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Hydroconversion of parafine LTP56-H over nickel/Na-mordenite catalysts

Research Article

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Abstract: Nickel catalysts supported on Na-mordenite were used for paraffin LTP56-H hydroconversion into liquid material as a possible component for engine fuels. The effects of none-catalytic thermal treatment and catalytic conditions-zeolite type and reaction conditions (solvent) on the process of liquefaction of LTP56-H paraffin and physicochemical properties of catalysts were studied. The physicochemical properties of catalytic systems were investigated using XRD, TPR, TPD-NH3 and SEM-EDS methods.

Keywords: *Nickel catalysts • Paraffin liquefaction • Mordenite • Hydroizomerization*

1. Introduction

Low temperature catalytic conversion of synthesis gas (CO-H_2) on iron catalysts known as the Low Temperature Fischer-Tropsch (FT) process leads mainly to a broad spectrum of olefinic and paraffinic hydrocarbons with a small amount of oxygenates possessing carbon number in the range C_{20} - $C_{40,}$ known as waxes. The contribution of waxes achieves up to 50% of total FT product. This rather undesirable solid FT product requires liquefaction as a possible source of liquid fuels (benzin gasoline, diesel). The unquestionable advantage is lack of sulfur and nitrogen compounds. In order to increase the yield of fuel fraction the paraffinic waxes should be convert into liquid hydrocarbons being the possible component of benzin and diesel fuels. The recommended processes are thermal and catalytic hydrogenation reactions [1,2]. The hydrocracking and hydroisomerization processes are two of the most promising processes for conversion of paraffin, which converts high-boiling molecules into more desirable lower molecular weight products with low olefin and high iso/linear paraffin yields by simultaneous or sequential hydrogenation and carbon bond breaking [3-5]. These two processes are basic in the petroleum refining industry, which produce a broad range of highly valuable chemicals, petrol, diesel oil and gasoline. These processes are carried out over bifunctional catalysts with two different components representing metallic and acidic functions. Different zeolites and zeolite-like solid acids and also acidic oxides are used as the acidic components. The most frequently used acidic components are decationized Y and mordenite zeolites. Selection of these materials is due to strong acidic properties combined with the specific pore geometry of these molecular sieves [6-9].

Typical hydrogenating/dehydrogenating components are usualy Pt, Pd, Ni, Co, Mo, their oxides and sulfides. The most active catalyst is platinum, and as little as 0.2–0.5 wt% is required to promote the activity of bifunctional materials. The classical mechanism of skeletal isomerization and hydrocracking of alkanes over bifunctional catalysts involves parallel and consecutive steps of dehydrogenation of the alkane molecule over metallic centers. Those steps lead to the formation

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of olefins which are highly reactive for conversion of carbenium ion, which rapidly undergo of isomerization and/or cracking into two smaller olefins over acidic sites. At the final step, olefinic intermediates are hydrogenated. Additionally, the rate of the alkane hydrocracking and isomerization is dependent on the activity of the metallic function [10-12]. Mordenite, a member of the large-pore zeolite family consists of main channels measuring 6.5×7.0 Å, which are connected by tortuous pores measuring 2.6×5.7 Å that form the so-called side pockets. Tortuous pores are too small for most molecules to enter, for this reason mordenite is generally regarded as a mono-dimensional zeolite. Mordenite is widely used in catalysis and in separation and purification because of its uniform, small pore size, high internal surface area, flexible framework, and controlled chemistry. The major drawback of mordenite and zeolites is generally a result of the limited size of the channels and cavities, and the lack of interconnectivity. This imposes diffusional limitations on reactions, limiting their activity, selectivity, and stability. It has been repeatedly proven that mass transfer limitations play an important role in industrial applications using zeolites [13-16].

In this work, nickel catalysts supported on Na-mordenite for paraffin hydroconversion into liquid material as a possible component for engine fuels were used. To successfully convert paraffin into transportation fuels, a catalyst combining hydrocracking and hydrogenation abilities is needed. Therefore, we used zeolite material as an appropriate support because of the base-acidic properties needed in hydrocracking process and metallic nickel for the hydrogenation process. We attempted this using Ni/Na-mordenite bifunctional catalysts, which have the relative strengths of the metal and base-acidic functions allowing a better balance between the hydrogenation and cracking functions and consequently, producing desired, clean, gasoline-like products.

2. Experimental procedure

2.1. Materials and catalysts preparation

The investigated paraffin wax (commercial paraffin denoted as LTP56-H) containing linear hydrocarbons with carbon number in the range C_{20}-C_{30} was used. The characteristic distribution of each individual hydrocarbon is presented in Fig. 6. The following commercial powdered support materials (by Alfa-Aesar) were used for Ni/Na-mordenite catalysts: Na-mordenite with surface area 426 m^2 g^{-1} and ratio SiO_2:Al_2O_3 = 13:1. Nickel/support catalysts containing 0.5, 1.5, 5 and 10 wt.% Ni were prepared by a wet impregnation method using aqueous solution of nickel nitrate as a metal precursor and commercial support sodium form of mordenite. After impregnation, catalysts were dried at 120°C and calcined for 4 h in air at 500°C. Catalyst sample (weight about 0.5 g) was reduced before catalytic test in a flowing stream of pure hydrogen with volume velocity 40 cm^3 per minute at temperature 400°C.

2.2. Methods of catalysts characterization

2.2.1 Temperature programmed reduction - (TPR-H_2)

The TPR-H_2 measurements were carried out in the automatic TPR system AMI-1 in the temperature range of 25-900°C with a linear heating rate of 10°C min^{-1}. Samples (weighing about 0.1 g) were reduced in hydrogen stream (5% H_2-95% Ar) using gas volume velocity of 40 cm^3 per minute. Hydrogen consumption was monitored by a thermal conductivity detector.

2.2.2 Temperature programmed desorption of ammonia-(TPD-NH_3)

The procedure of catalyst surface acidity measurement include: purification of catalyst surface, adsorption of ammonia and temperature programmed desorption. Catalyst sample purification (about 0.15 g) - removal of water from the system leading to surface dehydroxylation was completed in pure argon stream with a volume velocity of 40 cm^3 per minute at 400°C for 2 h and after cooling sample to 100°C argon stream was switched into a gaseous mixture of ammonia flowing 0.5 h through catalyst sample to entirely saturate its surface. After NH_3 adsorption the excessive amount of ammonia and removal of weakly and physically adsorbed NH_3 was undertaken by 1 h of catalyst sample purging in pure argon stream with volume velocity 40 cm^3 per minute. A temperature programmed desorption of ammonia-TPD-NH_3 run - was done in a temperature range of 100-500°C using a linear growth of temperature of (27°C min^{-1}) and a thermo-conductivity detector to obtain a TPD-NH_3 profile.

2.2.3 XRD measurements

Room temperature powder X-ray diffraction patterns were collected using a PANalytical X'Pert Pro MPD diffractometer in Bragg-Brentano reflecting geometry. Copper CuKα radiation from a sealed tube was utilized. Data were collected in the range of 5° - 90° 2θ with step of 0.0167° and exposition per one step of 27 s. Due to the fact that raw diffraction data contain some noise, the background during the analysis was subtracted using the Sonneveld, E.J. and Visser algorithm, and next the data were smoothed using a cubic polynomial. All calculations were done with X'Pert HighScore Plus computer software.

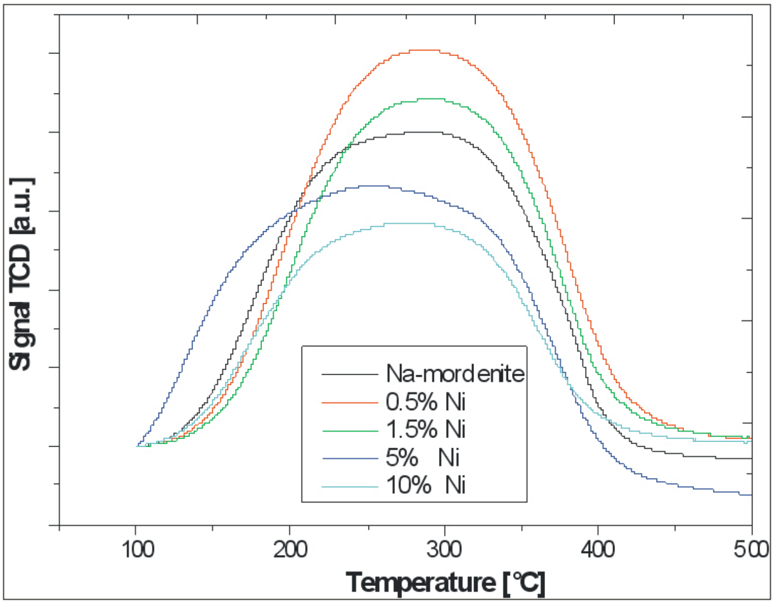

Figure 1. NH_3-TPD profiles for Na-Mordenite and Ni/Na-Mordenite.

2.2.4 SEM measurements

The SEM measurements were performed using a S-4700 scanning electron microscope HITACHI (Japan), equipped with an energy dispersive spectrometer EDS (Thermo Noran, USA). Images were recorded at several magnifications using secondary electron (SE) or BSE detector. The EDS method made it possible to determine the qualitative analysis of elements present in the studied micro-area of sample surface layer on the basis of the obtained characteristic X-ray spectra. A map of the distribution of elements on the studied micro-area was made. The accelerating volt age was 25 kV. For performing, measurements samples were coated with carbon target using Cressington 208 HR system.

2.2.5 Catalytic activity test

Catalytic activity of nickel supported catalysts in insolvency of LTP56-H paraffin with and without catalysts with a hexane as a solvent were studied in a stirred high pressure reactor (Pressure Reactor, Parr Instrument CO.) at two temperatures: 360 and 380°C, respectively. Before activity tests, all catalytic systems were reduced 2 h in pure hydrogen at 400°C. The pressure of the running reaction was in the range of 6 or 12 (starting) - 15 Mpa (final reaction temperature). The reaction time was 4h. Before activity tests, the starting source of hydrocarbons - LTP56-H paraffin was dissolved in hexane solution, paraffin: hexane weight ratio = 1:3 and after that, about 0.5 g of Ni catalysts was added into the reactor. The product composition and distribution were analyzed using the GC-MS technique.

3. Results and discussion

3.1. Temperature-programmed desorption

Temperature-programmed desorption of ammonia is a conventional method for characterizing acidity in zeolites [17-19]. The acidity of Na forms of mordenite and nickel catalysts containing 0.5, 1.5, 5 and 10 wt.% of Ni supported on Na-mordenite was evaluated by the TPD-NH_3 method, and ammonia desorption profiles are shown in Fig. 1. The TPD profile of the ammonium form of Na-mordenite shows only one desorption peak (Fig. 1). Similar results were obtained by González *et al*. [20] investigating the acidity of Na-mordenite. They observed only one NH_3-TPD peak for Na-mordenite with low intensity at 475 K [20-22]. This ammonia desorption profile has been assigned to ammonia weakly held or physically adsorbed on the surface of mordenite [20,21]. Additionally, TPD measurements of Ni/Na-mordenite catalysts showed that the increase of nickel loading results in a decrease of the amount of desorbed ammonia. Introduction of 5 and 10 wt.% of nickel caused the decrease of the TPD-NH_3 profile in comparison to support (mordenite-Na). This effect can be related to blocking pore of support by metal ions.However, in the case of 0.5% Ni/Na-mordenite and 1.5% Ni/Na-mordenite supported catalysts, we showed that increasing of the amount of adsorbed ammonia generates new centers of ammonia adsorption (see Table 1).

3.2. Temperature-Programmed Reduction

The reduction behavior of nickel supported catalysts was studied by the TPR method, and the results are shown in Fig. 2. In the case of Ni/Na-mordenite catalysts, one can observe two partially resolved reduction steps for catalysts containing 5 and 10% wt. Ni (see Fig. 2). These stages are connected with nickel oxide reduction. The first hydrogen consumption effect, whose maximum occurs at about 390°C, is attributed to the reduction of surface "free" nickel oxide NiO. The second effect is assigned to the reduction of nickel oxide interacting with the aluminosilicate surface or with reduction of Ni^{2+} species located in the channels of the zeolite [23]. The TPR profile recorded for 0.5% and 1.5%Ni supported catalysts did not show any reduction effect, what can be explained by fact that Ni^{2+} ions are not reducible being located into mordenite lattice structure.

Very similar reduction results on Ni/mordenite catalysts were obtained by Romero *et al.* [24] and Garrido [23]. These authors also observed two unresolved peaks. A peak centered at 380°C, which has been ascribed to the reduction of Ni^{2+} from the nickel oxide, originated from formed "free" NiO. The overall reduction of nickel oxide crystallites can be described by the following equation:

Table 1. TPD-NH_3 results for support (Na-mordenite) and catalytic systems.

Catalyst	Ni Content [%]	Total amount of desorbed NH_3 [mmol g^{-1}]
Na-mordenite	-	1.85
Ni/Na-mordenite	0.5	2.17
Ni/Na-mordenite	1.5	1.90
Ni/Na-mordenite	5	1.81
Ni/Na-mordenite	10	1.30

$$NiO + H_2 \rightarrow Ni + H_2O$$

The second unresolved peak is situated at higher temperatures (500 - 550°C), which could be assigned to the reduction of more stabilized Ni^{2+} species that were more difficult to reduce, probably due to their location in the channels of zeolite.

3.3. XRD measurements

XRD diffraction spectra of Ni supported catalysts after their calcination in air at 500°C for 4 h is given in Fig. 3. The phase composition studies carried out for samples after calcination showed that for all catalysts independent from nickel loading, the zeolite phase was observed. The reflexes of NiO phase were visible on the XRD spectra only for catalysts containing higher content of Ni (5 and 10% wt. Ni). The phase composition studies were also carried out for samples after reduction at 400°C in pure hydrogen for 2 h. The only difference observed for catalysts after reduction was appearance of metallic nickel phase, which comes from the reduction of nickel oxide phase (results not shown in this work). Metallic nickel phase was visible on the diffractograms in the case of supported catalysts containing 5 and 10 wt.% of Ni. The lack of reflexes in the case of lower Ni loading 0.5 and 1.5 wt.% of Ni indirectly suggest high monoatomic dispersion of Ni ions onto the surface of zeolite or the appearance of very small crystallites not visible by the XRD method.

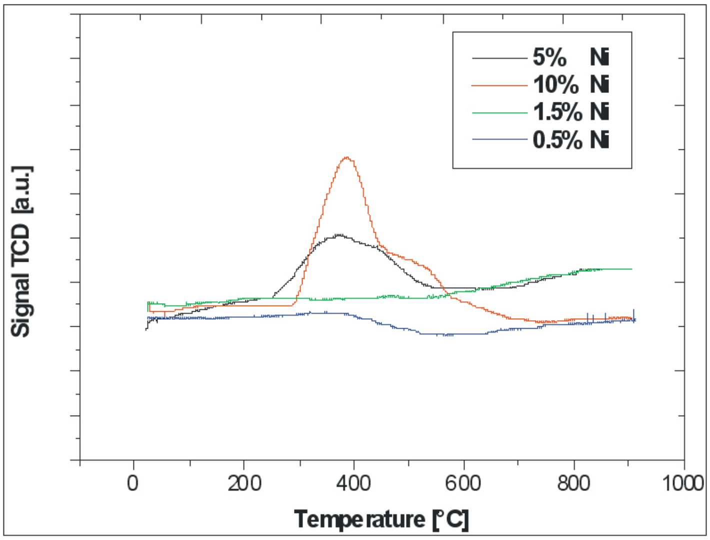

Figure 2. Temperature programmed reduction measurements for Ni/Na-Mordenite catalysts.

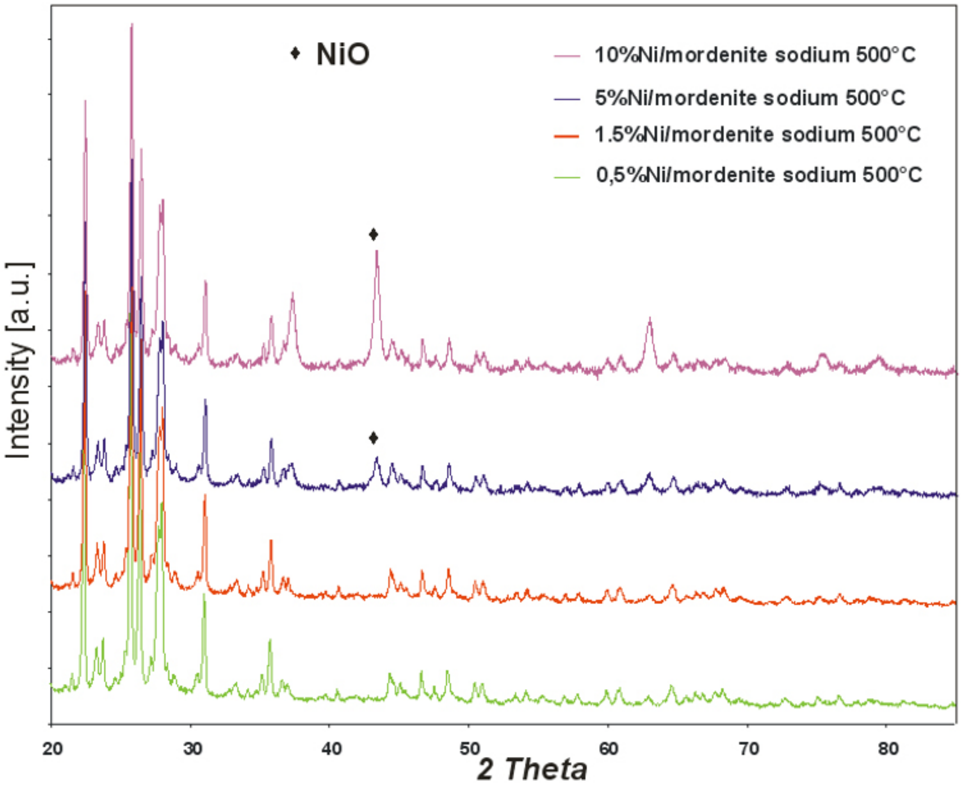

Figure 3. XRD patterns for catalysts after calcinations for 4 h in air atmosphere at 500°C Ni/Na-Mordenite catalysts.

3.4. SEM-EDS measurements

A scanning electron microscope (SEM) S-4700 (HITACHI, Japan), equipped with an energy dispersive spectrometer EDS (Thermo Noran, USA) was employed to characterize the morphology and determination of elemental distribution. The results of SEM-EDS measurements for monometallic 5% Ni/Na-mordenite supported catalyst after calcination and reaction are shown in Figs. 4a and 4b, respectively. The magnification was equal 20000 for 5% Ni catalyst after calcination and 5000 in the case of sample after reaction. The distribution of nickel, aluminum, silicon, and oxygen for both samples are also shown in Fig. 4. The SEM images showed that there were no differences between the pre- and postreaction catalysts. The distribution of each element is uniformly homogeneous, which confirms that one can not observe any changes on the catalysts surface after reaction.

3.5. Activity test measurements

The influence effect of catalyst and reaction conditions (solvent) in the paraffin LTP56-H hydroisomerization process was also studied in this work. The GC-MS technique was used to characterize the composition of LTP56-H paraffin. The results of hydrocarbon distribution in LTP56-H paraffin are given in Fig. 5. LTP56-H paraffin is a mixture of saturated linear hydrocarbons with carbon numbers in the range of C_{20}-C_{30}. It is worth to note that in the analyzed paraffin, the following molecules predominate: C_{20}-cosane (about 5%), C_{23}-tricosane (about 4%), C_{24}-tretracosane (about 11%), C_{25}-pentacosane (about 20%), C_{26}-hexacosane (about 31%) and C_{30}-triacontane (about 27%). The remaining 2% is a mixture of following hydrocarbons : C_{21}-heneicosane, C_{22}-docosane, C_{27}-heptacosane. The results of none catalytic thermal hydroconversion of LTP56-H paraffin conducted at 380°C in the pressure 12 MPa using hexane as a solvent and the GC-MS hydrocarbons distribution is presented in Fig. 6. The analysis of liquid products of LTP56-H paraffin after hydroconversion showed that the starting materials is cracked only slightly (see Table 2). The formation products were a mixture of saturated hydrocarbons containing from C_{10} to C_{19} carbon atoms in the molecule, and also branched hydrocarbons (4-methylooctane, 4-etylooctane, 5-methylononane) and aromatic hydrocarbons (etylobenzene, 1,3-dimetylobenzene, paraxylene). It is worth to note the considerable role of the methylation reaction combined with aromatization reaction.

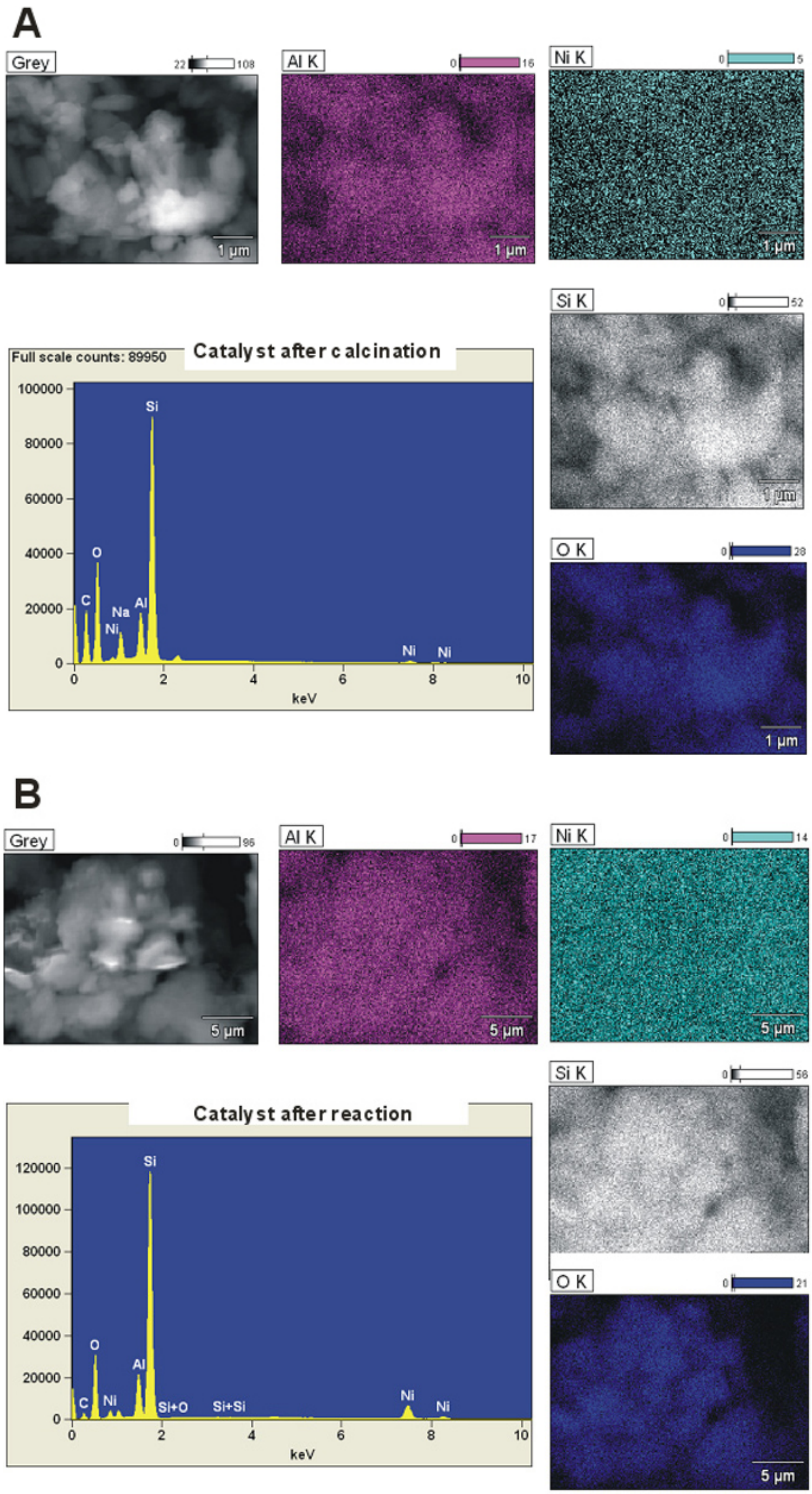

Figure 4. The results of SEM-EDS measurements for monometallic 5% Ni/Na-mordenite supported catalyst A) after calcination in air at 500°C for 4 h B) after reaction.

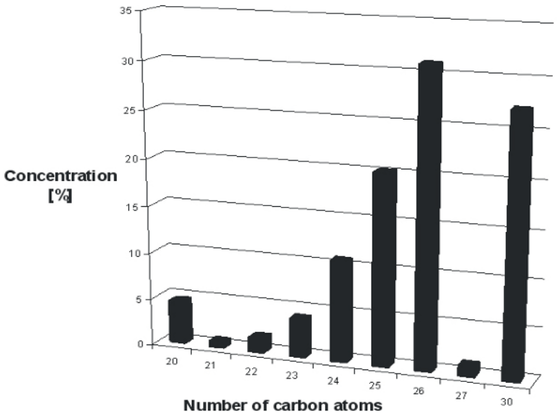

Figure 5. The results of LTP56-H paraffin composition study obtained using GC-MS technique (paraffin dissolved with hexane).

Totally different product distributions were obtained after catalytic hydroconversion of LTP56-H paraffin carried out at 360°C under the pressure 6 MPa with hexane as a solvent (Fig. 7) and without hexane (Fig. 8). High conversion of paraffin LTP56-H close to 100% in presence of solvent gave very brad spectra of products of many reactions covering the whole range of carbon number C_5-C_{30} such as cracking and hydroisomerization reactions. In the case of hexane-paraffin solution, hydrocarbons in the carbon range up to C_8 dominated, whereas paraffin alone catalytically decomposes giving very random and complicated spectra of hydrocarbon products (see Table 2). The main products come from hydroisomerization, cracking and aromatization reactions. Typical products were methyl-branched isomers and aromatics.

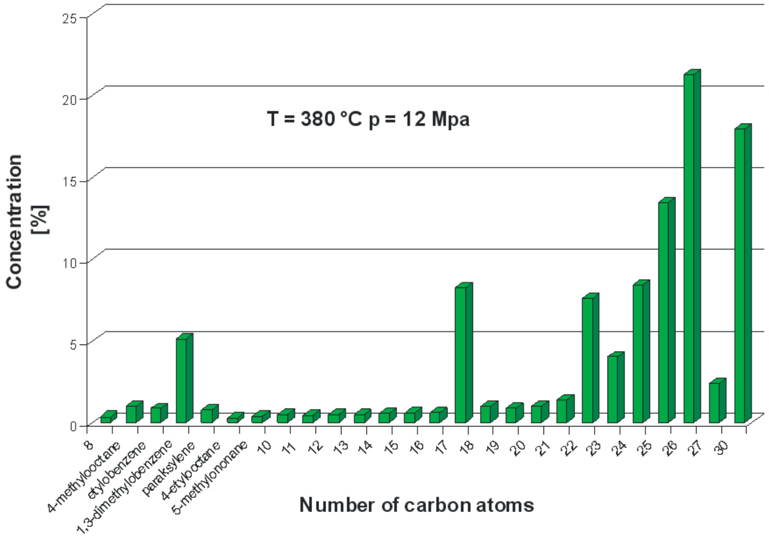

Figure 6. Hydroconversion of LTP56-H paraffin conducted for 4 h at 380°C without catalyst and in the pressure range 120-380 bar (paraffin dissolved with hexane).

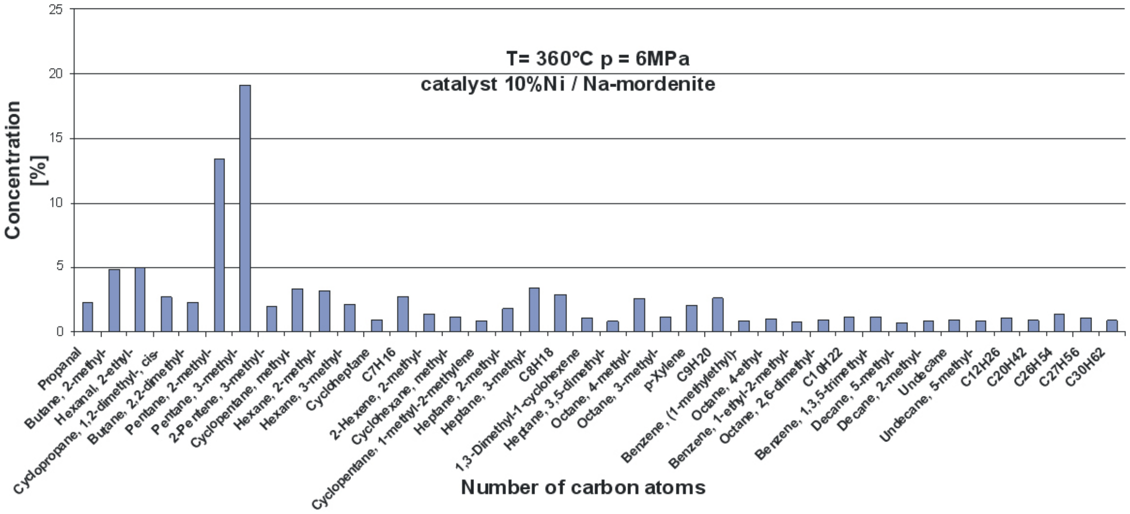

Figure 7. Hydroconversion of LTP56-H paraffin conducted for 4 h at 360°C over 10%Ni/Namordenite and in the pressure range 60-380 bar (paraffin dissolved with hexane, catalyst after reduction at 400°C in pure hydrogen for 2 h).

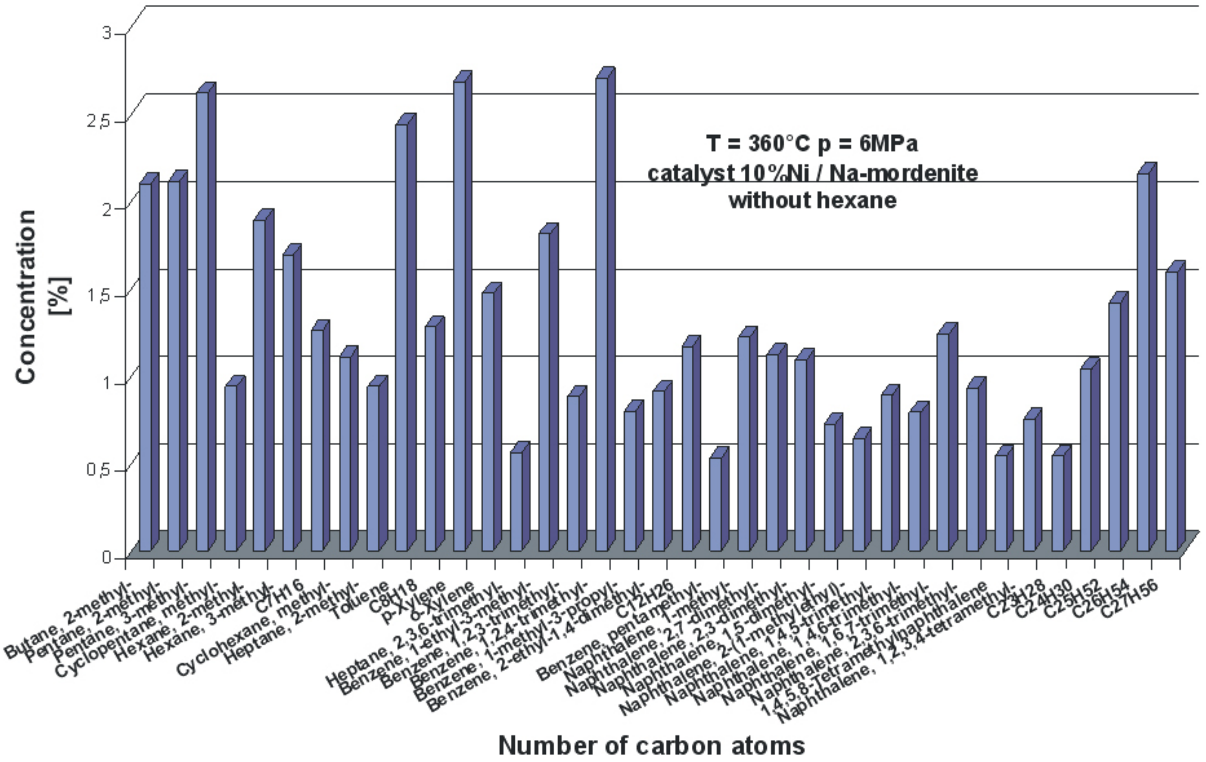

Figure 8. Hydroconversion of LTP56-H paraffin conducted for 4 h at 360°C over 10%Ni/Namordenite and in the pressure range 60-380 bar (without hexane, catalyst after reduction at 400°C in pure hydrogen for 2 h).

Table 2. The effects of none-catalytic thermal treatment and reaction conditions (solvent) on the selectivity of liquefaction LTP56-H paraffin process carried out over Ni/Na-mordenite catalysts (paraffin : hexane weight ratio = 1:3, g LTP56-H/g catalyst = 3, time = 4 h).

Catalyst	Temperature [°C]	P [Mpa]	Conversion [%]	Liquid Product Yield [%]		
				C_5-C_9	C_{10}-C_{19}	>C_{19}
No catalyst	380	12	33	9	14	77
10%Ni/Na-mordenite	360	6	97	85.5	10	4.5
10%Ni/Na-mordenite without hexane	360	6	100	56	26	18

4. Conclusions

The effect of catalytic treatment and application of solvent during hydroconverion of LTP56-H paraffin was studied in this work. The results showed that the Ni/Na-mordenite system is a promising catalyst for paraffin liquefaction, and enables the conversion of paraffin to liquid fuels. The product distribution strongly depends on the presence of a solvent. Application of solvent during hydroconverion of paraffin (hexane) causes the formation of mainly craking and hydroisomerization products. Furthermore, it can be concluded that the acid strength of nickel/Na-mordenite catalysts increases with a decrease in metal content.

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