Effect of Ce$_2$O$_3$, La$_2$O$_3$ and ZnO additives on the oxygenates conversion into liquid hydrocarbons

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Abstract. A selective modifying effect of cerium, magnesium and zinc oxide additives on the activity and the selectivity of a pentasil group zeolite catalyst in the reaction of conversion of oxygenates (methanol and dimethyl ether) to liquid hydrocarbons was found. It was found that zinc oxide contributes to the stable operation of the zeolite catalyst in the conversion of oxygenates in the synthesis gas stream and leads to the production of gasolines with low durene content (not more than 6.1 wt %). The obtained results demonstrate the rationale for producing hydrocarbons from synthesis gas without the stage of oxygenate separation with their subsequent conversion to synthetic gasoline.

1. Introduction

In recent years, serious attention is paid to the problems of environmental compatibility of the consumed fuel. This is primarily reflected in tightening the requirements for the quality of motor fuels and, in particular, limiting the content of aromatic hydrocarbons. Therefore, the search for new sources and technologies for production of high-octane gasolines with a low content of aromatic hydrocarbons is an important task.

Along with construction of production facilities based on the Fischer–Tropsch synthesis technology, the process for production of gasoline fractions from methanol (so-called MTG-process) is implemented in the production of the high-octane gasoline base component. The fuel produced from methyl alcohol has a research octane number of 94–96 and meets all the requirements for regular gasoline. Besides, it is fully compatible with refinery gasoline. One of the drawbacks of such gasoline is a high (up to 10–12%, hereinafter percentages are by weight, unless otherwise indicated) content of 1,2,4,5-tetramethylbenzene (durene) having a melting point of about 80 $^\circ$C and having a negative effect on the low-temperature and environmental properties of gasoline.

Currently, several research groups carry out intensive work on improving the technology of production of gasoline fractions from synthesis gas (SG). In contrast to the classical MTG-process, all stages of production of oxygenates and gasoline fractions are integrated into one circuit [1].

Earlier, in [2], a technological scheme, according to which SG produced from pine shavings and oak sawdust with a total content of H$_2$ and CO of 91.0 and 91.2 vol %, respectively, and
Table 1. Raw material composition.

| Component composition | Raw material 1 | Raw material 2* |
|-----------------------|---------------|-----------------|
|                       | ml/h**        | g/h             |
| Methanol              | 30.0          | 23.8            |
| Water                 | 3.3           | 3.3             |
| Dimethyl ether        | 16.7          | 11.2            |
| Total oxygenates + H₂O| 50.0          | 38.3            |

* In addition, synthesis gas of the following composition (vol %: H₂—52.0; CO—21.0; CO₂—10.0; N₂—17.0) was fed with a volume flow rate of 2000 h⁻¹.

** Based on liquid.

As catalysts for the second stage of the process, a pentasil group zeolite catalyst and zeolite samples modified with various oxide additives (cerium, magnesium and zinc oxides) were used. The goal of this study was to test the effectiveness of these two options for oxygenate processing and to choose the optimal oxide modifier for the catalyst and process conditions, which would allow to produce hydrocarbons with low content of durene having a negative effect on the low-temperature and environmental properties of gasoline from oxygenates.

2. Experimental part

Catalytic studies and analysis of the synthesis reaction products were carried out with the use of the methods and equipment described in detail in [2]. As a result of the synthesis, from oxygenates, several products, including gaseous and liquid hydrocarbons and reaction water, are formed. The assessment of the oxygenate conversion product yield was carried out directly, by measuring the weight of the liquid hydrocarbon catalyze, and indirectly, by calculating the molecular weight of the product gas (based on the chemical composition of the gas determined on the basis of the chromatogram data) and gas meter readings. Table 1 shows the composition of the used raw mixtures.

It is known that one of the possible ways of changing the catalytic properties of zeolites is directed modification of their acidic properties by removal of the strongest acidic sites and changing their nature. In this regard, the promising way is chemical modification of zeolite with compounds of boron, phosphorus, magnesium, silicon, and rare earth elements, which have an effect not only on the zeolite catalyst activity, but also on the selectivity in the conversion of various hydrocarbons, including oxygen-containing compounds [3–7]. As starting sample (sample 1), the zeolite catalyst of the following composition was used: 70.8%—highly siliceous pentasil group zeolite with silica modulus 50 mass portions of SiO₂ to 1 mass portion of Al₂O₃; 29.2%—Al₂O₃ binder. By the method of incipient wetness impregnation of the original zeolite catalyst, three samples of catalysts modified with various oxides, the composition of which is shown in table 2, were prepared from metal nitrate solutions. After impregnation, the samples were dried at a temperature of 90 °C and then calcined in air at a temperature of 500 °C.
Table 2. Catalyst composition.

| Sample number | 1   | 2   | 3   | 4   |
|---------------|-----|-----|-----|-----|
| Content of modifying additives | 0.65% of Ce₂O₃ | 2% of La₂O₃ | 2% of ZnO | none |
|                | 0.55% of La₂O₃ | 2% of ZnO | | 1.8% of ZnO |

Table 3. Results of the conversion of raw material 1 on catalyst samples 1–4 (%).

| Catalyst sample number | T, °C | Component composition of the obtained gasoline fractions | Conversion of methanol | Conversion of DME | Selectivity to liquid hydrocarbons |
|------------------------|-------|----------------------------------------------------------|------------------------|-------------------|----------------------------------|
|                         |       | Aliphatic hydrocarbons | Aromatic hydrocarbons |                   |                                  |
|                         |       | C₆ | C₇ | C₈ | C₉+ | durene |                   |                                  |
| 1                       | 310   | 63.2 | 0.2 | 2.6 | 12.4 | 21.6 | 11.1 | 80.4 | 82.2 | 86.4 |
|                         | 330   | 61.8 | 0.2 | 2.8 | 13.8 | 21.4 | 10.7 | 86.9 | 88.8 | 85.7 |
| 2                       | 310   | 61.6 | 0.1 | 2.9 | 13.7 | 21.7 | 14.0 | 97.7 | 58.6 | 80.4 |
|                         | 330   | 60.4 | 0.2 | 3.0 | 15.2 | 21.2 | 12.9 | 99.9 | 63.7 | 79.7 |
| 3                       | 310   | 53.6 | 0.2 | 3.3 | 16.2 | 26.7 | 8.6  | 83.5 | 83.7 | 89.2 |
|                         | 330   | 51.8 | 0.2 | 3.8 | 17.3 | 26.9 | 8.1  | 89.9 | 89.3 | 86.5 |
| 4                       | 310   | 51.7 | 0.2 | 5.7 | 21.2 | 21.2 | 6.4  | 81.2 | 84.1 | 90.2 |
|                         | 330   | 50.8 | 0.3 | 6.0 | 22.1 | 20.8 | 6.1  | 87.6 | 89.7 | 89.8 |

3. Results and discussion

Table 3 shows the results of the conversion of raw material 1 at a pressure of 1.0 MPa, volume flow rate of the oxygenate raw mixture of 1 h⁻¹ and two temperatures (310 and 330 °C).

Comparison of the catalytic properties of the original and modified zeolite catalyst samples showed that the modification of original sample 1 with various oxide additives did not always lead to improvement of the process performance. For example, sample 2 modified with a mixture of oxides Ce₂O₃, La₂O₃ and ZnO provided almost 100% conversion of methanol to hydrocarbons. At the same time, the conversion of dimethyl ether (DME) on it (58.0–64.0%) was very low, even lower than on the original sample. In addition, for this sample, in comparison with the other samples, the highest concentration of durene in the liquid reaction products (synthetic gasoline) (12.9 and 14.0% at 330 and 310 °C, respectively) is observed.

The best results were obtained for sample 4 containing only ZnO as a modifying additive. The conversion of methanol and DME on this sample was 81.0–88.6 and 84.0–91.0%, respectively, and the concentration of durene in the liquid products was the lowest (6.1–6.4%). It should be noted that an increase in the oxygenate conversion and selectivity of the formation of
Table 4. Results of the conversion of raw material 2 on catalyst samples 1–4 (%).

| Catalyst sample number | T, °C | Component composition of the obtained gasoline fractions | Conversion of methanol | Conversion of DME | Selectivity to liquid hydrocarbons |
|------------------------|-------|---------------------------------------------------------|------------------------|------------------|----------------------------------|
|                        |       | Aliphatic hydrocarbons | Aromatic hydrocarbons |                   | C6 | C7 | C8 | C9+ | durene |                   |
| 1                      | 310   | 65.6 | 0.2 | 3.9 | 12.5 | 17.8 | 9.7 | 80.6 | 86.9 | 84.4 |
|                        | 330   | 67.3 | 0.3 | 3.8 | 13.9 | 14.7 | 9.1 | 82.2 | 89.0 | 82.7 |
| 2                      | 310   | 61.7 | 0.3 | 4.1 | 13.9 | 20.0 | 13.2 | 82.4 | 57.2 | 79.4 |
|                        | 330   | 58.1 | 0.4 | 3.9 | 15.3 | 22.3 | 12.6 | 88.9 | 64.0 | 77.7 |
| 3                      | 310   | 58.4 | 0.3 | 3.5 | 17.2 | 20.6 | 7.8 | 83.7 | 83.4 | 87.2 |
|                        | 330   | 56.4 | 0.4 | 4.1 | 17.8 | 21.3 | 7.6 | 89.3 | 89.8 | 85.5 |
| 4                      | 310   | 56.7 | 0.4 | 5.6 | 18.5 | 18.8 | 5.6 | 84.3 | 81.5 | 89.2 |
|                        | 330   | 54.3 | 0.3 | 6.3 | 18.9 | 20.2 | 5.2 | 88.6 | 90.7 | 87.5 |

Aromatic hydrocarbons is observed for all catalyst samples with an increase in temperature. In addition, experiments on the conversion of the DME–methanol–water mixture with the addition of synthesis gas were carried out (see raw material 2 composition in table 1). The test results are shown in table 4.

Table 4 shows that the behavior of the catalyst samples in the SG flow is similar to that observed in experiments without the addition of synthesis gas (table 3). Sample 2 containing a mixture of Ce₂O₃, La₂O₃ and ZnO oxides was the most active in the conversion of methanol and showed the lowest conversion of DME and the highest concentration of durene in liquid products. The best results were obtained for sample 4 containing only ZnO as a modifying additive. It showed the highest degree of conversion of oxygenates, and the concentration of durene in liquid products was minimal (5.1–5.6%). It should be noted that lower levels of durene were observed for the oxygenate conversion reaction carried out in the stream of synthesis gas for all catalyst samples (see tables 3 and 4).

In addition, long-term (100 h of continuous operation) comparative tests were carried out for the sample, which gave the best results (according to preliminary experiments), sample 4, in the conversion of both a simple mixture of oxygenates (DME–methanol–water) and a mixture with addition of synthesis gas (figure 1).

During testing sample 4 in a mixture of oxygenates, the catalyst stability was not high enough. At the beginning of testing (first 8 h of operation), the conversion of methanol and DME was 88.6 and 90.7%, respectively, and the durene content was 6.4–6.5%. After 50 h of continuous operation, there was a significant decrease in the catalyst activity. By the end of the test, after 100 h of continuous operation, the conversion of methanol and DME decreased to 80.8 and 79.7%, respectively, while the selectivity of liquid product formation, distribution of aliphatic and aromatic hydrocarbons, and durene content in synthetic gasoline remained virtually unchanged.
During testing sample 4 in the synthesis gas stream, the catalyst demonstrated stable operation (for 100 h). The conversion of methanol and DME was 88.2 and 91.0%, respectively. There was some redistribution of the component composition of liquid products. After 10 h of continuous operation of the catalyst in the composition of liquid products (synthetic gasoline), the level of non-aromatic hydrocarbons began to increase. At the beginning of testing, the content of aliphatic and aromatic hydrocarbons in the liquid product was 54.3 and 45.7%, respectively. By the end of testing, the content of aromatic hydrocarbons decreased to 38.3%. In addition, the content of durene also decreased, from 5.2 to 4.5%. Such behavior of the catalyst can be due to promoting effects of carbon oxides [8], which appeared only during long-term interaction between synthesis gas and the zeolite catalyst.

4. Conclusions
The obtained results demonstrate the rationale for producing synthetic gasolines from synthesis gas without an intermediate stage of separation of oxygenates with their subsequent conversion to gasoline hydrocarbons. This will allow integrating the stages of production of oxygenates and gasoline hydrocarbons into one circuit and obtaining synthetic gasoline with low durene content.

Acknowledgments
The work was financially supported by the Ministry of Education and Science of the Russian Federation (project No. 14.607.21.0134, unique identifier RFMEFI60715X0134).

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