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CONVERSION OF METHANOL TO C_2-C_3 ALKENES ON MODIFIED HIGH-SILICA ZSM-5-TYPE ZEOLITES

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Abstract

To increase the selectivity for C_2-C_3 alkenes, catalysts based on ZSM-5 zeolite, modified with zinc, cobalt, gadolinium, and zirconium, were obtained using the impregnation method. The conversion of methanol to hydrocarbons was carried out in a flow reactor with a fixed catalyst bed in the temperature range of 300-350°C, under atmospheric pressure, in a nitrogen flow.

It has been shown that H-ZSM-5 has low selectivity for C_2-C_3 alkenes (24.0%).

The modified H-ZSM-5 with zinc, gadolinium, and zirconium improves selectivity for C_2-C_3 alkenes (52.6% - 63.6%) and reduces selectivity for C_1-C_5 alkenes (from 39.1% to 17.2% - 25.7%).

The highest selectivity for C_3 alkenes (65.5% - 68.7%) and propylene (38.4% - 42.2%) is achieved with the two-component modification of the zeolite on Gd-Zr-H-ZSM-5 and Zn-Zr-H-ZSM-5 samples.

Keywords: methanol, conversion, selectivity, C_2-C_3 alkenes, modification, zinc, gadolinium, zirconium.

Introduction

Lower alkenes C_2-C_3 are valuable raw materials for the petrochemical industry, primarily obtained in pyrolysis and catalytic cracking processes (1). In recent years, particular attention has been paid to methods for obtaining alkene hydrocarbons from alternative raw materials in the presence of zeolite catalysts [2],[4] .One type of alternative raw material is methanol, which is produced in industry from methane through syngas.

The process of converting syngas into lower alkenes through methanol was developed by Mobil Oil Corporation, UOP, and Norsk Hydro in the presence of molecular sieve-based catalysts of the SAPO-34 type at 450-500°C [6].

However, these catalysts do not achieve a high yield of propylene [7]. A more promising candidate for the conversion of methanol to C_2-C_3 alkenes is the ZSM-5 zeolite-based catalyst, which possesses nanoscale interconnected straight (0.51 × 0.53 nm) and sinusoidal channels (0.53 × 0.55 nm). Studies (9-19) have shown that the selectivity for C_2-C_3 alkenes can be improved by modifying the ZSM-5 zeolite with phosphorus compounds and transition metals [8] [9].

The aim of this study is to investigate the effect of two-component modification of high-silica ZSM-5-type zeolite with zinc, gadolinium, and zirconium on its selectivity in the conversion of methanol to C_2-C_3 alkenes.

Experimental part

For the preparation of catalysts, ZSM-5 zeolite produced by JSC "Nijnegorodskie sorbenti" was used, with a molar ratio of $SiO_2/Al_2O_3 = 33$.

To obtain the H-form, the initial Na-ZSM-5 zeolite was subjected to ion exchange with a 1 M NH_4NO_3 solution at 80°C for 2 hours. The ion exchange was carried out three times using a fresh salt solution each time. After ion exchange, the zeolite was thoroughly washed with distilled water to the absence of NO_3^- ions [10].

Then, the sample was dried for 24 hours at room temperature, followed by drying in a thermostat at 110°C for 6 hours. Subsequently, calcination was carried out in a muffle furnace at 250°C and 500°C for 4 hours each[1].

The obtained H-form of the ZSM-5 zeolite was modified using aqueous solutions of zinc acetate, lanthanum nitrate, and zirconium oxychloride [5].

The H-form of the zeolite was treated with the corresponding salt solutions under stirring and heating up to 95°C. The modified zeolites were then mixed with an alumina oxide suspension, calculated to contain 25 wt% dry Al_2O_3. The resulting extrudates were shaped, air-dried, granulated, and calcined at 500°C for 4 hours. The metal content in the catalysts was 0.5 wt%[3].

Experiments were conducted in a flow setup with a quartz reactor (length 18 cm, inner diameter 1.0 cm) with a stationary catalyst bed of 3.0 cm in length, in the temperature range of 250-450°C, with a methanol feed volumetric flow rate of 2.0-3.6 h^{-1} in the presence of nitrogen. The reaction products were analyzed using an Agilent GC782A gas chromatograph.

Results and Discussion

In the temperature range of 300-400°C, methanol, in the presence of unmodified ZSM zeolite, is converted into a mixture of hydrocarbons with compositions ranging from C_1 to C_{12}. The conversion of methanol on zeolite catalysts follows the scheme [].

$$2CH_3OH \xrightarrow{-H_2O} [CH_3OCH_3] \xrightarrow{-H_2O} alkenes\ C_2 - C_4 \begin{cases} \rightarrow & alkenes\ C_{5+} \\ \rightarrow & isoalkenes \\ \rightarrow & aromatic\ hydrocarbons \end{cases}$$

As seen in Figure 1, at a low methanol conversion of 10-20%, the main product of methanol conversion is ethylene. The ethylene content in the reaction products ranges from 61.5% to 68.8%. Increasing the reaction temperature above 300°C leads to a significant decrease in ethylene content. As the methanol conversion increases to 99.8%, the ethylene content decreases by a factor of 4.5, reaching 18.7%. At a methanol conversion of 20%, the propylene content is only 9.9%, and no butylenes are formed. Increasing the methanol conversion to 70% results in an increase in propylene content to 21.2%. Further increases in methanol conversion do not contribute to a higher propylene content.

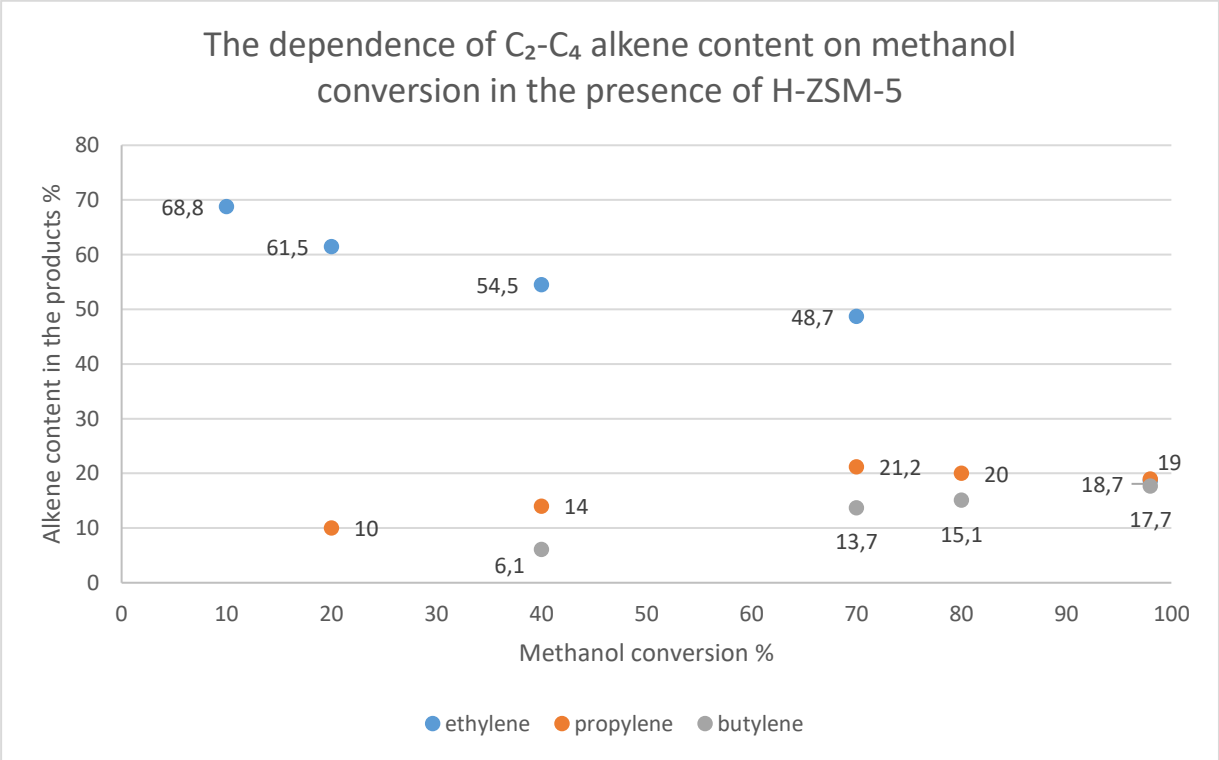

Figure 1. The dependence of C₂-C₄ alkene content on methanol conversion in the presence of H-ZSM-5

Butylenes are formed in the reaction products at a methanol conversion of 40%. The butylene content is 6.1%. Further increases in methanol conversion lead to an increase in butylene content. When the methanol conversion reaches 98%, the butylene content increases to 17.7%

Table 1.

The influence of the metal nature in H-ZSM-5 on its catalytic properties in methanol conversion to hydrocarbons.

Sample	Methanol Conversion	Gas yield %	Liquid product yield %	Composition of reaction products, wt%				
				C2H4	C3H6	C4H8	C1-C5 alkanes	C5+
H-ZSM-5	80.2	55.8	44.2	15.2	8.8	4.2	34.1	32.7
Zn-H-ZSM-5	85.3	75.2	24.8	23.2	29.4	5.6	25.7	16.1
Co-H-ZSM-5	83.2	58.2	41.8	18.8	15.2	4.5	45.7	15.8
Gd-H-ZSM-5	87.1	68.9	31.1	21.7	31.4	3.9	20.8	22.2
Zr-H-ZSM-5	87.2	80.1	19.9	30.2	33.4	3.3	17.2	15.9

As seen in Table 1, the H-ZSM-5 zeolite has low selectivity for alkenes, with alkanes predominating in the hydrocarbon fraction. The content of ethylene and propylene in the reaction products is 15.2% and 8.8% by weight, respectively. Modifying the H-ZSM-5 zeolite with metals alters the catalytic properties of the catalysts. Metal modification primarily affects the selectivity for C_1-C_5 alkanes and C_2-C_3 alkenes. Zinc modification increases the content of ethylene (up to 23.2%) and propylene (29.4%). Compared to ethylene, the propylene content increases by 3.3 times. At the same time, the content of C_1-C_5 alkanes decreases to 25.7%, and C_5+ hydrocarbons decrease to 16.1%. Cobalt modification has little effect on methanol conversion, and the content of ethylene increases by only 3.6%. However, there is a significant increase in the content of alkanes (up to 45.7%). Modification of the zeolite with gadolinium leads to a significant increase in propylene content (up to 31.4%) and a decrease in C_1-C_5 alkane content (down to 20.8%). The catalyst modified with zirconium shows high selectivity towards ethylene and propylene, with the content of ethylene and propylene

increasing to 30.2% and 33.4%, respectively. Furthermore, there is a significant decrease in the selectivity for C_1-C_5 alkanes.

Table 2.

The influence of bimetallic modification of H-ZSM-5 on the properties of catalysts in methanol conversion to hydrocarbons.

Sample	Methanol Conversion	Gas yield %	Liquid product yield %	Composition of reaction products, wt%				
				C2H4	C3H6	C4H8	C1-C5 alkanes	C5+
Zn-Gd-ZSM-5	96	68.6	31.4	23.6	31.2	5.7	21.2	18.3
Gd-Zr-ZSM-5	96.4	73.2	26.8	26.5	42.2	5.2	14.2	11.5
Zn-Zr-ZSM-5	95.7	72.1	27.9	27.1	38.4	6.8	11.4	16.7

Thus, the catalysts modified with zinc, gadolinium, and zirconium exhibit higher selectivity for ethylene and propylene compared to the catalyst modified with cobalt.

The effect of two-component modified H-ZSM-5 zeolites on the selectivity of methanol conversion products is shown in Table 2.

It is evident that in all cases, the selectivity for propylene increases. The highest selectivity for propylene is observed in the Gd-Zr-H-ZSM-5 sample, reaching 42.2%. This catalyst also exhibits high selectivity for the sum of ethylene and propylene (68.7%).

Conclusion

The conversion of methanol into C_2-C_3 alkenes on the H-form of ZSM-5 zeolite proceeds with insufficient activity and low selectivity for olefins. Modification of H-ZSM-5 zeolite with zinc, zirconium, and gadolinium leads to an increase in selectivity for C_2-C_3 alkenes. The highest selectivity for C_2-C_3 alkenes (65.5% - 68.7%) is achieved as a result of two-component modification of H-ZSM-5 zeolite with gadolinium and zirconium compounds.

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