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DEPENDENCE OF Cr-Cu-O CATALYSTS ACTIVITY IN THE REACTION OF ETHANOL DEHYDROGENATION ON THEIR PHASE COMPOSITION

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Abstract: *The work deals with the reaction of ethanol conversion over chromium copper binary oxide catalysts. It showed that acetaldehyde is the main product of the ethanol conversion reaction. As the temperature rises, the direction of the ethanol conversion reaction shifts toward dehydration of ethanol into ethylene. Studies revealed that the atomic ratio of chromium to copper in the composition of the catalyst also has a strong effect on the activity of chromium-copper oxide catalysts. It established that samples with high chromium content in the composition of the catalyst display the greatest activity in the reaction of acetic aldehyde formation. So, on the sample Cr-Cu = 6-4, the yield of acetaldehyde reaches 82.5% with a selectivity of 97.6%. X-ray studies found that Cr-Cu-O catalysts consist mainly of initial oxides and in some samples indicate the chemical compound. X-ray studies showed that as the copper content decreases, the degree of crystallinity increases in the studied catalytic system. Comparison of the activity of Cr-Cu-O catalysts with their crystallinity degree revealed that the rise in crystallinity degree of chromium-copper oxide catalysts leads to the increase of acetic aldehyde yield and its selectivity in the ethanol conversion reaction.*

Keywords: *ethanol dehydrogenation, binary catalysts, crystallinity.*
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Introduction

As is known, renewable bioethanol is one of the promising raw materials for the production of various chemical compounds [1-3]. The conversion reaction of ethanol makes it possible to obtain chemicals like acetaldehyde, acetic acid, diethyl ester, etc. For the reactions of ethanol conversion, various catalytic systems are used on the basis of oxides of chrome, zinc, copper, etc. [4, 5]. Previously we showed that at high speed the ethanol is converted into acetone, acetic acid on various binary chromium-copper containing catalysts [6,7]. It is known that the phase composition of the catalyst and its structural properties, can have a strong effect on its activity [8,9]. One of the structural properties of the catalyst is its crystallinity which depends both on basic compounds used for its preparation and on conditions under which it is prepared. For this reason, the present work deals with the study of the dependence of chromium-copper oxide catalysts activity in the dehydrogenation reaction of ethanol on their crystallization rate.

Experimental part

Binary chromium copper oxide catalysts of various compositions were prepared by means of co-precipitation from aqueous solutions of chromium and copper nitrate. The resulting mixture was successively evaporated and dried at 100-120°C, decomposed until nitrogen oxides were completely isolated at 250°C, and then calcined at 600°C within 10 hours. Thus, 9 catalysts with an atomic ratio of elements from Cr:Cu = 1:9 to Cr:Cu = 9:1 were

synthesized and the activity of the synthesized catalysts in the reaction of ethanol conversion and butene-1 isomerization explored in a flow unit with a tubular reactor in the temperature range 100 – 500°C. Also, 5 ml of the given catalyst with a grain size of 1.0–2.0 mm was loaded into the reactor, and its activity in the ethanol conversion reaction was studied. Ethanol conversion was carried out in a stream of nitrogen. Ethanol and its conversion products were determined by chromatography method. X-ray studies of binary chrome-copper oxide catalysts were carried out on a Bruker automatic D2 Phaser powder diffractometer (CuKα radiation, Ni filter, $3 \leq 2\theta \geq 80$ °).

Results and discussion

Studies found that the main product of ethanol over chrome-copper oxide catalysts conversion was acetic aldehyde. Ethylene, acetone, ethyl acetate, carbon dioxide, and carbon dioxide and other decomposition products were also formed as a by-product. Fig. 1 shows the effect of the reaction temperature on the yields of ethanol conversion products on a Cr:Cu = 6:4 catalyst. As can be seen from Fig. 1, acetic aldehyde is formed in the greatest amount on the Cr:Cu = 6:4 catalyst. Fig. 1 reveals that the reaction of ethanol conversion on the explored catalyst starts at a temperature of 150°C and at this temperature only acetic aldehyde is formed in an amount of 9.9%. Increase in the reaction temperature leads to the formation of other reaction products. Maximum yield of acetic aldehyde reaches 82.5% at 300°C.

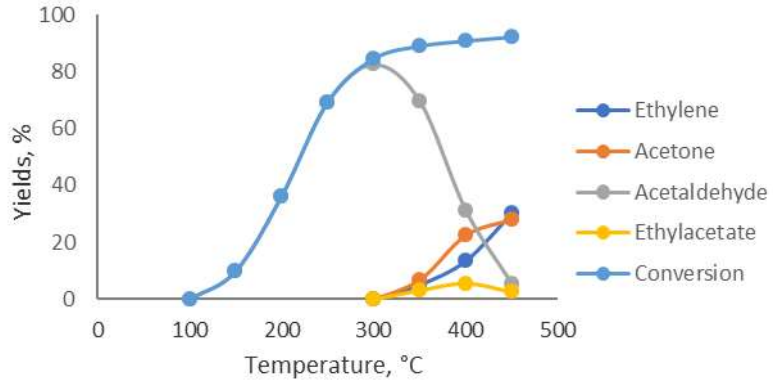

Fig. 1. Effect of temperature on the yields of ethanol conversion products on Cr:Cu=6:4 catalyst.

The formation of ethylene, acetone and carbon dioxide begins at a temperature of 350°C. Fig. 1 shows that the yields of ethylene and acetone increase as the reaction temperature rises. The highest yields of ethylene and acetone are observed at a temperature of 450° C to make up 30.2 and 28% respectively. As for the formation of ethyl acetate, it is observed in the temperature range 350 and 450°C and does not exceed 5.6%. The maximum ethanol conversion on the Cr: Cu = 1:9 catalyst reaches 92.1% at 450°C.

Our preliminary studies revealed that the atomic ratio of cerium to copper strongly affects the activity of chromium-copper oxide catalysts in the reaction of ethanol conversion. In this regard, we studied the effect of the composition of chromium copper catalyst on its activity. Table 1 shows the ethanol conversion, yields and selectivity of acetic aldehyde on chromium copper oxide catalysts of various compositions at a temperature of 300°C.

As can be seen from Table 1, the yield of acetic aldehyde with an increase in the chromium content in the catalyst composition first

decreases from 46.2% on the catalyst Cr:Cu = 1:9 to 32.3% on the catalyst Cr:Cu = 3:7 and then increases to pass through a maximum of 82.5% on the catalyst Cr:Cu = 6:4. The table also shows that the selectivity of the reaction for acetic aldehyde with an increase in the chromium content in the catalyst increases to almost 98% and then remains unchanged. The maximum ethanol conversion in the studied samples reaches 84.5%.

Table 1. Dependence of the yield and selectivity of acetic aldehyde on the atomic ratio of chromium to copper. T = 300°C.

Cr/Cu atom ratio	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Reaction products	Yields, %								
CH_3CHO	46.2	42.3	32.3	53.9	70.9	82.5	75.9	61.1	57
Conversion	73.8	63.3	58.6	67.9	72.6	84.5	75.9	62.5	57.8
Selectivity	62.6	66.8	55.1	79.4	97.6	97.6	100	97.8	98.6

Thus, based on the conducted studies, it can be said that acetic aldehyde is the main reaction product on chromium-copper catalysts and its yield reaches 82.5% with a selectivity of 97.6%. The yield and distribution of reaction products on chromium copper catalysts depends both on the reaction temperature and the atomic ratio of chromium to copper.

As is known, the phase composition of the catalyst, i.e., its structural properties, can have a profound effect on its activity. One of the structural properties of the catalyst is its crystallinity which depends both on basic compounds used for its preparation and conditions under which it is prepared. For this reason, we have studied the dependence of the activity of ethanol dehydrogenation reaction of catalysts synthesized by us on their crystallization rate.

X-ray studies of Cr-Cu-O catalytic system shows that in addition to phases of the two primary oxides the chemical compound phase $CuCr_2O_4$ is formed. The crystallographic characteristics of the identified phases are given in Table 2.

Table 2. Crystallographic properties of phases formed in the Cr-Cu-O catalytic system

Chemical compound	Syngonia	Volume group	Lattice parameters				Z, number of molecules
			a, Å	в, Å	c, Å	angle,	
CuO	Monoclinic	Cc	4.692	3.428	5.137	99.54	4
Cr_2O_3	Rhombohedral	$R\bar{3}c$	4.960	-	13.59	-	6
$CuCr_2O_4$	Tetragonal	$I\bar{4}2\,d$	6.04	-	7.78	-	4

Analysis of diffraction curves in the Cr-Cu-O system shows the formation of 3 phases - Cr_2O_3, CuO and $CuCr_2O_4$ in all samples. Fig. 2 shows combined diffraction curves of all nine ratios (m Cr/nCu). For comparative analysis, diffraction curves of Cr_2O_3 and CuO oxides are shown at the beginning and end of diffraction curves. X-ray analysis reveals that all samples contain mainly 2 phases, Cr_2O_3 and CuO. A regular change in the intensity of diffraction reflexes indicates the maintenance of the phase ratio of all components.

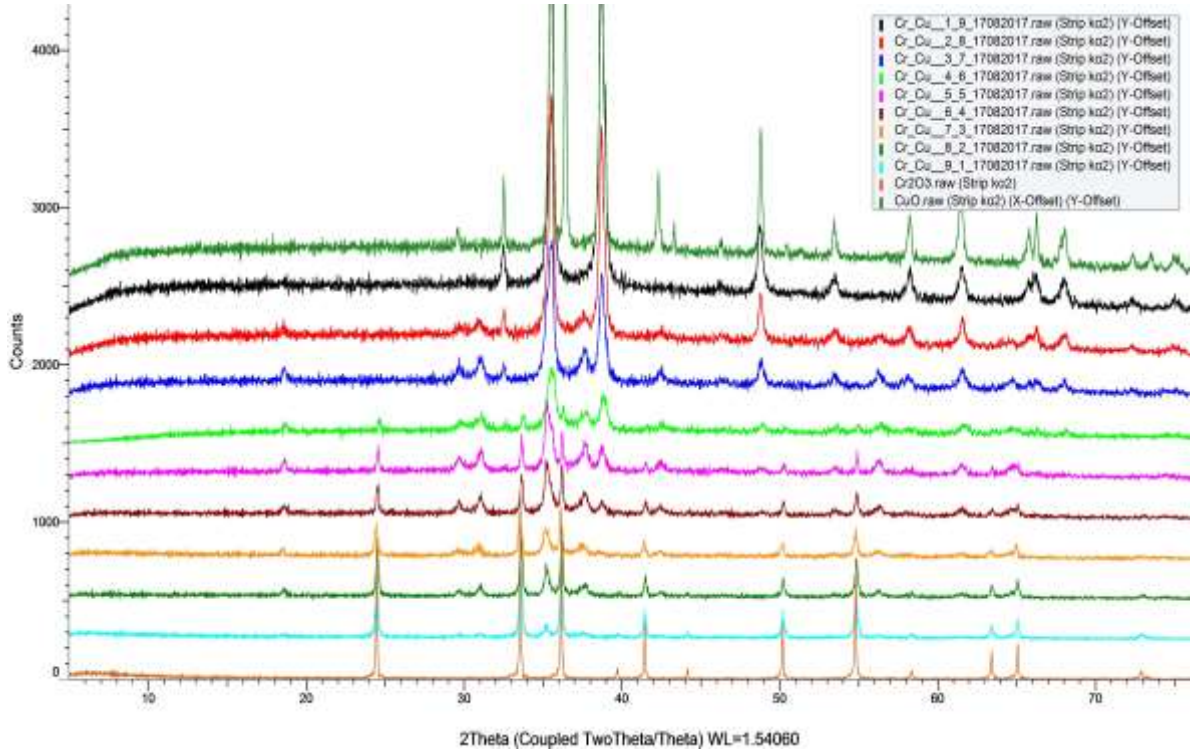

Fig. 2. Diffractograms of chromium and copper oxide, as well as Cr-Cu-O catalysts for all nine ratios.

Also, we calculated crystallization rates of all phases in the D2 Phaser using the DIFFRAC.EVA program. The results obtained are shown in Table 3. As can be seen from Table 3, the degree of crystallinity increases in the studied catalytic system as the copper content decreases. Thus, as the chrome content in the Cr-Cu-O catalytic system increases, the crystallization rate rises from 41.6% to 73.3%.

Table 3. Crystallinity degree of samples of Cr-Cu-O catalytic system.

Cr:Cu ratio	1:9	2:8	3:7	4:6	5:5	6:4	7:3	8:2	9:1
Degree of crystallinity, %	41.6	41.9	50.2	57.3	64.4	67.1	69.7	73.3	71.2

Fig. 3 shows the dependence of the yield of acetaldehyde, the selectivity of the process on acetaldehyde and the conversion of ethanol on the degree of crystallinity of binary chromium-copper oxide catalysts. Fig. 3 indicates that as the crystallinity of chromium-copper oxide catalysts increases, the yield of acetaldehyde, the selectivity of the acetaldehyde process, and the conversion of ethanol change symmetrically. Also, it has to be kept in mind that when the catalyst has a high crystallinity, the ethanol is converted to acetaldehyde at 100%. This indicates that the rise in the crystallinity of chromium-copper oxide catalysts increases the selectivity of acetaldehyde process. On that basis, in order to increase the selectivity of ethanol conversion into acetaldehyde, it is necessary to synthesize the catalyst with a high degree of crystallinity.

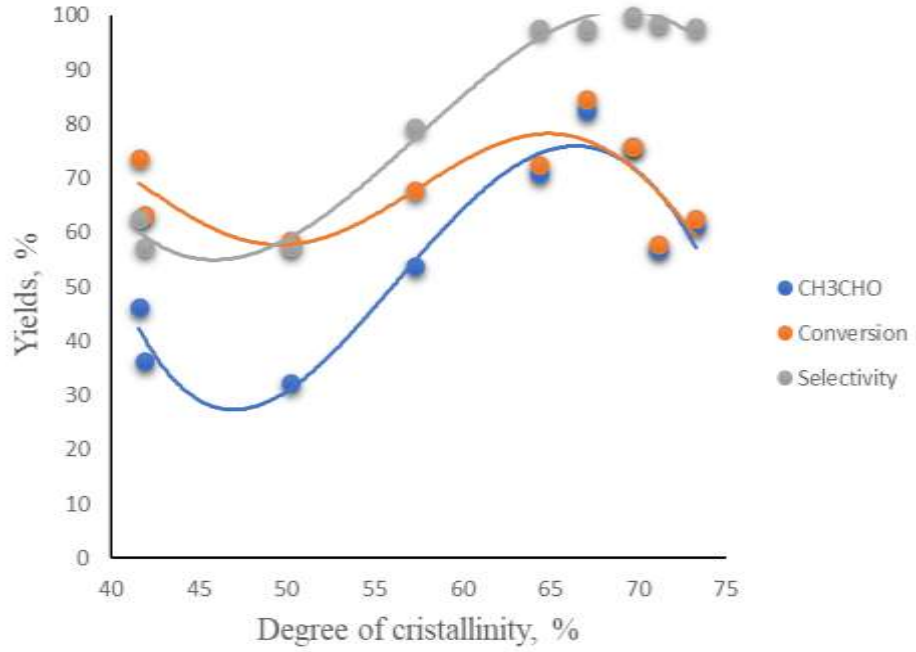

Fig. 3. Dependence of the activity of chromium-copper oxide catalyst in the ethanol dehydrogenation reaction on the degree of crystallinity. T = 300 °C.

Conclusions

- Main product of the ethanol conversion reaction over chromium-copper oxide catalysts is acetic aldehyde, and its yield reaches up to 82.5% with selectivity 97.6%.
- Increase in crystallinity degree of chromium-copper oxide catalysts leads to rise in the yield of acetic aldehyde and its selectivity in the ethanol conversion reaction.

References

1. Megumu Inaba, Kazuhisa Murata, Masahiro Saito & Isao Takahara. Ethanol conversion to aromatic hydrocarbons over several zeolite catalysts. *Reaction Kinetics and Catalysis Letters.* 2006, vol. 88, pp. 135–141.
2. Weiping Wang, Zhifei Wang, Yan Ding, Jinyu Xi & Gongxuan Lu. Partial Oxidation of Ethanol to Hydrogen over Ni–Fe Catalysts. *Catalysis Letters.* 2002, vol. 81, pp. 63–68.
3. Dapeng Liu, Yan Liu, Eileen Yi Ling Goh, Christina Jia Ying Chu, Chuandayani Gunawan Gwie, Jie Chang, Armando Borgna. Catalytic conversion of ethanol over ZSM-11 based catalysts. *Applied* Catalysis A: General, 2016, vol. 523, pp. 118–129.
4. Hala R. Mahmoud. Highly dispersed Cr_2O_3–ZrO_2 binary oxide nanomaterials as novel catalysts for ethanol conversion. *Journal of Molecular Catalysis A. Chemical*. 2014, vol. 392, pp. 216–222.
5. Isabel C. Freitas, Jean Marcel R. Gallo, José Maria C. Bueno & Clélia M. P. Marques. The Effect of Ag in the Cu/ZrO_2 Performance for the Ethanol Conversion. *Topics in Catalysis.* 2016, vol. 59, pp 357–365.
6. Mammadova S.H., Aghayeva K.Kh. Conversion of ethanol over binary copper containing catalysts. *Chemical Problems*. 2020, vol.18, no 2, pp. 199-205.
7. Mammadova S.H., Garaybayli S.A., Baghiyev V.L. A study of the phase composition of copper-cerium oxide system. In: 5th International School-Conference on Catalysis for Young Scientists, Catalyst

Design: From Molecular to Industrial Level, May 20-23, 2018, Moscow, Russia, ABSTRACTS, Novosibirsk, PP-V-12, p.188.
8. Kushal Singh, Kundan Kumar, Saurabh Srivastava, Anirban Chowdhury. Effect of rare-earth doping in CeO_2 matrix: Correlations with structure, catalytic and visible light photocatalytic properties. *Ceramics International*, 2017, vol. 43, issue 18, pp. 17041-17047.
9. Elena A.Baranova E.A, Monica A.Padilla, Barr Halevi, Tariq Amir, Kateryna Artyushkova, Plamen Atanassov. Electrooxidation of ethanol on PtSn nanoparticles in alkaline solution: Correlation between structure and catalytic properties. *Electrochimica Acta*, 2012, vol. 80, pp. 377-382.

ETANOLUN DEHİDROGENLƏŞMƏSİ REAKSİYASINDA Cr-Cu-O KATALUZATORLARININ AKTİVLİYİNİN ONLARIN FAZA TƏRKİBİNDƏN ASILILIĞI

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İşdə xrom və mis tərkibli binar oksid katalizatorları üzərində etanolun çevrilməsi reaksiyası öyrənilmişdir. Göstərilmişdir ki, etanolun çevrilməsi reaksiyasının əsas məhsulu sirkə aldehididir. Reaksiya temperaturunun məhsulların çıxımına təsiri öyrənilmişdir. Müəyyən edilmişdir ki, temperatur artdıqca etanolun çevrilmə reaksiyasının istiqaməti etanolun etilenə dehidratlaşması istiqamətinə doğru dəyişir. Tədqiqatlar göstərmişdir ki, xromun misə atom nisbəti katalizatorların aktivliyinə güclü təsir göstərir. Müəyyən edilmişdir ki, sirkə aldehidinin əmələ gəlməsi reaksiyasında katalizatorun tərkibində xromun miqdarı yüksək olan nümunələri daha çox aktivlik göstərir. Belə ki Cr-Cu=6-4 tərkibli nümunədə asetaldehidin çıxımı 82.5%, selektivlik isə 97.6% -ə çatır. Rentgenqrafik tədqiqatlar Cr-Cu-O katalizatorlarının əsasən oksidlərdən ibarət olduğunu göstərir, bəzi nümunələrdə eləcə də $CuCr_2O_4$ müşahidə olunur. Cr-Cu-O katalitik sistemdə misin miqdarı azaldıqca kristallik dərəcəsi artır. Kristalliklik dərəcəsi artıqca sirkə aldehidinin çıxımı, selektivliyi və etanolun konvensiyası artır.

Açar sözlər: *etanolun dehidrogenləşməsi, binar katalizatorlar, kristalliklik.*

ЗАВИСИМОСТЬ АКТИВНОСТИ Cr-Cu-O КАТАЛИЗАТОРОВ В РЕАКЦИИ ДЕГИДРИРОВАНИЯ ЭТАНОЛА ОТ ИХ ФАЗОВОГО СОСТАВА

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В данной работе реакция превращения этанола изучена на бинарных катализаторах, состоящих из оксида хрома и меди. Показано, что ацетальдегид является основным продуктом реакции превращения этанола. Установлено, что с повышением температуры направление реакции превращения этанола смещается в сторону дегидратации этанола до этилена. Исследования показали, что атомное отношение хрома к меди в составе катализатора также оказывает сильное влияние на активность катализаторов.

Установлено, что наибольшей активностью в реакции образования уксусного альдегида обладают образцы с высоким содержанием хрома в составе катализатора. Так, на образце Cr-Cu = 6-4 выход ацетальдегида достигает 82.5% при селективности 97.6%. Рентгеновские исследования показали, что катализаторы Cr-Cu-O состоят в основном из оксидов, а в некоторых образцах присутствует $CuCr_2O_4$. Рентгенографические исследования также показали, что с уменьшением содержания меди степень кристалличности исследуемой каталитической системы увеличивается. Сравнение активности Cr-Cu-O-катализаторов со степенью их кристалличности показало, что увеличение степени кристалличности хром-медно-оксидных катализаторов приводит к увеличению выхода уксусного альдегида и его селективности в реакции конверсии этанола.

***Ключевые слова**: дегидрирование этанола, бинарные катализаторы, кристалличность.*