Catalytic activity of hierarchical structure based on Ni-Al layered double hydroxide

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Abstract. In this paper, the characteristics of the composition and structure of NiAl layered double hydroxide as a precursor element of the catalytic system are determined. According to x-ray fluorescence analysis, nickel content in layered double hydroxide was 86%, aluminum - 13%. The obtained elements of the catalytic system have a specific surface area of 158 m²/g and stability at high temperatures and pressures. The results of the study of catalytic activity in cracking reactions of C₁₁-C₂₂ higher alkanes in the presence of Ni-Al layered double hydroxide at temperatures of 450°C and 500°C and a flow rate of 0.5 ml/min, with a ratio of raw materials to the catalyst equal to 30 are given. The products of catalytic conversion of the initial mixture of alkanes are C₇-C₁₄ normal- and isoalkanes. According to IR spectroscopy, unsaturated compounds were formed as the reaction products.

1. Introduction

Over the past decades, the share of hard-to-recover, including heavy high-viscosity oils and natural bitumen, has significantly increased in the world [1-3]. At the same time, scientists are interested not only in its production, but in more efficient processing [4-6]. Therefore, interest in catalytic processes has increased [7, 8].

In the catalytic systems industry, there has been a growing interest in hierarchical structures in recent years. The synthesis of hierarchical structures effectively maximizes the catalytic properties of compounds in processes, depending on the architecture of compounds. The degree of porosity in the hierarchical structure is known to perform a separate additional task: the micropores contain catalytically active areas, and access to them is facilitated by the newly introduced mesoporosity [9, 10]. The structure-forming agent by its modifications, for example, impregnation, insertion of various elements, etc., that is, by successive assembling, forms a hierarchical system. Also, the formation of hierarchical catalytic systems directly in the reaction medium is of large interest. The paper [11] shows the effect of catalysts formed in situ from precursors based on group VIII metals in catalytic cracking reactions of vacuum distillate. Hierarchical catalytic systems were obtained–silicon aluminum phosphates synthesized from precursors–nanocrystallites showed a record yield of isomer (79%) in n-heptane hydroisomerization [12]. In paper [13] improved characteristics of methanol–olefins conversion in the presence of highly mesoporous SSZ-13 catalysts obtained using quaternary ammonium salt surfactants were demonstrated in comparison with conventional SSZ-13. In turn, multifunctional polymer catalysts for biomass conversion demonstrated a high yield of hydroxymethylfurfural due to the formation of a
hierarchical structure (41%) [14]. Other authors [15] synthesized hierarchical structures by inserting interfacial nanodrops to the matrix surface: Au, Au-Pt and Au-Pd particles, such catalysts have demonstrated excellent catalytic activity in 4-nitrophenol reduction reactions. Hierarchical catalysts based on zeolite microspheres intercalated into iron and gold nanoparticles showed high conversion in catalytic reduction of 4-nitrophenol, as well as convenient magnetic separability, durability and reuse [16]. In paper [17] on the example of a catalytic system based on zirconium and aluminum in the reaction of 4-methoxybenzyl-second-butyl ether transformation from anisaldehyde and 2-butanol, it was proved that the increase in the size and charge of the hydrophilic part of the structure-forming reagents leads to an increase in the concentration of acid centers in aluminum-zirconium-silicate zeolites having hierarchical porosity. Also, on the basis of faujasite zeolite for the reactions of catalytic cracking, hierarchical structures were obtained [18].

In turn, layered double hydroxides are of particular interest, as they also form hierarchical structures. In such hierarchical structures, mixed oxides obtained by heat treatment of layered double hydroxides, there is an increase in catalytic activity. Their developed specific surface area, high concentration of active centers, as well as ease of production opens up opportunities for use as catalytic systems for oil refining processes [19].

Layered double hydroxides as precursors are used due to their possibility of regulating the structural and acid-base properties of catalysts by varying the ratio of $\text{M}^{2+}/\text{M}^{3+}$ metal cations, as well as the choice of anions occupying the interlayer space, thereby regulating the activity of the catalytic system in the reaction medium [20]. The selectivity of the obtained catalysts is based on the stereochemistry of hydrocarbon compounds [21-27], and it is based on their basal distance, given by the controlled synthesis of layered double hydroxides with a developed specific surface area. An additional advantage of layered double hydroxides is that they can be obtained using simple well-established methods, such as deposition methods, which are widely tested in industry.

The present article is concerned with revealing the activity of catalytic systems based on Ni-Al layered double hydroxide in homolytic reactions.

2. Experimental section

The objects of study are NiAl layered double hydroxide and oxide obtained on its basis. Nickel content in layered double hydroxide is 86%, aluminum - 13% (according to x-ray fluorescence analysis); this ratio remains the same after catalysis (indicating the stability of layered double hydroxides). A mixture of C_{11}, C_{12}, C_{13}, C_{16}, C_{17}, C_{20}, C_{22} higher alkanes, taken in equal proportions, was also chosen as the object of study. Layered double hydroxides were obtained by co-deposition method. Experiments on the transformation of petroleum hydrocarbons were carried out on a laboratory catalytic unit at a temperature of 500°C and a flow rate of 0.5 ml/min, with a ratio of raw materials to the catalyst equal to 30.

The resulting gases were analyzed using a Shimadzu GC - 2010 Plus gas chromatograph. The study of the composition of the initial mixture of n-alkanes and the resulting products was carried out on the chromatograph AutoSystem XL by Perkin Elmer using computer data processing in SIM mode. The phase composition of the obtained compounds powders was studied on a powder x-ray diffractometer by Bruker Axs with The Bragg-Brentano survey geometry, using the DIFFRAC.EVA software module and diffraction data database PDF-2 Release 2013. The qualitative analysis of initial compounds and products were performed on an infrared spectrophotometer Vector 22 (Bruker) in the range of 4000-400 cm\(^{-1}\). Elemental analysis of raw materials and products were performed by energy dispersive fluorescence x-ray spectrometer EDX-800HS2 by Shimadzu. Calculation of the specific surface was
performed by method of thermal desorption of nitrogen on the installation 2200e by Quantachrom company (USA).

3. Results and Discussions

The obtained catalysts based on layered double hydroxide according to x-ray diffraction analysis (Figure 1) correspond to the structure of hydrotalcite – a natural layered double hydroxide. The crystallite size of the resulting compound was determined to be 7 nm. The x-ray diffractogram of the obtained hierarchical system based on Ni-Al layered double oxide contains Nickel oxide with a reduced lattice parameter value associated with the substitution of some number of Ni$^{2+}$ cations for Al$^{3+}$ ones, the phase of mixed oxides of variable composition and the amorphous phase. The substitution of Ni$^{2+}$ for Al$^{3+}$ cations in nickel positions is 16%. The specific surface area of layered double oxides was determined to be 158 $\text{m}^2/\text{g}$. The crystallite size of the obtained oxide phases is 4 nm. The Ni-Al oxide phase consists of bunsenite-like octahedral layers with some spinel layers.

![Figure 1. X-ray diffractograms NiAl layered double oxide.](image)

According to x-ray fluorescence analysis, nickel content in layered double hydroxide equaled 86%, aluminum - 13%. After catalysis, this ratio remains almost the same, which indicates the stability of layered double hydroxides (figure 2).

![Figure 2. Microelement composition of the original NiAl layered double hydroxide and NiAl layered double oxide after catalytic cracking.](image)

The greatest contribution to the composition of the gas formed at the process temperature of 450°C, is made by methane, whose share equaled 72.5%. The content of C$_2$H$_6$ was 2.7%, C$_3$H$_6$ and C$_3$H$_8$ - 9.5%,...
iso-C\textsubscript{4} - 3.3\%. During the reaction at 500°C, iso-C\textsubscript{6} (19.8\%) appeared, the CH\textsubscript{4} content decreased to 9.9\%, which led to an increase in the proportion of the remaining components in the composition of the formed gas: the share of C\textsubscript{3}H\textsubscript{6} and C\textsubscript{5}H\textsubscript{8} was 30.8\%, C\textsubscript{2}H\textsubscript{6} - 17.6\% (Figure 3).

![Figure 3. Composition of the final gaseous products of catalytic cracking.](image)

The effect of temperature on the composition of the liquid end product is illustrated in Figure 4. In the investigated range of temperatures, the degree of n-alkanes conversion increases from 0.8 at a temperature of 450°C up to 6.0 at 500°C. With the increase of temperature, the selectivity for isoalkanes increases, while the selectivity for C\textsubscript{7}-C\textsubscript{14} alkanes is almost the same.

![Figure 4. Chromatogram of the final liquid products of catalytic cracking of C\textsubscript{11}-C\textsubscript{22} in the presence of NiAl hydroxides at temperatures of 450°C (a) and 500°C (b).](image)

According to IR spectroscopy data (Figure 5) unsaturated compounds were found to be formed in the reaction products. The iodine value was 0.172.
According to the chromatographic analysis, C_7-C_{14} alkanes and isoalkanes were formed in appreciable amounts in the products of catalytic conversion of the model mixture of alkanes. Aromatic compounds were formed in small quantities (Figure 4).

**Table 1.** Elemental analysis data of carbon and hydrogen content.

| Precursor and catalytic system element | C   | H   | C / H |
|---------------------------------------|-----|-----|-------|
| Al-Ni-LDH initial                     | 14.10 | 3.20 | 0.37  |
| Al-Ni-LDO (450°C)                     | 86.93 | 2.34 | 3.1   |
| Al-Ni-LDO (500°C)                     | 85.48 | 3.16 | 2.25  |
| C_{11}-C_{22}n-alkanes (initial mixture) | 77.43 | 11.72 | 0.55  |
| liquid cracking product C_{11}-C_{22} in the presence of NiAl hydroxides at 450°C | 77.36 | 11.67 | 0.55  |
| liquid cracking product C_{11} - C_{22} in the presence of NiAl hydroxides at 500°C | 75.64 | 9.79 | 0.64  |

**4. Conclusion**

The obtained catalyst carriers based on NiAl layered double hydroxide are stable compounds with a specific surface area of 158 m²/g. Methods of chromatographic analysis showed that the formed gas consisted of lower alkanes, including isoalkanes. The products of catalytic conversion of the initial mixture of alkanes are C_{7} - C_{14} normal- and isoalkanes. Thus, the catalytic activity of layered double hydroxides in homolytic reactions of higher alkanes transformation at temperatures of 450 and 500°C and raw material consumption of 0.5 ml/min was determined.
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