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X-Ray study of Mo-W-O, Ti-W-O and Cu-W-O catalysts

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Abstract: An X-ray study of the phase composition of Mo-W-O, Ti-W-O, and Cu-W-O catalysts was carried out. Analysis of X-ray diffraction patterns of the Mo-W-O catalytic system showed that in all samples, mainly the phases of molybdenum and tungsten oxides, namely MoO_3 and WO_3, are formed. It is shown that, in contrast to Mo-W-O catalysts, in addition to the initial titanium and tungsten oxides, the samples of the Ti-W-O catalytic system also contain phases of chemical compounds. So, in Ti-W-O samples, there are phases of titanium oxide (anatase), titanium oxide (rutile), and tungsten oxide. It has been established that the degree of crystallinity of binary titanium-tungsten oxide samples decreases with increasing titanium content in the catalyst composition from 83.4% to 70.2%. In the case of copper-tungsten oxide catalysts, in addition to the initial oxides of copper and tungsten also contain phases of the chemical compound of copper tungstate, and crystallinity degrees of binary copper-tungsten oxide samples changes in the ranges from 85.7% to 41.3%.

Keywords: binary catalysts, copper oxide, molybdenum oxide, phase analysis, titanium oxide, tungsten oxide

1. Introduction

Our studies have shown that binary tungsten-containing catalysts with molybdenum, titanium, and copper additives exhibit high activity in the reaction of partial ethanol oxidation. Thus, it was shown that on molybdenum-tungsten oxide catalysts rich in molybdenum, the reaction of dehydration of ethanol into ethylene occurs, while samples enriched with tungsten are active in the reaction of oxidative dehydrogenation of ethanol into acetic aldehyde [1]. The main product of ethanol conversion on titanium-tungsten oxide catalysts at temperatures up to 300°C is diethyl ether, while at higher temperatures, the reaction of ethanol dehydration into ethylene occurs [2]. At temperatures up to 300°C, acetic aldehyde is practically the only product of the ethanol oxidation reaction on copper-tungsten oxide catalysts [3,4]. Acetic aldehyde, acetone, carbon dioxide, and ethylene are also formed at higher temperatures.

Various factors, such as surface acidity, crystallinity, phase composition, etc, can cause such a change in the activity of binary tungsten-containing catalysts.

It is known that the phase composition of the catalyst and, consequently, its structural properties can strongly influence its activity [5-7]. Naturally, one of the structural properties of the catalyst is crystallinity, which in turn depends on both the conditions of preparation and the initial compounds taken for the preparation of the catalyst [8-10]. There are no materials in the periodical literature on the study of binary tungsten-containing catalysts' phase composition and crystallinity. In this connection, to explain how the structure of Mo-W-O, Ti-W-O, and Cu-W-O catalysts affect its catalytic activity, we have carried out for the first time X-ray diffraction studies of our catalysts to determine the phase composition and degree of crystallinity of the synthesized tungsten-containing catalysts.

2. Experimental

Molybdenum-tungsten oxide catalysts were prepared by co-precipitation from aqueous ammonium molybdate and ammonium tungstate solutions. 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 about 250°C. The obtained solid mass was calcined at 700°C for 10 hours. Thus, 9 catalysts with atomic ratio of elements from Mo: W=1:9 to Mo: W =9:1 were synthesized.

Titanium-tungsten and copper-tungsten oxide catalysts were prepared in the same sequence as molybdenum-tungsten oxide catalysts. Only titanium tetrachloride and copper nitrate were used as the second starting components. As a result, we prepared 9 samples in each catalytic system. In total, we

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prepared 27 catalysts satisfying the following conditions:

mA/nB, where A is Mo, Ti, Cu; B is W, m,n=1÷9, m+n=10.

Reagents used for the preparation of Mo-W-O, Ti-W-O, and Cu-W-O catalysts and their purity are given in Table 1.

Table 1. Reagents used for the preparation of catalysts and their purity.

Reagent	Chemical formula	Quality
Copper nitrate	$Cu(NO_3)_2$	Clean for Analysis
Ammonium molybdate	$(NH_4)_6Mo_7O_{24}x4H_2O$	Clean for Analysis
Ammonium tungstate	$(NH_4)_{10}W_{12}O_{41}x5H_2O$	Clean for Analysis
Titanium tetrachloride	$TiCl_4$	Clean for Analysis

X-ray diffraction studies of the phase composition of the synthesized Mo-W-O, Ti-W-O, and Cu-W-O catalysts were carried out on an automatic powder diffractometer "D2 Phaser" of "Bruker" (Germany) (CuKα-radiation, Ni-filter) in the reflection angle range $5° \leq 2\theta \leq 80°$.

3. Results and Discussion

Figure 1 shows the diffraction patterns of all nine mMo:nW ratios collected together. MoO_3 and WO_3 oxides are also represented at the beginning and end of these diffraction patterns. Analyses of X-ray diffraction patterns show that all samples consist of two phases, and the percentage ratio of the components is maintained in all of them, which is evidenced by the regular change in the intensities of the reflexes in the diffraction patterns.

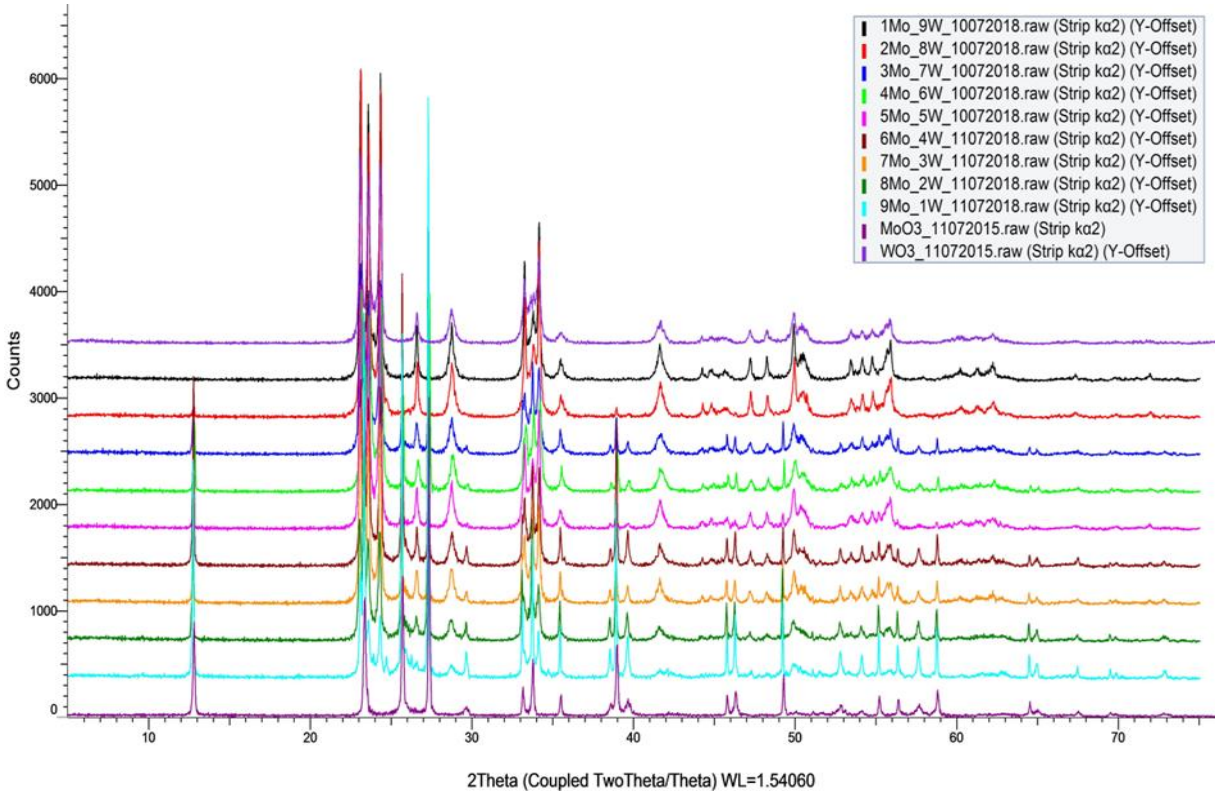

Figure 1. X-ray diffraction patterns of MoO_3, WO_3, and molybdenum-tungsten oxide catalysts of different compositions.

The phases formed in the studied Mo-W-O samples and their degrees of crystallinity are given in Table 2.

As can be seen from the results presented in Table 2, the Mo-W-O catalytic system forms mainly phases of molybdenum and tungsten oxides, namely MoO_3 and WO_3. Table 2 also shows that the degree of crystallinity of tungsten-containing catalysts with molybdenum additives depends little on the atomic ratio of molybdenum to tungsten and varies from 82.1% in the Mo-W=8-2 sample to 85.5% in the Mo-W=4-6 sample.

Table 2. Degrees of crystallinity of Mo-W-O catalytic system samples and phases present in these samples.

Atomic ratio of molybdenum to tungsten	Phases present	Degree of crystallinity, %
1:9	$MoO_3 + WO_3$	83.8
2:8	$MoO_3 + WO_3$	84.6
3:7	$MoO_3 + WO_3$	82.3
4:6	$MoO_3 + WO_3$	85.5
5:5	$MoO_3 + WO_3$	83.2
6:4	$MoO_3 + WO_3$	82.6
7:3	$MoO_3 + WO_3$	83.8
8:2	$MoO_3 + WO_3$	82.1
9:1	$MoO_3 + WO_3$	82.7

The diffraction patterns of all nine samples of the Ti-W-O catalytic system assembled and of the initial titanium and tungsten oxides, are shown in Figure 2.

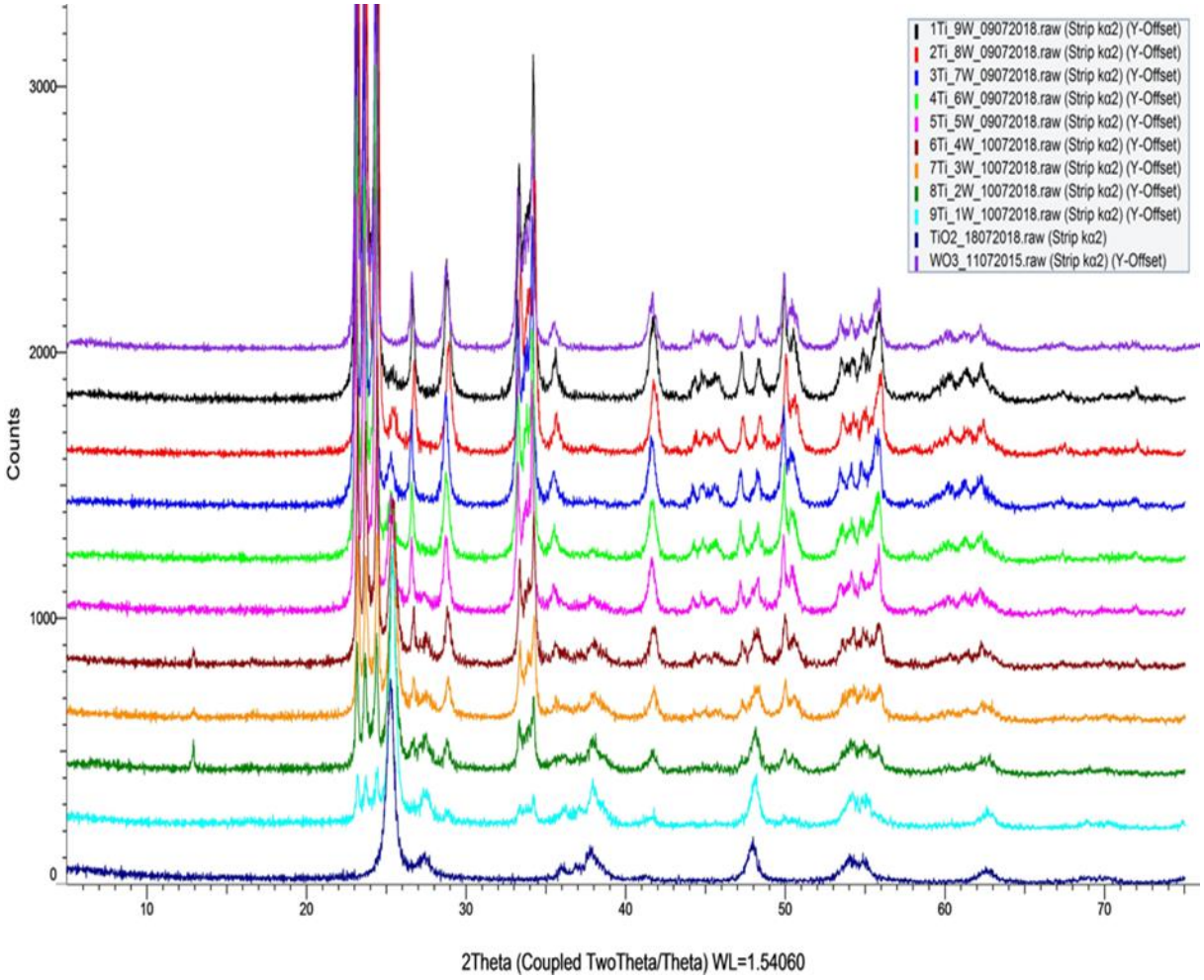

Figure 2. X-ray diffraction patterns of TiO_2, WO_3, and titanium-tungsten oxide catalysts of different compositions.

In contrast to the previous series of catalysts, in addition to the initial titanium and tungsten oxides, the Ti-W-O catalytic system samples contain phases of TiO_2 rutile. The phases formed in the Ti-W-O catalytic system and the crystallinity degrees of the samples are given in Table 3.

Table 3. Degrees of crystallinity of samples of catalytic system Ti-W-O and phases present in these samples.

Atomic ratio of titanium to tungsten	Phases present	Degree of crystallinity, %
1:9	TiO_2(anatase) + WO_3	83.4
2:8	TiO_2(anatase) + WO_3	82.1
3:7	TiO_2(anatase)+ WO_3	83.8
4:6	TiO_2(anatase) + WO_3	77.2
5:5	TiO_2(anatase) + WO_3	78.1
6:4	TiO_2(anatase) + WO_3 + TiO_2(rutile)	75.7
7:3	TiO_2(anatase) + WO_3 + TiO_2(rutile)	71.9
8:2	TiO_2(anatase) + WO_3 + TiO_2(rutile)	70.7
9:1	TiO_2(anatase) + WO_3 + TiO_2(rutile)	70.2

As can be seen from Table 3, in samples from Ti-W=1-9 to Ti-W=5-5, titanium oxide (anatase) and tungsten oxide phases are present. In samples from Ti-W=6-4 to Ti-W=8-2, there are also phases of titanium oxide (rutile) in addition to the above phases. In the sample Ti-W=9-1, there are phases of titanium oxide in the form of anatase, rutile, and tungsten oxide. Table 3 also shows that the degree of crystallinity of binary titanium-tungsten oxide samples decreases with increasing titanium content in the catalyst composition. So, the degree of crystallinity from 83.4% on the sample Ti-W=1-9 decreases to 70.2% on the sample Ti-W=9-1.

Figure 3 shows the diffraction patterns of all nine samples of the Cu-W-O catalytic system collected together and the initial copper and tungsten oxides presented.

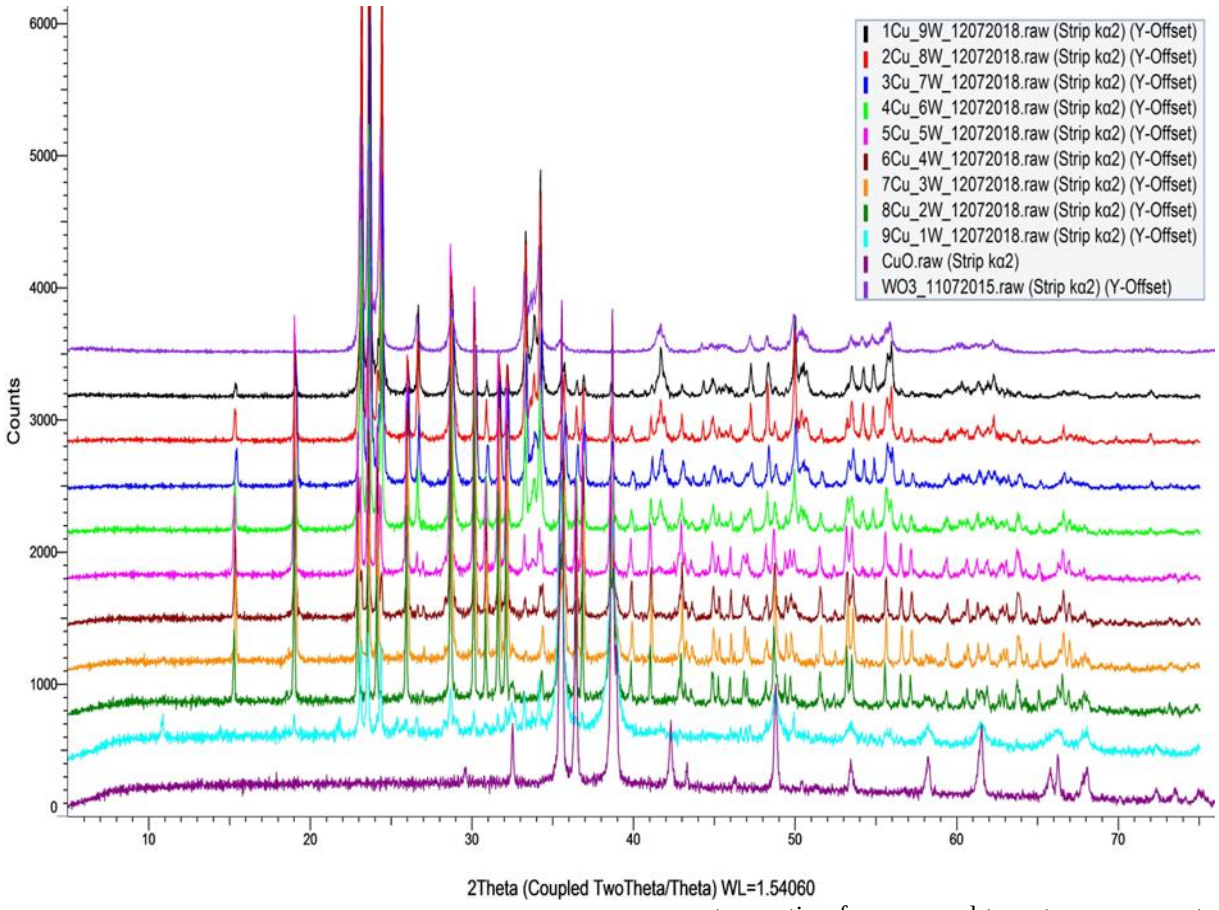

Figure 3. X-ray diffraction patterns of CuO, WO_3, and copper-tungsten oxide catalysts of different compositions.

As can be seen from Figure 3, analyses of the X-ray diffraction patterns show that in all samples, the Table 4 presents the phases formed in the catalytic system Cu-W-O, as well as the samples' crystallinity degrees.

percentage ratio of copper and tungsten components is maintained, evidenced by the regular change in the intensities of the reflexes in the diffraction patterns. In addition to the initial oxides of copper and tungsten, the samples of the Cu-W-O catalytic system also contain phases of chemical compounds.

Table 4. Degrees of crystallinity of the samples of the Cu-W-O catalytic system and the phases present in these samples.

Atomic ratio of copper to tungsten	Phases present	The degree of crystallinity, %
1:9	$CuO + WO_3 + Cu(WO_4)$	84.2
2:8	$CuO + WO_3 + Cu(WO_4)$	85.5
3:7	$CuO + WO_3 + Cu(WO_4)$	85.7
4:6	$CuO + WO_3 + Cu(WO_4)$	84.1
5:5	$CuO + WO_3 + Cu(WO_4)$	83.0
6:4	$CuO + WO_3 + Cu(WO_4)$	79.8
7:3	$CuO + WO_3 + Cu(WO_4)$	77.6
8:2	$CuO + WO_3 + Cu(WO_4)$	66.6
9:1	$CuO + WO_3$ + Cu(complex)	41.3

Table 4 shows that in all samples except Cu-W=9-1, phases of copper oxide, tungsten oxide, and copper tungstate chemical compounds are present. In the Cu-W=9-1 sample, apart from copper and tungsten oxides, phases of the copper compound with complex formula are also present. Table 4 also shows that the degree of crystallinity of binary copper-tungsten oxide samples with increasing copper content in the catalyst composition first slightly increases to 85.7% and then sharply decreases to 41.3% in the Cu-W=9-1 sample.

Conclusion

1. The samples of the Mo-W-O catalytic system consist mainly of molybdenum and tungsten oxide phases.
2. In samples of catalytic systems Cu-W-O, besides individual oxides of initial metals, there are also chemical compounds between initial elements.
3. The crystallinity of the studied Mo-W-O catalysts does not change much with the composition change. In contrast, for the catalytic systems Ti-W-O and Cu-W-O, the degree of crystallinity increases with the increase of tungsten in the catalyst composition.

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