

Performance of Ag-HZSM-5 Zeolite Catalysts in n-heptane Conversion

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The conversion of n-heptanes into aromatic hydrocarbons benzene, toluene and xylenes (BTX), by the chromatographic pulse method in the temperature range of 673 - 823K was performed over the HZSM-5 and Ag-HZSM-5 zeolites modified by ion exchange with AgNO₃ aqueous solutions. The catalysts, HZSM-5 (SiO₂/Al₂O₃ = 33.9), and Ag-HZSM-5 (Ag1-HZSM-5 wt. % Ag 1.02, Ag2-HZSM-5 wt. % Ag 1.62; and Ag3-HZSM-5 wt. % Ag 2.05 having different acid strength distribution exhibit a conversion and a yield of aromatics depending on temperature and metal content. The yield of aromatic hydrocarbons BTX appreciably increased by incorporating silver cations Ag⁺ into HZSM-5.

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

Much attention has been drawn to transformation of lower alkanes and alkenes into aromatic hydrocarbons BTX, both industrial and academic points of view. The aromatic hydrocarbons BTX can be utilized as a booster for high octane number gasoline and are fundamental raw chemical in the petroleum and organic chemical industry.

Csicsery [1-4], has described the dehydrocyclo-dimerization of lower alkanes over bifunctional catalysts such Pt/Al₂O₃ and Cr₂O₃/Al₂O₃.

HZSM-5 zeolites in combination with transition metals have been reported as the catalysts for aromatization of lower hydrocarbons [5, 6]. Platinum exhibit great dehydrogenation capacity of light alkanes and catalytic activity but is expensive and is also active in hydrogenolysis to form unreactive alkanes C₁ and C₂ and cyclic compounds, which decrease the selectivity to aromatics [7-9].

It has been established that the loading of zinc or gallium cations onto HZSM-5 greatly enhances the selectivity for aromatic hydrocarbons in the transformation of lower alkanes and alkenes. Gallium has the advantage over zinc of the lower volatility under reduced atmosphere at high temperature and of the low activity in hydrogenolysis [7-39].

Zinc ionic and zinc oxide exhibit good dehydrogenation activity and aromatization selectivity but under severe treatments (≥ 550°C) zinc metallic can be formed and eluted as Zn vapors from the catalyst [33-74]. The use of a zinc modified HZSM-5 instead gallium might be preferential, especially from the environmental point of view owing to the poisonousness and the high price of gallium.

Ni-HZSM-5 and Ag-HZSM-5 catalysts exhibit a good activity and selectivity towards BTX aromatics in conversion of light alkanes and alkenes [75- 84].

In this work, we demonstrate that Ag-HZSM-5 (ion exchanged) has high active catalytic activities in the transformation of n-heptane into aromatic hydrocarbons. However Ag-HZSM-5 has a lower activity and selectivity comparative with Ga-Al-HZSM-5 (isomorphous substitution) or Zn-HZSM-5 (ion exchanged).

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 (Aldrich), concentrated sulphuric acid (Riedel - de Haen), and distilled water [85].

Crystallization of the homogeneous gel took place over 24 h at autogenously pressure and 453 K in 0.150 L Teflon-lined autoclaves with intermittent stirring. The synthesis product 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 (15 mL 1M solution per gram zeolite), followed by drying and air calcinations at 823K for 6h. HZSM5 sample, was converted by ion exchange with 0.1 M solutions of AgNO₃ in Ag-HZSM-5 with different content of metal (wt. % Ag, 1.02, 1.62 and 2.5).

Characterization

The structure type, phase purity and degree of crystallinity were determined by X-ray powder diffraction pattern which were obtained 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 (fig. 1). The pattern confirms that the synthesized zeolite has the structure identical to MFI-type zeolite [86, 87]. 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 is presented in figure 2. It reveals the well-defined morphology of crystals indicating highly crystalline material. Catalytic tests on aromatization of n-heptane were carried out in a pulse microreactor coupled with a GCH gas chromatograph. The products of

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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).

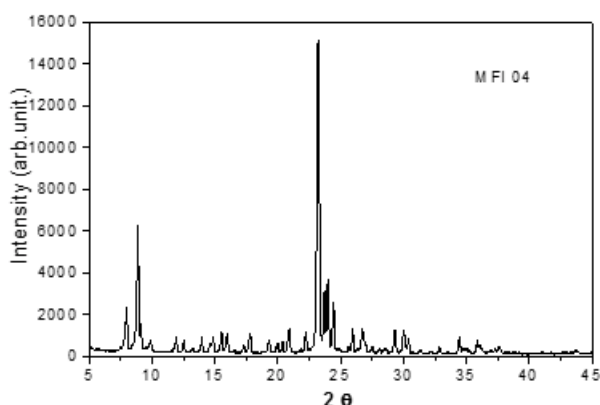


Fig. 1. X-ray diffraction pattern of NaZSM-5 zeolite

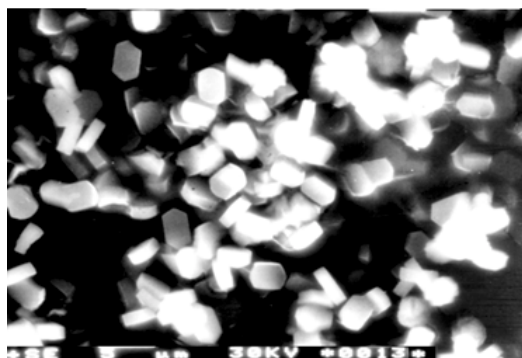


Fig. 2. SEM image of parent NaZSM-5 zeolite

The acidity and strength distribution on HZSM-5 and Ag-HZSM-5 catalysts were measured using Temperature Programmed Desorption (TPD) technique using ammonia. A known weight of the sample was activated in a dry N_2 at 500°C for 4h then cooled to 80°C when ammonia was admitted. The amount of ammonia desorbed from 373 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 ($\equiv Al$ and $\equiv Si^+$). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites M^{n+} , AlO^+). The temperature and the amount of desorbed ammonia give information about strength and number of the acid sites.

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 Ag-HZSM-5 catalysts are presented in table 1.

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
Ag1-HZSM-5	297.6	0.660	0.176	0.836
Ag2-HZSM-5	290.16	0.687	0.167	0.854
Ag3-HZSM-5	286.12	0.669	0.157	0.826

Table 1
PHYSICO-CHEMICAL
CHARACTERISTICS OF THE
STUDIED CATALYSTS

Temperature programmed desorption spectra of NH_3 revealed that the acid strength of HZSM-5 was considerably reduced by introducing Ag^+ cations.

It was indicated from the results that the acid sites distribution of the Ag-HZSM-5 changed after the metal incorporation in HZSM-5 (the incorporation of the Ni^{2+} ions into cationic positions), the medium and strong acid sites, in the catalysts weakened due the effect of Ag.

Catalytic studies

The catalytic properties of the H-HZSM-5 and Ag-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 than 0.1 g, were packed into a micro reactor and heated under a stream of N_2 at 823K 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 N_2 flow as carrier gas (1.32 L/h, n.c.) for each catalytic testing. The catalyst was dispersed in quartz wool to diminish the pressure drop. The temperature was varied from 673 to 823K measured with a thermocouple. Prior to the reaction, the catalyst was activated at 823K for 4 h under dried N_2 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 reaction of n-heptane over HZSM-5, Ag1-HZSM-5 (Ag wt. %, 1.02), Ag2-HZSM-5 (Ag wt. %, 1.62) and Ag3-HZSM-5 (Ag wt. %, 2.05) was carried out in the 673-823K range of temperatures and their total conversion and aromatic yields is plotted in figure 3 and 4.

The total conversion was slightly higher over Ag-HZSM-5 catalysts than over HZSM-5. The yields of aromatic hydrocarbons BTX appreciably increase by introducing silver cations into HZSM-5 zeolite.

The distribution of aromatic hydrocarbons in liquid fraction depends on the metal content of the catalyst and the working temperature as shown in figures 5-7.

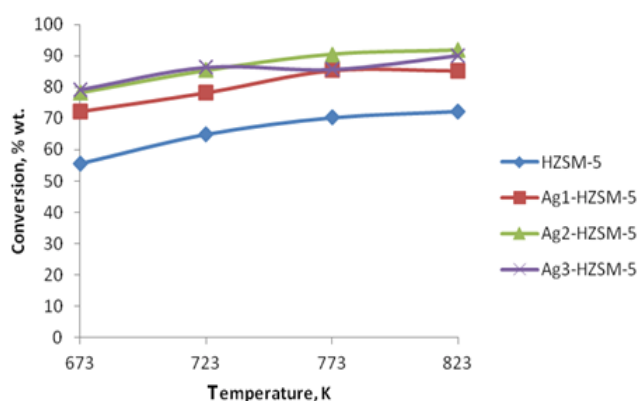


Fig. 3. Conversion of n-heptane vs. temperature on a HZSM-5 and Ag-HZSM-5 catalysts

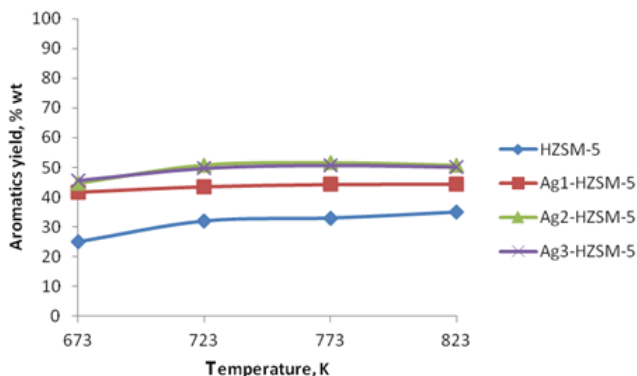


Fig. 4. Yield in aromatics vs. temperature on the HZSM-5 and Ag-HZSM-5 catalysts

The main component of liquid fraction is toluene, its concentration being controlled by the catalyst and by the working temperature. On Ag-HZSM-5 catalysts gives the greatest xylenes content and the lowest toluene content at higher temperatures of reactions comparative with Ga-Al-HZSM-5 or Zn-HZSM-5 [49, 54, 84-87].

As for the mechanism of the formation of aromatic hydrocarbons BTX, Poutsma [88] has proposed a mechanism involving Brønsted acid centers as active sites. Here, he proposed that aromatic hydrocarbons BTX molecules were formed from alkenes oligomers by successive deprotonation and hydride transfer to carbenium ions.

With this mechanism the formation of one molecule of aromatic hydrocarbons inevitably accompanies the formation of three molecules of alkanes. This mechanism is operative in conversion of light hydrocarbons over HZSM-5.

Enhancement of the aromatic yields over Ag-HZSM-5 are clear evidence that a mechanism other than the one described above is operative. One possibility is that silver species work as a dehydrogenation centers. In the presence of Ag⁺ cations, alkenes may undergo abstraction

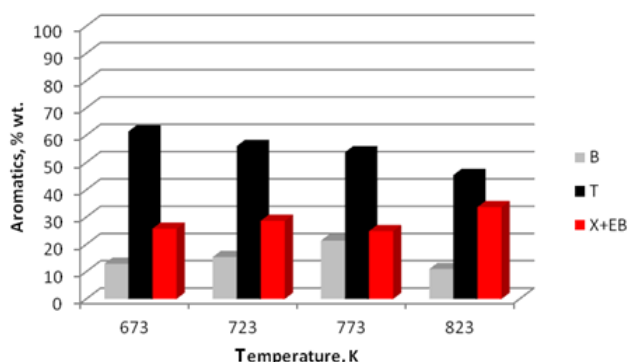


Fig. 5. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ag1-HZSM-5

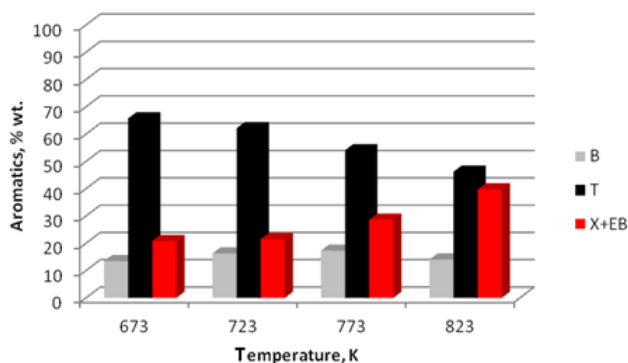


Fig. 6. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ag2-HZSM-5

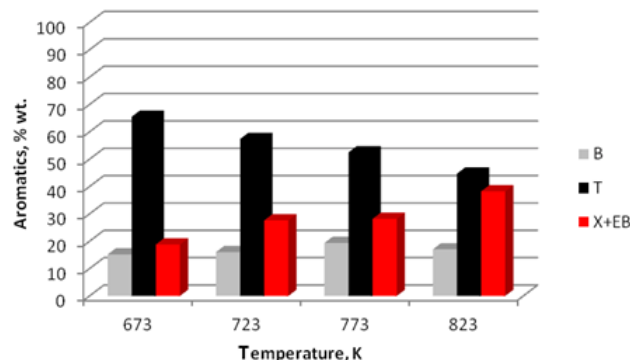


Fig. 7. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ag3-HZSM-5

of hydrogen atom (or ion) to form allylic species. Aromatic hydrocarbons may be formed by the successive abstraction of hydrogen atoms from higher alkenes or direct coupling of two allylic species with simultaneous production of hydrogen molecular [84].

Since the dehydrogenation path with metal cations (Ag⁺) does not result in the simultaneous formation of alkanes, there is essentially no limit to higher yield of aromatics. This explains the higher yield of aromatic hydrocarbons BTX over Ag-HZSM-5. Alkenes formed by cracking of alkanes (n-heptane) can be effectively transformed to aromatic hydrocarbons by dehydrogenation activity of these cations.

Consequently, it is clear that exist two types of activation of the reactant alkanes (n-heptane) molecules over Ag-HZSM-5, dehydrogenation by the action over Ag⁺ actions and cracking on Brønsted acid sites. Thus, relative contribution of the two types of activation seems to depend on both the nature of reacting alkanes and the primary reactions over acid sites.

Ag-HZSM-5 was much effective than HZSM5 in the aromatization of n-heptane. The difference in the product distribution between HZSM-5 and Ag-HZSM-5 is thought about by the difference in the acid strength of two catalysts. The silver cations Ag⁺ may be reduced by hydrogen which was produced during the dehydrogenation of hydrocarbons.

Kim, G.-J et al. [84] in study of X-ray diffractograms of the fresh and the used catalysts Ag-HZSM-5 observed as the formation of the Ag metal was found after using Ag-HZSM-5 as catalysts for 6h in the transformation of i-butane. These results indicate that the silver cations were reduced to Ag metals with resulting in the formation of acidic OH groups by hydrogen which was produced during the dehydrogenation of hydrocarbons:



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. 8). Therefore, when acidic nature of the catalyst is modified, the overall catalytic process in the zeolite pores would be greatly 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.

For Ag-HZSM-5 (and Zn-HZSM-5), formation of Brønsted acid sites was confirmed by presence a band at 1548 cm⁻¹ (pyridinium ion) a band at 1454 cm⁻¹ was observed in

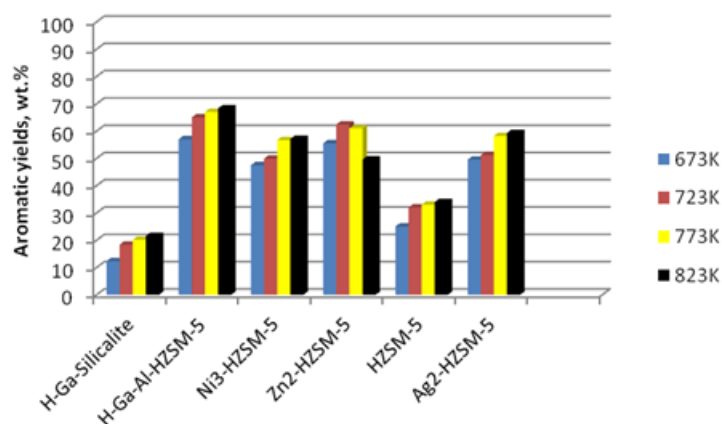


Fig. 8. Yield in aromatics vs. temperature on a series of the MFI catalysts

IR spectra, which was plausibly due to pyridine molecular interaction with Ag^+ (or Zn^{2+}) cations [84]. The yield of aromatic increased with increasing reaction temperature (up to 773K).

On the Ag-HZSM-5, xylenes were obtained in more quantity comparative with HZSM-5. These indicate that the aromatic hydrocarbons C_8 may be formed by the direct coupling of two butenes molecules (or by alkylation of benzene or toluene). The variety of the aromatic hydrocarbons BTX in products must be a reflection of the distributions of alkenes in the systems. This in turn implies that the oligomerization of alkenes and the aromatization steps are must faster than the interconversion among alkenes [84].

Conclusions

The yield of aromatics hydrocarbons BTX appreciably increased by introducing Ag^+ cations into HZSM-5 catalyst in aromatization of n-heptane. This may be attributed to the improvement of dehydrogenation activity of the catalyst by the presence of Ag species leading to the greater availability of olefins pool, which is the intermediate for aromatization.

The yield of aromatics increased with increasing reaction temperature. The aromatization activity of HZSM-5 and Ag-HZSM-5 catalysts depends on the acid-basic property and on the way in which occurs the aromatization resulted by hydrogen transfer.

Toluene was yielded as main aromatic product, followed by C_8 aromatics, and benzene from all the catalysts tested. On Ag-HZSM-5 catalysts xylenes and ethylbenzene were obtained in more quantity comparative with HZSM-5, Ni-HZSM-5 or Zn-HZSM-5

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