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THE ROLE OF THE BINDER IN THE COMPOSITION OF CATALYSTS FOR THE HYDROISOMERIZATION PROCESS



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The authors of the publication synthesized bifunctional catalysts based on mesoporous aluminosilicates (MAS) with different binder contents (80 and 65%, respectively) in two ways: the first method consisted in mixing the synthesized aluminosilicate with preliminarily activated bentonite, which was then promoted. Whereas, according to the second method, the synthesized mesoporous aluminosilicate was first promoted, only then mixed with bentonite. The synthesis of bifunctional bimetallic catalysts was carried out using the wet impregnation technique. Acid and physicochemical characteristics were studied using the DRIFT method, TPD-NH₃ and the standard nitrogen adsorption/desorption method. It was found that the samples of catalysts with the ratio MAS:H-bentonite = 35:65, prepared according to the first method, have optimal acid characteristics and physicochemical properties.

KEY WORDS: mesoporous aluminosilicates, bifunctional catalysts, acid centers, acidity.

ГИДРОИЗОМЕРЛЕУ ПРОЦЕСІ ҮШІН КАТАЛИЗАТОРЛАРДЫҢ ҚҰРАМЫНДАҒЫ БАЙЛАНЫСТЫРҒЫШТЫҢ РӨЛІ

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Мақала авторлары мезокеукті алюмосиликатқа (MAS) негізделген бифункционалды катализаторларды екі жолмен синтездеді (80 және 65%): бірінші әдіс бойынша синтезделген алюмосиликат алдын-ала белсендірілген бентонитпен араластырылды, содан кейін промотирленді. Ал екінші әдіс бойынша синтезделген мезокеукті алюмосиликат промотирленіп, содан кейін бентонитпен араластырылды. Бифункционалды биметалдық катализаторлардың синтезі дымқыл сіңдіру әдісін қолдану арқылы жүзеге асырылды. Қышқылдық, физикалық және химиялық сипаттамалары DRIFT әдісі, TPD-NH₃ және азотты адсорбциялау/десорбциялаудың стандартты әдісі арқылы зерттелді. Бірінші әдіспен дайындалған MAS:H-bentonite = 35:65 қатынасы бар катализатор үлгілері оңтайлы қышқылдық сипаттамаларға және физика-химиялық қасиеттерге ие екендігі анықталды.

ТҮЙІН СӨЗДЕР: мезоқұрылымды алюмосиликаттар, бифункционалды катализаторлар, қышқылдық орталықтар, қышқылдық.

РОЛЬ СВЯЗУЮЩЕГО В СОСТАВЕ КАТАЛИЗАТОРОВ ДЛЯ ПРОЦЕССА ГИДРОИЗОМЕРИЗАЦИИ

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Синтезированы бифункциональные катализаторы на основе мезопористых алюмосилкатов (MAS) с разным содержанием связующего (80 и 65 %, соответственно) двумя способами: первый способ заключался в смешивании синтезированного алюмосиликата с предварительно активированным бентонитом, который потом был подвергнут промотированию. Тогда как, по второму способу сначала синтезированный мезопористый алюмосиликат промотировали, только потом смешивали с бентонитом. Синтез бифункциональных биметаллических катализаторов были осуществлен с использованием методики влажной пропитки. Кислотные и физическо-химические характеристики были

изучены с использованием метода DRIFT, TPD-NH₃ и стандартного метода адсорбции/десорбции азота. Было установлено, что оптимальными кислотными характеристиками и физико-химическими свойствами обладают образцы катализаторов с соотношением MAS:H-bentonite = 35:65, приготовленные по первому способу.

КЛЮЧЕВЫЕ СЛОВА: мезоструктурированные алюмосиликаты, бифункциональные катализаторы, кислотные центры, кислотность.

Introduction

Today, the hydroisomerization process is more efficient, predictable, and popular than dewaxing [1,2]. Hydroisomerization is actively used for the synthesis of fuel with a high octane number, diesel fuel with a low pour point, as well as to increase the viscosity of paraffinic raw materials, which is associated with the process of isodewaxing [3]. This option of processing raw materials is much better suited for industry than the usual removal of n-alkanes from the mixture, which leads to potential loss of raw materials and an increase in the mass fraction of waste.

Bifunctional catalysts based on weakly acidic supports are suitable for the hydroisomerization of long-chain n-alkanes. Reactions involving bifunctional catalysts on such supports have good selectivity towards hydroisomerization, minimizing or eliminating the accompanying aromatization and cracking reactions. The catalysts themselves lose very little activity during regeneration, which prolongs their service life.

In this connection, the synthesis of bifunctional catalysts has become a worthy solution - acidity, porosity, specific surface area and balance between acidic and metallic functions of which can be varied at the stage of synthesis, as well as by modifying finished materials [4].

It was found [5] that the acid support, which provides the best selectivity for isomers, does not contain strong Brønsted acid sites, but only Lewis acid sites of medium strength. At the same time the catalyst with more Brønsted acid sites produced a higher amount of cracked products [6]. Li et al. [7] reported that the Al-MCF-17 support contains relatively no strong Brønsted acid sites and provides high isomerization selectivity via dehydrogenation on platinum and subsequent isomerization on medium strength Lewis sites and weak/medium strength Brønsted sites.

Based on the foregoing, the choice of the best method and synthesis conditions for obtaining bifunctional catalysts with the required acid characteristics and optimal values of the specific surface area, pore diameter and porosity is an important and practically significant task. However, current research in this field has focused on the acid characteristics of carriers such as zeolites, aluminosilicates, aluminophosphates, etc., without taking into account the fact that the binder can also have a significant effect on the strength of the acid sites of catalysts.

This work is devoted to the study of the influence of the introduction of a binder into the composition of the support on the acid characteristics and physicochemical properties of catalysts for the hydroisomerization process.

2. Experimental section

Material Synthesis

We utilized previous reported literature procedures and practices for synthesizing mesoporous aluminosilicates [8]. The synthesized sample of mesoporous aluminosilicate (MAS) became one of the components of the support of the bifunctional catalyst and was

placed in a porcelain bowl together with bentonite from the Tagan field (East Kazakhstan region, Kazakhstan). Two methods were used to synthesize bifunctional catalysts based on mesoporous aluminosilicates (MAS) with different contents of the binder, pre-activated bentonite clay, in the MAS:H-bentonite ratio of 20:80; 35:65. The first method consisted in mixing the synthesized aluminosilicate with preliminarily activated bentonite, which was then promoted. Whereas, according to the second method, the synthesized mesoporous aluminosilicate was first promoted, only then mixed with bentonite. The synthesis of bifunctional bimetallic catalysts was carried out using the wet impregnation technique. Ni and Mo sources were nickel carbonate NiCO_3 and ammonium molybdate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, respectively. Thus, 4 bifunctional bimetallic catalysts were synthesized: Ni-Mo/MAS – H-bentonite-1 (20:80), Ni-Mo/MAS – H-bentonite-1 (35:65), Ni-Mo/MAS – H-bentonite-2 (20:80), Ni-Mo/MAS – H-bentonite-2 (35:65). The numbers in the name of catalysts indicate the synthesis method (first or second), and the numbers in parentheses indicate the MAS:H-bentonite ratio.

Characterization of catalysts

The concentration and strength of acid sites was investigated using the method of temperature-programmed desorption of ammonia (TPD- NH_3). TPD- NH_3 was carried out on a USGA-101 unit. A sample weighing 0.1 g (fraction 0.30–0.50 mm) was placed in a quartz reactor, calcined at 512°C in a helium flow (139 min, 20 ml/min), and then cooled. Ammonia adsorption (7 vol.% NH_3 in N_2 , rate 40 ml/min) was carried out at 102°C for 1 h, after which the system was purged with helium (60 min). The TPD curves were recorded in a helium flow (8 ml/min) from 60 to 600 °C at a linear temperature rise rate of 8 °C/min.

Determination of Lewis/Brønsted acid sites in the synthesized catalysts was carried out using Diffuse reflectance infrared Fourier transform spectroscopy (DRIFT) on JASKO FT-IR-4700 spectrometer. Prior to these tests, the samples were pre-treated at 110° C to remove water adsorbed on the acidic sites. After pyridine adsorption, the samples were dried at 40°C, before DRIFT analysis, the background spectrum was recorded with KBr. The spectra obtained after pyridine desorption were subtracted from those measured before pyridine adsorption (fresh samples) to determine the bands relative to Lewis and Brønsted acid sites.

The specific surface area, volume and average pore diameter of the synthesized materials were studied using a standard nitrogen adsorption/desorption method using a Quanta ChromeAutosorb-6 sorbtometer.

3. Results and Discussion

The strength and concentration of acid-base sites in aluminosilicates have a strong influence on the qualitative and quantitative composition of the reaction products. In this regard, the study of the acid properties of mesoporous aluminosilicate catalysts is of great importance in terms of both elucidating the nature of their active centers and improving their selectivity by controlling their acid function and developing new efficient catalysts. The acid characteristics of the synthesized bifunctional catalysts were studied by the TPD- NH_3 method (*Figure 1* and *Table 1*).

According to *Figure 1* and *Table 1*, the peak below 190 °C was attributed to the desorption of ammonia adsorbed on weak acid sites. The range of 250-400 °C is intended for the desorption of ammonia adsorbed on acid sites of medium strength. The high temperature peak above 400°C corresponds to strong acid sites.

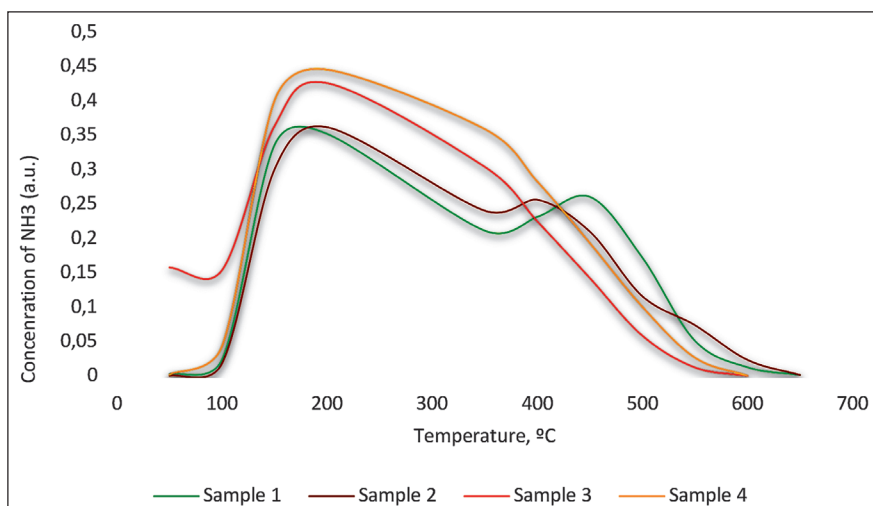


Figure 1 – TPD-NH₃ curves of synthesized bifunctional catalysts based on mesoporous aluminosilicates

Table 1 – Concentration and strength of acid sites of synthesized bifunctional catalysts based on mesoporous aluminosilicates

Nº of a sample	Sample	Temperature, °C	Amount of NH ₃ , µmol/g
1	Ni-Mo/MAS – H-bentonite-1 (20:80)	183	267
		452	153
2	Ni-Mo/MAS – H-bentonite-2 (20:80)	199	258
		398	141
3	Ni-Mo/MAS – H-bentonite-1 (35:65)	195	405
4	Ni-Mo/MAS – H-bentonite-2 (35:65)	198	491
		372	7

From the results of TPD-NH₃, it is shown that the concentration and strength of acid sites is affected by the content of activated bentonite. Reducing the content of pre-activated bentonite leads to a gradual decrease in the total acidity of the samples. For samples of catalysts supported by MAS-H-bentonite, where the content of bentonite is 65 wt.% is characterized by the presence of a larger number of weak acid centers. Compared to a sample of a catalyst with a high content of bentonite, in which there are strongly acid sites, a catalyst containing 65 wt.% bentonite is characterized by medium strength acid sites responsible for catalytic isomerization.

However, for an objective assessment of the acid characteristics of the synthesized catalysts, it is also necessary to determine the strength of the Brønsted and Lewis acid sites. For this purpose DRIFT analysis was carried out. DRIFT spectra of adsorbed pyridine on bifunctional catalysts are shown in Figure 2.

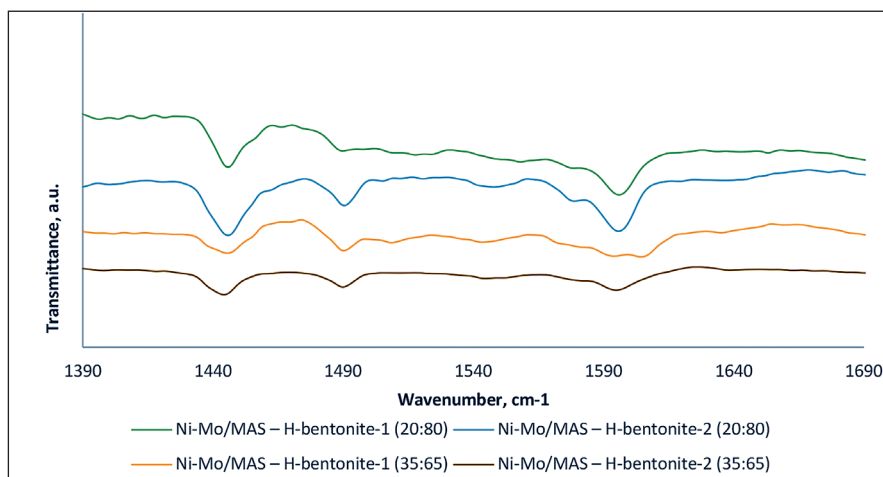


Figure 2 – DRIFT spectra of pyridine adsorbed on bifunctional catalysts

It can be seen from the data in *Figure 2* that absorption bands at 1445, 1490 and 1595 cm^{-1} are recorded on the studied samples. The observed bands at 1445 and 1595 cm^{-1} in the spectra are explained by the presence of hydrogen-bound pyridine adsorbed on Lewis acid sites [9, 10]. The band observed at about 1490 cm^{-1} is due to the adsorption of pyridine, both on the Lewis sites and on the Brønsted acid sites. According to the DRIFT analysis data, it was shown that Lewis acid sites are mainly present on the surface of the synthesized materials. However, the resulting peaks differ in intensity. Thus, the samples of bifunctional catalysts with the MAS:H-bentonite ratio of 20:80, regardless of the method of preparation, exhibit more pronounced and intense absorption bands in the range of 1445 and 1595 cm^{-1} than the samples of catalysts with the MAS:H-bentonite ratio of 35:65, which indicates the presence of stronger Lewis acid sites.

Thus, based on the studies performed, it can be concluded that the acidity of the catalyst is affected not only by the mesoporous aluminosilicate, but also by the binding agent, pre-activated bentonite. Samples of catalysts with the MAS:H-bentonite ratio of 35:65 have optimal acid characteristics - the higher the content of bentonite in the synthesized catalysts, the greater the strength and concentration of acid sites, which is not favorable for the hydroisomerization process. The catalytic efficiency of the developed catalysts was considered and confirmed in earlier studies by the authors of this article [8].

In the case of the acidic characteristics of the catalyst, the MAS: H-bentonite ratio had a significant effect, while the preparation method (first or second) influenced the specific surface area, volume and average pore diameter of the synthesized materials, which are shown in *Table 2*.


According to *table 2*, a decrease in the SSA and porosity of the catalysts synthesized by method 2 was observed. This is probably due to the partial blocking of the aluminosilicate pore system by promoting additives. A slight decrease in the surface area and pore volume indicates that part of the pores in the catalyst structure is closed by Ni and Mo metals. The average pore size of all samples is in the mesopore range. Thus, samples of catalysts synthesized by the first method (preliminary mixing of aluminosilicate with bentonite, followed by promotion) is a more preferable method for preparing bifunctional catalysts.

Table 2 – Physical properties of the samples

Nº of a sample	Catalyst	SSA, m ² /g	Porosity, cm ³ /g	Average pore size, nm
1	Ni-Mo/MAS – H-bentonite-1 (20:80)	214,9442	0,2489	3,9 и 6,2
2	Ni-Mo/MAS – H-bentonite-2 (20:80)	161,6055	0,1580	3,5 и 3,8
3	Ni-Mo/MAS – H-bentonite-1 (35:65)	375,1274	0,3523	2,9 и 3,5
4	Ni-Mo/MAS – H-bentonite-2 (35:65)	265,3722	0,2567	3,45 и 3,8

4. Conclusions

Based on the conducted studies, it can be concluded that the acidity of the catalyst is affected not only by the mesoporous aluminosilicate, but also by the binding agent, pre-activated bentonite. Samples of catalysts with the MAS:H-bentonite ratio of 35:65 with medium-strength acid sites, have optimal acid characteristics. Also, the catalysts prepared by the first method have the best physical characteristics (large specific surface area and porosity). As part of the research, a sample of the Ni-Mo/MAS - H-bentonite-1 (35:65) catalyst was synthesized in the most optimal way and has acidic and physico-chemical characteristics that are most beneficial for the hydroisomerization process.

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