Research Article

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The mesoporous aluminosilicate application as support for bifunctional catalysts for \( n \)-hexadecane hydroconversion

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Abstract: Mesoporous aluminosilicate (MAS) and bifunctional catalysts based on it were synthesized. The MAS synthesis is based on the method of copolycondensation of silicon and aluminum sources in the presence of alcohol. Hexadecylamine was used as a template for the formation of a porous structure. The catalysts were characterized by X-ray diffraction, Brunauer–Emmett–Teller, temperature-programmed desorption of ammonia, hydrogen-temperature programmed reduction, Fourier transform infrared spectroscopy, and diffuse reflectance infrared Fourier transform spectroscopic methods. The catalytic activity of Ni/MAS-H-bentonite and Mo/MAS-H-bentonite was investigated during the hydroconversion of \( n \)-hexadecane. It has been shown that a sample promoted with molybdenum and nickel based on MAS has the high activity and selectivity in the process of \( n \)-hexadecane hydroisomerization under optimal conditions (320°C, atm pressure).

Keywords: hydroisomerization, textural properties, Ni or Mo catalysts, acidity

1 Introduction

The attention of many scientists is focused on the investigation of mesoporous materials, which are promising components of industrial heterogeneous catalysts [1,2]. A major breakthrough in this area was made by the Mobile researchers [3], who described the synthesis of the ordered mesoporous aluminosilicates (MASs) in 1990. The method is based on the sol–gel synthesis of silicon dioxide solids and the use of long-chain surfactants’ self-assembling properties [3] in this synthesis. The great practical significance of Mobile studies is also confirmed by the fact that mesoporous materials which contain exclusively silicon have a chemically inert silicate framework and, therefore, do not contain acid sites [4]. And the introduction of aluminum into the framework of mesoporous materials made it possible to use regular porous structures. Also, along with it, it made it possible to carry out reactions with larger molecules due to specially selected porosity, much higher than that of zeolites and zeotypes [3]. It should be noted that a number of microporous materials, such as ZSM-22, ZSM-23, ZSM-48, and SAPO-11, were studied as functional supports for hydroisomerization catalysts. But because zeolite materials have diffusion limitations, mesoporous materials can be expected to solve this problem [5–10]. Mesopores, in comparison with micropores, provide faster mass transfer and perform the role of “molecular highways.” Intracrystalline or “configurational” diffusion of molecules in the pores of a zeolite is slow, and the diffusion coefficient is from \( 10^{-8} \) to \( 10^{-20} \, \text{m}^2/\text{g} \), which is about 10 orders of magnitude lower than the coefficient of diffusion mass transfer. Only a part of the zeolite is adsorptive and catalytically effective due to limited diffusion in micropores. Transport restrictions negatively affect both the activity and the selectivity of adsorbents and catalysts and shorten their service life. One of the vectors for solving this problem is shortening the diffusion path or...
increasing the diffusion efficiency in pores. This can be successfully implemented using mesoporous molecular sieves [11].

Since the priority direction of the use of MASs is in the oil industry, particularly the processes of isomerization and cracking of n-alkanes, a necessary condition for the successful operation of the catalyst is the combination of its acidic and metallic functions [3,12–15]. A worthy solution is the synthesis of bifunctional catalysts – acidity, porosity, and specific surface area (SSA). A second solution is a balance between acidic and metallic functions, which can be varied at the stage of synthesis by modifying the finished materials [16].

For example, the use of ionic surfactants as a structure-forming agent leads to the synthesis of MASs with a large SSA (up to 1,100 m²/g and pore size in the range from 20 to 100 Å and more) [17,18]. At the same time, the use of nonionic surfactants as a template makes it possible to obtain materials with pore size up to 500 Å. This exceeds the size of the molecules of most substances contained in petroleum feedstock [19]. In this regard, the use of nonionic surfactants as templates is of greatest interest for petrochemistry and oil refining. Materials synthesized on the basis of hexadecylamine have the highest SSA (up to 1,030 m²/g) in comparison with other widely used templates. For example, triblock copolymers of polyethylene and polypropylene oxide are only up to 750 m²/g [19].

The strength of acid sites is also one of the important characteristics of bifunctional catalysts, as the best selectivity to isomers is provided by acid support which does not contain strong Brønsted acid sites, but only Lewis acid sites of medium strength [20].

Another important issue in the synthesis of mesostructured aluminosilicates is the silicon to the aluminum ratio (Si/Al). At the high content of introduced aluminum (up to 85% Al₂O₃), the obtained aluminosilicates retain the uniformity of the mesopore distribution. At the same time, with an increase in the Al₂O₃/SiO₂ ratio, the deposition of aluminosilicates becomes more difficult due to the formation of poorly soluble AL(OH)₃ [11]. In addition, it was found [15] that the most optimal Si/Al ratio is 10. Thus, MASs with a high aluminum content possess a higher SSA of 1,030 m²/g compared to samples with a Si/Al ratio of 20, 40 (673, 963 m²/g, respectively). Also, they provide higher selectivity in the process of n-dodecane hydroisomerization. For this reason, in the present work, Si/Al ratio of 10 was used during synthesis.

Platinum and palladium have become widespread as metal centers for bifunctional catalysts [21], which cannot be applied to Kazakhstan oil due to the high content of contact poisons in them. To resolve this issue, it is proposed to use catalysts promoted with Ni and Mo. This is due to the fact that catalysts based on them possess a high hydrogenating activity even with significant sulfur content in the feed.

Based on the foregoing, the choice of the optimal method and synthesis conditions for the preparation of bifunctional catalysts is an important and practically significant problem. The purpose of this work is to synthesize a new hydroisomerization catalyst with Ni, Mo based on MAS and study the hydroconversion of n-hexadecane with these catalysts.

2 Materials and methods

2.1 Synthesis of MAS

In order to synthesize (Figure 1) MAS, the method of tetraethylorthosilicate Si(OC₂H₅)₄ and secondary aluminum butoxide (sec-BuO)₃Al copolycondensation was used. In this method, hexadecylamine was used as a structure-forming template [22]. First of all, in the polypropylene glass supplied with a magnetic mixer and a dropping funnel, solution of (sec-BuO)₃Al was dissolved in i-PrOH. Further, tetraethylorthosilicate Si(OC₂H₅)₄ solution was added dropwise at intensive stirring. The distilled water was added dropwise to the stirred solution for 5 min, after which the resulting solution was mixed for 30 min. At the same time, hexadecylamine and isopropanol were directly placed into the polypropylene flask supplied with a mechanical mixer and a dropping funnel followed by stirring and heating to 75°C. Then after complete dissolution of surfactants, 100 mL of the distilled water was added to the flask. To the resulting thick homogeneous mass containing a surfactant solution, a solution of silicon and aluminum compounds mixture (solution A) was added in portions. Next, after adding water dropwise and stirring for 10 min, the resulting mixture was stirred for 6 h at room temperature. Then it was kept without stirring at room temperature for 20 h. Further, the precipitate was filtered on a Buchner funnel, dried at room temperature for 24 h, and then slowly heated in an oven to 110°C for 3 h. The dried sample was transferred to a muffle furnace and heated to 300°C at a heating rate of 3°C/min. Then, at this temperature, the sample was kept in a muffle furnace for 1 h and heated to 550°C at a rate of 3°C/min. At this temperature, the sample was calcined for 6 h. Then the temperature was increased to 600°C, and the sample was calcined for another 3 h with intensive air circulation.
2.2 Synthesis of bifunctional catalysts

The obtained sample of MAS became one of the components of the bifunctional catalyst carrier (the synthesis scheme is shown in Figure 2) and was placed in a porcelain cup together with bentonite from the Tagan field (East Kazakhstan region, Kazakhstan), which was used as a binding agent. The resulting mixture was gently crushed for 20 min. With stirring, a solution of 0.53 mL of concentrated nitric acid in 42 mL of water was gradually added and triturated for 30 min. Then it was triturated for 20 min by heating the mixture on a hot water bath. After the mixture became viscous and plastic, it was placed in an extruder, resulting in extrudates with a diameter of 0.2 mm. The extrudates were dried for 20 h at room temperature and divided into pieces of 3–4 mm long. They were then blow-dried for 2 h at 50°C, then 2 h at 80°C, 2 h at 110°C, and another 2 h at 140°C. Next, the dried extrudates were calcined in a muffle furnace in airflow at 550°C for 3 h. Synthesis of bifunctional monometallic catalysts, 5% Ni/MAS-H-bentonite, and 1% Mo/MAS-H-bentonite, was prepared using the wet impregnation technique. First of all, samples of the carrier in the form of extrudates were calcined for 2 h at a temperature of 380–400°C, then cooled to 200°C in a dry argon atmosphere. The calculated amount of nickel nitrate, Ni(NO₃)₂, which was used as a source of Ni, was added to the calcined sample with stirring. Further, the resulting solution was mixed at a frequency of 1 time in 10 min for 2 h. The resulting samples were dried at room temperature for 24 h. The dried samples were reduced in a flow of dry hydrogen at a temperature of 550°C for 5 h. Monometallic bifunctional catalyst (1% Mo/MAS-H-bentonite) was synthesized by the same procedure as 5% Ni/MAS-H-bentonite, with the condition of using ammonium molybdate (NH₄)₆Mo₇O₂₄·4H₂O as a precursor of the Mo source.

2.3 Characterization of the samples

The ordering of the porous structure of the synthesized materials was analyzed using the method of X-ray small-angle scattering. X-ray diffraction patterns were taken on a Rigaku D/MAX 2200 diffractometer with a Cu Kα radiation source.

The characteristics of the porous structures of the synthesized samples and the SSA were determined using the standard method of nitrogen adsorption/desorption using a Quantachrome Autosorb-6 sorptometer. The IR spectrum of the samples was obtained on a Thermo Nicolet 8700 FTIR spectrometer with a spectral resolution of 4 cm⁻¹.
Temperature-programmed desorption of ammonia (TPD-NH₃) was carried out on a USGA-101 unit (Russia). A weighed quantity of a sample (0.1 g, fraction 0.30–0.50 mm) was placed into a quartz reactor, calcined at 512°C in a helium flow (for 139 min, at the flow rate of 20 mL/min), and then cooled. The adsorption of ammonia (NH₃/N₂ ratio of 7 by volume, at the flow rate of 40 mL/min) was carried out at 102°C for 1 h, after which the system was purged with helium (for 60 min). TPD-NH₃ curves were recorded in helium flow (at the flow rate of 8 mL/min) from 60 to 600°C at a linear temperature rise rate of 8°C/min.

Hydrogen-temperature programmed reduction (H₂-TPR) was carried out on a USGA-101 unit (Russia), which is equipped with a gas treatment system, a flow-type reactor (inner diameter is 4 mm) with a tube furnace, and a thermal conductivity detector. The sample (100 mg, fraction 0.30–0.50 mm) was preliminarily purged with Ar at 480°C for 40 min, followed by cooling to 50°C, and then heated at a rate of 10°C/min from 50 to 950°C in a mixture flow with H₂/Ar ratio of 10 by volume at a feed rate of 30 cm³/min. The analysis of the gas mixture was carried out using a thermal conductivity detector.

The Lewis and Brønsted acid centers in the synthesized catalysts were determined using diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy on PerkinElmer Spectrum One instrument. Before these tests, samples were pretreated at a temperature of 110°C to remove water adsorbed on acidic sites. After pyridine adsorption, the samples were dried at a temperature of 40°C, before analysis of DRIFT. The background spectrum was recorded using KBr. The spectra obtained after desorption of pyridine were subtracted from those measured before the adsorption of pyridine (fresh samples) to determine the bands relative to the Lewis and Brønsted acidic centers.

2.4 Hydroisomerization process of n-hexadecane

Pilot studies on testing were carried out on the installation of flowing type (Figure 3) with fixed-bed catalyst, in hydrogen current at a temperature interval of 280–340°C; fresh feed rate of 0.8–0.9 mL/min. The H₂:feed volume ratio of 100 was controlled with the help of a flowmeter. The catalyst (3) was placed in the quartz reactor (2) 500 mm long and with an internal diameter of 11 mm. Mass of the catalyst was 2.5 g and 3–4 mm long in length with a diameter of 0.2 mm, layer height ~ 80 mm. The raw materials with a pump for feeding liquid raw materials (1) came to the reactor and warmed by the furnace (4). Temperature in the reactor was installed with the help of a temperature regulator (5) and measured with a thermocouple (6). Liquid products of the reaction were collected in the receiver tank (7) supplied with the water direct...
For the prevention of products carried over by a hydrogen stream, after the refrigerator, a glass trap was installed with the cooling mixture (ice:salt = 3:1). Gaseous products of the reaction were collected in the gasometer. Hydrogen was given from a balloon through a reducer. The consumption of gas was regulated by the fine adjustment valve and measured with a flowmeter. Further hydrogen through a bottle with calcium chloride, for drying, came to the reactor. Purity degree of hydrogen is of 99.9%. Duration of experiments was varied from 40 min to 1 h. Then cooling of installation in hydrogen current was carried out. The liquid products, which were collected in a flask, weighed on scales with an accuracy up to 0.01. In order to study the activity of the synthesized catalysts, \( n \)-hexadecane was used as a model compound, as it is a part of the diesel fraction. Analysis of liquid products was carried out on the “Crystal 5000” chromatograph with linear programming of the temperature.

### 3 Results and discussion

#### 3.1 Characterization of catalysts

The X-ray scattering method was used to confirm the mesoporosity and orderliness of the porous structure of the synthesized materials (Figure 4). The small-angle scattering X-ray pattern of the synthesized MAS shows two well-resolved peaks in the \( 2\theta \) region of 0.8 and 2.1°, which can be indexed as (100) and (200), respectively, which indicates the mesoporous structure of the synthesized aluminosilicate with a hexagonal arrangement of pores [23–25]. The intensity peak in the 2.1° region at the wavelength of the radiation used corresponds to an interplanar distance of 4.2 nm. Compared with the X-ray diffraction pattern of the synthesized aluminosilicate, diffraction peaks of the Ni and Mo promoted catalysts (Figure 5) appear at \( 2\theta \) values of \( \approx 20^\circ, 27^\circ, \) and \( 50^\circ \), which belong to Ni and Mo formed at high calcination temperatures.
The nitrogen adsorption/desorption isotherms on the synthesized samples belong to type IV according to the classification of Brunauer, Emmett, and Teller. The presence of a hysteresis loop in them is associated with capillary condensation occurring in the mesopores. However, they differ in the type of hysteresis loop (Figure 6). Hysteresis loop of the MAS sample belongs to the H1 type and indicates a narrow pore size distribution and ordered structure. While hysteresis loops of the bifunctional catalysts belong to the H4 type and indicate narrow slit-shaped pores [26]. The induced deformation of the ordered mesoporous structure of these samples is associated with the penetration of Ni and Mo ions into the pores. Also, the synthesized materials differ sharply in SSA, mean pore diameter, and pore volume (Table 1). For example, MAS and bifunctional catalysts (Ni/MAS-H-bentonite and Mo/MAS-H-bentonite) possess SSA of 511.0, 151.7, and 283.6 m²/g, respectively. A decrease in the SSA and pore volume indicates that some of the pores in the catalyst structure are closed by the metals – Ni and Mo. As shown in Figure 6, the pore size distribution of the support materials and catalysts impregnated with Ni and Mo was rather narrow. In the case of the promoted catalysts, the bidisperse pore size distribution was observed in the lower pore size range. According to the data shown in Figure 6, the maximum on the pore size distribution curve is observed at 3.5–4.2 nm for the studied samples. The average pore size for all three samples is due to the presence of a small number of micro- and macropores.

FTIR spectroscopy was used to study the retention of crystalline ordering in the synthesized MASs. FTIR spectra of synthesized samples in the range of 400–4,000 cm⁻¹ are shown in Figure 7. FTIR complements X-ray diffraction in the search for changes in crystallinity by comparing peak intensities in the range from 1,300 to 300 cm⁻¹ [27]. These bands are grouped into two types of vibrations of TO₄ tetrahedral units (where T = Al or Si): vibrations associated

![Figure 5: Wide-angle X-ray scattering of Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts.](image1)

![Figure 6: Nitrogen adsorption/desorption isotherms of support material (MAS) and Ni, Mo impregnated catalysts.](image2)

| Samples                  | SSA, m²/g | Pore volume, cm³/g | Mean pore diameter, nm |
|--------------------------|-----------|--------------------|------------------------|
| MAS                      | 511.0     | 1.469              | 3.82                   |
| 5% Ni/MAS-H-bentonite    | 151.7     | 0.3565             | 1.67                   |
| 1% Mo/MAS-H-bentonite    | 283.6     | 0.2166             | 2.17                   |
with bonds between TO$_4$ tetrahedra, which are therefore sensitive to structural changes, and vibrations of TO$_4$ tetrahedra, insensitive to structural changes. According to the data in Figure 7, the appearance of the band in the 1,059 cm$^{-1}$ region can be attributed to asymmetric stretching vibrations of Si–O and Al–O within tetrahedra. While, the bands in the regions of 750 and 800 cm$^{-1}$ in the spectra of the studied materials indicate crystalline ordering [28], i.e., apparently, this is due to the internal vibration of TO$_4$ tetrahedra containing Al and Si. The absorption band at 450 cm$^{-1}$ corresponds to the bending vibrations of SiO$_4$. It should be noted that the average intensity band at 550 cm$^{-1}$ is specific to the identification of crystalline aluminosilicates and which is related to the vibrations of alternating SiO$_4$ and AlO$_4$ tetrahedra included in the lattice of the aluminosilicate framework, is absent in the spectra of the synthesized aluminosilicate samples. Probably, this is due to the increased silicon content in the aluminosilicate. The peaks obtained at 1,620 cm$^{-1}$ were attributed to molecular water adsorbed on the oxide surface [30]. Of particular interest is the peak at 520 cm$^{-1}$, which can be attributed to the O–H and Ni–OH hydrogen bonds in the NiOOH phase [32].

The curves of temperature-programmed hydrogen reduction (TPR-H$_2$) of Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts are shown in Figure 8. The TPR profile of Ni/MAS-H-bentonite has seven peaks: 328, 472, 532, 683, 792, 840, and 858°C. The peak at around 328°C

![Figure 7: FTIR spectra of synthesized samples: MAS, Ni/MAS-bentonite, and Mo/MAS-bentonite bifunctional catalysts.](image1)

![Figure 8: Temperature-programmed hydrogen reduction (TPR-H$_2$) of Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts.](image2)
correlates to the reduction of free NiO on the catalyst support [33,34]. This reduction peak corresponds to the reduction of the NiO species, which has minimal or no interaction with the Al₂O₃ supports. Reduction peaks in the range of 450°C to about 800°C may be attributed to the strong interaction of NiO and alumina support. The formation of strongly interacting NiO–Al₂O₃ phase is observed in the region between 550 and 750°C [35,36]. The peak centered at 532°C relates to the reduction of Ni⁴⁺ to Ni⁰ [37] and to the reduction of monolayer nickel oxide species on the catalyst surface [38]. The peak centered at 683°C corresponds to the reduction of the nickel oxide species having weak interactions with the alumina support (NiO–Al₂O₃) [39]. The high reduction temperatures (683, 792°C) may indicate the presence of NiAl₂O₄ spinel, which is difficult to reduce and is associated with high reduction temperatures of 600–780°C [40,41]. The Ni-promoted sample also presents reduction peaks at 840 and 858°C. These high reduction temperatures are attributed to the reduction of Ni²⁺ to Ni, strongly interacting with the alumina support due to the metal alloy effect [33,42].

In the case of Mo/MAS-H-bentonite catalyst four peaks were observed at 544, 658, 688, and 814°C. The peak at 544°C is due to tetrahedral molybdenum species reduction MoO⁴⁺ → Mo⁰ [43,44]. The peak at 658°C is assigned to the reduction of the Mo⁵⁺ phase to Mo⁰ [45]. Another reduction peak (688 and 814°C) might be due to the reduction of molybdenum oxide (Mo⁶⁺) to metallic molybdenum (Mo⁰) [46].

In agreement with TPR investigations of Mo/ZSM-5 catalysts, the first peak (565°C) can be assigned to the reduction of two kinds of Mo⁶⁺ species to Mo⁵⁺. The first kind is located on the external surface of the zeolite and, hence, reducible more readily, whereas the second kind (658°C) associated with Brønsted acid sites in the zeolite is difficult to reduce. At the end of the TPR profile, the peak that appears with a maximum at 658°C is usually attributed to the reduction of Mo⁵⁺ to metallic Mo⁰ [47].

Although the TPR profiles suggest a reduction temperature of over 550°C, the temperature for the reduction of catalysts was limited at 550°C to avoid the strong interaction between metal and catalyst support according to the calcination temperature of the Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts.

The strength and concentration of acid–base centers in the aluminosilicate have a strong influence on the qualitative and quantitative composition of the reaction products. In this regard, the study of the acidic properties of catalysts on the basis of MASs is of great importance from the point of view of both elucidating the nature of their active sites and improving their selectivity by regulating their acidic function and developing new effective catalysts. The acid characteristics of the synthesized bifunctional catalysts were investigated by TPD-NH₃ and DRIFT methods.

Thermal desorption curves of ammonia for catalysts based on MASs are shown in Figure 9. The amount of desorbed ammonia for each temperature is shown in Table 2. From the analysis of the obtained profiles, it follows that both samples have one broad peak. However, the concentration and strength of the acid sites are completely different. If for the Ni/MAS-H-bentonite catalyst, the peak is observed in the range of 100–450°C, with a maximum at \( T_{\text{max}} = 193°C \), with a small shoulder at \( T_{2\text{max}} = 635°C \). Then for Mo/MAS-H-bentonite, the peak is observed at 100–400°C, with maxima at \( T_{\text{max}} = 193°C \), \( T_{2\text{max}} = 241°C \), and \( T_{3\text{max}} = 358°C \). Compared to the nickel-promoted catalyst sample in which strong acid sites are present in small amounts, the molybdenum-promoted catalyst is characterized by medium-strength acid sites responsible for catalytic isomerization.

To determine the relative strength of the Brønsted and Lewis acidic centers on the surface of MASs and bifunctional catalysts based on them used in this study, we analyzed DRIFT spectra of adsorbed pyridine samples (Figure 10). The absorption bands at 1,445, 1,490, and 1,595 cm⁻¹ are fixed on the studied samples. The observed bands at 1,445 and 1,595 cm⁻¹ in the spectra are explained

![Figure 9: TPD-NH₃ profiles of Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts.](image)

| Sample                  | Temperature (°C) | NH₃ amount (μmol/g) |
|-------------------------|------------------|---------------------|
| Ni/MAS-H-bentonite      | 193              | 357                 |
|                         | 635              | 14                  |
| Mo/MAS-H-bentonite      | 193              | 70                  |
|                         | 241              | 42                  |
by the presence of hydrogen-bonded pyridine adsorbed on sites of Lewis acids [48, 49]. The band observed at approximately 1,490 cm\(^{-1}\) is due to the adsorption of pyridine in both the Lewis and the Brønsted acid sites [50–53]. It is clear from the DRIFT spectra that the sample of the Mo/MAS-bentonite catalyst has a higher acidity compared to Ni/MAS-H-bentonite, which is in good agreement with the TPD-NH\(_3\) data. Thus, on the basis of the data obtained, it can be argued that catalysts based on MAS promoted with nickel and molybdenum differ in strength and in the concentration of acid sites. The strongest acid sites are characteristic of a catalyst sample based on MAS promoted with molybdenum ions.

### 3.2 Hydroisomerization of \(n\)-hexadecane

The results of catalytic hydroconversion of \(n\)-hexadecane on Ni/MAS-H-bentonite and Mo/MAS-H-bentonite catalysts are presented in Table 3. It was found that an increase in the reaction temperature from 280 to 340°C leads to an increase in conversion from 10–12 to 82%. It should be noted that temperature affects not only the overall conversion but also the distribution of the product. At low reaction temperatures of 280–320°C, the main direction of \(n\)-hexadecane transformation is the isomerization process. In addition, the isomeric structures of the hexadecane are obtained due to the isomerization process without the participation of cracking. When the temperature rises from 320 to 340°C, along with the isomerization reactions, cracking reactions are also observed. The highest yield of the target products (iso-C\(_{16}\)H\(_{34}\)) during hydroisomerization of \(n\)-hexadecane is observed on a sample of the Mo/MAS-H bentonite catalyst at a temperature of 320°C and is 46% by mass with a selectivity of 91% and on a Ni/MAS-H catalyst sample at a temperature of 320°C and is 44% by mass with a selectivity of 95%. Thus, it can be concluded that both catalysts have good activity and selectivity for hydroisomerization of \(n\)-hexadecane.

![Figure 10: DRIFT spectra of pyridine adsorbed MAS, Ni/MAS-bentonite, and Mo/MAS-bentonite bifunctional catalysts.](image)

| Catalyst          | Temperature (°C) | Conversion (%) | Hydroisomerization | Hydrocracking |
|-------------------|------------------|----------------|--------------------|---------------|
| Ni/MAS-H-bentonite| 280              | 12             | 10 83              | 0 2           |
|                   | 300              | 31             | 30 97              | 0 1           |
|                   | 320              | 44             | 42 95              | 1 1           |
|                   | 340              | 86             | 30 35              | 10 46         |
| Mo/MAS-H-bentonite| 280              | 10             | 10 100             | 0 0           |
|                   | 300              | 30             | 30 100             | 0 0           |
|                   | 320              | 42             | 42 91              | 1 3           |
|                   | 340              | 82             | 30 37              | 12 40         |

Table 3: Catalytic performance of Ni/MAS-bentonite and Mo/MAS-bentonite bifunctional catalysts based on MAS in the process of \(n\)-hexadecane hydroisomerization
In the process of higher \( n \)-paraffins hydroisomerization, coke deposits are formed on the catalyst surface, leading to a gradual decrease in its activity. Determining the time of stable operation of the catalyst in the reaction cycle and the total number of “reaction–regeneration” cycles is very important from the point of view of the practical use of catalytic systems. The stability of the operation of the Ni/MAS-bentonite and Mo/MAS-bentonite catalysts during the hydroisomerization of \( n \)-hexadecane was measured at 320°C and fresh feed rate of 0.8–0.9 mL/min. It has been established that as a result of continuous 10 h tests at 320°C, the activity of catalysts based on both Ni/MAS-bentonite and Mo/MAS-bentonite practically does not decrease.

4 Conclusion

Thus, an ordered MAS and bifunctional catalysts based on it were synthesized. Tetraethylorthosilicate and aluminum sec-butoxide were used as sources of silicon and aluminum, respectively. Hexadecylamine was used as a template. The synthesized samples were examined using various physicochemical methods of analysis. The presence of a mesoporous and ordered structure in the synthesized aluminosilicates is confirmed by the data of low-temperature nitrogen adsorption/desorption, X-ray diffraction, and FTIR. According to the data of DRIFT and TPD-NH\(_3\) analyses, it was shown that the surface of the synthesized materials mainly contains acid sites of medium strength. The presented results on the study of the activity of the catalysts showed how the promoting additives of the catalysts deposited on the synthesized aluminosilicate affect not only their physical and chemical properties but also their activity in the hydroconversion of \( n \)-hexadecane. The maximum yield of isoparaffins on the studied samples of Ni/MAS-bentonite and Mo/MAS-bentonite is 44–46 wt\%, with a selectivity of 91–95%. It has been established that as a result of continuous 10 h tests at 320°C, the activity of bifunctional catalysts practically does not decrease.

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