Prediction of the catalytic activity of Ni-Al mixed oxide in the hydroisomerization of n-alkanes

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Abstract. This article discusses the possibility of using mixed Ni-Al oxides as catalyst systems for the hydroisomerization of n-alkanes. A number of instrumental analysis methods were carried out, on the basis of which elementary lattices of the synthesized mixed oxides were modeled. A preliminary study showed that systems based on mixed Ni-Al oxides have acidic, basic properties. Their structure makes it possible to speak of the presence of molecular sieve properties, which will make it possible to obtain mono- and dimethyl substituted isoalkanes, which will lower the pour point of diesel fuel and at the same time produce high-acetane products. According to preliminary data, the best result is shown by a sample of mixed Ni-Al oxide with a ratio of Ni²⁺/Al³⁺ cations equal to two in the synthesis.

1. Introduction

Alkanes of normal structure negatively affect the products of oil refining, as they have high pour points, which leads to a decrease in the operational properties of diesel fuels. However, n-alkanes have relatively high cetane numbers [1], which leads to a search for a compromise between the achievements of high cetane numbers and low pour points, ultimate filterability temperature and cloud point. The solution was to obtain monomethyl substituted and dimethyl substituted iso-alkanes from the alkanes in the diesel fraction, which have acceptable parameters compared to n-alkanes and highly branched iso-alkanes. This can be seen from table 1, where an example is the n-dodecane series [2]. Of particular interest are T-shaped isomeric structures [1].

| Hydrocarbon                  | Formula       | Pourpoint, °C | Cetanenumber |
|-----------------------------|---------------|---------------|--------------|
| n-dodecan                   |               | -12           | 72           |
| 3-ethyldecane               | C₁₂H₂₆        | -70           | 47           |
| 4,5-diethyloktan            |               | -70           | 20           |
| 2,2,4,6,6-pentamethylheptane|               | -70           | 9            |

Table 1. Cetane numbers of hydrocarbons.
Thus, hydroisomerization of n-alkanes into mono- and dimethyl substituted iso-alkanes allows one to obtain products that meet the requirements for winter and Arctic brands of diesel fuels [3]. The demand for such fuels according to Infineum Worldwide Winter Diesel Fuel Quality Survey 2018 [4] has increased, which is associated primarily with the diesel disengagement and development of the northern regions of the world.

Of the currently proposed catalytic systems, the most effective in the hydroisomerization reactions of C\textsubscript{7+} paraffins are bifunctional catalysts based on zeolite materials of a specific structure: SAPO-11, MeAPO-11, SAPO-31, SAPO-41, ZSM-22, ZSM-23, ZSM-48. The pore mouth size of conventional zeolites (ZSM-5, Eu-1, MCM-22) is such that only paraffins of normal structure can be selectively penetrated into the zeolite micropores, blocking access to larger molecules [5], which prevents further isomerization of the necessary mono- and dimethyl substituted isoalkanes. However, the size of the 10-R channels of the zeolite is such that the diffusion of bulk isomers from large zeolite cavities is very difficult. The consequence of this is the intensive hydrocracking reactions of highly branched isomers with the formation of low molecular weight products [6, 7]. The selectivity of zeolite-based catalysts in hydroisomerization reactions varies slightly with increasing chain length of the paraffin used as feed. Moreover, the use of paraffins with a longer chain length as a raw material leads to an increase in the number of highly branched isomers formed [8, 9]. Thus, it can be said that zeolite-based catalysts have serious drawbacks, and the development of catalytic systems with high conversion and selectivity in hydroisomerization reactions is still a relevant trend in the field of catalysis [10].

Recently, catalytic systems based on oxides of mixed phase composition have been of increasing interest. This is primarily due to the simplicity of the preparation, a wide range of cations, which makes it possible to control the catalytic activity [11], and the presence of a “memory effect” allows one to obtain catalytic systems with a controlled highly developed surface [12].

It was described in [13] that NiAl mixed oxide obtained by calcined layered double hydroxides showed a relatively higher catalytic activity than the same mixed oxide obtained by physical mixing or by impregnation. The results showed that NiAl-MO has a semi-metallic characteristic. Electron transfer from the Al and O atom to the Ni atom was observed, which is useful for electron transfer from the surface and improves catalytic activity. In our previous studies, which the article [14] is devoted to, the catalytic activity of NiAl-MO in the process of catalytic cracking of a mixture consisting of C\textsubscript{11}-C\textsubscript{22} n-alkanes was revealed. The results of the study showed a high yield of isomer alkanes in both gases and liquid products, which confirmed that the main centers of the catalytic system have isomerizing properties. As for the surface itself, in papers [15] the influence of the content of metallic Ni and NiO on the surface of the formed spinel after calcination of its precursor layered double hydroxide at temperatures below 500°C was studied. Thus, a high nickel content leads to an increase in surface area to 220 m\textsuperscript{2}/g, and also such a catalytic system under hydrogenation conditions was more resistant to deactivation caused by coking than systems with a lower Ni content. In the works of Siberian scientists [16], it was proved that the calculated lattice parameter a of NiO (4.162 Å) obtained during the calcination of structures (LDH) is less than that for pure NiO (4.177 Å).

In this work, several goals were set:

- determination of the possibility of using mixed oxides as catalytic systems for the process of isomerization of n-alkanes;
- identification of the relationship between the ratio of Ni\textsuperscript{2+} and Al\textsuperscript{3+} cations in the synthesis of complex oxides and their molecular sieve and catalytic properties.
2. Methodology

2.1. Materials and synthesis

The synthesis of the initial layered double hydroxides containing cations of bivalent and trivalent metals of various nature was carried out by the coprecipitation method described in detail in [17]. For this purpose, mixtures of aqueous solutions of nickel and aluminum nitrates with a molar ratio of $M^{2+}/M^{3+} = 2:4$ were prepared. The resulting solutions were added dropwise to 100 ml of distilled water. During the synthesis, a constant $pH = 10$ was maintained by adding a NaOH solution (3 M). The synthesis temperature was $25^\circ C$. To control the pH, an electrode with an integrated temperature sensor (Mettler Toledo) was used. After adding the entire salt solution, the suspension was stirred for 48 hours at the synthesis temperature. This hydroxide was washed with distilled water until a neutral pH of the wash water was obtained, filtered and dried for 4 hours at 110°C. The hydrotalcites synthesized in this way contained carbonate anions between brucite-like layers, which subsequently facilitated the transition to the oxide phase [11]. The oxide phase was formed by calcining Ni-Al hydrotalcites at 450°C in a furnace for 4 hours.

2.2. Analysis

The phase composition of the studied samples was carried out on a Bruker Axs powder X-ray diffractometer with Bragg-Brentano geometry in the range of angles $2\theta$ from 5 - 70°. Screening step 0.02°, exposure time 1 s/step. The phase composition was determined using the DIFFRAC.EVA software module and the PDF-2 Release 2013 diffraction database. The specific surface was determined by thermal desorption of nitrogen on a Quantachrome NOVA® 1200; the specific surface was calculated using the BET method. Micrographs of the test materials were obtained with a Hitachi TM 1000 microscope. The construction of theoretical models of mixed oxide crystals based on the analysis results and n-dodecane homolog molecules was carried out using the Avogadro program.

3. Results and Discussions

X-ray diffraction patterns of the obtained mixed oxides are shown in Figure 1. All samples have a peak of $2\theta=43.4$, which indicates the presence of a NiO phase. The narrower this peak, the greater the probability of the formation of larger and less stable crystallites. The diffraction pattern of calcined Ni-Al hydrotalcites corresponds to bunsenite with a reduced lattice parameter, which is associated with the replacement of part of the Ni$^{2+}$ cations by Al$^{3+}$ in tetrahedral positions, the phase of mixed oxides of variable composition and the amorphous phase. On the diffraction patterns of Ni-Al-MO (2:1) and Ni-Al-MO (3:1), diffraction reflections of Al$_2$O$_3$ were not detected. At the same time, Ni-Al-MO (4:1) has a part of aluminum in the form of X-ray amorphous aluminum oxide, as indicated by $2\theta=53.4$. It is possible that Ni-Al oxide contains an insignificant amount of spinel octahedral-tetrahedral layers.

The substitution of Ni$^{2+}$ for Al$^{3+}$ at the positions of nickel and $S_{BET}$ is shown in Figure 2. From this graph it is seen that with an increase in the Ni/Al ratio, the content of substituted Al$^{3+}$ nickel structures having a high specific surface area in comparison with NiO decreases.
Figure 1. Diffractograms of mixed oxides after catalysis.

Figure 2. The relationship between the substitution of $\text{Ni}^{2+}$ for $\text{Al}^{3+}$ and the specific surface area.
Photographs of samples obtained by optical microscopy are shown in Figure 3. The mixed oxide phase is represented by spherical particles. The sizes of aggregates increase with increasing ratio of cations in the synthesis of precursors.

![Microphotographs of samples](image)

**Figure 3.** Microphotographsof a) Ni-Al-MO (2:1), b) Ni-Al-MO (3:1), c)Ni-Al-MO (4:1).

The lattice parameters and crystallite sizes were also calculated, which are presented in Table 2. The compounds obtained are represented by cubic syngony, space group Fm3m, structure type NaCl.

| Cationic composition | Lattice parameter, Å | Unit cell volume, V |
|----------------------|----------------------|--------------------|
| Ni-Al-MO (2:1)       | 4.139                | 70.906             |
| Ni-Al-MO (3:1)       | 4.163                | 72.147             |
| Ni-Al-MO (4:1)       | 4.172                | 72.616             |

Based on the data obtained, elementary lattices of three samples were created in the Avogadro program, which are presented in Figure 4.

The diameters of the effective cross section of various molecules of mono- and dimethyl substituted homologues of n-dodecane were calculated, which are presented in Table 3. Based on the data obtained, a prediction was made of the passage of alkane molecules of normal and isomeric structure through the pores of the obtained catalytic systems.
Figure 4. Unit cells of a) Ni-Al-MO (2:1), b) Ni-Al-MO (3:1), c) Ni-Al-MO (4:1).

Table 3. The diameters of the effective cross section of the molecules.

| Molecule                  | Diameter  |
|---------------------------|-----------|
| n-dodecan                 | 3.089     |
| 2-methylundecane          | 4.346     |
| 6-methylundecane          | 4.352     |
| 2,10-dimethyldecane       | 4.339     |
| 3-ethyldecane             | 5.632     |
All catalyst systems theoretically show an acceptable result. However, a Ni-Al-MO sample (2:1) containing a significant amount of aluminum near the surface and close to the spinel structure will most likely show the best result, according to the article [2]. It proved that:

- the acidity of zeolites in a decisive way affects the activity, but weakly affects the selectivity of the catalysts;

- a decrease in the size of zeolite crystals and the creation of a mesopore system in their structure positively affects the hydroisomerization indices;

- reducing the particle size of the deposited metal, including through the use of a second metal component, leads to an increase in the activity of hydroisomerization catalysts.

4. Conclusions

Taking into account the data obtained in [14] and the data obtained in this, it can be judged that mixed Ni-Al oxides can act as catalytic systems for the hydroisomerization of n-alkanes, and the catalytic systems do not change much after the catalysis. Based on the research, a theory was put forward according to which a catalytic system based on Ni-Al mixed oxide has both acidic and basic properties, due to the mesopore system it has molecular sieve properties. In addition, it was suggested that in this process, the Ni-Al-MO system (2:1) will show the best result, which is primarily associated with increased acidity, a higher specific surface area due to the lower ratio of Ni to Al cations in the synthesis of layered double hydroxide precursors.

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