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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≤2θ≥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.

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
DEPENDENCE OF Cr-Cu-O CATALYSTS

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 CuCr₂O₄ 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

<table>
<thead>
<tr>
<th>Chemical compound</th>
<th>Syngonia</th>
<th>Volume group</th>
<th>Lattice parameters a, Å</th>
<th>b, Å</th>
<th>c, Å</th>
<th>angle,</th>
<th>Z, number of molecules</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuO</td>
<td>Monoclinic</td>
<td>Cc</td>
<td>4.692</td>
<td>3.428</td>
<td>5.137</td>
<td>99.54</td>
<td>4</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>Rhombohedral</td>
<td>R₃c</td>
<td>4.960</td>
<td>-</td>
<td>13.59</td>
<td>-</td>
<td>6</td>
</tr>
<tr>
<td>CuCr₂O₄</td>
<td>Tetragonal</td>
<td>42 d</td>
<td>6.04</td>
<td>-</td>
<td>7.78</td>
<td>-</td>
<td>4</td>
</tr>
</tbody>
</table>

Analysis of diffraction curves in the Cr-Cu-O system shows the formation of 3 phases - Cr₂O₃, CuO and CuCr₂O₄ in all samples. Fig. 2 shows combined diffraction curves of all nine ratios (m Cr/nCu). For comparative analysis, diffraction curves of Cr₂O₃ and CuO oxides are shown at the beginning and end of diffraction curves. X-ray analysis reveals that all samples contain mainly 2 phases, Cr₂O₃ and CuO. A regular change in the intensity of diffraction reflexes indicates the maintenance of the phase ratio of all components.

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

<table>
<thead>
<tr>
<th>Cr/Cu atom ratio</th>
<th>Yields, %</th>
<th>Conversion</th>
<th>Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:9</td>
<td>46.2</td>
<td>73.8</td>
<td>62.6</td>
</tr>
<tr>
<td>2:8</td>
<td>42.3</td>
<td>63.3</td>
<td>66.8</td>
</tr>
<tr>
<td>3:7</td>
<td>32.3</td>
<td>58.6</td>
<td>55.1</td>
</tr>
<tr>
<td>4:6</td>
<td>53.9</td>
<td>67.9</td>
<td>79.4</td>
</tr>
<tr>
<td>5:5</td>
<td>70.9</td>
<td>72.6</td>
<td>97.6</td>
</tr>
<tr>
<td>6:4</td>
<td>82.5</td>
<td>84.5</td>
<td>100</td>
</tr>
<tr>
<td>7:3</td>
<td>75.9</td>
<td>75.9</td>
<td>97.8</td>
</tr>
<tr>
<td>8:2</td>
<td>61.1</td>
<td>62.5</td>
<td>97.6</td>
</tr>
<tr>
<td>9:1</td>
<td>57</td>
<td>57.8</td>
<td>98.6</td>
</tr>
</tbody>
</table>
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.**

<table>
<thead>
<tr>
<th>Cr:Cu ratio</th>
<th>1:9</th>
<th>2:8</th>
<th>3:7</th>
<th>4:6</th>
<th>5:5</th>
<th>6:4</th>
<th>7:3</th>
<th>8:2</th>
<th>9:1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Degree of crystallinity, %</td>
<td>41.6</td>
<td>41.9</td>
<td>50.2</td>
<td>57.3</td>
<td>64.4</td>
<td>67.1</td>
<td>69.7</td>
<td>73.3</td>
<td>71.2</td>
</tr>
</tbody>
</table>

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

ETANOLUN DEHİDROGENLƏŞMƏSİ REAKSİYASININDA Cr-Cu-O KATALUZATORLARININ AKTİVLİYİNİN ONLARIN FAZA TƏRKİBİNDƏN ASILİLİĞİ

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İşdə xrom və mis tərkibli binar oksid katalizatorları üzərində etanolun çevriləşdi reaksiyasının qarmaqda tərəfdar olmağı sübut edilmişdir. Gəstərlər让更多 di, etanolun çevriləşdi reaksiyasının asas məhsul sırka aldehididir. Reaksiya temperaturunun məhsulların çıxıma təsirindən qısa öyrənilmişdir. Müşəyyən edilmişdir ki, temperatur artdıraca etanolun çevriləşdi reaksiyasının istiqamətini etanolun etilənə dehidratlaşması istiqamətinə doğru dayışır. Tədqiqatlar göstərməkdir ki, xromun misə atom nisbatı katalizatorların aktivliyini güçlü təsir göstərir. Müşəyyən edilmişdir ki, sırka aldehidinin ənənə gələn reaksiyasında katalizatorların tərkibi xronun miqdəri yüksək olan nümunələrdir daha çox aktivlik göstərir. Belə ki Cr-Cu=6-4 tərkibli nümunə asetaldehidin çıxımı 82.5%, selektivlik isə 97.6% -ə çatır. Rentgenqrafik tədqiqatlar Cr-Cu-O katalizatorlarının asasan oksidlərdən ibarət olduğunu göstərir, bəzi nümunələrdə elə cə arcsə CuCr₂O₄ məşahidə olunur. Cr-Cu-O katalitik sistəmdə məninin miqdəri azaldıqda kristallik dərəcəsi artır. Kristallik dərəcəsi artıraca sırka aldehidinin çıxımı, selektivliyi və etanolun konvensiya artırır.

Açar sözlər: etanolun dehidrogenləşməsi, binar katalizatorlar, kristalliklik.

ZAVİSİMİCİ İAKTİVİNCİ CR-CU-Ö KATALİZATÖRƏRİ Vİ REAKŞİYON DƏĞİDİRİRƏNI ETANOLƏS İÇİN Vİ FAZƏVƏ OÇTAÇABA

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V danın rəhbərə reaksiyanın əvəz etilənə dəvəticə etanolun düztda izuchan bina qatalizatorlar, xronun oksidan xrom və medi. Təsdiq edilmişdir, ki qənti aldehididir. Reaksiyanın qına reaksiyanın qına xronun miqdəri yüksək olan nümunələrdə daha çox aktivlik göstərir. Belə ki Cr-Cu=6-4 tərkibli nümunə asetaldehidin çıxımı 82.5%, selektivlik isə 97.6% -ə çatır. Rentgenqrafik tədqiqatlar Cr-Cu-O katalizatorlarının asasan oksidlərdən ibarət olduğunu göstərir, bəzi nümunələrdə elə cə arcsə CuCr₂O₄ məşahidə olunur. Cr-Cu-O katalitik sistəmdə məninin miqdəri azaldıqda kristallik dərəcəsi artır. Kristallik dərəcəsi artıraca sırka aldehidinin çıxımı, selektivliyi və etanolun konvensiya artırır.
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 CuCr₂O₄. 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.