CONVERSION OF BIOETHANOL OVER OXIDE CATALYSTS

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ABSTRACT

The conversion of bioethanol over supported oxide catalysts (CuO, ZnO, Cr₂O₃ CeO₂) was studied, among which the most active in the production of hydrogen is 3% CuO/ γ -Al₂O₃. Modification of 3% CuO/ γ -Al₂O₃ catalyst with Cr₂O₃, ZnO and CeO₂ promotes the growth of hydrogen yield. The highest concentration of hydrogen at 300 °C and a space velocity of 1 h⁻¹ on CuO-ZnO/ γ -Al₂O₃ was 48% by volume. The acidity of catalysts for adsorption-desorption of pyridine by infrared spectroscopy (ITI Matson FTIR) was determined. When the content of CuO in the catalyst is increased from 1 to 3%, the amount of Lewis acidic centers (LAS) increases from 58 to 82 μmol/ g_{cat}-Modification with chromium oxide of the copper catalyst increases the number of LAS from 82 to 156 μ mol/ g_{cat} by adsorption of pyridine at 150 °C and from 79 to 120 μ mol/g_{cat} with pyridine adsorption at 250 °C. It has been established that an increase in the number of Lewis acid sites has a positive effect on the yield of hydrogen in the conversion of bioethanol. According to electron microscopy, the modification of catalysts leads to an increase in the dispersity of the catalyst and to a uniform distribution of particles on the surface of the catalyst, which also contributes to its greater activity in the production of hydrogen.

Keywords: bioethanol, catalyst, modification.

Introduction

The steady rise in prices for oil feedstock and reduction of stockpiles around the world leads to an increase in prices of basic petroleum products. Currently under active search for new basic raw materials that can replace oil as a fuel in the production and in the chemical industry [1, 2]. Typically alternatively treated natural gas or coal, but they, like oil, are non-renewable energy sources. The most promising renewable raw materials with virtually unlimited inventory that meets the latest environmental standards for chemical raw materials include bioethanol, from which is obtained a wide range of intermediate and final products of large-scale petrochemical and fine organic synthesis [3, 4].

The use of bioethanol in fuel purposes is largely limited, mainly due to its high hygroscopicity and possible freezing of dissolved water at low temperatures in cold regions [5, 6]. Therefore, the development of bioethanol conversion technology, which provides a perspective replacement of oil in the production of gasoline range hydrocarbons and other valuable petrochemical products, determines the relevance of the study.

Processing of bioethanol to valuable petrochemical products is promising for Kazakhstan, as our country is rich in agriculture from which you can get bioethanol [7]. The development of the technology for the conversion of bioethanol in our Republic is actual today, as Kazakhstan is the ninth state in the world in terms of the area of the territory that has huge land. Therefore, interest in Kazakhstan is manifested not only as an oil power, but as a country with rich land resources, where it is possible to produce renewable energy sources. In addition, there are bioethanol production plants in the Republic of Kazakhstan, such as LLP «BM», the capacity of the enterprise is 30 thousand tons of products per year (Zhambyl region); «Biokhim» (Taiynshinsky district, North-Kazakhstan region) should resume its work in the first half of 2018. At the construction stage two more factories belonging to LLP «BM» in Taraz and Uralsk. As the initial reagent will be used bioethanol produced in our country, which eliminates the shortage of raw materials.

In the development strategy on a global scale several directions of the conversion of bioethanol to high-value products dominate [8-10]: the synthesis of aromatic hydrocarbons, the synthesis of ethylene, the

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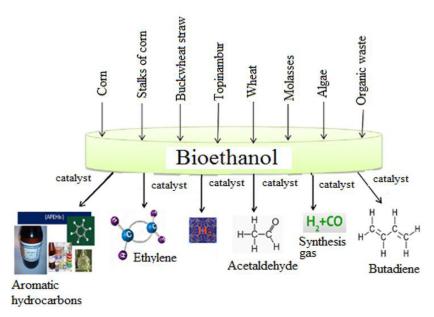


Fig. 1. Raw materials for bioethanol production and its catalytic conversion to valuable products.

production of hydrogen, the synthesis of acetaldehyde, synthesis-gas synthesis and divinyl synthesis by the Lebedev-Ipatiev method (Fig. 1).

Hydrogen takes the first place among the energy carriers by the heat of combustion. Hydrogen is also used as a raw material in organic chemistry, petrochemistry, oil and gas processing. In the chemical industry hydrogen is one of the main intermediates used in the production of ammonia, methanol, synthetic fuels, deep oil processing and the production of high-octane motor fuel. Hydrogen is widely used in low-tonnage, science-intensive industries: electronic, pharmaceutical, food, metallurgy, the synthesis of chemically highly active substances and other industries. Consumption of hydrogen all over the world is steadily growing.

The special properties of hydrogen (the easiest, having the greatest heat of combustion, etc.) open up a tempting prospect of its application for environmentally friendly energy production. The «hydrogen problem» is now attracting a lot of attention of scientists in the field of science all over the world for many reasons: hydrogen as fuel is economically effective. Industrial interest lies in the fact that the technology of hydrogen production from renewable raw materials of bioethanol is ecologically impeccable. In addition H₂ allows to accumulate large energy reserves, pumping hydrogen to the place of incineration and obtaining energy is 10-15 times cheaper than transporting electricity [8]. To celebrate the «hydrogen idea» a large amount of H2 is needed. One of the possible ways of obtaining such an amount of hydrogen is the conversion of renewable bioethanol feedstock.

Hydrogen production by ethanol steam reforming over oxide catalysts, including Cu containing catalysts, is described in [11-13]. Different catalysts, including metal oxides, mixed metal oxides, supported base metals (Ni, Co, Cu), and supported noble metals (Pd, Pt, Rh, Ru, Ir), have all been extensively studied for the SR, POX, and OSR reactions [14].

In this article, we presented the results of the conversion of bioethanol on oxide catalysts.

Experimental

Experiments on testing the efficiency of catalysts during the catalytic conversion of bioethanol were carried out on a flow-through catalytic unit (Fig. 2) with the output of a programmed chromatographic analysis of reaction products at atmospheric pressure in a temperature range of 200-400 °C. The starting materials and reaction products were identified on the «CHROMOS GH-1000» instrument using the absolute calibration method and thermal conductivity detectors. Separation of the components was carried out on two columns (length 2 m, internal diameter 3 mm) filled with NaX zeolite and porapak-T, carrier gases - helium and argon. Physical-chemical characteristics of the catalysts were studied by scanning and transmission electron microscopy and infrared spectroscopy. The catalysts were prepared by the method of capillary impregnation of the carrier by moisture absorption with aqueous solutions of metal salts. After impregnation, the catalyst was kept at room temperature for 12 hours, then dried at 140 °C and calcined at 300 °C.

Results and discussion

Table 1 shows the concentrations of gaseous and liquid products of the ethanol conversion reaction in the presence of 1% oxide catalysts on γ -Al₂O₃. The



Fig. 2. Flow catalytic setup.

investigated catalysts were 1% $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$, 1% $\text{ZnO}/\gamma\text{-Al}_2\text{O}_3$, 1% $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$, 1% $\text{CeO}_2/\gamma\text{-Al}_2\text{O}_3$. The best results for hydrogen were obtained on a 1% $\text{CuO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, where the hydrogen yield was 9%. Further a catalyst containing 3% CuO was studied. As follows from Tables 1 and 2, an increase in the content of CuO in the catalyst from 1 to 3% positively affects the concentration of hydrogen, which increases from 9 to 20%.

To increase the activity of the copper-containing catalyst, the influence of modifying additives (Cr_2O_3 , CeO_2 and ZnO) was studied. Modification of 3% CuO/γ - Al_2O_3 with chromium and zinc oxides significantly increases hydrogen yield from 20 to 46% with the addition of 2% Cr_2O_3 and from 20 to 48% in the case of 2% ZnO. When modified with cerium oxide, the yield of hydrogen decreases from 20 to 4%. Thus, the results

showed that the highest hydrogen concentration - 48 vol.% is observed at 300 °C and a space velocity of 1 $h^{\text{-}1}$ by 3% CuO + 2% ZnO/ γ -Al $_2$ O $_3$. An increase in the yield of hydrogen to 48% is possibly due to the formation of new phases between the copper and zinc oxides, which are active in the production of hydrogen from ethanol. This change would require further, more detailed study.

The catalysts were analyzed by various physical chemical methods: BET, scanning (SEM) and transmission (TEM) electron microscopy, and acidity determination by adsorption-desorption of pyridine*. The texture characteristics of the developed catalysts were studied by the BET method (Table 3).

It is shown that the specific surface area and the specific pore volume of the catalysts vary insignificantly. The surface morphology of the catalysts was studied by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The results are shown in Figs. 3-5.

As can be seen from Fig. 3, in the composition of catalysts there presents dispersed particles of different size and forms. When the copper catalysts are modified with zinc and chromium oxides (Fig. 4), the dispersion of the catalysts increases.

Modification of the $\text{CuO/Al}_2\text{O}_3$ catalyst with chromium oxide leads to an increase in the dispersion of the catalyst. Nanoparticles with sizes of 2-5 nm are observed in the composition of the catalyst (Fig. 5).

The determination of the acidity of the studied catalysts on Bronsted and Lewis was measured by infrared spectroscopy (IRS) using pyridine as the probe molecule.

Table 1Composition of ethanol conversion products on various catalysts

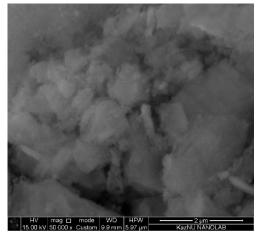
Catalysts (wt.%) on γ-Al ₂ O ₃	Products of ethanol conversion, vol.%							
	H_2	CO	C_2H_4	CH_4	CO_2	Acetaldehyde	Toluene	Xylene
1CuO/Al ₂ O ₃	9	3	6	0.2	0.4	8	1.3	1.1
$1ZnO/Al_2O_3$	3	17	4	0.6	-	1	-	1
$1Cr_2O_3/Al_2O_3$	4	3	34	-	0.4	2	-	1.4
$1CeO_2/Al_2O_3$	0.5	2.7	3.8	-	0.2	5	-	-

Table 2 Effect of modifiers on catalyst activity during bioethanol conversion at $T_p = 300$ °C and GHSV = 1 h⁻¹

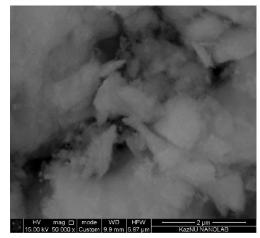
Catalysts (wt.%) on γ-Al ₂ O ₃	X _{ethanol} ,%	Yield of products, %			
		H_2	C_2H_4	Acetaldehyde	Butanol
3CuO	56	20	25	8	-
3CuO+2ZnO	75	48	0.5	15	4
$3CuO+2Cr_2O_3$	78	46	0.3	19	2
3CuO+2CeO ₂	22.5	4	4	12.5	1.8

Table 3Textural characteristics of copper-containing catalysts

Catalysts (wt.%) on γ–Al ₂ O ₃	Specific surface area m ² /g	Specific volume pore, cm ³ /g
3 CuO	174.9	0.075
3 CuO+2 ZnO	172.7	0.074
$3 \text{ CuO} + 2 \text{ Cr}_2 \text{O}_3$	176.5	0.076

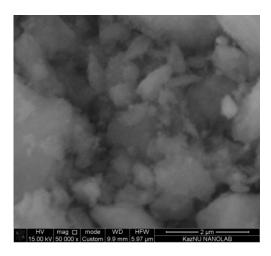


1 wt.% CuO/Al_2O_3

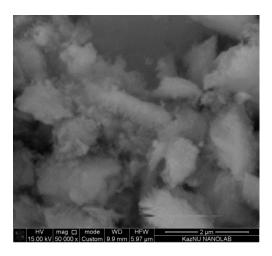


3 wt.% CuO/Al₂O₃

Fig. 3. SEM micrographs of catalysts.



3 wt.% CuO+2 wt.% Cr₂O₃/Al₂O₃



3 wt.% CuO+2 wt.% ZnO/Al₂O₃

Fig. 4. SEM micrographs of catalysts.

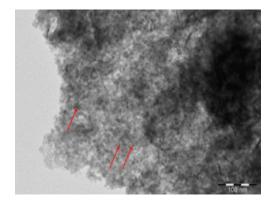
It is shown that copper-containing catalysts contain only Lewis acid sites (LAS). With an increase in the CuO concentration from 1 to 3%, the amount of LAS increases from 58 to 82 μ mol/g_{cat} (Table 4).

Modification with chromium oxide, increases the number of LAS for Cr_2O_3 from 82 to 156 μ mol/ g_{cat} by adsorption of pyridine at 150 °C and from 79 to 120 μ mol/ g_{cat} by adsorption of pyridine at 250 °C. At 350 °C, Lewis acid sites were not detected on all the catalysts studied.

Thus, it has been established that an increase in the number of Lewis acid sites has a positive effect on the yield of hydrogen in the conversion of bioethanol.

Conclusion

The oxide catalysts CuO, ZnO, Cr_2O_3 , and CeO_2 supported on γ -Al $_2O_3$ have been studied during the conversion of bioethanol to hydrogen. The optimal catalyst for the production of hydrogen is 3% CuO/ γ -Al $_2O_3$ (20% H $_2$). Modification of 3% CuO/ γ -Al $_2O_3$ with chromium oxide or zinc oxide helps increase the hydrogen yield to 46-48 vol.% at 300° C and a space velocity of 1 h $^{-1}$. Based on the results of electron microscopy, the presence of nanoparticles with dimensions of 2-5 nm is observed on the investigated catalysts. The modification of catalysts with ZnO or



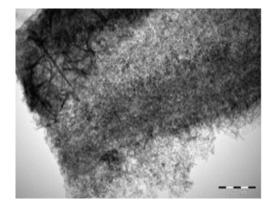


Fig. 5. Micrographs of a TEM-nanophase CuO-Cr₂O₃/Al₂O₃ catalyst.

Table 4 IRS of pyridine

Catalysts (wt.%) on γ-Al ₂ O ₃	150 °C	250 °C	
	Lewis acid sites (µmol/pyridine/g _{cat})		
1 CuO	58	19	
3CuO	82	79	
3CuO+2ZnO	84	74	
$3CuO+2Cr_2O_3$	156	120	

 Cr_2O_3 leads to an increase in the dispersion of the catalyst, which contributes to an increase in the activity of the catalyst in the direction of hydrogen production. The IRS of pyridine showed that coppercontaining catalysts contain only Lewis acid sites (LAS), the number of which increases from 58 to 82 μ mol/g_{cat} with an increase in the CuO concentration from 1 to 3%. Modification with chromium oxide increases the number of LAS from 82 to 156 μ mol/g_{cat} upon adsorption of pyridine at 150 °C and from 79 to 120 μ mol/g_{cat} with the adsorption of pyridine at 250° C. Thus, an increase in the Lewis acid sites of the catalyst has a positive effect on the yield of hydrogen in the conversion of bioethanol.

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*Analyzes for determination of acidity by adsorptiondesorption of pyridine were carried out in the Laboratory of Industrial Chemistry and Reaction Engineering Abo Akademi University, Finland.

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Конверсия биоэтанола на оксидных катализаторах

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АННОТАЦИЯ

Изучена конверсия биоэтанола на нанесенных оксидных катализаторах (CuO, ZnO, Cr $_2$ O $_3$, CeO $_2$) среди которых наиболее активен в получении водорода 3% CuO/ γ -Al $_2$ O $_3$. Модифицирование 3% CuO/ γ -Al $_2$ O $_3$ катализатора Cr $_2$ O $_3$, ZnO и CeO $_2$ способствует росту выхода водорода в продуктах реакции. Наиболее высокая концентрация водорода при T_p -300 °C и объемной скорости 1 ч $^-$ 1 на CuO-ZnO/ γ -Al $_2$ O $_3$ составила 48 об.%. Определена кислотность катализаторов по адсорбции – десорбции пиридина с помощью инфракрасной спектроскопии. При увеличении содержания CuO в катализаторе от 1 до

3% количество Льюисовских кислотных центров (ЛКЦ) увеличивается от 58 до 82 мкмоль/гкт. Модифицирование оксидом хрома медного катализатора повышает число ЛКЦ от 82 до 156 мкмоль/гкт при 150 °C и от 79 до 120 мкмоль/гкт при 250 °C. Установлено, что увеличение числа Льюисовских кислотных центров в составе катализатора оказывает положительное влияние на выход водорода при конверсии биоэтанола. По данным электронной микроскопии модифицирование катализаторов приводит к повышению дисперсности катализатора и к равномерному распределению частиц на поверхности катализатора, что также способствует его большей активности в получении водорода Ключевые слова: биоэтанол, катализатор, модифицирование.

Оксидті катализаторлар негізінде биоэтанолды конверсиялау

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АННОТАЦИЯ

Тасымалдағышқа отырғызылған оксидті катализаторлар қатысында (CuO, ZnO, Cr_2O_3 , CeO_2) биоэтанолдың конверсиясы зерттелді, CuO/у-Al₂O₃ катализаторы сутек алуда белсенділік көрсетті. 3%CuO/ γ -Al₂O₃ катализаторын Cr₂O₃, ZnO және CeO₂ оксидтерімен модифицирлеу өнімдегі сутегі мөлшерін арттыратыны анықталды. Сутегінің өнімдегі ең жоғары концентрациясы (48 көл. %) Т_р-300 °C және көлемдік жылдамдық 1сағ-1 тең болғанда $CuO-ZnO/\gamma-Al_2O_3$ катализаторы қатысында байқалды. Катализатордың қышқылдығы инфрақызыл спектроскопия көмегімен пиридиннің адсорбциясы және десорбциясы арқылы анықталды. Катализатордың құрамындағы СиО мөлшерін 1% дан 3% жоғарлатқанда Льюис қышқылдық орталықтарының мөлшері (ЛҚО) 58 ден 82 мкмоль/ гкт артатыны байқалды. Хром оксидімен модифицирленген мыс құрамды катализаторда ЛҚО-ның мөлшері 150 °С -де 82 ден 156 мкмоль/гкт дейін, ал 250 °С-де 79-дан 120 мкмоль/гкт дейін артатыны анықталды. Катализатор құрамындағы Льюис қышқылдық орталықтарының мөлшерінің артуы

биоэтанол конверсиясы нәтижесінде шығатын сутегінің шығымына оңтайлы әсер етеді. Электрондық микроскоптық зерттеулердің нәтижесінде катализаторларды модифицирлеу оның дисперстілігінің жоғарлауына және катализатор бетінде бөлшектердің біркелкі орналасуына алып келеді, бұл өзгерістер катализатордың сутегі алудағы белсенділігіне оңтайлы әсер етеді.

Түйін сөздер: биоэтанол, катализатор, модифицирлеу