Methylcyclohexane conversion over ZSM-11 zeolite

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ZSM-11 zeolite samples differing by their active sites (H^+ and Zn^{2+}) have been studied in the conversion of methylcyclohexane. It was observed that both the conversion and the selectivity to aromatic hydrocarbons are increased with the zinc content. It has been shown that dehydrogenation of the hydrocarbon, leading directly to toluene, is the initial stage for Zn-ZSM-11 zeolite showing very low cracking activity. These factors make zeolite ZSM-11 with Zn^{2+} as counter ion a competitive catalyst for naphthene aromatization.

Keywords: H-ZSM-11; Zn-ZSM-11; methylcyclohexane conversion; active sites; aromatization

1. Introduction

Pentasil zeolites modified by Zn^{2+} and Ga^{3+} cations are active in the transformation of light paraffins and olefins into aromatic hydrocarbons [1–7]. Studies have been made on the catalytic properties of Zn^{2+} modified ZSM-5 zeolite for aromatization of cyclohexane [8]. Methylcyclohexane has been used as a probe molecule to investigate the cracking behavior of naphthenes over zeolite Y catalysts [9]. Smirniotis and Ruckenstein [10] examined the influence of temperature on the product distribution, for the reforming of methylcyclopentane and methylcyclohexane using Pt impregnated β zeolite. In this work, the transformation of methylcyclohexane into aromatic hydrocarbons using ZSM-11 type zeolite with proton and Zn^{2+} as active sites is studied.

2. Experimental

Zeolite type H-ZSM-11 and Zn-ZSM-11 were synthesized by published methods [11,12] and characterized by XRD, FT-IR and TPAD [13]. The Si/Al ratio was 17 for both catalysts. 99.9%, Fluka methylcyclohexane (MCH) was used without further purification. All the reactions were performed using a fixed bed flow reactor, on line with a gas chromatograph equipped with FID.

MCH was delivered by a motor-driven syringe to be vaporized in the preheating zone of the reactor. The reaction products were analyzed chromatographically on a Gow-Mac 750P instrument using a capillary column 30 m AT-1, connected on line.

In order to investigate the effects of the reaction conditions, H-ZSM-11 zeolite and Zn-ZSM-11 zeolite with 0.84 Zn/Zn + H were used. To study the effect on Zn loading, zeolites with various Zn contents were prepared. The operating conditions were as follows: temperature 400–520°C, contact time 2–100 g h/mol, pressure 1 atm, reaction time 30 min. Conversion, yield and product distribution were expressed on a carbon-atom basis.

3. Results and discussion

Figs. 1 and 2 show the influence of the temperature on aromatic selectivity and aromatic yield for MCH conversion over H-ZSM-11 and Zn-ZSM-11. MCH conversion was higher over Zn-ZSM-11 than H-ZSM-11 in the whole range of temperature studied, indicating that Zn^{2+} species enhanced MCH ring activation.

The lower MCH conversion and aromatic selectivity produced over H-ZSM-11 than Zn-ZSM-11 zeolites,suggest a different type of interaction between MCH with protonic center (Brønsted sites) and aprotonic center (Lewis sites). As we can see in fig. 1, the aromatic selectivity decreases with temperature, which is in good agreement with the proteolytic cracking increase observed simultaneously.

Under the conditions employed in this study, the reactions which take place over ZSM-11 zeolite are competitive and may occur simultaneously (cracking, ring opening, hydrogen transfer, dehydrogenation, isomerization).

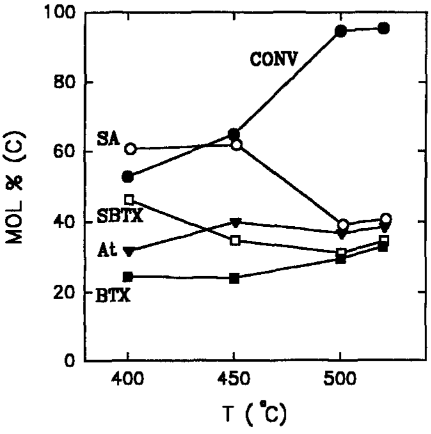

Fig. 1. Aromatic yield (At), benzene–toluene–xylenes yield (BTX) and aromatic selectivity (SA), and BTX selectivity (SBTX) from MCH conversion (CONV), over H-ZSM-11 zeolite as a function of temperature, $w/f = 58$ g h/mol after 30 min on stream.

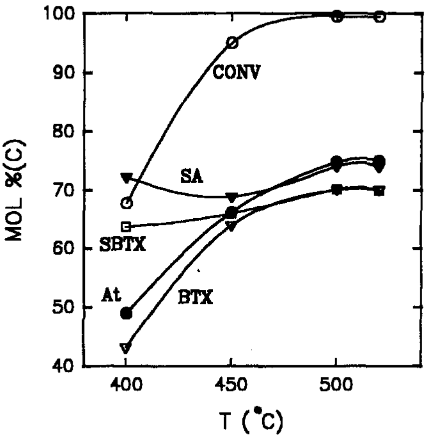

Fig. 2. Aromatic yield (At), benzene–toluene–xylenes yield (BTX) and aromatic selectivity (SA), and BTX selectivity (SBTX) from MCH conversion (CONV), over Zn-ZSM-11 zeolite as a function of temperature, $w/f = 58$ g h/mol after 30 min on stream.

There are two ways for ring opening when catalysts with protons as active sites are considered, in accordance with Corma et al. [9]:

(A) *By protolysis*, the primary formed carbocation could desorb as heptane after producing hydride abstraction, or desorb as heptene by deprotonation. Moreover, it could crack after or before isomerization giving an alkene and a sorbed carbenium ion. The carbenium ion could desorb giving an alkane or an alkene by hydride transfer or deprotonation.

(B) *By β-scission*, the methyl cyclohexyl carbocation could produce heptadiene, heptene or products with less than seven carbon atoms.

Fig. 3 shows a different behaviour of H-ZSM-11 and Zn-ZSM-11 in toluene and heptane selectivities, with temperature. The analysis of the results give the relative rate of the C_6 ring opening reaction and hydride transfer reaction. In fig. 3, the decrease of toluene and heptane yields over 450°C suggests that cracking of MCH by protolysis is predominant in the presence of H-ZSM-11 zeolite.

Yields for cracking derivatives were always higher than for heptene and heptane, Cyclo-olefins were not detected in the products due to their high reactivity.

Cracking products could be originated by ring opening reactions. It seems that heptane and heptene initially formed by ring opening are readsorbed to produce secondary cracking products. This would mean that heptene and heptane were non-stable primary products [9]. Results illustrated in fig. 3b show that the toluene selectivity was higher over Zn-zeolite than H-ZSM-11 zeolite, in the whole range of temperature studied.

In fig. 4, toluene, heptane and heptene yields at different MCH conversion levels are shown. As can be seen, according to the results obtained by using the standard optimum performance envelope technique [14], see fig. 4, heptane and heptene

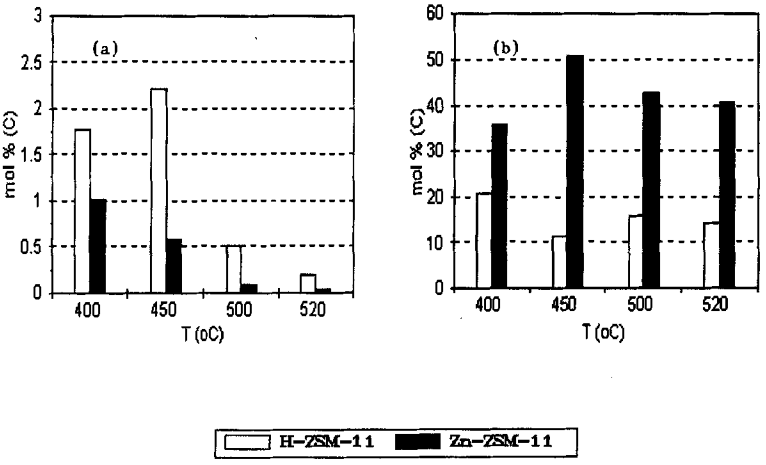

Fig. 3. *n*-heptane selectivity (a), and toluene selectivity (b), from MCH conversion over H-ZSM-11 and Zn-ZSM-11 as a function of temperature, $w/f = 58$ g h/mol after 30 min on stream.

appear as unstable primary products, while toluene is found to be a stable primary product over Zn-ZSM-11.

In figs. 5 and 6 the MCH conversion and individual aromatic yield are plotted versus contact time at 450°C using Zn-ZSM-11 and H-ZSM-11. Zn-ZSM-11 showed high activity and produced more aromatic hydrocarbon than H-ZSM-11, indicating the dehydrogenation effect of the Zn^{2+} species. This interpretation is supported by the high relative yields of toluene/heptane (fig. 3). As for fig. 4, it can be seen that initial activity for toluene yield is higher than for heptane and heptene yield.

In agreement with ref. [15] and with our above mentioned results, toluene could be formed by three consecutive dehydrogenation reactions in the presence of Zn^{2+} species:

MCH → methylcyclohexene → methylcyclohexadiene → toluene

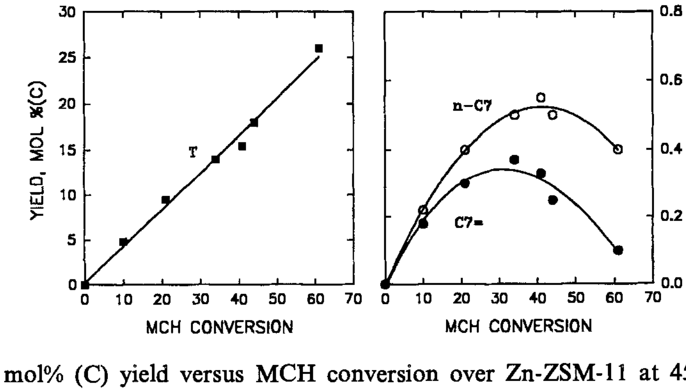

Fig. 4. Plots mol% (C) yield versus MCH conversion over Zn-ZSM-11 at 450°C. (a) Toluene, (b) *n*-heptane, 1-heptene.

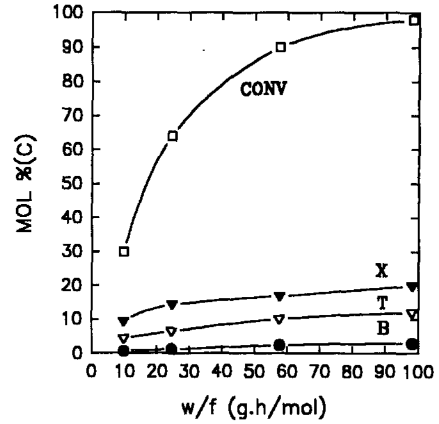

Fig. 5. Change in the distribution of aromatic products with contact time in the reaction of MCH over H-ZSM-11 at 450°C. Conversion (CONV), benzene (B), toluene (T) and xylenes (X).

Thermodynamically, the first step has a low frequency factor. The high initial selectivity to toluene could be attributed to the dehydrogenating action of Zn^{2+} species. Thus, *β-scission* reaction would be depressed with respect to hydride abstraction over Zn-ZSM-11 zeolite.

The dehydrogenation action of Zn^{2+} would lead to methylcyclohexene (MCH=) as an intermediate. MCH= could work as alkene and naphthene, being a proton acceptor. The generated methyl cyclohexyl carbenium ion could be an hydride acceptor, increasing the dehydrogenation action and leading to aromatics. However, toluene could be produced by direct dehydrogenation of MCH= [8]. Xylenes and benzene formation require alkylation, dealkylation or disproportionation reactions. In this way, we could expect different individual aromatic selectivities over Lewis or Brønsted sites. Fig. 7 shows individual aromatic selectivities on

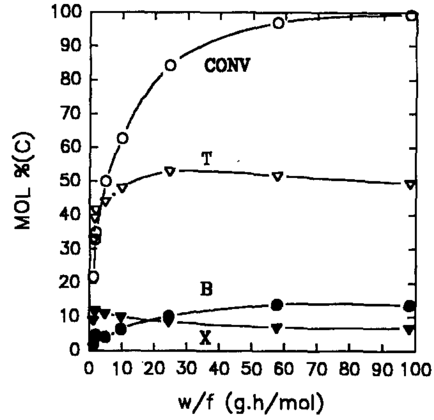

Fig. 6. Change in the distribution of aromatic products with contact time in the reaction of MCH over Zn-ZSM-11 at 450°C. Conversion (CONV), benzene (B), toluene (T) and xylenes (X).

H-ZSM-11 type zeolite with different Zn loading. Xylenes selectivity over H-ZSM-11 is higher than observed on Zn-ZSM-11, probably because of an enhancement methylation with Brønsted acidic sites. A catalyst with $Zn^{2+}/Zn^{2+}+H^{+}$ molar fraction of 0.84 is seven times more selective on toluene than H-ZSM-11, see fig. 7.

According to IR studies presented earlier [13], absorption bands for OH groups (Si–OH) with maximum at 3740 cm^{-1} were observed for both samples (H-ZSM-11 and Zn-ZSM-11), whereas the band at 3610 cm^{-1} (bridging OH groups) was absent in H-ZSM-11 loaded with zinc. According to the above mentioned IR results, the samples used in this study, most probably will present sites of type:

(I) $[Si(OH)Al]_{Lattice}$ Brønsted sites,

(II) $[Si(O)Al]_{Lattice}$- - -$Zn^{\delta+}$- - -$[Si(O)Al]_{Lattice}$.

Therefore, differences in the selectivities of the protonic form and aprotonic form of the catalysts can be explained in terms of changes of the nature and concentration of active sites. Thus, the introduction of Zn as counter ion is responsible for the creation of dehydrogenation and aromatization centers. Also, the lowering of the strong Brønsted sites decreases the cracking activity by protolysis or β-scission, producing high aromatic selectivity.

4. Conclusions

According to the experimental data obtained with H-ZSM-11 and Zn-ZSM-11, the activation mode of MCH is different for both catalysts. For the first one, the ring opening (by protolysis or β-scission) seems to be determinant, whereas for the Zn-loaded zeolite, the dehydrogenation functions of electron-acceptor sites produced by the incorporation of Zn^{2+} as counter ion diminish the concentration of the strong Brønsted sites and produce toluene directly with high selectivity. When

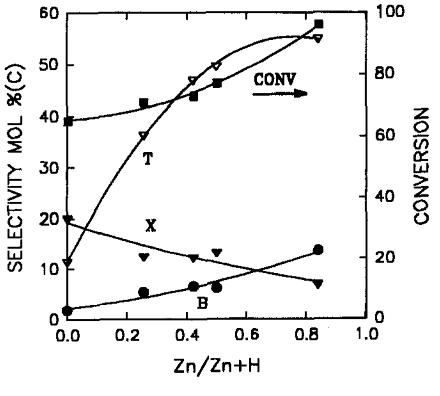

Fig. 7. The effect of the Zn concentration in H-ZSM-11 on the MCH conversion and aromatic selectivity at 450°C and $w/f = 58$ g h/mol. Conversion (CONV), benzene (B), toluene (T) and xylenes (X).

Zn-ZSM-11 zeolite is used for the conversion of MCH, heptane and heptene are unstable primary reaction products, whereas toluene is a stable primary product.

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