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DEPENDENCE OF THE ACTIVITY IN THE REACTION OF ETHANOL OXIDATION OF MOLYBDENUM-TUNGSTEN OXIDE CATALYSTS ON THE SPECIFIC SURFACE AREA

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Abstract. The activity of molybdenum-tungsten oxide catalysts in the ethanol oxidation reaction has been studied. It is shown that on molybdenum-tungsten oxide catalysts rich in tungsten, the reaction of dehydration of ethanol to ethylene proceeds, while samples enriched in molybdenum are active in the reaction of oxidative dehydrogenation of ethanol to acetaldehyde. It has been established that with an increase in the content of molybdenum in the composition, the specific surface area of the samples changes in the range from 0.4 m2/g to 26.5 m2/g. It is shown that with an increase in the specific surface area, the ethylene yield first sharply decreases and then practically does not change, while the yield of acetaldehyde first sharply increases and then practically does not change with an increase in the specific surface area.

Keywords: *Molybdenum-tungsten oxide catalysts, Ethanol oxidation, Acetaldehyde, Acetic acid, Specific surface area.*

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1. Introduction

It is known from periodic literature that catalysts based on tungsten oxide exhibit high activity in the reactions of partial oxidation of organic compounds. Thus, the adding of tungsten oxide into the composition of the Rh/TiO2 catalyst leads to an increase in activity in the partial oxidation of methane, which indicates the promoting effect of tungsten oxide on the initial sample (Akhlaghian *et al.*, 2012). At the same time, the partial oxidation of acrolein to acrylic acid was studied on a series of catalysts of the general formula Mo_8V_2WcOx with different contents of tungsten ($0 \leq c \leq 5$) (Endres *et al.*, 2007). The conducted studies showed that catalysts with small additions of tungsten showed the highest activity in the studied reaction. Thin films of initial and platinum-doped tungsten oxide were studied in the reaction of partial oxidation of methanol (Polášek *et al.*, 2019). It was found that doping tungsten oxide with platinum leads to a significant increase in the yield of hydrogen and a decrease in the proportion of carbon monoxide in the reaction products. According to the authors, this is due to the strong electronic interaction between WOx and platinum, which increases the acidity of the reaction centers of tungsten oxide. The effect of the amount of tungsten oxide modifier on the activity of copper-cerium catalysts in the CO oxidation reaction was studied in this work (Gan & Si, 2021). It is shown that the introduction of tungsten oxide (WO3) significantly changes the metal-carrier interaction, which leads to an improvement in the catalytic activity of copper-cerium catalysts in the oxidation of carbon monoxide. Previously, we have shown that tungsten-based catalysts are highly

active in the reaction of partial oxidation of ethanol (Aghayeva & Baghiyev, 2018; Mammadova & Kh, 2020). Main reaction products on these catalysts are acetaldehyde and diethyl ester. It is known that in reactions occurring on heterogeneous catalysts, the conversion of feedstock into reaction products occurs on the surface of the catalyst. The developed surface of the catalyst is one of the important properties of the catalyst that affect its activity. In this study (Kim *et al.*, 2022), the characteristics and catalytic activity of nickel-added tungsten carbide catalysts in tar hydrocracking reactions using various Ni/(Ni + W) ratios were studied. As a result, the yield of commercial liquid was maximum and coke formation on the NiWC(20) catalyst with a Ni/(Ni + W) ratio of 23 mol.% was significantly reduced. Alumophosphates with transition metals have been studied in this paper (Vijayasankar & Govindaraju, 2020). To understand the structural and textural properties, the obtained samples were characterized by various methods. It has been found that the mesoporous nature of vanadium aluminophosphate with high surface acidity and surface area leads to an increase in catalytic activity compared to pure aluminophosphates. One of the main surface properties of catalysts is its specific surface area. Therefore, in this work, we studied the effect of the specific surface area of the synthesized catalysts on their activity in the ethanol oxidation reaction.

2. Experimental part

Molybdenum-tungsten oxide catalysts were prepared by coprecipitation from aqueous solutions of ammonium molybdate and ammonium tungsten. The obtained mixture was evaporated at 95-100°C, then the formed precipitate was dried at 100-120°C and then decomposed to complete release of nitrogen oxides at a temperature of about 250-300°C. The resulting solid mass was calcined at a temperature of 700°C for 10 hours. Thus, 9 catalysts were synthesized with the atomic ratio of elements from Mo:W=1:9 to Mo:W=9:1.

The activity of the synthesized catalysts in the reaction of ethanol conversion was studied on a flow-through unit at a volumetric feed rate of 1200 h^{-1} in the temperature range 100-500°C. The yields of acetaldehyde, acetic acid and other organic compounds were determined on a chromatograph with a flame ionization detector on a 2 m column filled with a Polysorb-1 sorbent. Carbon dioxide yields were determined on a chromatograph with a column 6 m long filled with sorbent celite with petroleum jelly applied on it.

The specific surface area of the synthesized samples was determined by the method of thermal desorption of nitrogen.

3. Results and discussion

The conducted studies have shown that the products of the reaction of ethanol oxidation on binary molybdenum-tungsten oxide catalysts are acetaldehyde, ethylene, acetic acid and carbon oxides. The effect of temperature on the activity of the Mo-W=5-5 catalyst in the ethanol conversion reaction is shown in Fig. 1.

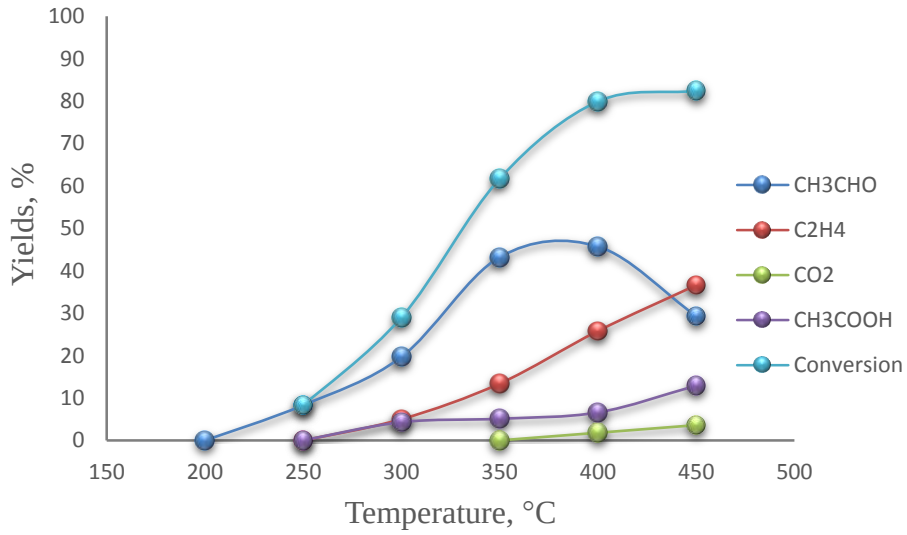

Fig. 1. Effect of temperature on the yields of ethanol oxidation products on the Mo-W =5-5 catalyst

It can be seen that the ethanol oxidation reaction on the studied catalyst starts at a temperature of 250°C with the formation of 8.3% acetaldehyde. With an increase in the reaction temperature, the yield of acetaldehyde on the studied catalyst passes through a maximum at 400°C and is equal 45.7%. The reaction for the formation of ethylene, the product of ethanol dehydration, begins at 300°C, and with increasing temperature, the yield of ethylene sharply increases and reaches 36.6% at 450°C. As can be seen from figure 1, the yields of acetic acid and carbon dioxide slightly increase with increasing reaction temperature and their yields do not exceed 12.9% and 3.6%, respectively. Figure 1 also shows that on the Mo-W=1-9 catalyst, the conversion of ethanol increases with increasing reaction temperature and at 450°C it is equal 82.4%. Similar results were obtained for other binary molybdenum-tungsten oxide catalysts.

We have also studied the dependence of the activity of binary molybdenum-tungsten oxide catalysts on their composition. Table 1 shows the dependence of the activity of molybdenum-tungsten catalysts on their composition in the ethanol oxidation reaction at a temperature of 300°C. It can be seen that acetaldehyde is the main reaction product on all catalysts. The dependence of the yield of acetaldehyde on the atomic ratio of molybdenum to tungsten has the form of a curve with two maxima on the samples Mo-W=3-7 and Mo-W=7-3. As can be seen from table 1, the yields of ethylene and acetic acid slightly depend on the atomic ratio of molybdenum to tungsten.

Table 1. Dependence of the activity of molybdenum-tungsten oxide catalysts in the reaction of ethanol oxidation on their composition. T=300°C

Reaction products	Yields of reaction products, %								
Mo/W atomic ratio	1:9	2:8	3-7	4:6	5:5	6:4	7:3	8:2	9:1
CH3CHO	27,2	24,8	33,6	22,9	19,7	24,8	28,7	22,9	25,5
C2H4	10,5	10,4	4,8	5,1	5	4,5	4,5	5,5	7,5
CO2	2,9	0	0	0	0	0	0	0	0
CH3COOH	6,6	6,6	3,2	4,5	4,3	5,3	2,4	2,6	0
Conversion	47,2	41,8	41,6	34,5	29	32,6	35,6	31	35

Another character of the dependence of the yields of reaction products on the atomic ratio of molybdenum to tungsten is observed at temperatures above 300°C (table 2.). It can be seen that with an increase in the content of molybdenum in the composition of the catalyst, the yield of ethylene decreases, while the yield of acetaldehyde increases. Thus, the ethylene yield decreases from 69% on the Mo-W=1-9 catalyst to 19.5% on the Mo-W=9-1 catalyst, and the acetaldehyde yield increases from 6.9% on the Mo-W=1-9 catalyst to 35.6% on catalyst Mo-W=9-1. From Table 2 it is also seen that the composition of the catalyst has little effect on the yields of acetic acid and carbon dioxide. It should also be noted that at a temperature of 450°C, ethanol is converted to ethylene with high selectivity on catalysts rich in molybdenum.

Table 2. Dependence of the activity of molybdenum-tungsten oxide catalysts in the reaction of ethanol oxidation on their composition. T=450°C

Reaction products	Yields of reaction products, %								
Mo/W atomic ratio	1:9	2:8	3-7	4:6	5:5	6:4	7:3	8:2	9:1
CH3CHO	7,2	17,1	21,3	30,6	29,3	32,2	32,6	34	35,6
C2H4	69	54,3	45,7	43,6	36,6	35,3	33,5	27,8	19,5
CO2	5,4	4,5	6,2	4,6	3,6	5,1	4,6	3,4	2,1
CH3COOH	9,6	12,9	16,1	16,1	12,9	12,3	10,3	9,8	16,3
Conversion	91,2	88,8	89,3	94,9	82,4	85	81	75	73,5

Based on the results obtained, it can be said that on molybdenum-tungsten oxide catalysts rich in tungsten, the reaction of dehydration of ethanol to ethylene occurs, while samples enriched in molybdenum are active in the reaction of oxidative dehydrogenation of ethanol to acetaldehyde.

It is known that heterogeneous catalytic reactions are a complex type of processes involving the interaction of initial gaseous substances with the surface of a solid catalyst. One of the main properties of catalysts that affect its catalytic activity is the specific surface area (Jung *et al*., 2012; Yu *et al.*, 2022). In this regard, we determined the specific surfaces of the studied catalysts. For comparative evaluations, we also measured the specific surfaces of individual oxides of molybdenum and tungsten. Thus, the specific surface area of molybdenum oxide is 1.9 m2/g, and that of tungsten oxide is 4.3 m2/g. The results of measuring the specific surface area of Mo-W-O catalysts by the method of thermal desorption of nitrogen are shown in Table 3. As can be seen from Table 3, for molybdenum-tungsten oxide catalysts, with an increase in the content of molybdenum in the composition, the specific surface area of the samples increases from 0.4 m2/g on the sample Mo-W=1-9 to 26.5 m2/g on the sample Mo-W=9- one. -O.

Table 3. Specific surfaces area of Mo-W-O catalysts, m2/g

Mo/W atom ratio	1-9	2-8	3-7	4-6	5-5	6-4	7-3	8-2	9-1
S, m^2/q	0.4	1.7	0.7	2.5	12.3	15.5	22.9	25.9	26.5

Comparing the obtained data, we can say that the introduction of molybdenum into the composition of the binary catalyst increases the specific surface area of tungsten-containing catalysts.

We have also studied the dependence of the yields of reaction products on the specific surface area of the catalysts. The dependence of the yields of acetaldehyde, ethylene, acetic acid and ethanol conversion on the specific surface area of molybdenum-tungsten oxide catalysts is shown in Fig. 2.

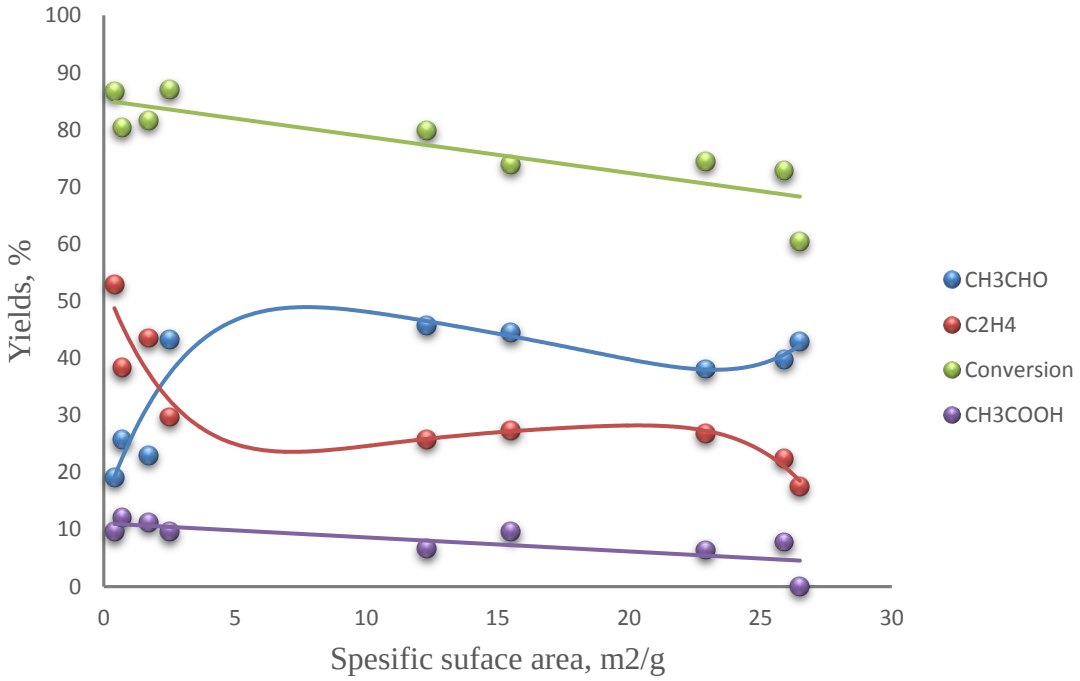

Fig. 2. Dependence of the activity of molybdenum-tungsten oxide catalysts in the ethanol oxidation reaction on the specific surface area

Fig. 2 shows that with an increase in the specific surface area, the yield of acetic acid decreases. From the data shown in Fig. 2 it is also seen that with an increase in the specific surface area, the ethylene yield first sharply decreases, and then practically does not change. The yield of acetaldehyde first increases sharply, and then practically does not change with an increase in the specific surface area. It can also be seen from the obtained data that the conversion of ethanol decreases with an increase in the specific surface area of the catalyst.

4. Conclusion

1. Molybdenum-tungsten oxide catalysts rich in tungsten are active in the reaction of dehydration of ethanol to ethylene, while samples enriched in molybdenum are active in the reaction of oxidative dehydrogenation of ethanol to acetaldehyde.
2. The introduction of molybdenum into the composition of a binary catalyst increases the specific surface area of tungsten-containing catalysts.
3. As the specific surface area increases, the yield of acetic acid and the conversion of ethanol decrease. At low specific surfaces of catalysts, an increase in the specific surface leads to an increase in the yield of acetaldehyde and a decrease in the yield of ethylene.

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