Catalytic activity of H-ZSM-5 and Cu-HZSM-5 zeolites of medium SiO_2/Al_2O_3 ratio in conversion of n-hexane to aromatics

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ARTICLE INFO

ABSTRACT

H-ZSM-5 and Cu-HZSM-5 composite zeolites with a medium SiO_2/AL_2O_3 ratio was successfully synthesized using a incipient-wetness impregnation method and characterized via physico-chemical analysis, such as X-ray diffraction (XRD), scanning electron microscope (SEM), N_2-physisorption, BET, and temperature programmed desorption of ammonia (NH_3-TPD). Activity of the catalysts and acid properties of high-silica zeolite H-ZSM-5 modified with Cu was investigated for conversion of hexane into value-added hydrocarbons. It was noticed that the introduction of the modified metal Cu during the stage of impregnation synthesis changed catalytic and acid properties of the original zeolite. The obtained results display that the amount of Cu metal content plays a centric role in the formation of Cu-HZSM-5 zeolite catalyst. Comparing to H-ZSM-5 and 1.5Cu-HZSM-5, the 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts exhibited more catalytic efficiency in the aromatization process of the investigated alkanes, as well as increased the products of aromatic/gasoline-ranged hydrocarbons and diminished the products of hydrocarbon gases.

1. Introduction

One of the essential and critical environmental problems is the release of volatile organic compounds (VOCs) (e.g. hexane) in great amounts firstly due to global and rapid industrialization. As well as, these compounds are considered as the primary contaminants in indoor air, causing a significant impact not only indoor air quality but also human health (Wang et al., 2007). Several methods have been investigated to mitigate these compounds and among the various mechanisms/approaches, a catalytic conversion is considered as the most promising because of the advantages, such as low operating temperature, high efficiency (Tursunov and Tilyabaev, 2017; Tursunov et al., 2017a, 2017b) and no secondary contamination. On the anther hand, at the beginning of the 21st century there have been significant changes in views on the future of world energy and the role of various sources of hydrocarbon raw materials. There is no doubt that the processes of processing lower alcohols into petroleum-based hydrocarbons will play an important role in the economy, which will gradually have to replace the currently used engine fuel from petroleum raw materials. Most industrial processes are also based on catalytic reactions, and their improvement is usually associated with the development of new catalysts.

It is known that acid-base type heterogeneous catalysts accelerate the dehydration reaction of oxygen-containing substances of different classes (Mika et al., 2018; Scholz et al., 2018; Palinko, 2018). By varying the parameters of the ethanol conversion process, it is possible to obtain a diverse set of hydrocarbons of the gasoline series. The decisive factor for the successfulness of the process is solely based on the design of the catalytic system. The numerous research studies have been conducted using the catalysts based on noble metals, like Pd and Pt due to their activity and efficiency during the reaction process. Nevertheless, these particular catalysts are susceptible to higher operating temperatures, relatively expensive comparing to other metal based catalysts (Wyrwalski et al., 2007), and have a poor resistance to sulfur poisoning. Therefore, inexpensive and affordable catalytic elements or substances, such as metal oxides (e.g. Cu, Ce, Mn, Co etc.), are the potential substitutes which nowadays attract the vast interest of researchers. Although, at low temperatures, these metals may be less active, but upon increasing the temperature their activity may be analogous to that of noble metals (Sinha and Shankar, 1993; Kamiuchi et al., 2010; Liotta, 2010; Adamski et al., 2011; Azalim et al., 2011). In this connection, if only highly active transition metals and their compounds function as catalysts can be successfully elaborated for the of

volatile organic compounds conversion, they will be preferred.

Zeolite Socony Mobil – 5 (ZSM-5) modified with metal oxides (e.g. Cu, Fe, Co, Ce, Mn etc.) exhibits catalytic properties to those of Pd and Pt catalysts, and this type of catalysts have been applied in several chemical reactions, such as the decomposition of nitrogen monoxide (NO) (Zhang et al., 1995a, b; Bai et al., 2017; Wang et al., 2018), synthesis of methanol (Beznis et al., 2010; Zhuang et al., 2018), CO_2 and CO hydrogenation (Alaba et al., 2017; Srikkarin et al., 2018; Zhao et al., 2018), dry reforming of methane (Izhab et al., 2017; Jang et al., 2018), methanol dehydration (Hosseini et al., 2012; Li et al., 2013) and conversion of ethanol (Injongkol et al., 2017; Xia et al., 2017; de Oliveira et al., 2018).

In studies carried out by Shibata et al. (2005), Cu-ZSM-5 catalysts exhibited an efficiency to convert benzene to phenol and the same study has been investigated by the research team of Kubacka et al. (2007). Cu-ZSM-5 has also been used for CH_4 (methane) conversion into CH_3OH (methanol) using molecular oxygen as an oxidant (Smeets et al., 2005; Groothaert et al., 2005). Moreover, various quantum chemical calculations and infrared investigations indicate that ZSM-5 modified by copper is able to activate double and triple bonds in alkynes, alkenes, acetones and benzene (Broclawik et al., 2005). As well as, it is also proven that metal loading on ZSM-5 induces synergetic effects because of the interactions between acid sites of zeolite and metals species. During the methanol conversion to hydrocarbons, the selectivity of binding of aromatic compounds to hydrocarbons was enhanced by metal oxides loading on zeolite, as mentioned earlier, because of the interaction of basic sites of metal oxides with acid sites of ZSM-5/11 (Conte et al., 2012). Moreover, the interaction of zeolite's acid sites with metal oxides involves alterations in ZSM-5's acidic properties. Chang et al. (1995) reported that the acid stability of ZSM-5/11 was mitigated after the introduction of transition metal oxides species on the ZSM-5 surface, this lead to suppressing objectionable reactions; for instance, limit the cracking level of hydrocarbon products. Moreover, Zhang et al. (1995a, b) suggested that to generate active sites, the hydrogen dissociated on metals' oxides relocates on the surface of zeolite ZSM-5 support. Hence, the synergetic effects highly depend on loaded metal oxide species.

Copper containing H-ZSM-5 catalysts is a proper candidate for transformation or conversion of hexane into value-added hydrocarbon products too; however, this particular process has not been researched broadly. Thus, the purpose of this work is to examine copper-modified high-silica zeolite-containing catalysts in hexane aromatization reactions and the effect of Cu metal loading in C_6H_{14} conversion process under the reaction pressure of 2.0 MPa and temperature of 400–550 °C.

2. Experimental section

2.1. Catalyst preparation

In this study, the catalyst was prepared using incipient-wetness impregnation method (Conte et al., 2012; Tursunov et al., 2017a). We used commercial samples NH_4^+ - type ZSM-5 zeolite catalysts with SiO_2/Al_2O_3 molar ratio of ~60 and $Cu(NO_3)_2 \cdot 6H_2O$ which were purchased from PQ Cooperation & Zeolyst International and Spectrum Chemical MFG Corporation.

Prior the hexane conversion reactions, the catalysts were forwarded to calcinations process in airflow at 550 °C for 4 h with a heating rate of 1–2 °C/min to decompose the ammonium ions to receive H-form of catalyst zeolite. The obtained catalysts were denoted as "H-ZSM-5". Afterwards, the catalyst with Cu-metal loading of 1.5, 3, 6 and 9 wt% was prepared using above-mentioned incipient-wetness impregnation method. Generally, this method is based on the impregnation of H-ZSM-5 in an aqueous solution which contains a metal salt containing a supported amount of $Cu(NO_3)_2 \cdot 6H_2O$. Next, the resultants were retained at room temperature for 12 h and then dried at the temperature of 120 °C for 6 h. Ultimately, the dried samples were re-forwarded for calcination
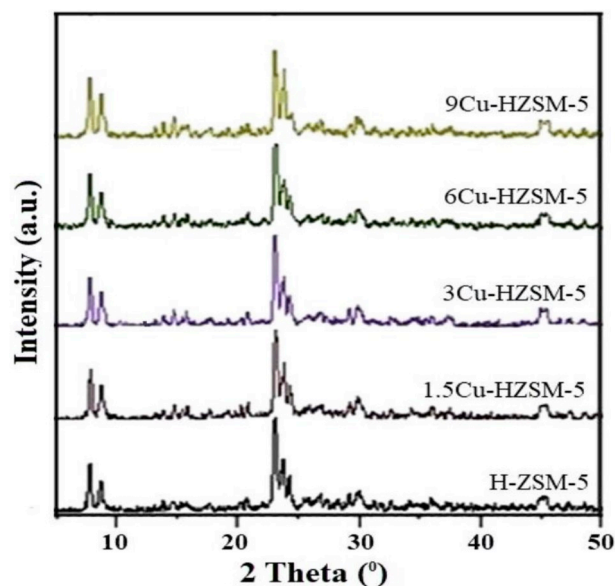

Fig. 1. XRD patterns of pure H-ZSM-5, 1.5Cu-HZSM-5, 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts.
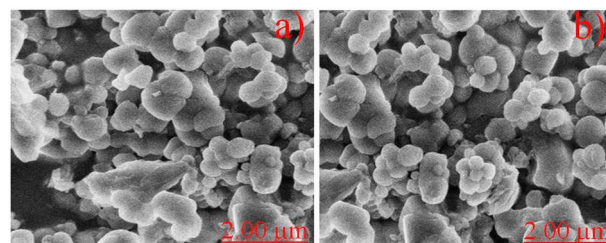

Fig. 2. SEM image of the surface of H-ZSM-5 (a) and 6Cu-HZSM-5 (b) catalysts.

process in airflow at 550 °C with a heating rate of 1–2 °C/min for 4 h, and the obtained catalysts were denoted as XCu-HZSM-5 (X-wt% of Cu).

2.2. Catalyst characterization

To distinguish the crystal structure of the catalysts, X-ray diffraction (XRD) analysis/or tests were employed on the D/MAX-2400 diffractometer with *Cu Ka* radiation with a scanning rate of 4^0/min in the ranges 2 between 10 and 80^0, the voltages and current were 40 kV and 100 mA.

Secondary electron images/or scanning electron microscopy (SEM) of the catalysts were investigated via Scanning Electron Microscope (JEOUL JSM-7610) with high probe current up to 200 nA, voltage 15 kV and built-in r-filter enabling user selectable mixture of backscattered electron and secondary electron images, as well as with large specimen chamber (sample diameter of 200 mm).

Accelerated surface and porosimetry system - Micrometrics ASAP 2020 BET/Porosimeter was used to measure N_2-physisorption isotherms at – 200 °C. First of all, the samples were dehydrated at 105 °C until the vacuum pressure was reached to lower than 5 m Hg. The surface area of the prepared samples was defined by using the Brunauer-Emmett-Teller (BET) equipment for the relative pressures within the range of $P/P_0 = 0.05$–0.2.

Above-mentioned XRD, SEM, N_2-adsorption-desorption and BET specific surface area characterizations of the prepared samples were investigated according to our previous studies (Tursunov and Tilyabaev, 2017; Tursunov et al., 2017a).

The acidities of the supports were recorded by NH_3-temperature programmed desorption (HH_3-TPD) using the Micrometrics Pulse
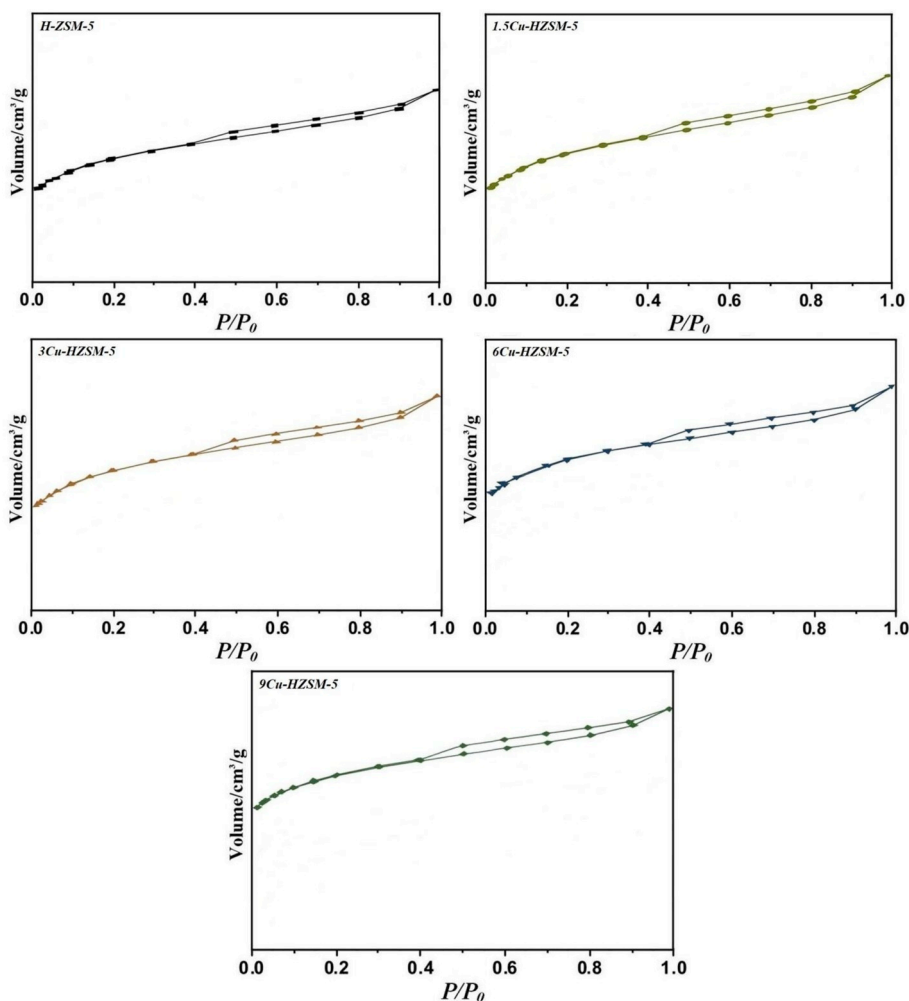
Fig. 3. N$_2$ adsorption-desorption isotherms of H-ZSM-5, 1.5Cu-HZSM-5, 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts.

Table 1
Textural characteristics of H-ZSM-5 and Cu-HZSM-5 with different Cu loadings.

Sample	SiO$_2$/Al$_2$O$_3$ ratio	Surface area (m^2 g^{-1})			Pore volumes (cm^3 g^{-1})	
		S$_{BET}$	S$_{Micro}$	S$_{external}$	V$_{Total}$	V$_{Micro}$
H-ZSM-5	60	386	288	98	0.198	0.109
1.5Cu-HZSM-5	60	353	264	89	0.165	0.097
3Cu-HZSM-5	60	320	224	96	0.151	0.092
6Cu-HZSM-5	60	285	192	93	0.139	0.092
9Cu-HZSM-5	60	268	183	85	0.127	0.091

Chemisorption Chemisorb 2720 analyzer. Initially, catalyst sample was pretreated in helium (He) with a flow rate of 40 ml min^{-1} at 500 °C for 1 h, and then cooled down to 100 °C. The adsorption of NH$_3$/He (40 ml min^{-1}) was done at 100 °C for 1.5 h, then the physically adsorbed ammonia (NH$_3$) on the sample surface was removed by the same He wit a flow rate of 40 ml min^{-1} at 100 °C. Measurements of NH$_3$-TPD were performed within the range of 100–650 °C under the heating rate of 5.0–10.0 °C/min. The thermal conductivity detector (TCD) was applied to detect the amount of desorbed NH$_3$.

2.3. Catalytic test

Catalytic conversion of hexane (ACS 99.5+ %, Sigma-Aldrich) to hydrocarbons was tested in a fixed-bed continuous flow reactor following our previous studies (Tursunov and Tilyabaev, 2017; Tursunov
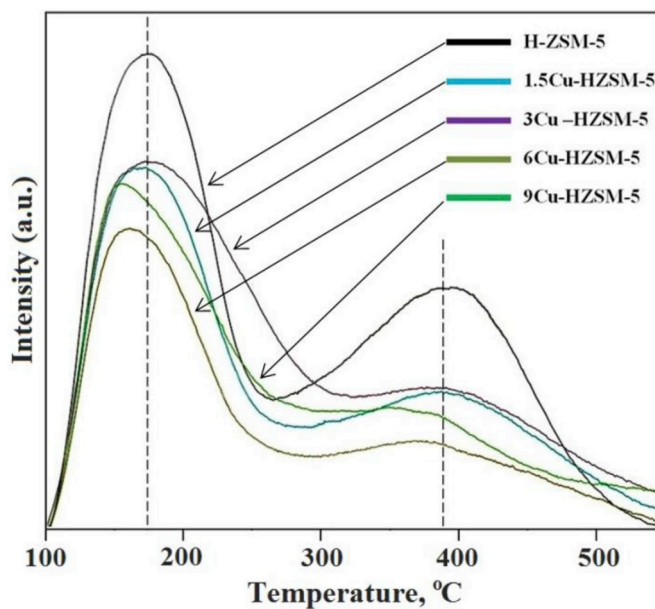

Fig. 4. NH$_3$-TPD spectra of H-ZSM-5, 1.5 Cu-HZSM-5, 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts.

Table 2
The total acid amounts of H-ZSM-5, 1.5 Cu-HZSM-5, 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts calculated by NH_3-TPD.

Samples	Total number of acid site (µmol/g)
H-ZSM-5	721
1.5Cu-HZSM-5	733
3Cu-HZSM-5	719
6Cu-HZSM-5	689
9Cu-HZSM-5	695

et al., 2017a). A stainless steel tubular reactor with a tube's inner diameter of 10 mm and complete length of 200 mm equipped with the K-type thermocouple was employed. The catalysts were crashed and diluted with quartz sands (mesh size of 20–40) in order to avoid hot spots due to exothermal reaction. Prior to catalysis reaction test, the catalyst sample with weight of 0.5 g was mounted into the quartz tubular reactor, and afterwards, it was reduced in a mixture of H_2/N_2 with flow rate of 80 mL min^{-1} at 290 °C for 3 h, and then the reactor was cooled down to 190 °C. After completion the reduction process, a reactant (hexane concentration 50%) was fed with a micropump (PerkinElmer S200), which was vaporized together with a flow rate of 80 mL min^{-1} of high purity nitrogen (N_2), and a mass flow controller was applied to control this process. The catalytic activities of the catalysts in conversion of n-hexane to high value aromatic hydrocarbons were measured under reaction conditions of 400–550 °C, 2.0 MPa and the weight of catalyst to the flow rate ratio of hexane was 9.0 g_{cat} h mol^{-1}. The excurrent hydrocarbon products/yields were analyzed using an online system connected with Gas Chromatography (GC) (Agilent 6820) equipped with a two-column analytical system: molecular sieve and Porapak Q columns which are connected to the thermal conductivity (TC) and the flame ionization (FI) detectors. The product-yields liquefied via condensation at normal room temperature were analyzed using the Gas Chromatography (Agilent 6820).

The conversion of hexane was calculated by Eq (1). The C-containing hydrocarbon product-yields were calculated based on the reaction methods of atomic carbon.

$$C_6H_{14} \, conversion \, (\%) = \frac{[C_6H_{14}]in \, - \, [C_6H_{14}]out}{[C_6H_{14}]in} \times 100 \qquad (1)$$

3. Results and discussion

3.1. 1Catalyst characterization

Fig. 1 highlights the X-ray Diffraction patterns of the H-ZSM-5, 1.5 Cu-HZSM-5, 3Cu-HZSM-5, 6 Cu-HZSM-5 and 9Cu-HZSM-5 catalysts. H-ZSM-5 catalyst's diffraction peaks were observed at 2 = 7.9^0, 8.8^0, 22.9^0, 23.8^0 and 24.5^0 which is standard characteristics of H-ZSM-5 zeolite structure which is consistent with the studies carried out by Ding et al. (2014), Lai et al. (2015) and Lin at al. (2017). After calcinations and loading of Cu on H-ZSM-5, the XRD intensity and diffraction peak position did not alter, inferring that the H-ZSM-5 zeolite structure is well retained and remains intact after adding Cu. The CuO diffraction peaks were not detected for both unmodified and modified catalysts, displaying that the species of copper are splendidly dispersed on the surface of the H-ZSM-5.

Fig. 2 demonstrates the SEM images of H-ZSM-5 and 6Cu-HZSM-5 catalysts. The obtained results indicate that H-ZSM-5 catalyst exhibits the irregular or spherical morphology. The morphology of 6Cu-HZSM-5 catalyst is virtually unaltered even after the addition of copper. It can be explain that the catalystsH-ZSM-5 and 6Cu-HZSM-5 (average pore size of 2.5–3.0 nm) are easily aggregated to form nanoparticles and hence, the modification of H-ZSM-5 with copper did not alter the physical morphology of the H-ZSM-5catalyst.

N_2 adsorption-desorption isotherms of the H-ZSM-5 and Cu-HZSM-5 catalysts with different copper loadings are highlighted in Fig. 3, and the textural characteristics of these catalysts are shown in Table 1 respectively. According to Brunauer et al. (1940) and IUPAC classifications, all shapes of the adsorption isotherms curves are categorized as Type I and Type IV, which indicates the type of microporous solids, precisely saying that the composite zeolite is definitely microporous. According to the figure, with the increase of Cu contents, the shape of adsorption-desorption isotherms altered imperceptibly compared with unmodified H-ZSM-5 catalyst which signifies that the modification of zeolite H-ZSM-5 catalyst has arguably minor impact on the pore shapes of the H-ZSM-5. In addition, it can be seen from Table 1 that the catalysts' specific surface area, micropore specific area and total pore volume decreased with addition and increase of Cu content from 1.5 wt% to 9 wt%, which might be because of the faintly discernible changes of channel structure after addition of copper and the binary magnification H-ZSM-5 crystals. As well as, it can also be related to the matter of fact that the copper species embrace an external surface of H-ZSM-5, thereby blockading numerous zeolite channels.

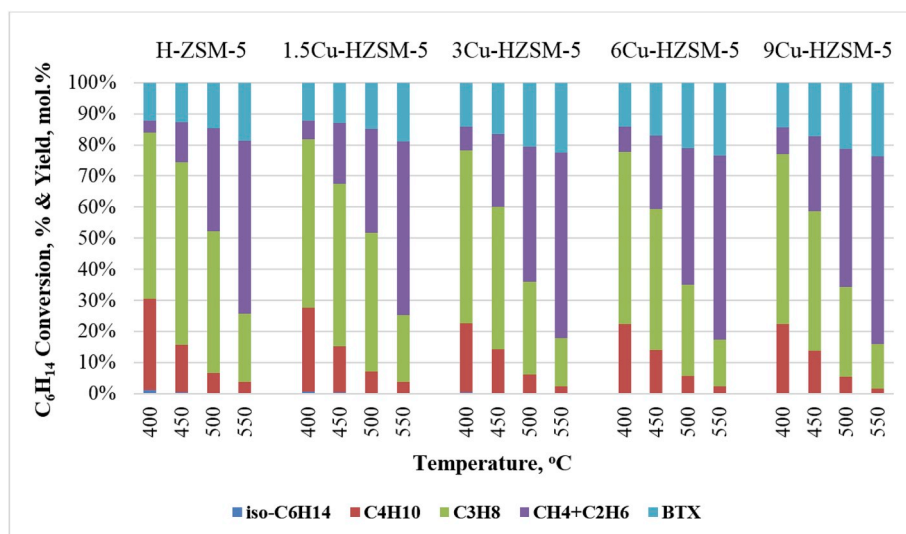It is well-known that acid sites of catalysts play a substantial role in

Fig. 5. Effect of reaction temperature on C_6H_{14} conversion and products over H-ZSM-5, 1.5Cu-HZSM-5, 3Cu-HZSM-5, 6Cu-HZSM-5 and 9Cu-HZSM-5 catalysts.

Table 3

Product yield resulting from n-hexane conversion to hydrocarbons over H-ZSM-5 and modified by Cu loading H-ZSM-5 catalysts. Reaction conditions: 1.0 g catalyst, P = 2 MPa, WHSV$_{n\text{-hexane}}$ = 9.0 g$_{cat}$ h mol^{-1}, N$_2$ flow rate = 80 mL min^{-1}.

Hydrocarbons (mol. %)	H-ZSM-5				1.5Cu-HZSM-5				3Cu-HZSM-5				6Cu-HZSM-5				9Cu-HZSM-5			
	Temperature, ^{0}C				Temperature, ^{0}C				Temperature, ^{0}C				Temperature, ^{0}C				Temperature, ^{0}C			
	400	450	500	550	400	450	500	550	400	450	500	550	400	450	500	550	400	450	500	550
BTX	11.9	12.6	14.5	18.7	11.9	12.8	14.6	18.9	13.8	16.3	20.3	22.4	13.9	16.6	20.8	23.4	14.1	16.9	21.2	23.6
CH$_4$ + C$_2$H$_6$	3.7	12.7	32.8	55.5	5.8	19.1	33.2	55.8	7.6	22.9	43.2	59.7	7.9	23.2	43.6	59.1	8.3	23.6	43.9	60.3
C$_3$H$_8$	52.4	58.2	45.2	22.0	53.2	51.1	44.3	21.4	54.3	44.9	29.4	15.5	54.2	44.5	28.9	15.2	53.8	44.1	28.5	14.4
C$_4$H$_{10}$	28.8	15.1	6.5	3.7	26.4	14.7	6.9	3.8	21.9	13.8	6.1	2.3	21.8	13.7	5.7	2.2	21.7	13.4	5.4	1.5
iso-C$_6$H$_{14}$	1.0	0.3	0	0	0.6	0.3	0	0	0.3	0.1	0	0	0.1	0	0	0	0.1	0	0	0
C$_6$H$_{14}$ conv.%	99.9	99.9	100	100	99.9	100	100	100	99.9	100	100	100	100	100	100	100	100	100	100	100

the transformation or conversion of VOCs to value-added hydrocarbon products. Therefore, the investigation of the acid properties of the catalysts modified with the different Cu loadings was carried out by the NH$_3$-TPD method in the temperature range of 100–550 °C (Fig. 4). Two desorption peaks at 177 and 390 °C can be observed for the H-ZSM-5 catalyst. The peak at the temperature of 177 °C is attributed to physisorbed ammonia species or NH$_3$ and can primarily refer to the Lewis acidic cites, and the desorption peak at the temperature of 390 °C is attributed to ammonia absorbed at the strong acidic sites which is probably belong to the strong Brønsted acidic sites. After the addition of copper, the NH$_3$-TPDprofiles have apparently changed and the desorption peak at the temperature of 390 °C drastically decreased and is significantly lower than that of H-ZSM-5 because of the fact that the Brønsted acid protons were replaced by Cu^{2+} (Martins et al., 2008). As well as, it can be inferred that the copper species interacted with the H-ZSM-5 zeolite's acid sites to weaken their acidic strength. According to Suzuki et al. (2008), the peak at higher temperatures (e.g. 300–600 °C) corresponds to ammonia desorption from catalytically active acid sites.

Table 2 shows the concentration of total acid amounts in the catalysts which are evaluated from the peak at higher temperature. It can be seen that by the increase of copper loading, the total number of acid sites decreases to 719 (3Cu-HZSM-5), 689 (6Cu-HZSM-5) and 695 (9Cu-HZSM-5) μmol/g compared to the initial H-ZSM-5 (721 μmol/g) and 1.5Cu-HZSM-5 (733 μmol/g). Szostak (1989) stated that the total amount of acid is proportional to the aluminum (Al)content of the framework which means that the increase or decrease in the total number of acid site could be also due to the large or small pore volume of Cu-HZSM-5 that alleviate NH$_3$ desorption.

As highlighted in Fig. 5, the aromatic/gasoline-ranged hydrocarbons yield (benzene, toluene and xylenes) was significantly improved when copper loading was enriched to 3 wt%, whilst by the further enrichment in the copper loading, the minor increase in the aromatic/gasoline-ranged hydrocarbons yields was observed, which, according to NH$_3$-TPD profiles, corresponds to the variations in the peak at higher temperature. Hence, it can be inferred that the weak acid sites generated by the loading of copper species on H-ZSM-5 obviously played a significant role in the selective synthesis of aromatic/gasoline-ranged value-added hydrocarbon yields (benzene, toluene and xylenes). Additionally, the loading of Cu on zeolites H-ZSM-5 did not lead to the catalytic polymerization and cracking of product-yields due to moderate/or mild acid strength.

Product yields resulting from n-hexane conversion to high value aromatic hydrocarbons and the effect of reaction temperature on n-C$_6$H$_{14}$ conversion over H-ZSM-5 and modified by Cu loading H-ZSM-5 catalystsare shown in Table 3 and Fig. 5 respectively. On the initial stage, the conversion of hexane, using unmodified zeolite H-ZSM-5, was 99.9% at the temperature of 400 and 450 °C. The total yield of gasoline – ranged aromatic hydrocarbon products BTX (benzene, toluene and xylenes) was 11.9 mol. % and the total yield of cracking products (methane- CH$_4$, ethane - C$_2$H$_6$, propane - C$_3$H$_8$ and butane - C$_4$H$_{10}$) was 84.9 mol. %. With an increase in the catalytic reaction temperature up to 550 °C, the yield of BTX increased to 18.7 mol. % as well as the conversion of n-hexane reached 100%, and the content of cracking products decreased to 81.2 mol. %.1.5Cu-HZSM-5 provided similar results as unmodified H-ZSM-5 catalysts with n-hexane conversion of 99.9% at 400 °C, the BTX yield was 11.9 mol. % and the total yield of cracking products was85.4 mol. %. Temperature increment up to 550 °C resulted to increase of BTX yield (18.9 mol/%) as well as the n-hexane conversion reached 100%, while the total yield of cracking products decreased to 81.0 mol %. However, when Cu species of3 wt% was loaded on H-ZSM-5 (3Cu-HZSM-5), the BTX yield was higher (13.8 mol. %) than those H-ZSM-5 and 1.5Cu-HZSM-5 zeolite catalysts at the temperature of 400 °C. The total yield of cracking products was 83.8 mol. %.Undoubtedly, by increasing the temperature to 550 °C the BTX yield increased to 22.4 mol. % which is also significantly higher compared with H-ZSM-5 and 1.5Cu-HZSM-5 catalysts, while the total yield of cracking products significantly decreased to 77.5 mol. %.A similar tendency or even a slightly better result was observed when Cu content on H-ZSM-5 catalysts was further increased to 6 wt% and 9 wt% (6Cu-HZSM-5 and 9Cu-HZSM-5) with BTX yield of 13.9 mol. % and 14.1 mol. % at 400 °C and the total yield of cracking products were 83.9 mol. % and 83.8 mol. %. By increasing the temperature to 550 °C, the BTX yield was also increased up to 23.4 mol. % for 6Cu-HZSM-5 and 23.6 mol. % for 9Cu-HZSM-5 catalysts, while the total yield of cracking product diminished to 76.5 mol. % and 76.2 mol. %. Regarding the n-hexane conversion, all catalysts displayed the identical degree of conversion percentage. The initial n-C$_6$H$_{14}$ conversion was reached to ~99.9% and when temperature amplified the n-hexane conversion enhanced and reached even 100% at 550 °C, independent of copper loading, specifying that the content of copper on H-ZSM-5did not impact the total transformation or conversion of n-hexane to value-added hydrocarbons.

Thus, the modification of zeolite with a proper weight percentage of copper loading leads to an increase in the yield of aromatic/gasoline-ranged value-added hydrocarbons BTX (benzene, toluene and xylenes) in comparison with H-ZSM-5 catalyst, which indicate the reaction's improved selectivity. It can be noted that the copper loading on H-ZSM-5 zeolite catalyst would embrace the acid sites inducing the cracking of hydrocarbons and hence causing the amelioration in the aromatic/gasoline-ranged hydrocarbon yields (mostly benzene, toluene and xylenes). In addition, the observed dynamics of increase in the yields of BTX and a decrease in the yields of cracking products with increasing reaction temperature for both H-ZSM-5 and Cu loaded on H-ZSM-5 zeolite catalysts indicates secondary aromatization reactions from the hydrocarbons formed as a result of n-hexane destruction.

4. Conclusion

The catalytic activity of the synthesized H-ZSM-5 and Cu-HZSM-5 zeolites of medium (60) SiO$_2$/Al$_2$O$_3$ ratio was studied for comprehensive conversion of n-hexane into value-added aromatic hydrocarbons. The hybrid catalyst consisting of 1.5 wt% Cu-HZSM-5 exhibited very

identical catalytic activities to the unmodified H-ZSM-5 catalyst. However, a further increase of Cu content (3, 6 and 9 wt %) in the H-ZSM-5 catalyst provided more qualitative catalytic activity than those of H-ZSM-5 and 1.5Cu-HZSM-5. Moreover, a further increase in the copper loading, without the cracking of the products, enhanced the gasoline-ranged aromatic hydrocarbon yields BTX. As well as, according to the NH$_3$-TPD profiles, the high copper loading on H-ZSM-5 diminished the acidic sites and attenuated the acidic strength of H-ZSM-5 catalyst. These particular results indicate that copper species interact with the acidic sites of H-ZSM-5 catalyst in order to confect the acidic strength mild, and this interaction also lead to the cracking of the products by maintaining substantial ability of the n-hexane conversion to value-added aromatic hydrocarbon product-yields, and restraining the surplus polymerization. Moreover, an increment in the reaction temperature led to a recession in the yield of hydrocarbon gases and a rise in the yield of aromatic hydrocarbons (benzene, toluene and xylenes). Hence, Cu-HZSM-5 catalyst with an appropriate copper loading could serve as an effective mechanism for vigorous and sustainable conversion of volatile organic compounds into value-added gasoline-ranged aromatic hydrocarbons.

Acknowledgement

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