The study of using HZSM-5/silicate mesopores in the catalytic reaction of n-heptane isomerization

M. H. Peyrovi[a], B. Derakhshan[a] and N. Parsafard[b*]

[a]Department of Physical and Computational Chemistry, Faculty of Chemistry Science and Petroleum, Shahid Beheshti University, Tehran, Iran, 1983963113
[b]Department of Applied Chemistry, Kosar University of Bojnord, North Khorasan, Iran

C H R O N I C L E	A B S T R A C T
	Micro/mesopore composite catalysts containing platinum with HZSM-5 zeolite and three different silicate mesopores (SBA-3, KIT-6, and KCC-1) were prepared to investigate the influence of different silicate mesopores in the isomerization reaction of n-heptane at the temperature of 200-350 °C The structural characteristics and morphology of the prepared catalysts were studied by various methods such as XRD, FT-IR, N2 adsorption-desorption, XRF, and SEM. The obtained results indicate that the prepared catalysts have high conversion and high selectivity of multi-branched isomers compared to mono-branched isomers and low development of aromatic compounds. The most suitable results and selectivity were obtained in the n-heptane isomerization reaction related to the Pt/HZSM-5-SBA-3 catalyst.

1. Introduction

The isomerization process is a process of converting linear paraffins to their branched isomers by selecting a suitable acid catalyst. This reaction is performed with bifunctional catalysts containing noble metal deposited on a solid containing acidic sites.[1, 2] In the past, there were various techniques[3] to increase the octane number of gasoline, including the application of tetra ethyl lead, as well as oxygenated compounds, such as tert-butyl ether and methanol, which are now banned owing to their environmental problems. Increasing the octane number of light naphtha using isomerization reaction is one of the known techniques to improve fuel quality, which the mentioned bans have growing interest in it.[3]

Further limits on the amount of aromatic substances, such as benzene in gasoline, have led to greater interest in the isomerization process of linear alkanes. The existence of benzene in the final gasoline produces carcinogens during combustion. One way to reduce benzene is to remove the hydrocarbons that make up benzene, such as hexane, and to use long chain alkanes such as n-heptane.[4] In addition, n-heptane with zero octane can be changed up to 42-112 by isomerization reaction.[5] Also, the increasing demand of the industry to produce high-octane gasoline has led to the research and development of efficient catalysts for n-heptane isomerization.[6]

Calemma and co-workers have investigated the influence of paraffin chain length on the isomerization reaction. They concluded that the cracking process rises with increasing carbon chain length.[7] Therefore, it is desirable to design catalysts that the selectivity of the isomerization reaction is higher than the cracking reaction.[1]

* Corresponding author. Tel.: +98 58 32258865; Fax: +98 58 32427408
E-mail address n-parsafard@kub.ac.ir (N. Parsafard)

A variety of catalysts have been investigated to perform the isomerization reaction, such as Pt on MOR,[8] Beta,[9] SAPO-11,[10] ZSM-5,[11] and ZrO$_2$.[12]

Although zeolite catalysts have good properties, including large internal surface and crystallinity, etc., but also have limitations. The micropores of zeolites cause diffusion constraints for large molecules. As a result, it reduces the efficiency of the zeolite catalyst. Recently, more attention has been given to the synthesis of micro/mesoporous composite materials.[13] By adding a mesoporous phase to microporous zeolites, micro/mesoporous composites are formed with a hierarchical pore structure, which reduces diffusion limitations. Therefore, the application of micro/mesoporous catalysts can be suitable for n-heptane isomerization.[14]

Various micro/meso composite materials have been reported so far. HZSM-5-HMS,[15] BETA-KIT-6,[16] and BETA-MCM-41,[17] are some of the composites that have been reported as catalytic supports for the n-heptane isomerization reaction. But most of them have disadvantages.
The HZSM-5 catalyst has a high external surface area, a large volume of pores with a small diameter, and good stability of pores. But it has a high selectivity for the development of aromatics. Due to the high acidity of the active pore surfaces, carbon is deposited over its active sites.[18]

The isomerization reaction of n-heptane was discussed in our previous works. These works included the analysis of Pt/HZSM-5(x)-HMS composites and the influence of different ratios of HZSM-5 and HMS,[15] and also in the later works, the influence of HZSM-5 composite with different mesopores of SBA-15, FSM-16 and MCM-41.[19] Now, in this research, which is a continuation of the previous works, we synthesize new composite catalysts from zeolites HZSM-5 and various silicate mesopores. In this work, we synthesize new composite catalysts from HZSM-5 zeolites and different silicate mesopores. The aim of this work is to improve the performance of micro/mesoporous composites, including the decrease in aromatic compounds and the increase of multi-branched isomers compared to mono-branched that we achieved this goal.

2. Results and Discussion
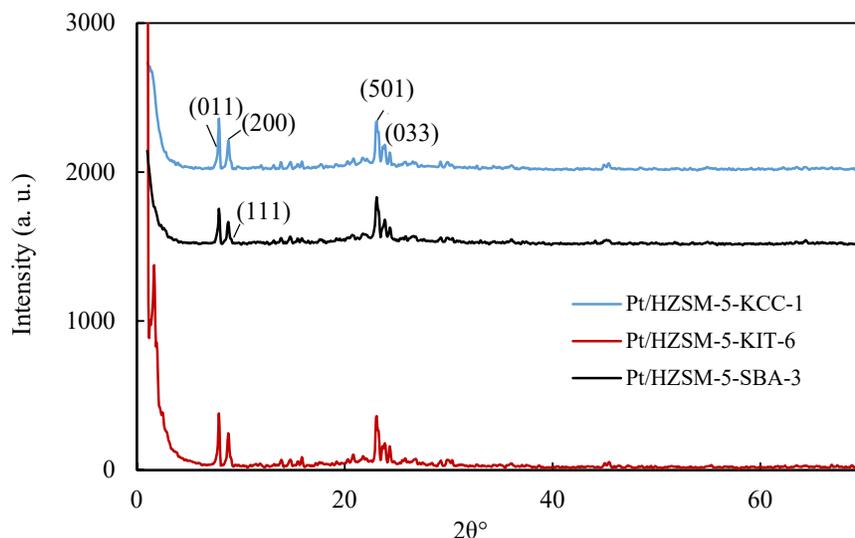
Fig. 1. XRD patterns of the prepared platinum catalysts in the range of 2θ=1-70°.

Fig. 1 shows the powder XRD patterns of platinated catalysts after calcination. As shown in this Figure, sharp peaks in the range of 2θ=7-11° and 2θ=22-25° as well as a large number of fine peaks in the 2θ= 30-65° range, are related to HZSM-5 zeolite. Platinum peaks should be seen in the 40-80° range, but the synthesized catalysts do not show a separate peak for the loaded metal, which has been added owing to the small amount of metal. Basically, the addition of the metal increases the irregularity and flattening of the peaks and shortening the height of the main peak.[15,20] The sharp peak is observed in the low-angle region (2θ = 1.09°), indicates the three-dimensional and regular structure of mesoporous particles. [15,20]

The FT-IR spectra are shown in **Fig. 2**. The peak in the area of 550-555 cm^{-1} indicates the existence of 5- and 6-membered rings of T-O-T (T = Si or Al) HZSM-5 zeolite. The peak in the range 450-460 cm^{-1} can be a sign of tetrahedral Si-O bending vibrations. The peaks in 960-980 cm^{-1} and 800-815 cm^{-1} are related to the symmetric and asymmetric stretching vibrations of Si – O – Si bonds. There are a number of peaks at the range of 450-460 cm^{-1}, 1080-1090 cm^{-1} and 1230-1240 cm^{-1}, which indicate the asymmetric bending and stretching vibrations of Si-O-Si composite catalysts. All spectra in the 1640-1635 cm^{-1} region have an average peak that indicates the bending vibrations of the hydroxyl group of the adsorbed water on the surface of the catalysts. The peak observed in the region of 3636-3454 cm^{-1} is connected to the stretching vibrations of the terminal Si – OH groups and the OH group of water molecules adsorbed by the catalyst support.
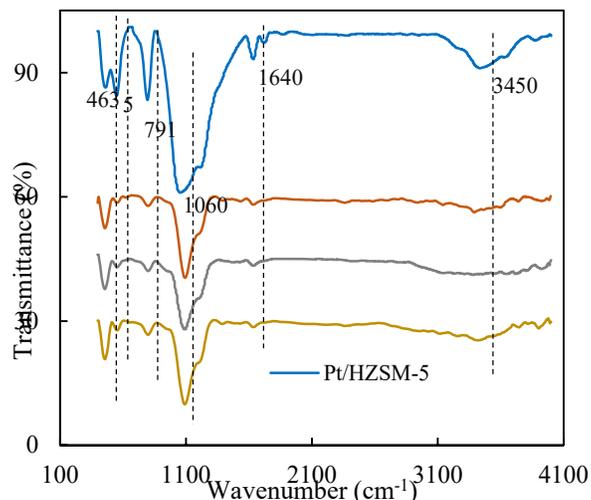
Fig. 2. FT-IR spectra of the prepared platinum catalysts.

Scanning electron microscopy (SEM) images of platinum-containing composite catalysts are shown in **Fig. 3**. As can be found in these figures, silica particles with different shapes are seen among the zeolite particles, which indicates that the composite catalysts are biphasic. The elliptical granules of KIT-6, as well as the spherical structure KCC-1 and the hexagonal structure of SBA-3 are almost visible among the HZSM-5 zeolite particles. It can be seen a considerable particle's coalescence and agglomeration. It is expected that this observed state of solids affects the activity of catalysts. The isotherms of nitrogen adsorption and desorption of catalysts are shown in **Fig. 4**. According to the IUPAC classification, isotherm curves are type IV with different hysteresis loop that are related to mesoporous structures. The Pt/HZSM-5-KIT-6 catalyst shows a hysteresis loop of type H1, which is characteristic of mesoporous material with a narrow pore size distribution of cylindrical pores. The Pt/HZSM-5-KCC-1 catalyst shows an H3-type loop hysteresis that typical characteristic of KCC-1 lamellar mesopore. Pt/HZSM-5-SBA-3 catalyst with limited hysteresis loops is observed which connected to regular and uniform SBA-3 mesoporous material. For comparison, the textural properties of the catalysts are reported in **Table. 1**. These catalysts have quite good BET surface (672 m^2g^{-1}) and mesoporous d_p (3.0-5.9 nm). The largest surface area and volume of pores belong to Pt/HZSM-5-KIT-6 catalyst and large pore diameter belongs to Pt/HZSM-5-KCC-1.

(a)

(b)

(c)

(d)

(d)

(e)
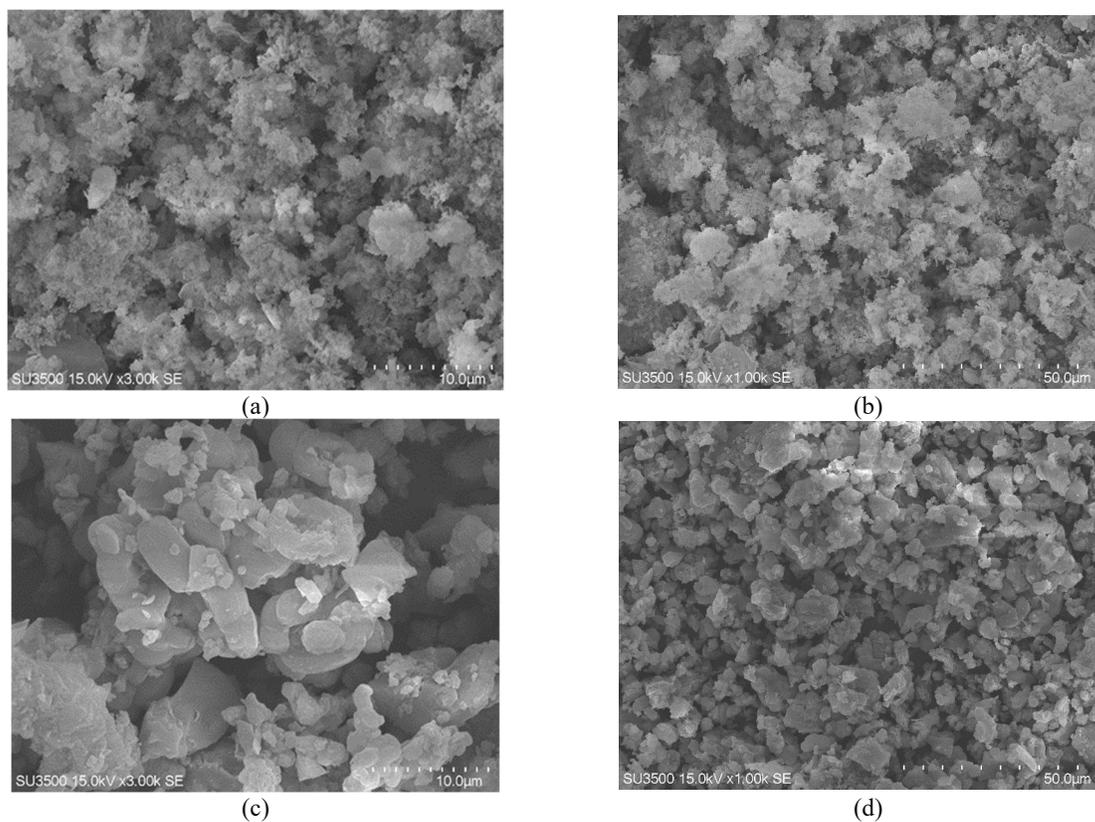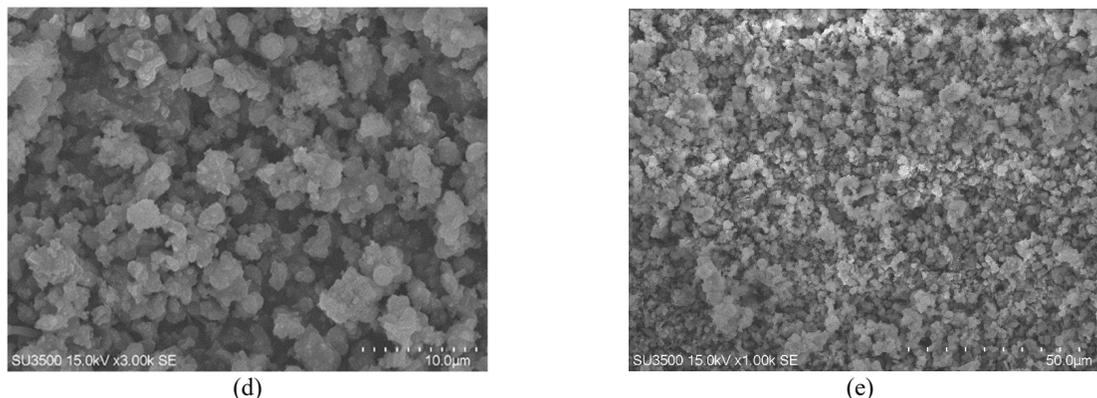
Fig. 3. SEM micrographs of Pt catalysts: (a and b) HZSM-5-KCC-1, (c and d) HZSM-5-KIT-6, and (e and f) HZSM-5-SBA-3
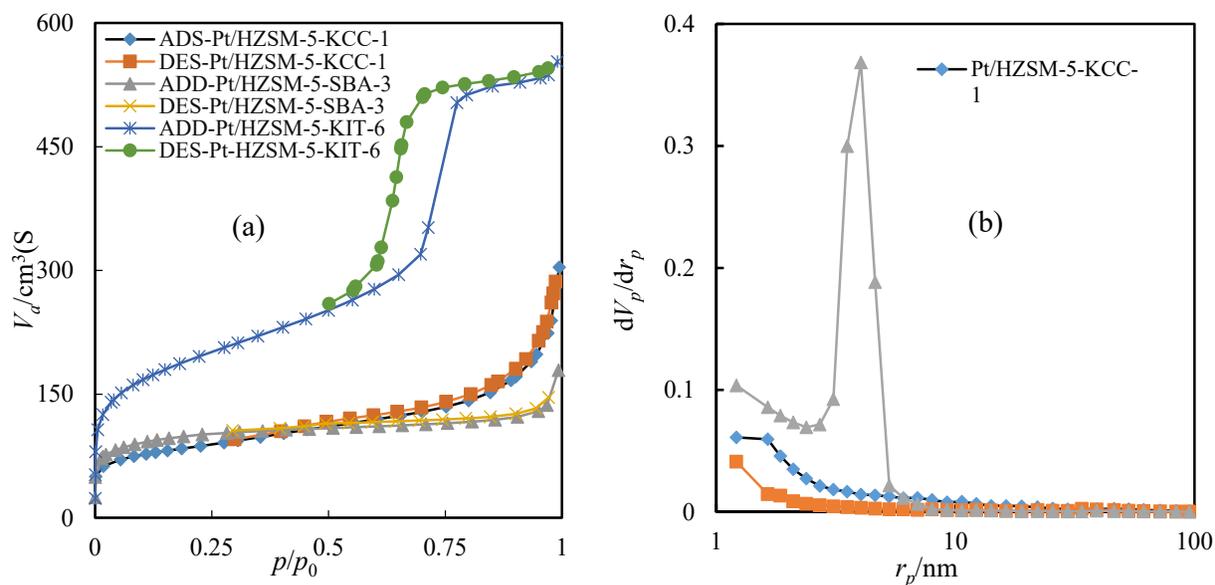
Fig. 4. (a) Adsorption (ADS)-desorption (DES) isotherms of N_2, and (b) pore size distribution patterns of the prepared platinum catalysts.

The highest conversion rate at 200-350 °C is connected to the Pt/HZSM-5-KIT-6 catalyst, which has the largest pore volume and surface area. It is observed that the conversion of n-heptane to isoheptane (i-C_7) decreases with increasing temperature. This observation is consistent with the thermodynamic drawbacks of the isomerization reaction because the isomerization reaction of n-heptane is a mildly exothermic reaction. Therefore, high temperatures are not useful for the isomerization reaction and the production of isomers (i-C_7). The adverse reactions also occur at high temperatures. Various factors such as acidity, pore geometry, metal dispersion, etc. affect the isomerization reaction of catalysts. Smaller pores in most catalysts, owing to the larger molecular size of the branched isoheptans than normal heptane, prevent the formation, excretion and diffusion of the branched isoheptans inside it and usually cause cracking which makes forming a multi branched (MUB) more challenging than a mono branched (MOB) isomers. However, the results indicate that the prepared catalysts have a good selectivity to the MUB. These results show that the mesoporous diameter of the catalyst composite has a predominant role in the creation of the MUB isoheptane.

Table. 1. Surface and pore properties of Pt supported composites.

Catalyst	S_{BET} (m^2g^{-1})[a]	d_p (nm)[b]	V_p (cm^3g^{-1})[c]	S_{Lang} (m^2g^{-1})[d]
Pt/HZSM-5-KCC-1	301	5.9	0.4	279
Pt/HZSM-5-KIT-6	672	5.1	0.8	506
Pt/HZSM-5-SBA-3	359	3.0	0.3	317

[a] BET surface area by Brunauer–Emmett–Teller method.
[b] Mean pore diameter by BJH method.
[c] Total pore volume (p/p₀=0.990) (V_p) by BET plot.
[d] Langmuir surface area by Langmuir plot.

Table. 2 shows the conversion of n-heptane, selectivity to MOB and MUB isomeric products and other products.

Table. 2. Catalytic activity, selectivity and coke amount over Pt synthesized catalysts

catalyst	T/°C	coke (%)	conv.(%)	MOB	MUB	i-C$_7$	crack.	hydro.
Pt/HZSM-5-KCC-1	200		50.9	7.9	21.6	29.5	6.1	47.2
	250		52.9	8.0	19.1	27.1	11.2	57.7
	300	9.3	75.2	0.1	25.3	25.4	12.4	55.1
	350		82.5	0.2	17.3	17.5	12.5	56.2
Pt/HZSM-5-KIT-6	200		53.2	7.8	24.7	32.5	7.7	56.4
	250		54.1	5.0	24.3	29.3	9.3	58.8
	300	7.7	87.1	1.0	27.7	28.7	11.6	55.0
	350		100.0	0.2	0.1	0.3	12.3	83.0
Pt/HZSM-5-SBA-3	200		49.9	10.1	24.8	34.9	7.3	48.0
	250		52.7	2.6	30.0	32.6	13.6	33.0
	300	7.7	83.7	0.3	30.1	30.4	13.1	55.1
	350		97.4	0.0	12.2	12.2	13.9	72.9

Although our goal in this investigation is to increase the isomerization products of heptane, the side reactions of cracking, hydrogenolysis, aromatization, etc. are performed. In the prepared catalysts, the amount of cracking rises with increasing temperature up to 350 °C. According to the literature,[15] the mesoporosity of the catalysts comforts the hydrogen transfer reactions between the olefinic and the cyclic intermediates and increases the aromatic and cracking properties. The catalysts produced do not contain any aromatic substances except the Pt/HZSM-5-KIT-6 at 350 °C. Also, acidity, kind of acid site, geometry and balance between acid and metal performance are factors that affect these competitive reactions.

To evaluate the stability of the prepared catalysts against coking and to evaluate their activity, the isomerization process is performed at 300 °C for 6 h with the same H$_2$/HC ratio. The plots of feed conversion vs. time on stream (TOS) for all catalysts are shown in **Figure 5**. The conversion of all catalysts decreases with increasing TOS. As mentioned before, the isomerization reaction is less performed at high temperatures. On the other hand, at high temperatures, the side reactions of cracking, hydrogen transfer, etc. are increased, which cause the development of coke and the activity of catalysts decreases with the creation of carbon deposition on the active sites of the catalysts.
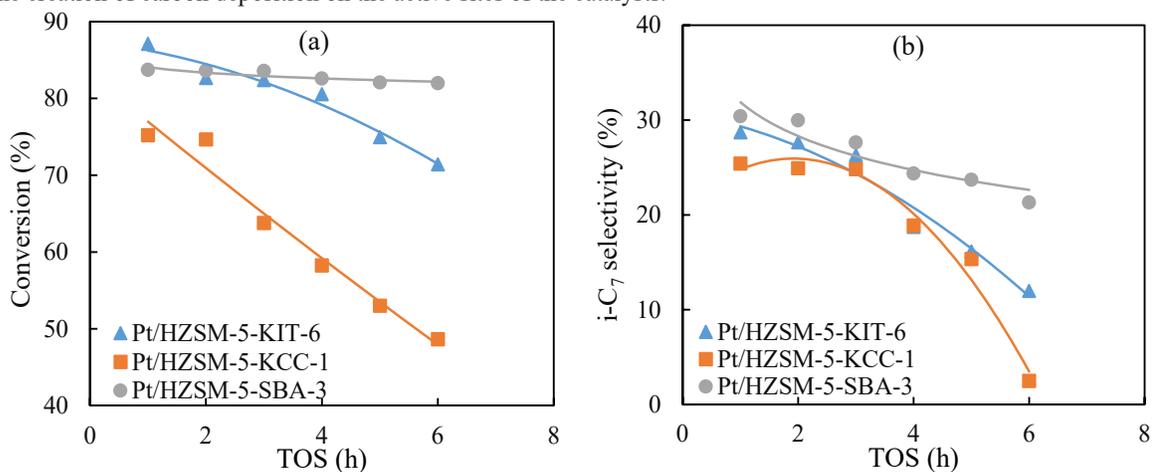
Fig. 5. (a) n-C$_7$ conversion (%) and (b) i-C$_7$ selectivity (%) vs. TOS (h) at 300 °C.

The highest rate of coking is connected to Pt/HZSM-5-KCC-1 catalyst and the lowest is connected to Pt/HZSM-5-KIT-6 catalyst. As can be found in **Fig. 5**, the highest conversion fall vs. time on stream is connected to Pt/HZSM-5-KCC-1 catalyst, which has the highest coking among catalysts. As can be seen in the Figure, the conversion and selectivity to isomeric products both decline with time, indicating the deactivation of the catalyst with time owing to coke deposition. However, in relation to **Fig. 5b**, a regular trend is not observed, which is possibly due to the non-uniform deactivation of acidic sites.

In order to obtain the amount of coking of the catalysts, after performing the stability test, coke poisoned catalysts are first placed in an oven at a temperature of 120 °C to remove their moisture and then these solids are weighed. Immediately after weighing, these catalysts are put in the oven at 300 °C for one hour. When they cool, they are weighed again immediately. The result of their weight difference with coke poisoned catalysts is the amount of coke over the catalysts.

3. Conclusions

The objective of this research was to synthesize catalysts that reduce aromatic compounds and increase MUB

compounds in the n-heptane isomerization reaction. The synthesized catalysts have performed well for this purpose. By investigation the structure and morphology properties of the produced catalysts, it was observed that the synthesized two-phase catalyst has a suitable mesopority. The outcomes of the reactor tests demonstrate that the Pt/HZSM-5-SBA-3 catalyst has the best performance in the n-heptane isomerization reaction with 86% conversion, 30.4% i-C_7 selectivity and 30.1% MUB compared to the other synthesized catalysts in this work. Coke deposition reduces the activity of the catalyst, and the highest amount of conversion drop in the stability test belongs to the Pt/HZSM-5-KCC-1 catalyst which has the highest amount of coke. The utilization of different silicate mesopores to composite with HZSM-5 zeolite can change the acidity, structural and morphological properties of the composite. According to the results, the influence of the kind of silicate mesopore used in the composite catalyst can be understood in the isomerization reaction.

4. Experimental

4.1. Materials

Protonated form of Zeolite Socony Mobil–5 (ZSM-5) with Si/Al = 14 was purchased from Zeolyst International. Pluronic P123 (a symmetric triblock copolymer comprising poly(ethylene oxide) and poly(propylene oxide)) was prepared from Sigma (China). Cetyl trimethyl ammonium bromide (CTAB) was purchased from Sigma Aldrich (Germany). Tetra ethyl ortho silicate (TEOS) served as a silica source, normal butanol, normal heptane (n-C_7), hydrogen chloride (HCl), toluene, ammonium hydroxide (urea, NH_4OH), ammonium nitrate (NH_4NO_3), and hexa chloro platinic acid ($H_2PtCl_4.6H_2O$) were purchased from Merck. The deionized (DI) water was made in our laboratory.

4.2. Preparation methods

4.2.1. Preparation of composite HZSM-5-KIT-6

To prepare the composite HZSM-5-KIT-6, KIT-6 was prepared as reported[21] and ZSM-5 was added during synthesis. 2 g of P123 was placed in 72 ml of DI water and 3.8 g of HCl (35%) on the heater stirrer. After a clear solution was obtained, 2 g of normal butanol was added. The solution was stirred for one hour. Then one gram of ZSM-5 was added to the solution and after stirring for half an hour, 4.3 g of TEOS was added to it and placed on the heater for 24 h (all steps were performed at 35 °C and vigorous stirring). It was transferred the resulting gel to an autoclave and then placed in an oven at 100 °C for 24 h. After filtering and washing, the obtained solid was dried in an oven overnight and calcined at 550 °C for 6 h.

4.2.2. Preparation of composite HZSM-5-KCC-1

To prepare the composite HZSM-5-KCC-1, KCC-1 was prepared as reported[22] and then ZSM-5 was added during synthesis. 0.5 g of zeolite was also added to 2.34 ml of butanol and 54.24 ml of toluene and then it was placed on the stirrer for half an hour. Then, while stirring, 5 ml of TEOS was added and it was left until stirred (Solution 1). Simultaneously another solution containing 1.86 g of CTAB and 1.1702 g of urea in 55.199 ml of DI water was made for half an hour on the stirrer to obtain a clear solution (Solution 2). Quickly solution 2 was added to solution 1 while stirring. After an hour of vigorous stirring, the resulting gel was transferred to the autoclave and was left in the oven at 120 °C for 4 h. The obtained product was filtered, washed, dried in the oven overnight and then calcined at 550 °C for 6 h.

4.2.3. Preparation of HZSM-5-SBA-3 composite

1 g of CTAB was dissolved in 20 ml of HCl (37%) and 50 ml of distilled water at room temperature on a stirrer. 0.5 of zeolite was added to it. After stirring for 30 min, 5 ml of TEOS was added drop by drop. After stirring for 24 h at room temperature, the obtained gel was filtered and washed. The resulting material was dried in an oven for 3 h and calcined at 550 °C for 8 h.

All prepared samples (HZSM-5-KIT6, HZSM-5-SBA-3, and HZSM-5-KCC-1) were ion exchanged with NH_4NO_3 solution (0.1 M) for 12 h at 70 °C and finally these solids were washed with distilled water. The ion-exchanged products were dried at 110 °C for 3 h and then calcined at 550 °C for 6 h.

Platinum with the same concentration (0.6 wt%) was loaded onto the composites by an impregnation method with an aqueous $H_2PtCl_4.6H_2O$ solution according to the reported method.[14] After evaporating the solvent and drying, the catalysts were calcined in air at 300 °C for 4 h. The amount of platinum impregnation over the catalysts was checked by X-ray fluorescence (XRF-8410 Rh 60 kV) to ensure the deposition of platinum over the synthesized supports.

4.3. Characterization method

The micro/mesoporous catalysts were characterized by XRD on an X-PERT diffractometer with a nickel filter using Cu k_α radiation (wavelength = 1.54 Å) as an X-ray source. Patterns were recorded with scanning step of 0.06° in a range of

2θ=1–70°.

The Fourier transform infrared (FT-IR) spectra (BOMEM FT-IR spectrophotometer model Arid-Zone TM, MB series) was used to characterization of the chemical bonds of the catalysts in the region from 400 to 4000 cm^{-1} using the KBr method.

The surface area was measured by BET method based on the adsorption and desorption data with relative pressure (P/P$_0$) between 0.05 to 0.3 and average pore diameter (d$_p$) using Barret-Joyner-Holland method (BJH). Also, the cumulative pore volume (V$_p$) of the isotherms at P/P$_0$ = 0.99 was obtained by the BET equation. Nitrogen adsorption-desorption isotherms were obtained using samples that were removed from the adsorbed gas molecules under vacuum at 623 K for 10 h before measurement. These isotherms were recorded at -196 °C with a Belsorp mini II device made in Japan.

Scanning electron microscopy (SEM) was performed on a HITACHI SU3500 instrument with 15 kV accelerating voltage to investigate the morphology of catalysts.

4.3. Catalytic test

The catalytic isomerization of n-heptane was performed using a continuous fixed bed reactor with 0.2 g of catalyst in the presence of H$_2$ at an atmospheric pressure and in the temperature range of 200-350 °C. The desired temperature was continuously controlled using a thermocouple located next to the catalyst bed. The catalysts were pre-treated with an H$_2$ flow of 40 ml/min at 400 °C for 2 h. Liquid feed (n-heptane) was injected into the reactor using a syringe pump with the space velocity (LHSV) 1 h^{-1}. To obtain the best selectivity of the desired products, hydrogen was introduced in the optimized value of H$_2$/HC = 7 molar ratios. The performance of the catalysts was tested after 1 h time on stream (TOS) at the mentioned temperatures for each experiment. To study the deposition of coke, the catalytic performance of all samples was investigated at 300 °C for 6 h time on stream. The products obtained from the reaction were analyzed by gas chromatography (Agilent Technologies 7890A) equipped with a flame ionization detector (FID).

References

1. Guisnet M. (**2013**) "Ideal" bifunctional catalysis over Pt-acid zeolites. *Catal. Today*, 218, 123-134.
2. Parsafard N., Asil A. G., and Mirzaei S. (**2020**) Reliable prediction of n-heptane isomerization over Pt/(CrO$_x$/ZrO$_2$)-HMS via comparative assessment of regularization networks and surface response methodologies. *RSC Adv.,* 10(44), 26034-26051.
3. Valavarasu G., and Sairam B. (**2013**). Light naphtha isomerization process: A review. Petroleum Science and Technology, 31(6), 580-595
4. Fahim, M.A., Al-Sahhaf, T.A. and Elkilani, A. (**2009**) Fundamentals of petroleum refining. Elsevier.
5. Alemán-Vázquez L.O., Cano-Domínguez J.L., Torres-García E., and Villagómez-Ibarra J.R. (**2011**) Industrial application of catalytic systems for n-heptane isomerization. *Mol.*, 16(7), 5916-5927.
6. Kalashnikov I. M., Belopukhov E. A., Smolikov M. D., Kir'yanov D. I., and Belyi A. S. (**2018**) Isomerization of n-heptane on zeolite-supported platinum catalysts. In AIP Conference Proceedings (Vol. 2007, No. 1, p. 020012). AIP Publishing LLC.
7. Calemma V., Peratello S., and Perego C. (**2000**) Hydroisomerization and hydrocracking of long chain n-alkanes on Pt/amorphous SiO$_2$–Al$_2$O$_3$ catalyst. *Appl. Catal. A: Gen.*, 190(1-2), 207-218.
8. Belopukhov E. A., Kalashnikov I. M., Kir'yanov D. I., Smolikov M. D., and Belyi A. S. (**2019**) The region of hydroisomerization reactions of n-heptane and a benzene/n-heptane mixture over Pt-containing catalysts based on BEA and MOR zeolites. In AIP Conference Proceedings (Vol. 2143, No. 1, p. 020025). AIP Publishing LLC.
9. Guo Z., Li X., Hu S., Ye G., Zhou X., and Coppens M.O. (**2020**) Understanding the role of internal diffusion barriers in Pt/Beta zeolite catalyzed isomerization of n-heptane. *Ange. Chem.*, 132(4), 1564-1567.
10. Chen Z., Dong Y., Jiang S., Song W., Lai W., Yi X., and Fang W. (**2017**) Low-temperature synthesis of hierarchical architectures of SAPO-11 zeolite as a good hydroisomerization support. *J. Mat. Sci.*, 52(8), 4460-4471.
11. Oenema J., Harmel J., Vélez R.P., Meijerink M.J., Eijsvogel W., Poursaeidesfahani A., Vlugt T.J., Zečević J., and De Jong K.P. (**2020**) Influence of nanoscale intimacy and zeolite micropore size on the performance of bifunctional catalysts for n-heptane hydroisomerization. *ACS Catal.*, 10(23), 14245-14257.
12. Smolikov M.D., Shkurenok V.A., Yablokova S.S., Kir'yanov D.I., Paukshtis E.A., Leont'eva N.N., Belyi A.S., and Drozdov V.A. (**2017**) Preparing and studying Pt/WO$_3$/ZrO$_2$ catalysts for the isomerization of n-heptane. *Catal. Ind.*, 9(1), 54-61.
13. Bijanzad K., Tadjarodi A., Akhavan O. (**2015**). Photocatalytic activity of mesoporous microbricks of ZnO nanoparticles prepared by the thermal decomposition of bis (2-aminonicotinato) zinc (II). *Chin. J. Catal.*, 36(5), 742-749.
14. Vu X.H., Armbruster U., and Martin A. (**2016**) Micro/mesoporous zeolitic composites: Recent developments in synthesis and catalytic applications. *Catal.*, 6(12), 183.
15. Parsafard N., Peyrovi M.H., and Rashidzadeh M. (2014) n-Heptane isomerization on a new kind of micro/mesoporous catalyst: Pt supported on HZSM-5/HMS. *Microporous Mesoporous Mat.*, 200, 190-198.
16. Gao L., Etim U.J., Shi Z., Xing W., Wu P., Han D., Bai P., and Yan Z. (**2019**) Predicting catalytic performance of micro-

mesoporous Pt/Beta-KIT-6 catalyst in n-heptane hydroisomerization using indexed isomerization factor and experimental verification. *Ind. Eng. Chem. Res*., 58(13), 5146-5157.

17. Gao L., Shi Z., Etim U.J., Wu P., Han D., Xing W., Mintova S., Bai P., and Yan Z. (**2019**) Beta-MCM-41 micro-mesoporous catalysts in the hydroisomerization of n-heptane: Definition of an indexed isomerization factor as a performance descriptor. *Microporous Mesoporous Mat*., 277, 17-28.

18. Lee K., Lee S., Jun Y., and Choi M. (**2017**) Cooperative effects of zeolite mesoporosity and defect sites on the amount and location of coke formation and its consequence in deactivation. *J. Catal*., 347, 222-230.

19. Peyrovi M. H., Parsafard N., and Anajafi H. R. (**2018**) Catalytic performance of micro-mesoporous materials as the supports for Pt catalysts in n-heptane isomerization. *Chem. Phys. Let*., 713, 32-38.

20. Zhang W., Yu D., Ji X., and Huang H. (**2012**) Efficient dehydration of bio-based 2, 3-butanediol to butanone over boric acid modified HZSM-5 zeolites. *Green Chem.,* 14(12), 3441-3450.

21. Wang W., Qi R., Shan W., Wang X., Jia Q., Zhao J., Zhang C., and Ru H. (**2014**) Synthesis of KIT-6 type mesoporous silicas with tunable pore sizes, wall thickness and particle sizes via the partitioned cooperative self-assembly process. *Microporous Mesoporous Mat*., 194, 167-173.

22. Febriyanti E., Suendo V., Mukti R.R., Prasetyo A., Arifin A.F., Akbar M.A., Triwahyono S., and Marsih I.N. (**2016**) Further insight into the definite morphology and formation mechanism of mesoporous silica KCC-1. *Langmuir*, 32(23), 5802-5811.