

Performance of MFI Zeolite Catalysts in n-heptane Conversion Reaction Test

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The aromatization of n-heptane, one of the main components of light naphtha, has been investigated over HZSM-5 (Si/Al = 33.9) and Zn-HZSM-5: Zn1-HZSM-5 (0.86% Zn); Zn2-HZSM-5 (1.35% Zn) and Zn3-HZSM-5 (2.89% Zn) catalysts prepared by the ion exchange with 10M aqueous solution of Zn(NO₃)₂. The catalytic activity measurement was performed by the chromatographic pulse method in the temperature range of 673 - 823K. The presence of zinc in Zn-HZSM-5 catalysts provided a significant increase in total aromatics selectivity due to the improvement of dehydrogenation activity by Zn incorporation. The Zn species facilitated the aromatization by converting paraffin's into corresponding olefins which, in turn, were the aromatics precursors. Therefore, both acidity and zinc incorporation played important roles in the aromatization of n-heptane. Over 773 K the activity and selectivity of the Zn-HZSM-5 catalysts decrease very probably due to the loss of zinc ions.

Keywords: aromatization, n-heptane, BTX, HZSM-5, Zn-HZSM-5

The aromatization of n-alkanes is a profitable reaction for the transformation of naphtha to more valuable components as aromatics (BTX - benzene, toluene, and xylene isomers). Aromatic hydrocarbons, BTX, obtained can be used as essential raw materials for production of a wide variety of petrochemical or octane booster for commercial gasoline. ZSM-5 zeolite (MFI) of the Pentasil family is well known as a potential acidic catalyst for the aromatization of lower alkanes (C₃ - C₅) [1-3].

The high activity of HZSM-5 catalysts in the aromatization of alkanes is attributed to its high acid strength and correct pore geometry [4, 5]. Although the HZSM-5 catalysts provided a high conversion, the selectivity to aromatics was quite low due to the low dehydrogenation ability of HZSM-5. Therefore, the addition of metal on the HZSM-5 catalysts was introduced to improve the aromatics selectivity. The study on the aromatization of light hydrocarbons over HZSM-5 catalysts with addition of Ga, Zn, and Pt indicated that the highest aromatics selectivity was observed on Ga-HZSM-4 or Zn-HZSM-5 [6-74].

Nevertheless, Pt-HZSM-5 catalyst yielded less aromatic selectivity than HZSM-5. This might be due to the fact that the hydrogenolysis property of Pt leads to the production of a large amount of lower alkanes, especially methane and ethane.

Ni-HZSM-5 and Ag-HZM-5 catalysts exhibit a good activity and selectivity towards BTX aromatics in conversion of light alkanes and alkenes [75- 87].

Although the metal-modified HZSM-5 catalysts exhibit a significant improvement in the selectivity to total aromatics, the detailed reaction pathways of the aromatization on such catalysts have not yet been understood but extensively discussed. Giannetto et al. [12, 13] suggested that the direct aromatization of n-hexane and n-heptane yielding toluene, C₈ aromatics and benzene, respectively, took place over Ga-HZSM-5 catalysts, thereby proposed that the direct aromatization occurred via the

dehydrogenation step on the metal sites, followed by cyclization over acid sites. Recent reports on the aromatization of n-heptane over Zn-HZSM-5 and Ga-HZSM-5 catalysts proposed that the aromatization started with cracking of n-heptane, followed by oligomerization to higher alkenes, before the dehydrocyclization steps. Moreover, the direct dehydrocyclization of n-heptane to toluene could possibly occur on the Zn modified HZSM-5 [46, 49, 65, 76, 85].

This paper studies the activity and the selectivity of HZSM-5 and HZSM-5 modified with Zn in the conversion of n-heptane into C₆-C₈ aromatic hydrocarbons.

Experimental part

Synthesis

The parent Na-ZSM5 was synthesized with ethylene glycol as the template organic molecule. The starting materials were: sodium silicate solution (29.63 % SiO₂, 9.55 % Na₂O and 60.8 % H₂O), aluminum sulphate Al₂(SO₄)₃ · 18 H₂O, concentrated sulphuric acid, and distilled water [88].

Crystallization of the homogeneous gel took place over 24h at autogenously pressure and 453 K in stainless steel autoclaves with intermittent stirring. The synthesis products were filtered, washed repeatedly with distilled water, dried at 383K in air for 6h and calcined at 823 K in air for 6 h in order to remove the organic agent.

The calcined Na-ZSM5 was converted into H-form by three successive ion exchanges with 1 M NH₄NO₃ solution at 353K for 6h (solid: liquid ratio (1÷5)). Then, the zeolite is separated from the solution by filtering and washing with distillate water. After that, the catalyst is dried overnight at 383K and calcined in air at 823K for 6h. HZSM5 sample was converted by ion exchange with 0.1 M aqueous solutions of ZnNO₃ in Zn-HZSM-5 with different content of metal (wt. % Zn, 0.86, 1.35 and 2.89).

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Sample	BET surface area, m ² /g	Acidity, mmol. NH ₃ /g		Total acidity
		low-peak LT 353-573K	high-peak HT 573-873K	
HZSM-5	302.46	0.618	0.282	0.900
Zn1-HZSM-5	298.5	0.615	0.256	0.871
Zn2-HZSM-5	291.75	0.654	0.200	0.854
Zn3-HZSM-5	285.50	0.667	0.153	0.820

Table 1
PHYSICO-CHEMICAL CHARACTERISTICS OF THE STUDIED CATALYSTS

Characterization

The structure type, phase purity and degree of crystallinity were determined by X-ray powder diffraction technique; registering XRD patterns on a Philips PW 1830 diffractometer using Ni filtered Cu K_α radiation at a scanning speed of 0.02° s⁻¹ in the range of 6° - 45, 2θ. XRD powder pattern of the Na-ZSM-5 sample exhibit only diffraction lines proper to MFI structure high crystallinity. The pattern confirms that the synthesized product has the structure identical to MFI-type zeolite [4]. The morphology and size of the individual crystals were obtained by scanning electron microscopy (SEM) with a Microspec WDX-2A using a 25 kV accelerating potential. The SEM image of parent NaZSM-5 reveals the well-defined morphology of crystals indicating highly crystalline material [25, 26, 61]. Catalytic tests on aromatization of n-heptane were carried out in a pulse microreactor coupled with a GCH gas chromatograph. The products of reactions (only aromatic BTX) were on-line analyzed by a gas chromatograph Carlo Erba VEGA equipped with a 25 m capillary column filled with SE -52 and flame ionization detection (FID).

The acidity and strength distribution on HZSM-5 and Zn-HZSM-5 catalysts were measured using Temperature Programmed Desorption (TPD) technique using ammonia. A known weight of the sample was activated in a dry N₂ at 773K for 4h then cooled to 353K when ammonia was admitted. The amount of ammonia desorbed from 373K to 1073K (at a heating rate of 283K/min) was quantitatively monitored by absorption in 1M HCl. The ammonia desorbed represents the total acidity (weak and strong) of the sample. The TPD ammonia desorption presents two peaks, one at low temperature (LT) and one at high temperature (HT) (table 1). Temperature peak correspond to higher acid strength and is done to ammonia bound to strong structural Brönsted sites (Si-O-Al bridging OH), and possible to strong Lewis sites (≡ Al and ≡ Si⁺). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites Mⁿ⁺, AlO⁺). The temperature and the amount of desorbed ammonia give information about strength and number of the acid sites [25, 26, 61].

The BET specific surface area applying the BET equation was determined using a Carlo Erba Sorptomatic Series 1800 instrument at -469K and at sub-atmospheric pressure with nitrogen as the analysis gas.

The values of the BET specific surface area and acidity of the HZSM-5 and Zn-HZSM-5 catalysts are presented in table 1

Temperature programmed desorption spectra of NH₃ revealed that the acid strength of HZSM-5 was considerably reduced by introducing Zn²⁺ cations [25, 61].

The obtained results indicate that the distribution of the acid sites on Zn-HZSM-5 surface has been changed after the metal incorporation in HZSM-5 framework (the incorporation of the Zn²⁺ ions into cationic positions), while the medium and strong acid sites, in the catalysts weakened due the Zn effect. All physico-chemical parameters calculated from the obtained results are listed in table 1.

Catalytic studies

The catalytic properties of the H-HZSM-5 and Zn-HZSM-5 samples were tested in acid-catalyzed reaction of n-heptane aromatization. The catalysts were pressed, crushed and sorted into grains smaller than 0.147 mm and then 0.1 g, were packed into a micro reactor and heated under N₂ flow, at 823 K for 4 h. The catalytic activity measurements in the n-heptane aromatization were carried out in a pulse micro reactor containing 0.1 g catalyst, with 0.2 mL n-heptane pulse in N₂ flow as carrier gas (1.32 L/h, N.C.) for each catalytic test. The catalyst was dispersed in quartz wool to diminish the pressure drop. The temperature was varied from 673 K to 823 K measured with a thermocouple. Prior to the reaction, the catalyst was activated at 723 K for 6h under dried N₂ flow (22 mL/min).

The products of reactions (only aromatic BTX) were on-line analyzed by a gas chromatograph Carlo Erba VEGA equipped with a 25 m capillary column filled with SE -52 and flame ionization detection (FID).

Results and discussions

The conversion of n-heptane over HZSM-5, Zn1-HZSM-5 (Zn 0.86 wt. %), Zn2-HZSM-5 (Zn 1.35 wt. %) and Zn3-HZSM-5 (Zn 2.89 wt. %) was carried out in the 673-823K range of temperature and their total conversion and aromatic yields are plotted in figure 1 and 2, respectively.

The addition of Zn on the HZSM-5 catalyst significantly increased n-heptane conversion and aromatics yield. The

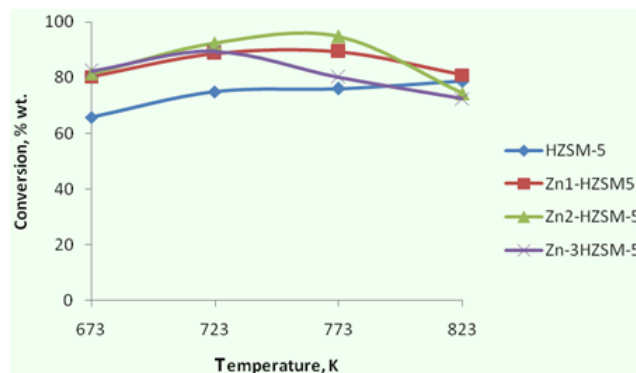


Fig. 1. Conversion of n-heptane vs. temperature on HZSM-5 and Zn-HZSM-5 catalysts

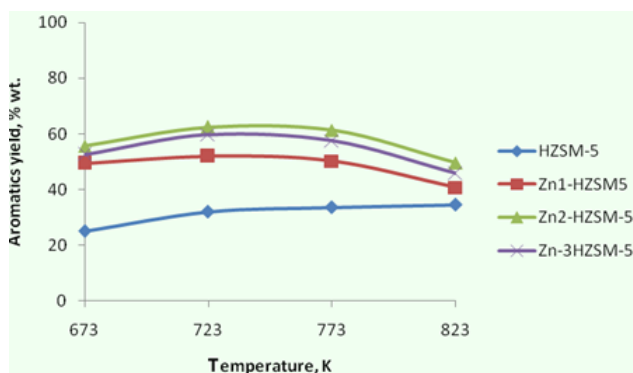


Fig. 2. Variation of the aromatics yield with temperature on HZSM-5 and Zn-HZSM-5 catalysts

incorporation of Zn^{2+} into cationic positions of HZSM-5 zeolite affects the acidity and the large attraction of Zn for hydrogen is responsible for higher conversion and aromatic yield for n-heptane aromatization. Catalytic conversion of n-heptane and aromatic yield on Zn-HZSM-5 catalysts decreased at temperature higher than 723K because of sublimation or migration of Zn from the active sites.

The aromatic hydrocarbons distribution depends on the metal content of the catalyst and the working temperature as shown in figures 3-5.

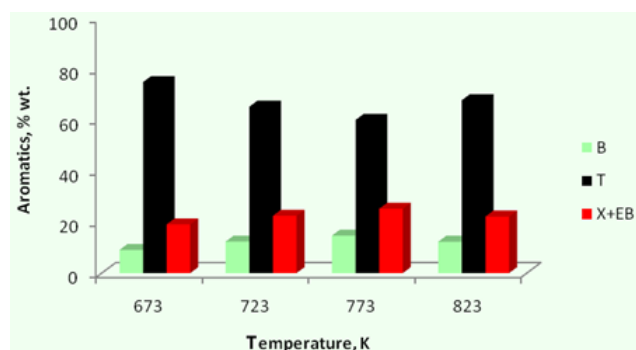


Fig. 3. BTX-aromatics distribution (wt %) vs. temperature in n-heptane conversion reaction over Zn1-HZSM-5

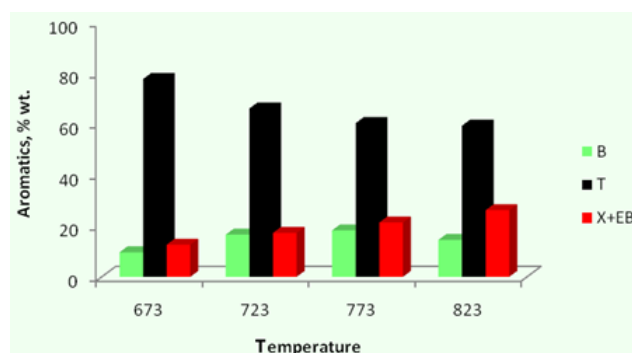


Fig. 4. BTX-aromatics distribution (wt. %) vs. temperature in n-heptane conversion reaction over Zn2-HZSM-5

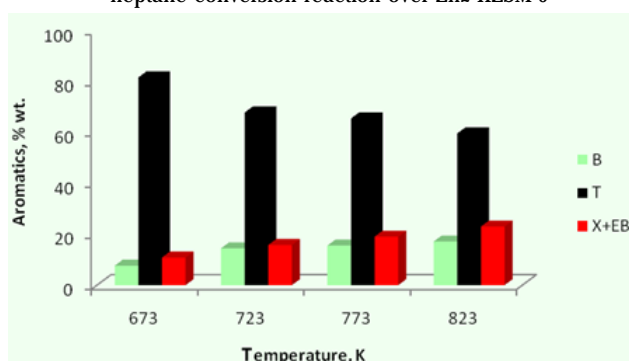


Fig. 5. BTX-aromatics distribution (wt. %) vs. temperature in n-heptane conversion reaction over Zn3-HZSM-5

In addition, toluene was yielded as the main aromatic product, followed by C_8 aromatics (xylenes and ethyl benzene) and benzene from all the catalysts tested.

An important aspect observed in the aromatic product distributions is the decrease in the selectivity ratios of toluene to total aromatics and increase of benzene and the aromatics C_8 with temperature increase. These results may imply that toluene is involved in secondary reaction for production of C_8 aromatics, leading to toluene disproportionation.

Based on preliminary results, the reaction pathways of the n-heptane aromatization over HZSM-5 (monofunctional) and Zn-HZSM-5 (bifunctional catalyst) take place by direct dehydrogenation and cyclization and by

hydride transfer which lead to the cracking of n-heptane followed by oligomerization, cyclization and dehydrogenation. The Zn^{2+} cations catalyze, the dehydrogenation / hydrogenation steps, while H^+ sites of zeolite are responsible for the other aromatization reaction sequence which implies hydride transfer and deprotonation to carbenium ions. It was reported that the olefinic fragments are the precursors for aromatics [25,57, 68]. The presence of zinc as dehydrogenation component facilitates formation of high concentration of these precursors leading to a significant increase in the production of BTX-aromatics from n-heptane aromatization.

The bifunctional nature of catalyst is important for aromatization of hydrocarbons. The acidic sites are responsible for oligomerization of alkenes and the metal cations are responsible for dehydrogenations of alkenes or oligomerized products. Acidic sites are also responsible for cracking of oligomers and hydrogen transfer reactions (fig. 6). Therefore, when acidic nature of the catalyst is modified, the overall catalytic process inside zeolite pores would be significantly changed and the selectivity's to the products be altered. The difference in the acidic properties should have a great influence on the reaction pathway of aromatization.

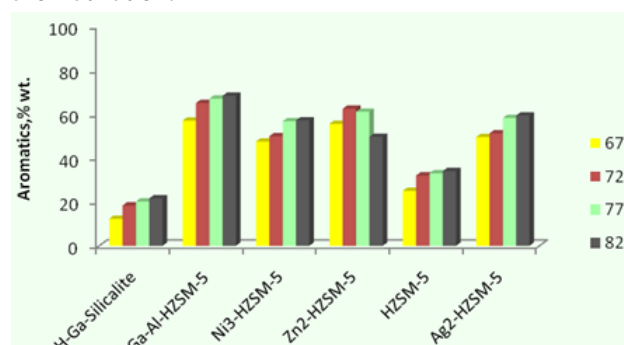
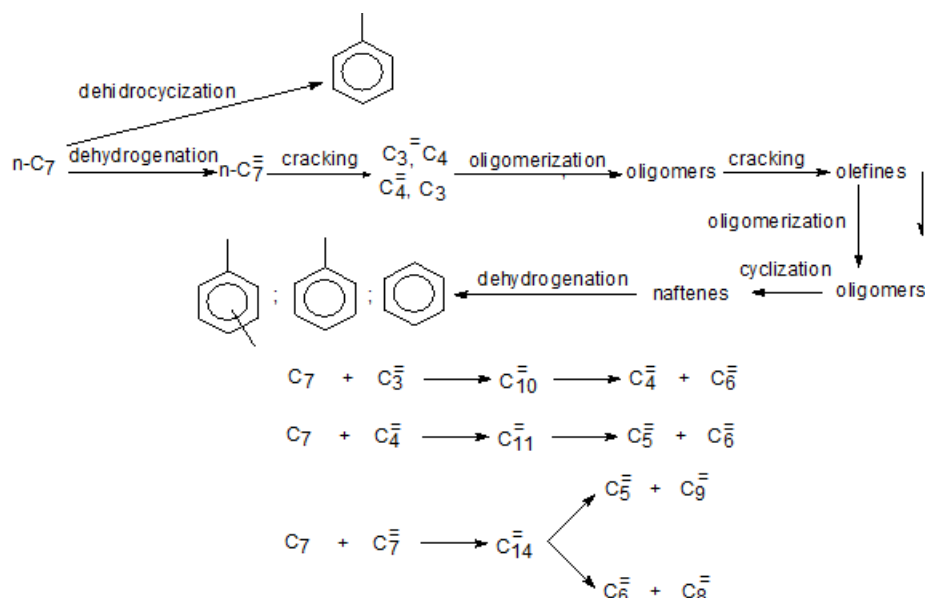


Fig.6. Aromatics yield vs. temperature on a series of MFI catalysts

It is accepted that the aromatization of n-heptane over monofunctional (H-form) and bifunctional (Me-HZSM-5) catalysts take place by direct dehydrogenation and cyclization and by hydride transfer which lead to the cracking of n- C_7 , followed by oligomerization, cyclization and dehydrogenation. The gallium catalyses, the dehydrogenation steps and H^+ acidic sites of zeolite are responsible for the other aromatization reaction sequences which involve hydride transfer and deprotonation. The activity and selectivity for n-heptane aromatization is higher than on the other studied MFI catalysts.

The incorporation of Zn^{2+} , Ni^{2+} or Ag^+ into cationic positions of HZSM-5 zeolite affects the acidity and the strong attraction of metal cations for hydrogen is responsible for higher conversion and aromatic yield for n-heptane aromatization. Catalytic conversion of n-heptane and aromatic yield on Zn-HZSM-5 decreases at temperature higher than 723K because of sublimation and/or migration of Zn from the active sites. The conversion of n-heptane on Ag-HZSM-5 is similar to that on Zn-HZSM-5 but the aromatic distribution is different. The increase of temperature determines an increase of xylenes concentration. Ni-ion exchange ZSM-5 was less effective in the aromatization of n-heptane than Ag- and Zn-HZSM-5 [82, 83].

n-Heptane conversion over Metal-HZSM-5 obtained by ionic exchange occurs via a complex sequence of cracking, dehydrogenation, and/or H transfer, oligomerization, isomerisation, cyclization, β -scission (scheme 1) [12, 49, 82, 83].



Scheme 1

Conclusions

In conclusion, the density of Bronsted acid sites and dehydrogenation activity play essential roles in the aromatization process of n-heptane. The modification of HZSM-5 framework with Zn ions enhances the n-heptane conversion as well as the selectivity to aromatics. This may be attributed to the improvement of dehydrogenation activity of the catalyst by the presence of Zn species leading to the greater availability of olefin pool, which is the intermediate for aromatization. This strongly suggests that Zn species effectively dehydrogenate intermediates into aromatics.

Toluene was yielded as the main aromatic product, followed by C₈ aromatics (xylenes and ethyl benzene) and benzene on all tested catalysts.

The aromatization activity of the HZSM-5 and Me-HZSM-5 catalysts increase with increase of the reaction temperature, while by incorporation of the metal in HZSM-5 framework decreases the cracking reaction on the catalysts, and at same time increasing the reaction that may result in the production of BTX-aromatic hydrocarbons (i.e. dehydrogenation and dehydrocyclization).

Catalytically conversion of n-heptane and aromatics yield on Zn-HZSM-5 catalysts decreased at temperature higher than 723K, very probably, because of sublimation and/or migration of Zn from the active sites.

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