Study on *n*-heptane Conversion Over Ni-HZSM-5 Zeolite Catalysts

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The conversion of n-heptanes by the chromatographic pulse method in the temperature range of 673 - 823K on the MFI zeolites modified by ion exchange with Ni(NO₃)₂ aqueous solutions was studied. The catalysts, HZSM-5 (SiO₂/Al₂O₃ = 33.9), and Ni-HZSM-5 (wt. % Ni, 0.57, 1.09, 1.34,) having different acid strength distribution exhibit a conversion and a yield of aromatics depending on temperature and metal content. The highest selectivity for n-heptanes aromatization was obtained on the catalyst Ni3-HZSM-5 (wt. % Ni 1.34) at 823K. The metal actions and the acidic properties of zeolites have an important effect on the aromatization of n-heptanes.

Keywords: aromatization, n-heptanes, BTX, HZSM-5, Ni-HZSM-5

Benzene, toluene and xylenes hydrocarbons (BTX) have two main industrial uses [1]:

- because of their high octane number they constitute a significant part of gasoline pool (\sim 30%) even if due to antipollution legislation their utilization tends to decrease;

- they are also an important source of petrochemicals: aromatic chemicals represent about 30% of the total of some 8 million known organic compounds.

BTX are now obtained by catalytic reforming of naphtha's. However lights hydrocarbons, in particular liquefied petroleum gas (LPG), are becoming an attractive feed for the production of aromatics. Light alkanes aromatization over zeolite based catalysts is well known [2-5].

On MFI catalysts, low cost liquefied petroleum gas (LPG) can be transformed into valuable aromatics (mainly C_{e} -C_a) and into hydrogen. Unfortunately methane and ethane are also produced in significant amounts. A reduction of the production of these unwanted compounds would render the aromatization process economically more attractive. The reaction pathways of light alkanes aromatization were established on HZSM-5 and Metal (Pt, Ga, Zn) -HZSM-5. On H-ZSM-5 the first step is the dehydrogenation and the cracking of the reactants through carbonium ion intermediates. The resulting alkenes undergo rapid successive reactions via carbenium ion intermediates: oligomerization, cyclization and hydrogen transfer. The selectivity toward aromatics is limited because of the formation of alkanes by hydrogen transfer (three moles of alkanes are formed for one mole of aromatics hydrocarbons).

It has been known that HZSM-5 zeolite can be modified by incorporation of metal or metal oxides in order to obtain catalysts for selective hydrocarbon conversion [6-8]. Activity, selectivity and stability of these catalysts for those shape selective reactions depend not only on the porous structure of the zeolite but also on the density of acid sites distribution a metal support interactions [9].

Platinum exhibit great dehydrogenation capacity of light alkanes and catalytic activity but is expensive and is also active in hydrogenollysis to form unreactive alkanes C_1 and C_2 and cyclic compounds, which decrease the selectivity to aromatics [10 – 14].

Gallium improves both the rate and selectivity of light hydrocarbons aromatization. Gallium has the advantage over zinc of the lower volatility under reduced atmosphere at high temperature and of the low activity in hydrogenollysis [15-37].

Zinc ionic and zinc oxide exhibit good dehydrogenation activity and aromatization selectivity but under severe treatments (\geq 550°C) zinc metallic can be formed and eluted as Zn vapours from the catalyst [38 - 59]. 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-HZM-5 catalysts exhibit a good activity and selectivity towards BTX aromatics in conversion of light alkanes and alkenes [60- 69]. MFI-zeolites modified with, Sn, Zr, Cu, and Ge exhibit also a good activity in conversion of light alkanes and alkenes into aromatics [70-72].

The present work deals with the results obtained by investigation of aromatization of n-heptane on the HZSM-5 type ion-exchanged with Ni(NO₂), aqueous solutions.

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 (SO₂) $_{3}$ x 18 H₂O (Aldrich), concentrated sulphuric acid (Riedel - de Haën), and distilled water [73].

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

order to remove the organic agent. The calcined Na-ZSM5 was converted into H-form by three successive ion exchanges with 1M NH₄NO₃ solution at 353 K for 6 h (15 mL 1M solution per gram zeolite), followed by drying and air calcinations at 823 K for 6 h. HZSM5 sample, was converted by ion exchange with 0.1M solutions of Ni(NO₃)₂ in Ni-HZSM-5 with different content of metal (wt. % Ni, 1.34, 1.09, 0.57).

Characterization

The structure type, phase purity and degree of crystallinity were determined by X-ray powder diffraction

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pattern which were obtained on a Philips PW 1830 diffractometer using Ni filtered Cu K_a radiation at a scanning speed of 0.02° s⁻¹ in the range öf 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 zeolite has the structure identical to MFI-type zeolite [74]. 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. It reveals the well-defined morphology of crystals indicating highly crystalline material. Catalytic tests on aromatization of nheptane were carried out in a pulse micro reactor 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 Ni-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 (\equiv Al and \equiv Si⁺). Low temperature peak correspond to less acidic sites (terminal OH groups, cationic sites \dot{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 Ni-HZSM-5 catalysts are presented in table 1.

It was indicated from the results that the acid sites distribution of the Ni-HZSM-5 changed after the metal incorporation in HZSM-5 (the incorporation of the Ni²⁺ ions into cationic positions), the medium and strong acid sites, in the catalysts weakened due the effect of Ni (decreasing the number of Brönsted strong acid sites and increasing the Lewis acid sites).

Catalytic studies

The catalytic properties of the H-HZSM-5 and Ni-HZSM-5 samples were tested in acid-catalyzed reaction of nheptane 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, 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 N₂ 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 K to 823 K measured with a thermocouple. Prior to the reaction, the catalyst was activated at 823 K for 4 h under dried N₂ flow (22 mL/min).

The products of reactions (only aromatic BTX) were online 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 catalytic activity was investigated in the temperature range of 673-823 K with 0.2 mL n-heptane pulse in N₂ flow as carrier. Conversion vs. temperature on of the MFI catalysts is presented in figure 1.

Catalytically conversions on n-heptanes increase as temperature increases, but not exceed 90%. Also, nheptane conversion increased with metal cations (Ni²⁺) content in Ni-HZSM-5 catalysts.

BTX aromatics yield variation with temperature in the reaction of n-heptane flavoring is represented in figure 2.



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

Fig. 2. Yield aromatics vs. temperature on of the MFI catalysts

On the catalysts Ni-H-ZSM-5 BTX aromatics yields is higher in comparison with HZSM-5. It also found a slight increase in aromatic yield with Ni content of the catalysts Ni-HZSM-5.

There is a general acceptance that the major role of the metal in the catalyst is to accelerate the combination of surface hydrogen, which formed from the dehydrogenation processes involved in key steps in the conversion of light hydrocarbons to aromatics hydrocarbons via alkenic intermediates. The Ni may have a more marked tendency to accelerate the combination of surface hydrogen than HZSM-5, so the aromatics selectivity of the Ni-HZSM-5 is higher that of HZSM-5. The relatively less medium and strong acid sites in Ni-HZSM-5 than the HZSM-5 is potentially related to the higher aromatization activity of the former.

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

The main component of liquid fraction is toluene, its concentration being controlled by the catalyst and by the working temperature. As long as the working temperature increases, takes place an increase of benzene and C₈ aromatics concentrations, probably due to the disproportionation reaction as well as toluene alkylation / desalkylation. Toluene, as primary product of aromatization



Fig. 3. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ni1-HZSM-5



Fig. 4. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ni2-HZSM-5



Fig. 5. Aromatics, BTX, distribution (wt %) vs. temperature on conversion of n-heptane over Ni3-HZSM-5

of n-heptane over Metal-modified catalysts is the result of a successive transformations of 1,2-hexenes following in principal the $C_1 - C_6$ ring closure. n-Heptane molecule in the cavity of intersection of two channels of MFI zeolite (0.85-0.9 nm diameter) is adsorbed on C_1 atom on a Metal/ aluminum site and, because the length of hydrocarbon chain exceed the diameter of cavity, the molecule adopt the structure of C_1 - C_6 ring.

In a bifunctional čatalyst, Ni-HZSM-5, Ni²⁺ species are responsible for dehydrogenation (because they exert strong hydrogen attracting action) and for the disposal of H₂ in the gas phase (consequently enhance aromatization) and the acidic sites (zeolitic protons) catalyze the cyclization of olefinic intermediates and cracking.

The formation of toluene illustrates that cyclization may occur by a mechanism involving 1, 6 - ring closure.

It is stated that the protons associated to the framework Al are responsible for the strong Bronsted acidity of zeolites. The results are comparable with those reported on HGa[AlZSM5] obtained by ion exchange [18].

It is accepted that the aromatization of n-heptane over monofunctional (H-Form) and bifunctional catalysts 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 metal cations catalyses, the dehydrogenation/hydrogenation steps and H⁺ acidic sites of zeolite are responsible for the other aromatization reaction sequences which involve hybrid transfer and deprotonation of carbenium ions (fig. 6).



Fig. 6. Yield in aromatics vs. temperature on a series of the MFI catalysts

The forming of toluene over aluminosilicate catalyst decreases with increasing of temperature because of coke generation and deposition. In the same time, the benzene and especially of xylenes content over H/AlMFI catalyst is increasing with the increasing of reaction temperature. The aromatic hydrocarbons distribution over Me-HZSM-5 catalysts is correlated with reaction temperature and acidity: the toluene remains the principal component (primary product) and the xylenes exceed the benzene (secondary products). In this case, the toluene is a result (partially) of a direct aromatization of n-heptane via 1, 6-cyclization and byproducts, benzene and xylenes, mainly by disproportion and alkylation of toluene.

The incorporation of Ni (II) into cationic positions of HZSM5 zeolite affects the acidity and the strong attraction of Ni for hydrogen is responsible for higher conversion (~ 70%) and aromatic yield (~ 40%) for n-heptane aromatization. Aromatic yield on Zn-HZSM5 decreases at temperature higher than 723 K because of sublimation and/ or migration from the active sites. The conversion of n-heptane on Ag-HZSM5 is similar to that on Zn-HZSM5 but the aromatic distribution is different. The increase of



temperature determines an increase of xylenes concentration. Ni - ion exchange ZSM5 was less effective in the aromatization of n-heptane that Ag- and Zn- HZSM-5.

Conclusions

In the n-heptane aromatization on modified MFI zeolites, the conversion, and the aromatic yield depend on the metal cations (incorporated by ionic exchange) where they serve as active sites for dehydrogenation and for olefins interconversion and less for cracking.

The catalytic activity is correlated with acidity of catalysts by conversion, aromatic yield and aromatic hydrocarbons distribution.

The aromatization of n-heptane within temperature range 673-823 K is situated in the following series:

Ni3-HZSM5 \geq Ni2-HZSM5 > Ni1-HZSM5 > HZSM5.

n-Heptane conversion over HZSM-5 occurs via a complex sequence of cracking, oligomerization, isomerisation, cyclization, β -scission and H transfer.

n-Heptane conversion over Me-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).

On HZSM-5 n-heptane undergo cracking over Brönsted sites of zeolites to give lower olefins and smaller paraffin's. Lower olefins formed by cracking of alkanes dimerize to yield higher olefins which undergo cracking to regenerate lower olefins. Isomerization of olefins proceeds simultaneously with dimerization and cracking over acid sites. The combination of these reactions leads to the formation of a variety of olefins. Then, repeated hydride abstraction and deprotonation of higher olefins yield aromatics.

Since the formation of one molecule of aromatic hydrocarbons accompanies the formation of three molecules of alkanes, the yield of aromatics is limited [75].

In presence of zinc, silver and nickel cations, alkenes may undergo direct abstraction of a hydrogen atoms (or ions) to form allylic species. Aromatic hydrocarbons may be formed by the successive abstraction of hydrogen atoms (or ions) from higher alkenes or by direct coupling of two allylic species with simultaneous production of hydrogen. All elementary reactions found over HZSM-5 also proceeds over and Ni-HZSM-5 by action of Bronsted acid sites. The incorporation nickel species does not generate acidic centers capable of catalyzing hydride-transfer reactions. Since the dehydrogenation path with metal cations does not result in the simultaneous formation of the alkanes, there is essentially no limit to higher yield of aromatics. Alkenes formed by cracking of alkanes can be effectively transformed to aromatic hydrocarbons by the dehydrogenation activity of these cations. Consequently, it is clear that there exist two types of activation of reactant alkanes molecules over, Metal-HZM-5, dehydrogenation by the action of Ni cations and cracking on Brönsted acid sites.

Scheme 1

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