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Conversion of n-alkanes C₁₁-C₂₂ using a catalyst based on Ni-Al mixed oxides

S Petrov^{1,2}, A Valieva¹

¹Kazan National Research Technological University, 68 Karl Marx St., Kazan, Russia

²Kazan Federal University, 18 Kremlevskaya Str., Kazan, Russia

E-mail: psergeim@rambler.ru

Abstract. During the work composition and properties of Ni-Al mixed oxides samples were investigated. These oxides were obtained from Ni-Al layered double hydroxide using thermal and hydrothermal methods. Catalytic cracking of a model mixture of alkanes was carried out in the presence of Ni-Al mixed oxides samples. Gas chromatography, chromatography-mass spectrometry, and IR-spectroscopy were used for the analysis of gaseous and liquid products. X-ray structural, X-ray fluorescence, IR-Fourier spectrometry, the specific surface analyzer, particle size analyzer, microphotographic analysis were used for the analysis of the composition and properties of catalytic systems. According to X-ray structural and X-ray fluorescence analyzes, the composition of the supporting structure of the catalyst Ni-Al mixed oxide did not change after catalysis. The content of their low-boiling homologs increases, alkanes of a branched structure is formed in the products of n-alkanes cracking in the presence of the obtained mixed Ni-Al oxide.

1. Introduction

To date, the latest research in the field of catalysts set a goal to increase the catalytic activity and the specific surface area of catalytic systems for secondary refining processes.

In recent decades, layered double hydroxides are of particular interest in the global scientific communities due to the developed specific surface, high concentration of active centres, the possibility of varying metal cations, thereby changing the acid-base properties, as well as ease of preparation. They are used widely in the field of heterogeneous catalysis, mainly as precursors for the synthesis of catalysts based on mixed oxides. Through the use of various transition metals, it is possible to control compatibility and interconnection of metal-substrate. All these features extend the catalytic scope of layered hydroxides [1].



When the LDH is heated at about 250 °C, the water in the interlayer space is released with following dehydroxylation of hydroxide layers and non-stoichiometric mixed metal oxides with characteristic properties form. They are used as active catalysts for many catalytically important reactions [2]. The advantages of the basic and / or redox properties of layered double hydroxides are used in catalysis, since the dispersion of cations in hydroxylated layers is preserved after calcination, which leads to the formation of well-stabilized metal particles [3].

In the literature [4], various forms of layered double hydroxides such as calcined, rehydrated, functionalized and as supporting structure, have been studied in various catalytic processes, such as partial oxidation and steam reforming of methane to produce hydrogen, one-step liquid-phase heterogeneous synthesis, combined oxidation and dry reforming of methane to synthesis gas, alkylation, isomerization, aromatization of olefins, selective oxidation of phenol to catechin and hydroquinone, benzene to phenol, benzyl hydroxylation, liquid phase oxidation of aromatic hydrocarbons and etc.

The catalytic activity of the catalyst supporting structure based on Ni – Al mixed oxides in the process of higher alkanes cracking is determined in this work.

2. Materials and Methods

The layered hydroxide was obtained by the coprecipitation method [5]. Samples of mixed oxides were obtained in two ways. Ni-Al mixed oxide (sample No. 1) obtained by calcination at 450-500 °C for 4 hours in a nitrogenous medium. Ni-Al mixed oxide (Sample No. 2) was obtained in the reaction medium by heating the reactor 450-500 °C for one hour.

The phase composition of the catalytic system was investigated on a BrukerAxs X-ray diffractometer with Bragg-Brentano geometry using the DIFFRAC.EVA software module and the PDF-2 Release 2013 diffraction data base.

The textural characteristics of the catalytic system were investigated by the method of nitrogen thermal desorption on the NOVA 2200e of the Quantachrom company. The specific surface was calculated by the Brunauer–Emmet–Teller method.

Spectrometric analysis of the samples was carried out on a IR-Fourier spectrometer of the Frontier PerkinElmer.

The elemental composition was obtained using an energy dispersive fluorescence X-ray spectroscopy EDX-800HS2 of the company "Shimadzu".

The size of the aggregates of the samples was determined by scattering and detection of reflected / refracted laser light, red and blue spectra (650 and 405 nm), in accordance with ISO 13320-1 on a laser analyzer of particle size distribution HORIBA LA-950. Measurement range: from 0.01 µm to 3000 µm, measurement frequency 5000 per second. Micrographs of the studied materials were obtained on a Hitachi TM 1000 microscope.

A model mixture of C₁₁H₂₄, C₁₂H₂₆, C₁₅H₃₂, C₁₆H₃₄, C₁₇H₃₆, C₂₀H₄₂, C₂₂H₄₆ was selected as the feedstock. The ratios of n-alkanes illustrated in Figure 1. Catalytic cracking of n-alkanes of C₁₁-C₂₂ using 1 and 2 samples were carried out on the laboratory "REXO Engineering" catalytic cracking unit with automated reactor system. The process was carried out at a

temperature of 500 °C, a pressure of 5 atm and a consumption of feedstock of 0.5 ml/min. The multiplicity of feedstock to the catalyst was 9 in experiment No. 1, in experiment No. 2 this ratio equalled 22.

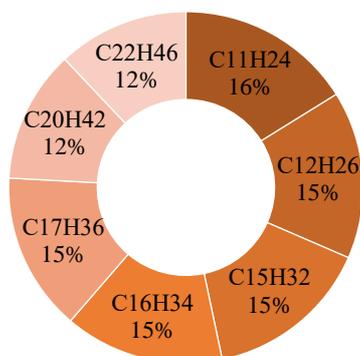


Figure 1. The composition of the model mixture.

The products of conversion were analyzed by gas-liquid chromatography on Crystal-2000M devices of the company Hromatek with a flame ionization detector, a DB-1 capillary column is 15 m long, internal diameter of 0.32 mm, in the linear programming mode temperature from 50 to 320 °C at a rate of 20 °C/min. The sample volume is 1 ml, the dilution is 1:20 in CCl₄, PerkinElmerClarus 680 with a SQ8 MS mass spectrometric detector, a capillary column, in the temperature programming mode from 70 to 270 °C. Gas analysis was investigated on a GC 2010 Plus Shimadzu gas chromatograph.

3. Results and Discussions

The resulting catalyst supporting structure based on layered double hydroxide correspond to the structure of hydrotalcite, which is a natural layered double hydroxide. The coherent scattering region was 7 nm. The diffractogram of the obtained system based on Ni-Al layered double oxide (sample No. 1) contains nickel oxide with a reduced lattice parameter value, which is due to the replacement of a part of Ni²⁺ cations with Al³⁺. The substitution of Ni²⁺ for Al³⁺ in nickel positions is 16 wt %. The crystallite size of the oxide phases is 4 nm. The Ni-Al oxide phase consists of bunsenite-like octahedral layers with a certain number of spinel layers. The specific surface area of sample No. 1 was 169.9 m²/g. The diffractogram of the obtained systems is shown in Figure 2.

According to X-ray fluorescence and X-ray diffraction analyzes, the composition of the samples studied remained unchanged. The nickel content in the resulting layered double hydroxides was 86 wt %, aluminium – 14 wt %. This ratio remains the same after catalysis. Layered double hydroxides were preliminarily deposited on ceramic wool, which explains its presence on diffractograms and in elemental composition. The appearance of iron and chromium in the catalytic system after the reaction is explained by the fact that the reactor is made of alloyed steel, the particles of which were adsorbed on the catalyst. Traces of

elements such as sulfur, zirconium, calcium, potassium are explained by the degree of purity of the raw materials used in the preparation of layered double hydroxides. All these data can see from Figures 3 and 4.

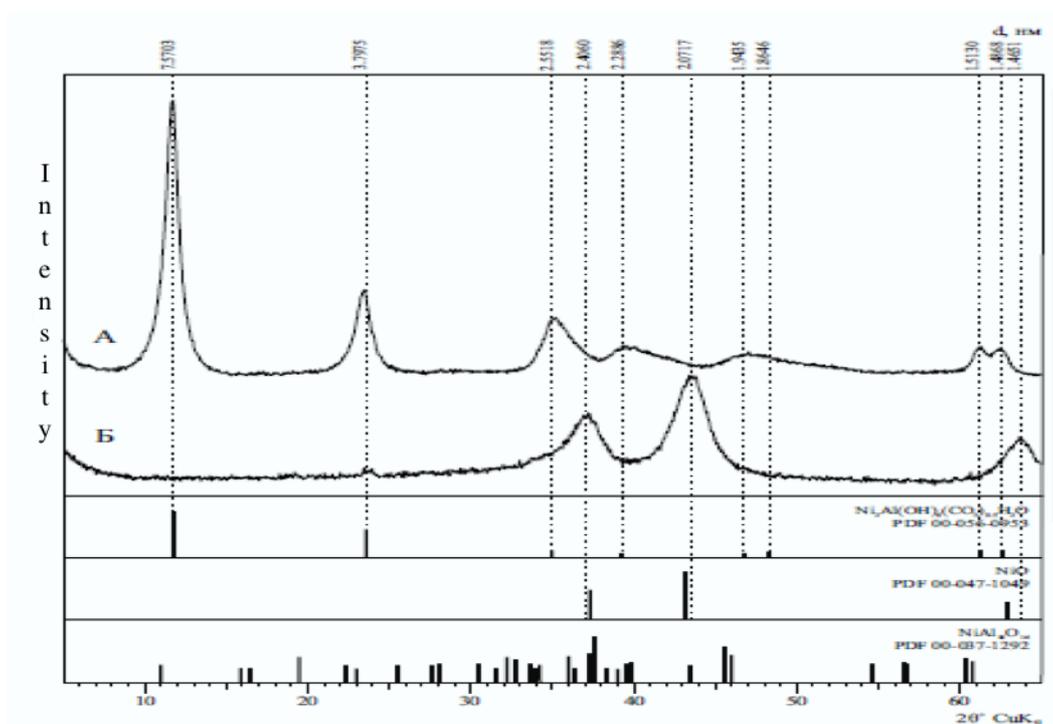


Figure 2. Diffractograms a) Ni-Al layered double hydroxide, b) Ni-Al mixed oxide (sample No.1).

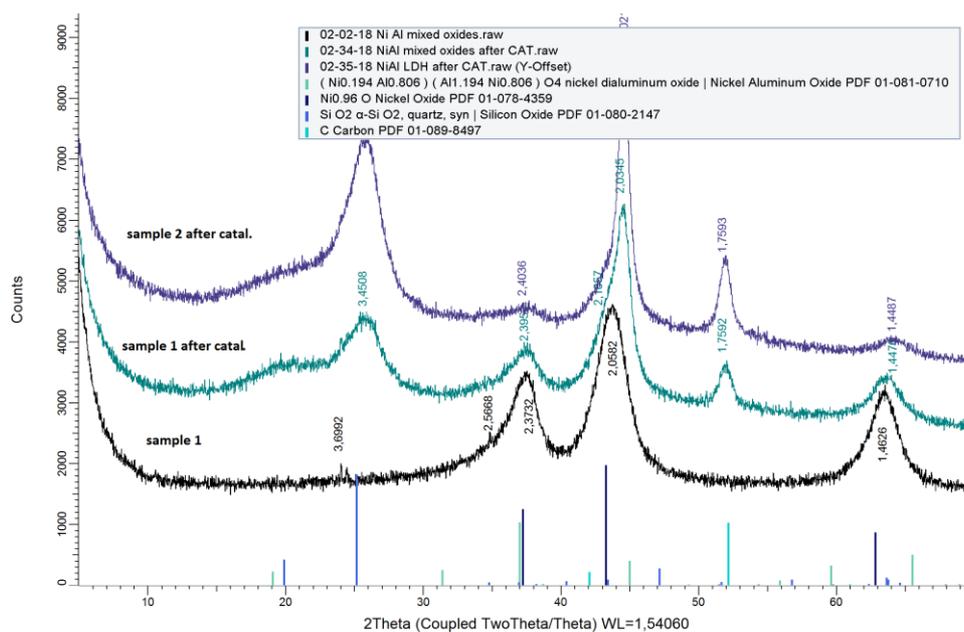


Figure 3. Diffractograms of mixed oxides before and after catalysis.

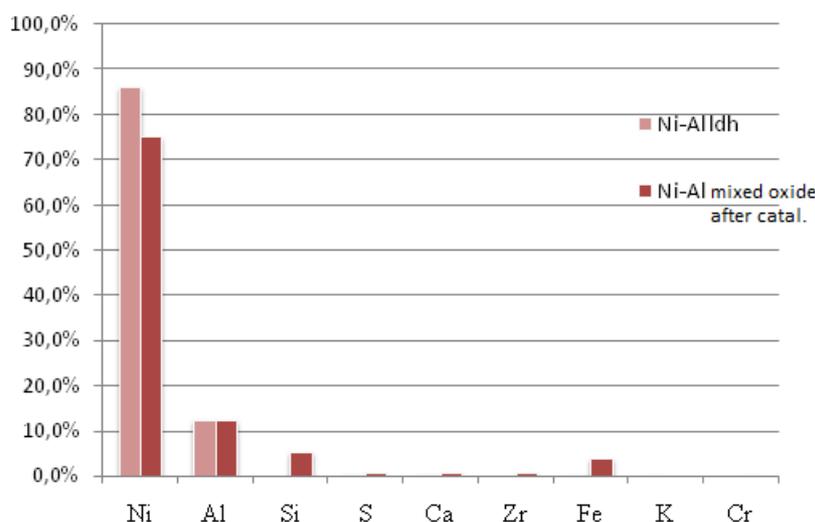


Figure 4. X-ray fluorescence analysis of layered binaries hydroxides before and after catalysis.

The IR spectra of Ni-Al layered double hydroxide, which is shown in Figure 5, have bands characteristic of layered double hydroxides. Reflexes with wavelengths less than 800 cm^{-1} (770.06 cm^{-1} and 561.15 cm^{-1}) are attributed to oscillations in brucite-like layers, the corresponding oscillations of metal – oxygen and the band with a maximum of about 3450 cm^{-1} are oscillations of hydroxyl groups. The interval $3000\text{--}3150\text{ cm}^{-1}$ corresponds to the stretching oscillations of water molecules in the interlayer space. The band with a maximum of 1360.17 cm^{-1} indicates the presence of O–C–O carbonate anions in the interlayer space, and the band of 1650 cm^{-1} reflects the deformational oscillations of water in the interlayer space [6]. In the IR spectra of samples 1 and 2, an absorption band of 1050 cm^{-1} is observed, which is characteristic of the ether –C–C–C bond. The formation of this compound is associated with the oxidation process, accompanied by the release of heat, which is confirmed by the data of thermal analysis.

Analysis of microphotographs, which are presented in Figure 6, allows us to conclude that the surface of the LDH is composed of rod-like aggregates with dimensions of 245 nm and diameters of $50\text{--}80\text{ nm}$. In turn, the aggregates form agglomerates larger than 1 micron . During calcination, the relief is represented by pronounced rod-like forms of nickel oxide particles with a length of 600 nm , and the mixed oxide phase is represented by spherical particles with a diameter of 131 nm . When a layered double hydroxide is converted to a mixed oxide under the cracking conditions of the initial mixture of n-alkanes at a temperature of $500\text{ }^{\circ}\text{C}$, there are no obvious changes in the grain size in the composition of the aggregates, however, the boundaries of their contact degenerate. The probable cause of the observed effects may be coke formation products, which are deposited on the supporting structure surface in the amount of $5\text{ wt } \%$.

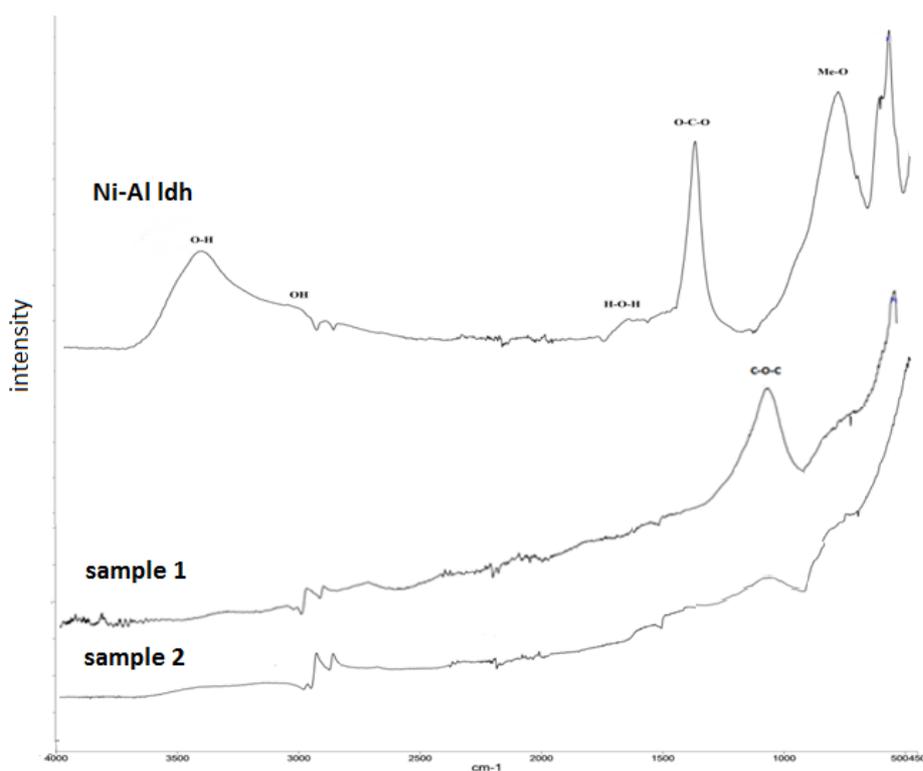


Figure 5. IR spectra of layered double hydroxide and mixed oxides after catalysis.

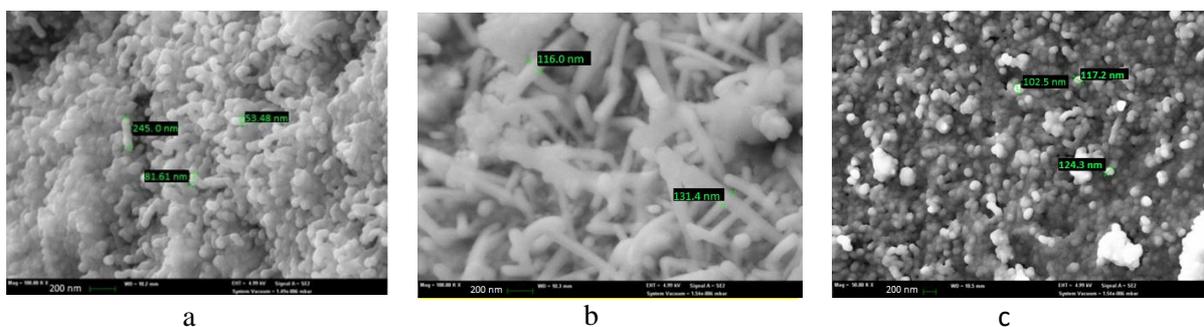


Figure 6. Microphotographs of a) NiAl layered double hydroxides, b) NiAl mixed oxides of oxides (sample No. 1) c) NiAl mixed oxides of oxides after catalysis (sample No. 2).

The composition of the gases produced is shown in the diagram in Figure 7.

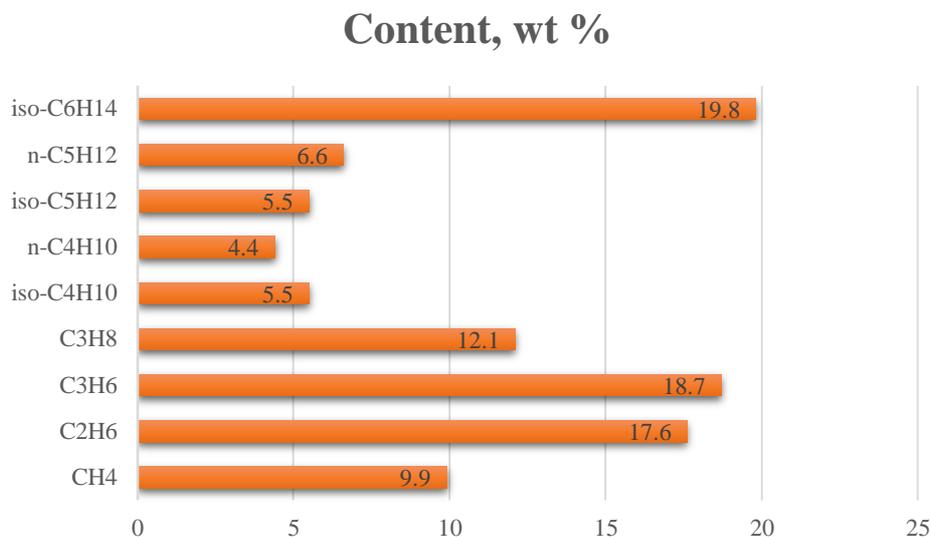


Figure 7. The composition of the resulting gases.

According to the Figure 8, the highest yield of newly formed hydrocarbons is 16.32 wt % of sample No. 2. The yield of hydrocarbons for sample No. 1 was 11.13 wt %. For the studied samples, the selectivity for isoalkanes is observed and amounts to 7.3 wt % (sample No. 2) and 5.5 wt % (sample No. 1). Conversion of sample No. 1 was 39.66 wt %, sample No. 2 was 28.37 wt %. The high conversion for sample No. 1 is associated with a lower feedstock / catalyst ratio. The increase in yield of newly formed hydrocarbons in the presence of sample No. 2 is associated with the calcination mode. According to [7], the maximum concentration of the basic centres is observed at a calcination temperature of 450 °C. The share of the basic centres decreases at 500 °C. The basic centres of the catalytic system have isomerizing functions, which were confirmed by the experiments.

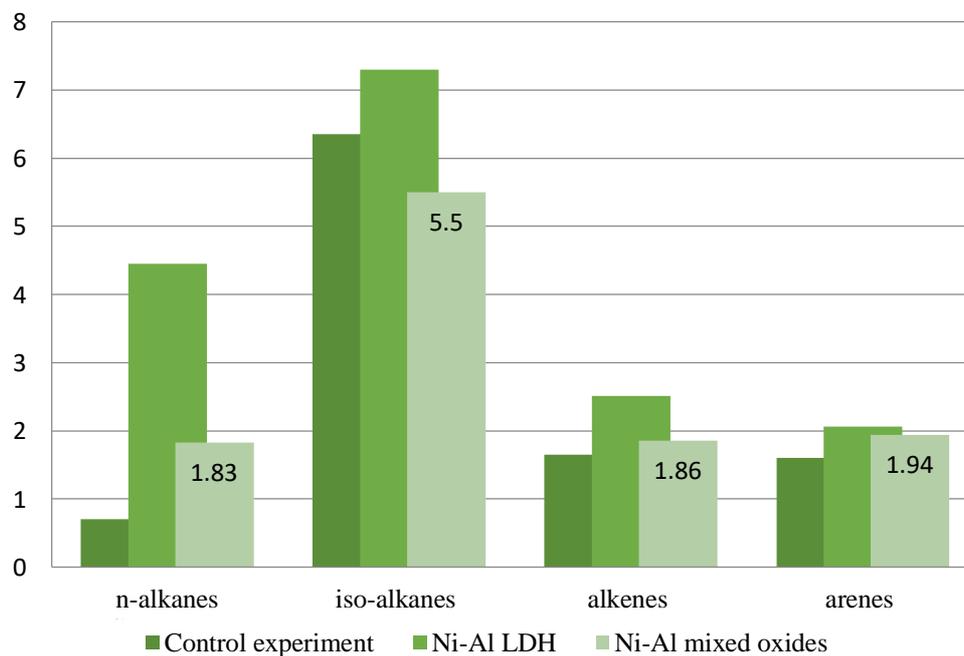


Figure 8. The composition of the resulting hydrocarbons.

4. Conclusions

The composition of Ni-Al mixed oxides samples, which was obtained from Ni-Al layered double hydroxide, was studied. Catalytic cracking of a model mixture of alkanes was carried out in the presence of Ni-Al mixed oxides samples. According to X-ray structural and X-ray fluorescence analyzes, the composition of the supporting structure of the catalyst Ni-Al mixed oxide did not change after catalysis. According to the resulting data, sample No. 2 has the highest yield of iso-alkanes, which is associated with a high concentration of the basic centres on its surface. Conversion for sample No. 1 was 39.66 wt %, and for sample No. 2 equalled 28.37 wt %.

Acknowledgments

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