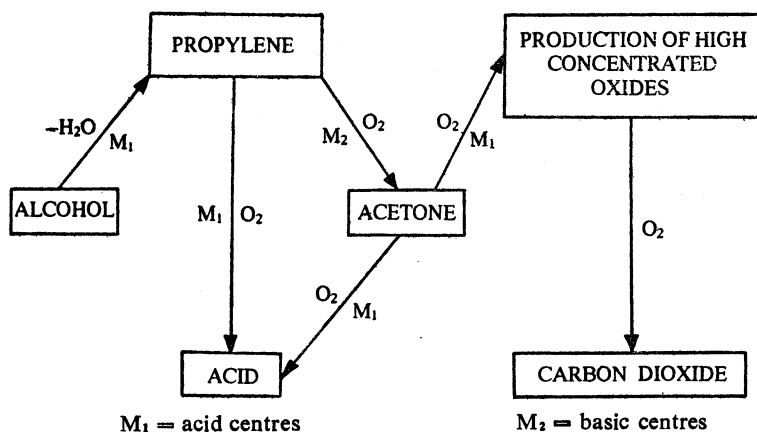
(Ratio of alcohol : air = 1 : 15, Volume speed of gas mixture = 3420 hr⁻¹)

At 170–200°C if KOH content increases, propylene accumulation velocity will decrease, and at higher temperature the velocity is reached a maximum. The increasing of KOH concentration in catalyst leads to a marked decrease in complete oxidation reaction and when catalyst contains KOH reached 0.5% of mass, CO₂ was not formed.

The observed changes of Sn–Mo–O catalysts acidic-basic characters in presence of KOH can be explained by the slowing of acid accumulation speed, accompanied by increase of KOH content in the catalysts, as this reaction occurs on the surface of acid centres. We suggest that acids, acetone and propylene are formed on the acidic centres in the oxidation reaction.

The decrease in acetone accumulation speed (W_{acet}) indicates that its formation occurs on the surface of basic centres, decrease in (W_{acet}) in case by increasing temperature, is due to increase in the rate of acetone oxidizing conversion into acid and carbon dioxide. The results in Fig. 1. allow us to propose that propylene formation occurs on acidic centres. It may explain decrease of isopropanol dehydration speed with KOH containing catalyst at temperature between 170–200°C. An extreme character of $W_{\text{C}_3\text{H}_6}$ values dependency on containing alcohol of catalyst is observed at higher temperatures (230, 260°C), and is considered to be due to acidic-basic characters influence.

Propylene formation may occur on the weaker acidic centres and its secondary conversion on centres of great acidic potency. Deposition of small amounts of KOH leads to blocking of the more acidic centres, and is accompanied by decrease of propylene secondary conversions, while alcohol dehydration is still pronounced. It may explain increase of propylene accumulation speed with catalysts containing 0.5% of alkali. A decrease of propylene output was observed by further increasing KOH concentration, and is due to slowing of alcohol dehydration speed. Fig. 1.



show that complete oxidation occurs on strong acid centres of the catalyst. According to a study by Alkhazov³, we can propose that : acetone is firmly adsorbed on these centres, and exposed to oxidizing conversions with formation of highly oxidized products which finally gives carbon dioxide. From the above facts it is concluded that the process of isopropanol oxidation by Sn-Mo-O catalysts can be presented by the following scheme (on page 889).

According to previous studies^{6,7} it does not take in to consideration acid oxidation into CO₂. Our results show the possibility of a marked increase of acetone production during the isopropanol oxidation on Sn-Mo-O catalysts containing alkali and a marked decrease in acetone content by raising temperature (Table 2).

TABLE 2
THE EFFECT OF CONCENTRATION KOH IN Sn-Mo-O CATALYST
AND TEMPERATURE OF ISOPROPANOL OXIDATION ON
ACETONE PRODUCTION
(RATIO ALCOHOL : AIR = 1 : 15, VELOCITY = 3420 h⁻¹)

KOH content mess % in catalysts	Acetone Products			
	170°C	200°C	230°C	260°C
0.0	11.2	09.1	05.3	02.1
0.1	27.0	20.5	12.5	04.5
0.5	51.4	45.1	31.4	14.7
1.0	59.0	53.6	45.8	27.6

REFERENCES

1. F. B. Kacemov and K. Yu. Adjamov, *J. Phys. Chem.*, T. 56, 8 (1982).
2. T. G. Alkhazov, K. Yu. Adjamov, F. M. Poladov and V. L. Vagev, *Oil and Chemistry*, T. 20, 1 (1909).
3. T. G. Alkhazov, K. Yu. Adjamov, E. A. Mamedove and V. B. Vaceleovckii, *Kinetics and Catalysts*, T. 20, 1 (1989).
4. M. A. Wassel, N. KH. Allkhverdova. K. Y. Adjamov and T. G. Alkhazov, *J. of Serb. Chem. Soc.* (in press).
5. A. E. Lucosickii, Z. A. Tablov and T. G. Alkhazov, USSR Conference on Mechanism of Catalytic Reactions, Moscko (1989).
6. K. Yu. Adjamov and T. G. Alkhazov, USSR Conference on Mechanism of Catalytic Reactions, Moscko (1989).
7. V. L. Vagev, Ph. D. Thesis, USSR-baky (1979).

[Received: 24 June 1991; Accepted: 2 August 1991]

AJC-366