Characterization and catalytic activity of Ni/mesoporous aluminosilicate HMS and Mo/mesoporous aluminosilicate HMS in the conversion of n-hexadecane

Gulzira Vassilina [a], Kamilla Umbetkaliyeva [a,*], Nuray Oktar [b], Birce Pekmezci Karaman [b], Tursunay Vassilina [c]

[a] Al-Farabi Kazakh National University, SRI New Chemical Technologies and Materials, Almaty, Kazakhstan
[b] Department of Chemical Engineering, Gazi University, Ankara, Turkey
[c] Kazakh National Agrarian University, SRI New Chemical Technologies and Materials, Almaty, Kazakhstan

ARTICLE INFO

ABSTRACT

Mesoporous aluminosilicate HMS was synthesized and adopted as a support for Ni and Mo-containing catalysts. Characterization of various samples was performed through XRD and DRIFT techniques. Textural and morphological characteristics were examined using nitrogen adsorption/desorption isotherms. The presence of a mesoporous and ordered structure in the aluminosilicate and catalysts based on it is confirmed by the data of low-temperature adsorption/desorption of nitrogen and X-ray diffraction. A correlation was established between the structural, acidic and catalytic properties of HMS-based catalyst samples. The catalytic activity of Ni/HMS-H-bentonite and Mo/HMS-H-bentonite was investigated during the conversion of n-hexadecane. It was shown that the sample of molybdenum-promoted HMS-based catalyst possesses the highest activity and selectivity in the process of hydroisomerization of n-hexadecane under optimal conditions (320 °C, 1 h^{-1}). The yield of isoparaffins on this sample is 42 wt% with a selectivity of 91%.

1. Introduction

In 1959, hydrocracking, a new catalytic process, began to be used in the industrial practice of foreign refineries. The licensor of this process is Chevron. Both processes, hydroisomerization and hydrocracking of long-chain alkanes, play a key role in the petrochemical industry, in which heavy distillates and oil residues are converted into more valuable products, such as gasoline, jet fuel, other middle distillates and lubricating oils [1]. The branching of the alkanes chain during the process of hydroisomerization is one of the ways to increase the octane number of gasoline and improve the performance of diesel fuel at low temperatures [2,3]. This is especially true for Kazakhstan with a sharply continental climate and low air temperatures in winter, sometimes reaching even −50 °C. Indicators such as pour point, freezing point, viscosity and viscosity index are significantly improved with the introduction of side chains along linear hydrocarbon chains [2,3]. Today, about 90% of all industrial chemical products are produced using bifunctional catalysts [2-5]. This is also applicable to the process of hydroisomerization of diesel oil fractions, since the bifunctional catalyst allows combining the hydrogenating-dehydrogenating functions of metal centers and the isomerizing functions of acidic centers, which are responsible for the rearrangement of the carbenium ion [2,6].

Currently, in the oil refining industry of our Republic, mainly Pt-containing catalysts based on synthetic zeolites are used. A significant disadvantage of this type of catalysts is the diffusion limitations of the transport of large molecules in their porous system, leading to a decrease in the selectivity of the process for poly-branchedisoalkanes [2,6,7]. A solution to this problem can be found by creating catalysts based on mesostructured aluminosilicates, which make it possible to convert the higher normal alkanes that

make up the initial diesel fractions into branched isomeric hydrocarbons. As the acidic components of hydroisomerization catalysts, mesostructured aluminosilicates are of interest due to their structural features, since their pore size exceeds the size of most of the molecules that make up the feedstock. In addition, the acidity spectrum of mesoporous aluminosilicates can be varied both at the synthesis stage and by modifying already prepared materials [3,5,8–11]. In addition, platinum and palladium impart dehydrogenating properties to the catalysts, but they are not resistant to the toxic effect of contact poisons present in the diesel fraction. To address this issue, it is proposed to use catalysts promoted with metals such as Ni and Mo. This is due to the fact that the catalysts based on them have a high hydrogenating activity even with a significant sulfur content in the feedstock.

The aim of this work is a comparative analysis of bifunctional catalysts based on mesoporous aluminosilicate promoted with nickel and molybdenum during hydroisomerization of n-hexadecane.

2. Experimental part

In order to synthesize mesostructured aluminosilicates (HMS) with a high aluminum content, the copolycondensation method of $Si(OC_2H_5)_4$ tetraethylorthosilicate and aluminum secondary butoxide $(sec\text{-}BuO)_3Al$ were used [10,12]. In this method, hexadecylamine was used as a structure-forming template. The obtained sample became one of the components of the bifunctional catalyst carrier and was mixed with bentonite of the Tagan deposit (East Kazakhstan region), which was used as a binding agent (35% HMS and 65% H-bentonite). The synthesis of bifunctional monometal catalysts, 5% Ni/HMS-H-bentonite, and 1% Mo/HMS-H-bentonite, were prepared using wet impregnation techniques.

The characteristics of the porous structures of the synthesized samples and the surface area of the BET were determined using the standard method of nitrogen adsorption/desorption using a Quanta ChromeAutosorb-6 sorptometer.

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 K radiation source.

The Lewis/Brønsted acid centers in the synthesized catalysts were determined using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) on PerkinElmer Spectrum One instrument.

The process of catalytic conversion of n-hexadecane was carried out in a laboratory setup with a fixed-bed catalyst under hydrogen in the temperature range of 280–340 °C; feed rates were 1 h^{-1}, hydrogen/raw materials ratio equal to 1000 nm^3/m^3, hydrogen pressure in the reactor is of 3 MPa. Analysis of liquid products was carried out on the "Crystal 5000" chromatograph with linear programming of the temperature from 35 °C to 250 °C.

3. Results and discussion

Nitrogen adsorption/desorption isotherms on all the studied samples (Figs. 1 and 2) are of type IV according to the classification of Brunauer, Emmett and Teller, the presence of a hysteresis loop in it, as well as a narrow pore size distribution indicate their ordered pore structure in the mesoporous range [11]. As follows from the
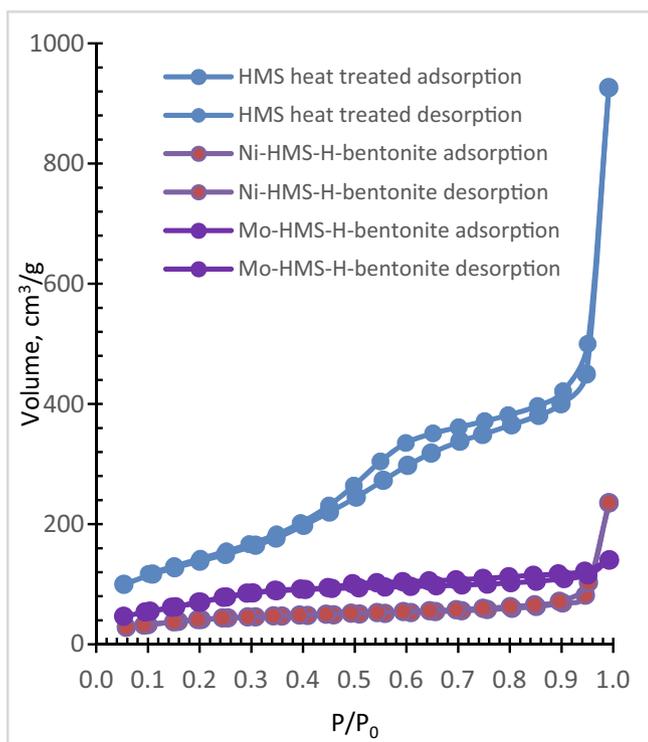
Fig. 1. Nitrogen adsorption/desorption isotherms of support material and Ni, Mo impregnated catalysts.
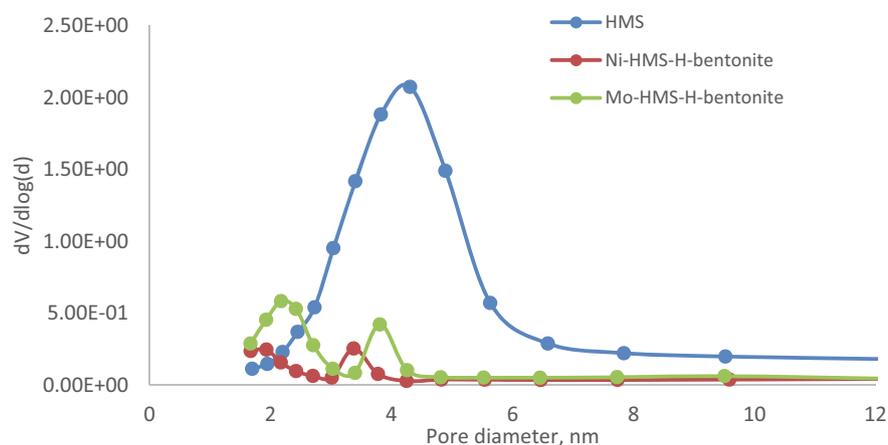
Fig. 2. Pore-size distributions of HMS, Ni/HMS-H-bentonite and Mo/HMS-H-bentonite.

Table 1
Physical properties of the catalysts.

Samples	SSA, m²/g	Pore Volume, cm³/g	Mean pore diameter, nm
HMS	511.0	1.469	3.82
5% Ni/HMS-H-bentonite	151.7	0.3565	1.67
1% Mo/HMS-H-bentonite	283.6	0.2166	2.17
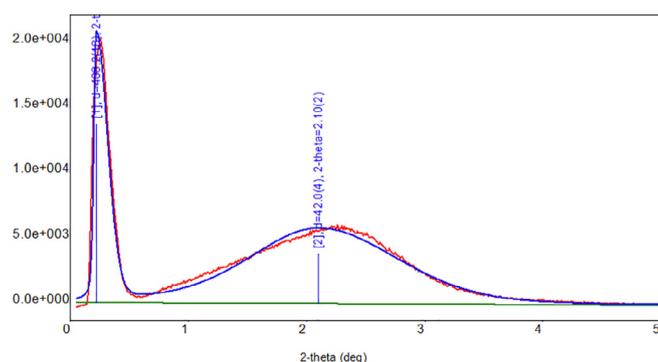
Fig. 3. Low angle XRD patterns of HMS support.

data in Fig. 1, the nitrogen adsorption/desorption isotherm for the HMS sample is characterized by a wider hysteresis loop, as compared to the Ni/HMS-H-bentonite and Mo/HMS-H-bentonite samples, which is probably due to the presence of larger pores in the HMS. The promotion of samples of catalysts based on mesoporous aluminosilicate by nickel and molybdenum leads to significant changes in the structural characteristics of the catalyst (Fig. 2). On the pore size distribution curve by effective diameters, three maxima are observed, one of which corresponds to mesoporous aluminosilicate, the second -to bentonite and the third - to the promoting additive. The surface area, average pore diameter and pore volume decreased from 511 m²/g to 151.7 m²/g, from 3.82 nm to 2.17 nm and from 1.47 cm³/ g to 0.21 cm³/g, correspondingly, as a result of impregnation of Ni and Mo (Table 1). These results showed that most of the Ni and Mo was penetrated into the mesopores and deposited on the pore surface of this catalyst. This was also facilitated by a shift in the pore size distribution towards smaller pores as a result of impregnation of Ni and Mo. These results showed that some nickel was deposited on the outer surface of the HMS for Ni/HMS-H-bentonite and Mo/HMS-H-bentonite.

To confirm the mesoporosity and ordering of the porous structure of the synthesized materials, the X-ray scattering method was used. As an example, Fig. 3 shows X-ray diffraction patterns of small-angle scattering of mesoporous samples of HMS support, according to which the presence of pronounced peaks in the range
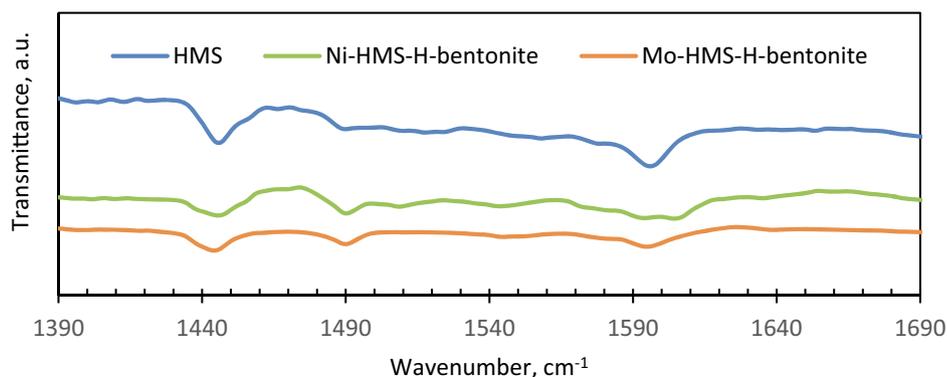
Fig. 4. DRIFTS spectra of pyridine adsorbed on mesoporous aluminosilicate and bifunctional catalysts based on it.
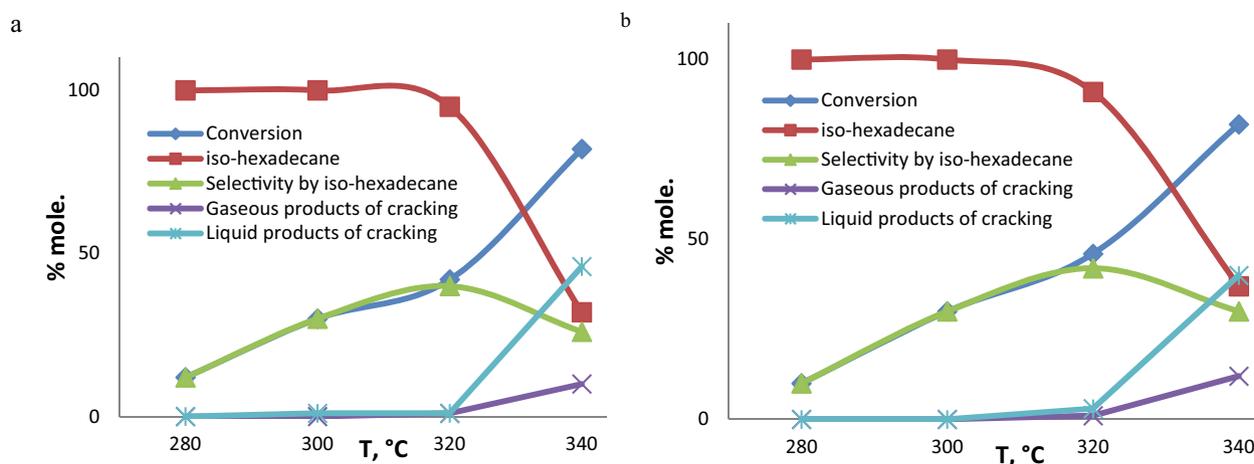
Fig. 5. Catalytic activity of (a) Ni/HMS-H-bentonite and (b) Mo/HMS-H-bentonite during the conversion of n-hexadecane.

of 2θ 2.1° angles indicates the presence of a mesoporous structure. For HMS and Mo/HMS-H-bentonite samples, the intensity peak is in the region of 2.1°, and for Ni/HMS-H-bentonite − 2.3°, which corresponds to an interplanar distance of 4.2 at the wavelength of the radiation used, and 3.9 nm, respectively.

To determine the relative strength of the Brønsted and Lewis acidic centers on the surface of mesoporous aluminosilicates and bifunctional catalysts based on them used in this study, we analyzed IR spectroscopy using diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) of adsorbed pyridine samples (Fig. 4). The absorption bands at 1445, 1490, and 1595 cm^{-1}are fixed on the studied samples. The observed bands at 1445 and 1595 cm^{-1}in the spectra are explained by the presence of hydrogen bonded pyridine adsorbed on sites of Lewis acids [13,14]. The band observed at approximately 1490 cm^{-1}is due to the adsorption of pyridine in both the Lewis and Brønsted acid sites. The introduction of Ni (5 wt%) and Mo (1 wt%) into the mesoporous aluminosilicate leads to a significant decrease in the intensity of the bands of 1445, 1490, and 1595 cm^{-1}, indicating that some of the alumina oxygen tetrahedra are blocked by the modifier. DRIFT spectra provide clear evidence that Mo/HMS-H-bentonite has a higher acidity than Ni/HMS-H-bentonite.

The catalytic conversion of n-hexadecane on (a) Ni/HMS-H-bentonite and (b) Mo/HMS-H-bentonite catalysts is shown in Fig. 5. From the obtained experimental data, it can be seen that, under conditions of low temperature aluminosilicate catalysis (320 °C), the basic direction of the hexadecane conversion is the isomerization process. It should also be noted that isomerized hexadecane structures are obtained due to the isomerization process, without the participation of cracking. When the temperature rises from 320 °C to 340 °C, along with isomerization reactions, the cracking reaction also proceeds. The highest yield of the target products (iso-$C_{16}H_{34}$) during hydroisomerization of n-hexadecane is observed on a sample of the catalyst Mo/HMS-H bentonite at a temperature of 320 °C and is 42 mass. % with a selectivity of 91%. Slightly low activity of the Ni/HMS-H-bentonite sample in the process under study is probably due to the low acidity necessary for hydroisomerization of n-hexadecane [15,16].

4. Conclusion

The ordered mesoporous HMS carrier was prepared using copolycondensation method. Nickel and molybdenum-containing catalysts deposited on a mesoporous aluminosilicate containing 5 wt% Ni and 1 wt% Mo were synthesized by wet impregnation method. The prepared samples were studied using various characterization methods, namely BET, nitrogen adsorption/desorption, XRD and DRIFT. The presence of a mesoporous and ordered structure in the aluminosilicate and catalysts based on it is confirmed by the data of low-temperature adsorption/desorption of nitrogen and X-ray diffraction. A correlation was established between the structural, acidic and catalytic properties of HMS-based catalyst samples. The catalytic activity of Ni/HMS-H-bentonite (a) and Mo/HMS-H-bentonite (b) was investigated during the conversion of n-hexadecane. It was shown that the highest activity and selectivity in the n-hexadecane hydroisomerization process under optimal conditions (320 °C, 1 h^{-1}) is possessed by a sample molybdenum-promoted HMS-based catalyst. The yield of isoparaffins on this sample is 42 wt% with a selectivity of 91%.

CRediT authorship contribution statement

Gulzira Vassilina: Supervision, Project administration, Conceptualization, Methodology, Writing - review & editing. **Kamilla Umbetkaliyeva:** Conceptualization, Writing - review & editing, Investigation, Formal analysis. **:** . **Nuray Oktar:** Formal analysis, Resources. **Birce Pekmezci Karaman:** Formal analysis, Resources. **Tursunay Vassilina:** Investigation, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] V.M. Benitez, J.C. Yori, J.M. Grau, C.L. Pieck, C.R. Vera, Energy Fuels 20 (2006) 422–426.
[2] M. Zhang, Y. Chen, L. Wang, Q. Zhang, C.-W. Tsang, C. Liang, Ind. Eng. Chem. Res. 55 (2016) 6069–6078.
[3] Y. Liu, T. Hanaoka, K. Murata, K. Sakanishi, Recent Progress in Mesostructured Materials, Elsevier, 2007, pp. 781-785.
[4] M. Shamzhy, M. Opanasenko, P. Concepcion, A. Martinez, Chem. Soc. Rev. 48 (2019) 1095–1149.
[5] M. Abdi-Khanghah, M. Adelizadeh, Z. Naserzadeh, Z. Zhang, Chin. J. Chem. Eng. 26 (2018) 1330–1339.
[6] A. Soualah, J.L. Lemberton, L. Pinard, M. Chater, P. Magnoux, K. Moljord, Appl. Catal., A: Gen. 336 (2008) 23–28.
[7] R. Henry, M. Tayakout-Fayolle, P. Afanasiev, C. Lorentz, G. Lapisardi, G. Pirngruber, Catal. Today 220–222 (2014) 159–167.
[8] G. MuthuKumaran, S. Garg, K. Soni, M. Kumar, J.K. Gupta, L.D. Sharma, K.S. Rama, Rao, G. MuraliDhar, Microporous Mesoporous Mater. 114 (2008) 103–109.
[9] A.V. Vutolkinaa, A.P. Glotova,b , A.V. Zaninaa , D.F. Makhmutova, A.L. Maximovc, S.V. Egazar'yantsa, E.A. Karakhanova, Catal. Today 329 (2019) 156-166.
[10] T. Chiranjeevi, G. MuthuKumaran, J.K. Gupta, G. MuraliDha, Thermochim. Acta 443 (2006) 87–92.
[11] R. Huirache-Acuna, B. Pawelec, C.V. Loricera, E.M. Rivera-Munoz, R. Nava, B. Torres, J.L.G. Fierro, Appl. Catal., A 125 (2012) 473–485.
[12] G. Vassilina, R. Moisa, T. Abildin, A. Khaiyrgeldinova, K. Umbetkalieva, 2016 International Conference on Computational Modeling, Simulation and Mathematics, Bangkok, Thailand 2016, pp. 308-311.
[13] J. Aguado, J.M. Escola, M.C. Castro, B. Paredes, Appl. Catal., A, Gen. 284 (2005) 47–57.
[14] B. Chakraborty, B. Viswanathan, Catal. Today 49 (1999) 253–260.
[15] G. Cordoba, R. Arroyo, J.L.G. Fierro, M. Viniegra, J. Solid State Chem. 123 (1996) 93–99.
[16] B. Mile, D. Stirling, M.A. Zammitt, A. Lovell, M.J. Webb, J. Catal. 114 (1998) 217–227.

Further Reading

[1] N. Alam, R. Mokaya, J. Mater. Chem. A. 3 (2015) 7799–7809.