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ANALYSIS OF CARBON DIOXIDE DESORPTION FROM THE SURFACE OF DME SYNTHESIS CATALYST

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АНАЛИЗ ПРОДУКТОВ ДЕСОРБЦИИ ДИОКСИДА УГЛЕРОДАС ПОВЕРХНОСТИ КАТАЛИЗАТОРОВ ПОЛУЧЕНИЯ ДМЭ

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В статье представлено изучение продуктов десорбции диоксида углерода с поверхности катализаторов получения диметилового эфира из смеси CO и H_2 методом температурно-программированной десорбции с масс-спектрометрическим анализом. Показано, что температурная область десорбции CO_2 с поверхности промышленного и синтезированного образцов одинакового состава $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$ находится в области 100-600 °C с $T_{мах}$=331 °C и $T_{мах}$=352 °C соответственно. Предположительно, низкая каталитическая активность синтезированного $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$,используемого в качестве катализатора дегидратации метанола до диметилового эфира в совмещенном процессе получения диметилового эфира из CO и H_2 связана с недостаточной температурой катализа, так как CO_2 десорбирует в более высокой температурной области.

Zeolites are crystalline aluminosilicates containing cations of elements of I and II groups of periodic system. They belong to a group of skeletal aluminosilicates,representing complex compounds from the chemical and structural points of view. It is noteworthy that natural zeolites are not widely used as catalysts, while a number of synthetic analogues have been used successfully in practice. Synthetic zeolites have unique desorption, ion exchange, and molecular sieve properties that can effectively be used them in purification processes, production of detergents, NO_x removal, manufacturing of synthetic fuel. Also, they are widely used as catalysts in various petrochemical processes such as cracking of petroleum fractions, isomerization, disproportionation and alkylation of aromatic hydrocarbons, conversion of alcohols to hydrocarbons, etc.[1-3]. The catalytic activity of zeolites is caused by both molecular sieve and acidic properties of the surface [2, 4]. For example, zeolites can be used as catalysts for the dehydration process toproduceDME, which is a useful chemical intermediate tomanufacture various important chemicals such as dimethyl sulfate, methyl acetate, light olefins, and is also used in propellant aerosols. It was also suggested that DME can be used as a clean alternativeadditive to fuel for diesel engines [4].

In the article [5] thesynthetic zeolite HZSM-5 (IPC SB RAS, Tomsk) was used as a catalyst for methanol dehydration to DME. Thecommercial catalyst Katalco-58 (Johnson Matthey Catalysts)with the composition of 13%CuO/27% ZnO/60% Al_2O_3, % wt (hereafter denoted as R-1)was used as a catalyst for methanol synthesis. Earlier in work [6] it was shown that there is an opportunity to obtain DME for the case of layering charge.

In this paper the process to obtain DME from CO and $H_2$was studied over the synthesized $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$ (IC SB RAS, Novosibirsk)catalyst for methanol synthesis, which was prepared by co-precipitation of solutions of copper, zinc and aluminum nitrates and sodium carbonate solution at a constant pH and temperature in continuous process.

In work [5] it was shown that in case of layered charge of R-1 catalyst and the HZSM-5 (30)synthetic zeolite the DME output of 39 %vol. was achieved in the combined process to produce DME from a mixture of CO and H_2. When the synthesized catalyst for methanol synthesis ($Cu_{0,2}/Zn_{0,7}/Al_{0,1}$) and HZSM-5 (30) were tested under the same conditions (T = 220 ^{0}C, P = 3 MPa, H_2/CO = 2) the DME output was insignificant (3 %vol.)with30% CO conversion.

Since a significant role in the transformation of CO and H_2 to methanol and methanol to DME is played by the acid-base state of the catalyst surface, the method of temperature-programmed desorption combined with mass spectrometry (TPD-MS) was used to study the basic properties of the synthesized $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$catalystas well as the R-1 and HZSM-5 (30) catalysts using chemisorption analyzer Chemisorb 2750 equipped with a gas mass spectrometer UGA 300 for the qualitative analysis of the reaction products (CO_2).

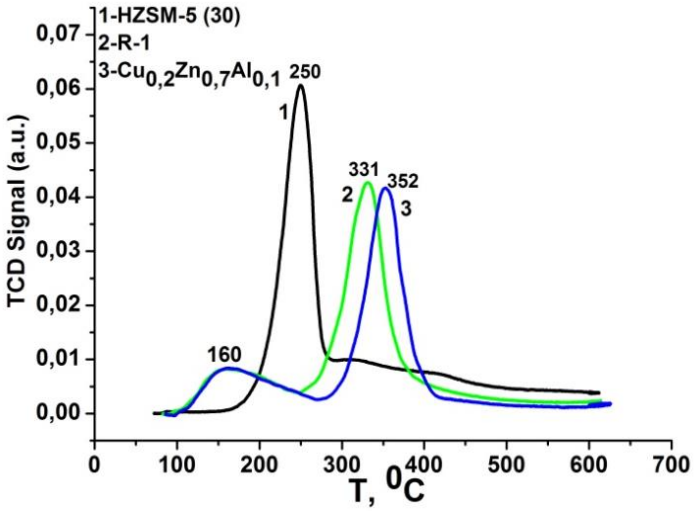

Fig. 1. CO_2-TPD profiles from catalysts after CO_2 adsorbtion at 100 °C for 30 minutes.

Figure 1 shows that the surface of all the samples of desorbed carbon dioxide in several forms. According to [4, 5] there are both acidic and basic sites on the surface of HZSM-5 (30) zeolite catalyst. Desorption of carbon dioxide from HZSM-5 (30) zeolite takes place in the temperature range of 110–600 °C with T_{max}=250 °C, which corresponds to the temperature range of catalytic experiments. The largest part around 280 °C is present and there are two shoulders with T=310 °C and T=412 °C. This suggests strong CO_2 adsorption and its desorption at least in two forms.

On the surface of the copper-zinc catalysts, having basic propertiesby nature, CO_2 desorbed throughout the temperature range of 100–600 °C. For both samples the characteristic peak is appeared at 110–250 °C, which is associated with the release of physically adsorbed carbon dioxide. However, the maximal temperature of the release for R-1 is 331 °C, and for $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$ is 352 °C. It can be assumed that the surface of the synthesized $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$catalyst with maximal allocation of desorbed carbon dioxide is shifted to a higher temperature region. This partly explains the low catalytic activity sincethe working temperature was 220 °C in catalysis. Release of carbon dioxide in molecular form is confirmed by mass spectra presented in figure 2. Release of small amounts of CO are also characteristic forCO_2desorption. The appearance of water (Fig. 2) is most likely connected with the presence of physically adsorbed water on the surface of the HZSM-5 (30) sample. Water is determined in mass spectrum in the temperature range of 100-600°C for the case of copper-zinc catalysts. Mass spectra are almost identical. The blurring of the spectrum, which is characteristic for both samples, is probably

connected withthe desorption of physically adsorbed and weakly coupled water.

Thus, it can be assumed that the increase in the yield of DME in the combined process to obtain DME from a mixture of CO and H_2 in a single reactor with a layered loading of the synthesized catalyst for methanol synthesis ($Cu_{0,2}/Zn_{0,7}/Al_{0,1}$) and HZSM-5 (30) zeolite catalyst is necessary to increase the temperature of the catalysis.

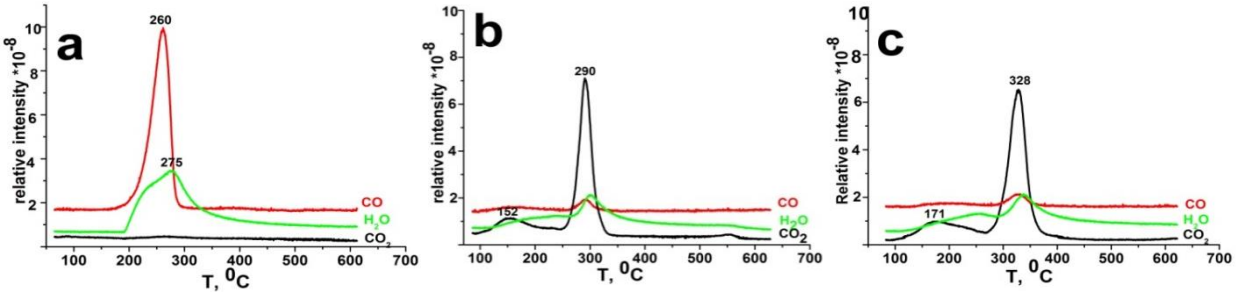

Fig. 2. Mass spectra of the products of CO_2 desorption from the surface of a) HZSM-5 (30); b) R-1; c) $Cu_{0,2}/Zn_{0,7}/Al_{0,1}$.

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