Zn-ZSM-11 zeolite catalyst for LPG aromatization

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LPG transformation into aromatic hydrocarbons using Zn^{2+} modified pentasil zeolites has been studied at 450–540°C and 10–58 g h/mol. The conversion and selectivity to aromatics obtained over Zn-H-ZSM-11 catalysts with different degree of exchange suggest, the primary role of the Zn^{2+} species is in C–H activation and the transformation of the intermediates into aromatic hydrocarbons.

Keywords: Zeolites; Zn-H-ZSM-11; LPG conversion; selectivity to aromatics

1. Introduction

H-ZSM-5 and H-ZSM-11 zeolites catalyze the transformation of light paraffins into aromatic hydrocarbons with great success [1–3]. Zn-ZSM-5 zeolite is more active and more selective than H-ZSM-5 in the production of BTX [2,4–6]. We have reported that Zn-ZSM-11 shows excellent aromatization behavior for C_3, C_5 and C_6 paraffins [7,8]. In this paper we report the results obtained for conversion of LPG (propane 30%; butane 70%) over 0.84Zn-0.16H-ZSM-11 material. The zinc species enhanced the aromatics yield, and the effect of zinc loading on the H-ZSM-11 zeolite performance was studied using propane as reactant.

2. Experimental

Zeolite type ZSM-5 and ZSM-11 were synthesized by known methods according to Mobil Patents [9,10] with some modifications [11]; the zinc-exchanged forms of ZSM-11 zeolite were obtained by the procedure reported in ref. [8]. The catalysts with different degree of zinc content were prepared at various times of exchange, obtaining the following material with different $Zn^{2+}/H^{+}+Zn^{2+}$ (Zn molar fraction): sample (a): 0; (b): 0.256; (c): 0.422; (d): 0.5; (e): 0.84;

(f): 0.88. The Si/Al ratios obtained by chemical analysis were: (a), (b), and (c): 20.7; (d), (e) and (f): 20.81. H-Zn-zeolites (samples (a)–(f)) were obtained by heating ammonium-Zn-zeolites in the flow of N_2 (20 ml/min) from 50 to 540°C, at heating rate of 10°C and heating it in inert atmosphere for a further period of 60 min at 540°C. The nitrogen flow was then switched over to air (20 ml/min) at 540°C for a period of 120 min. In the calcined samples under controlled atmosphere of N_2 and air, the zinc was preferentially incorporated in the crystallite; SEM-EDX analysis from the catalyst samples registered that the content of Zn with respect to other elements is nearly constant. The XPS data of Si/Zn was 15 to 40 times greater than the total ratio; thus the zinc was not on the outer surface of the zeolite.

LPG and propane transformation were carried out in a flow reactor on line with a gas chromatograph for products analysis. The operating conditions were: temperature 450–540°C; contact time 10–58 g h/mol; pressure 1 atm; reaction time 30–60 min.

3. Results and discussion

In table 1 we show the catalytic activity of various zeolites for LPG transformation in mol% C at 500°C and w/f = 18 g h/mol. As can be seen in table 1, the zinc-zeolites showed increased activity and produced more aromatic hydrocarbons than H-ZSM with the best BTX selectivity.

In fig. 1 the conversion of LPG, the aromatics yield, aromatics selectivity and BTX selectivity are plotted against contact time at 540°C using sample (e). The conversion increased with the contact time (5–20 g h/mol) and then showed a modest increase (20–58 g h/mol). The aromatics yield and aromatics selectivity passed through a maximum at contact time 18 g h/mol. The BTX yield in the

Table 1
Conversion and selectivity data for the LPG reaction over various zeolites [a]

Catalyst	T (°C)	Conv. (%)	Total aromatic	Aromatics selectivity	BTX selectivity
H-ZSM-5	500	40.2	13	32.2	28.3
H-ZSM-11	500	39.1	11.5	29.4	25
Zn-ZSM-5 [b]	500	82.5	54.9	66.5	63.5
Zn-ZSM-11 [c]	450	49	34	69.3	66
	480	71	48.8	67.6	64
	500	82	52	63.4	59.1
	540	83	53.4	64.3	59

[a] Contact time 18 g h/mol. Results are in molar%C basis.
[b] Si/Al = 34; Zn/Zn + H = 0.76.
[c] Sample (e).

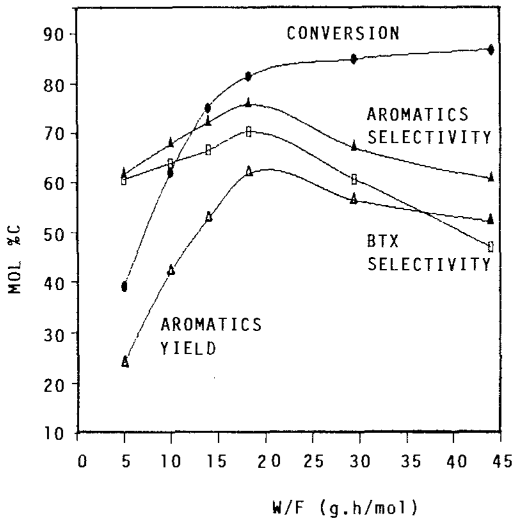

Fig. 1. Change in total conversion (●), yield of aromatics (△), selectivity to aromatics (▲) and BTX selectivity (□) with contact time at 540°C using sample (e).

total aromatic was 100% at contact time below 5 g h/mol. The aromatics distribution varies with the contact time, as can be seen in fig. 2. Xylenes fell steeply from w/f 5 to 58 g h/mol, while toluene was almost constant. The increased proportion of benzene and C_{9+} species with the contact time probably arises from demethylation and secondary transalkylation reactions.

The effect of the zinc loading on the H-ZSM-11 zeolite for the conversion and aromatics yield at 500°C and w/f = 18 g h/mol is given in fig. 3. The zinc

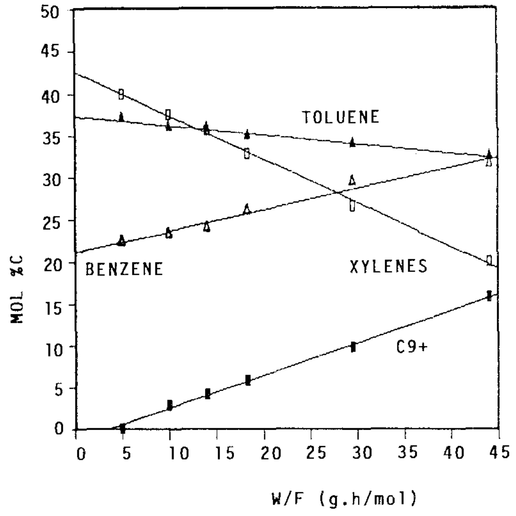

Fig. 2. Aromatics distribution at 540°C and different contact times using sample (e): benzene (△), toluene (▲), xylenes (□), C_{9+} (■).

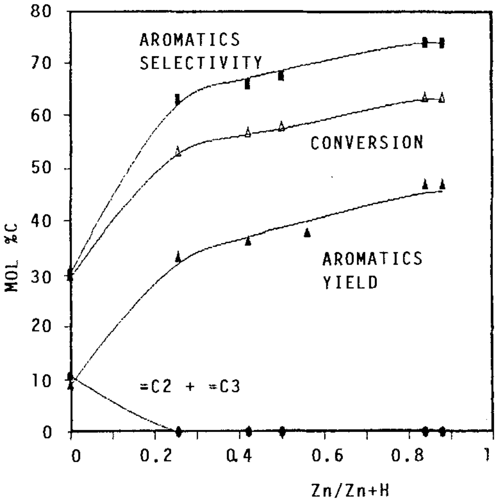

Fig. 3. The effect of the Zn concentration in H-ZSM-11 on the catalytic properties at 500°C and w/f = 18 g h/mol. Propane conversion (△), aromatics yield (▲), aromatics selectivity (■), and $=C_2+=C_3$ yield (●).

species caused an important effect on the propane conversion, as well as in aromatics yield. Olefins with two and three carbon atoms were only detected when we used sample (a). As the zinc loading increased, ethylene and propene were introduced into the polymerization, cyclization, dehydrogenation and aromatization complex mechanism.

Taking into account that the acidic properties of Zn-ZSM-11 zeolite and H-ZSM-11 zeolite [8] are similar, the increase of the activity and selectivity to aromatic hydrocarbons of Zn-ZSM-11 in propane conversion would not be attributable to a change in acidic properties. However, TPD spectra of ammonia from NH_4-Zn-ZSM-11 zeolites with different zinc content showed that zinc first blocked the strong Brønsted acidic sites [12], generating new and strong Lewis acidic sites [13]; thus the residual protons produced by thermal ammonia desorption were weak or medium Brønsted acidic sites [13,14]. In addition, calculations of the partial charge of hydrogen by Sanderson electronegativity for samples (b)–(f) showed that zinc lowered the partial charge on residual protons [15]. The results obtained by FT-IR of pyridine desorbed at different temperatures were in concordance with the ammonia desorption (not ammonia preadsorbed) and Sanderson electronegativity calculation [15]. Thus, if the remaining Brønsted acidic sites catalyze any step of the reaction, this step needs medium or weak acidic sites. It appears more likely that the function of zinc species is activation of paraffins and aromatization of the intermediate products [2,8,16]. The direct abstraction of a hydride from propane, producing a carbenium-like surface species (propyl-carbenium ion), and then by deprotonation propene, which can react further with the formation of higher-molecular-weight oligomers, is now well established [2,17–19].

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