Aromatisation of *n*-heptane over ZSM-5 prepared without the aid of a template

A.R. Pradhan, N. Viswanadham, S. Suresh, O.P. Gupta, N. Ray,
G. Muralidhar, Uma Shanker and T.S.R. Prasada Rao

Indian Institute of Petroleum, Dehradun 248005, India

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ZSM-5 was prepared without the aid of an organic template. Effect of synthesis parameters on its catalytic activity in aromatisation of *n*-heptane are discussed. Addition of seed material increased the crystallinity of the ZSM-5 phase. The catalytic activity was comparable with a sample prepared using an organic template. Formation of higher amount of C_{9+} aromatics was observed over the non-templated zeolite.

Keywords: *n*-heptane aromatisation; ZSM-5; non-templated

1. Introduction

Zeolite ZSM-5 is well known for its various applications in petroleum and petrochemical industries [1]. Usually, this zeolite is prepared using quaternary ammonium compounds, amines and other organic compounds as templating agents [2]. The role of these structure-directing agents has been discussed as gel modifier by interacting physically and chemically with different gel components and as void filler [3]. These organic compounds are expensive, corrosive and need to be removed before the zeolite is put to actual application. Because of these disadvantages, synthesis of pentasil zeolite ZSM-5 without the aid of an organic template is very attractive. There are reports in literature on such synthesis; however, these syntheses resulted in products of lower crystallinity and formation of impurity phases [4,5]. The present study was undertaken with a view to getting further insight into the zeolite synthesis and exploring the possibility of its application in aromatisation of *n*-heptane.

2. Experimental

2.1. ZEOLITE CRYSTALLISATION

Synthesis of zeolite ZSM-5 without the aid of an organic template was carried out by mixing appropriate amounts of silica gel (mesh 200–300), sodium hydroxide

(AR, Merck), aluminium sulphate (AR, Sarabhai Chemicals) and deionised water. The chemical composition of the initial gel was $3Na_2O : Al_2O_3 : 30SiO_2 : 825H_2O$.

Final pH of the reaction mixture was adjusted to 10.5 using 1 : 1 H_2SO_4 to get gel suspension. At this stage an appropriate amount of the seed material was added to the reaction gel. The mixture was stirred for 15 min before transferring it to a stainless steel autoclave (500 ml capacity). All preparations were carried out at 150°C, 72 h crystallisation time and under static conditions. At the end of the crystallisation the reactor was quenched to room temperature.

The white crystalline solid was collected on a filter, washed repeatedly with deionised water and dried at 120°C for 6 h in an air oven. ZSM-5 zeolite with template was made using a gel composition $1.5(TPA)_2O : 3Na_2O : Al_2O_3 : 30SiO_2 : 825H_2O$.

The zeolite sample thus obtained was calcined at 480°C for 12 h in presence of dry air to remove organic matter. All samples were then ion exchanged repeatedly with 5 N NH_4NO_3 solution till the residual sodium is less than 100 ppm. Extrudates (1 mm diameter) of the catalyst were made using alumina as the binder.

2.2. PHYSICO-CHEMICAL CHARACTERISATION

X-ray diffraction (XRD) powder patterns were recorded on a Rigaku model D.max 111B diffractometer using Cu K_α radiation. The percentage crystallinity was determined by comparing the intensities of the peaks in the 2θ range of 22–25° with those for the respective peaks of the reference sample. The ZSM-5 zeolite sample obtained using the organic template with the same silica-to-alumina ratio was considered to be 100% crystalline and used as a reference sample. Diffuse reflectance infrared patterns were recorded with a Perkin Elmer model 1700 X using KBr discs. The thermogravimetric analysis was carried out using DuPont model 951 Thermogravimetric analyser. The thermal stability of the samples was also confirmed by calcining zeolite samples at different temperatures and examining the X-ray diffraction powder patterns. Their crystal morphology was examined with a scanning electron micrograph Philips model 525 fitted with a tungsten filament. The zeolite samples were coated with Au·Pd film for the study. Adsorption measurements were performed on a static high vacuum volumetric adsorption unit.

2.3. CATALYTIC STUDIES

The catalytic studies were carried out in a high pressure microreactor unit with 5 ml of the catalyst loaded in the constant temperature zone of a stainless steel reactor (10 mm id). The catalyst was activated at 500°C in presence of air before the reaction. *n*-heptane was fed at an LHSV of 2 h^{-1} using nitrogen as a carrier gas. The reaction product was cooled and separated into gaseous and liquid products in a high pressure separator. The liquid product was analysed using a Hewlett Packard gas chromatograph model 5730A fitted with a TCEP column and FID detector. Gaseous products were analysed using a squalane column. All experiments were carried out at 400°C, 10 kg/cm^2 pressure and a nitrogen-to-hydrocarbon mole ratio of two. After each experiment the catalyst was regenerated in a flow of air at 500°C for 6 h.

3. Results and discussion

3.1. NON-TEMPLATED SYNTHESIS

Before each synthesis, the stainless steel autoclave was cleaned with hot KOH solution. NH_4-ZSM-5 zeolite having 2–3 μm size and the same silica-to-alumina ratio as that of the reaction gel was used as seed material. Crystallisation temperature and pH of the reaction gel were kept low to prevent breeding of seed material [6].

Fig. 1 presents a comparison of the X-ray diffractograms of ZSM-5 zeolite samples prepared with and without the aid of the organic template. Both diffractograms match well.

The effect of addition of seed material on BET surface area and crystallinity of the zeolite sample is presented in table 1. The surface area of the ZSM-5 zeolite sample increased from 170 m^2/g in the absence of the seed material to 295 m^2/g in the presence of 10 wt% of the same. Simultaneously the crystallinity of the sample

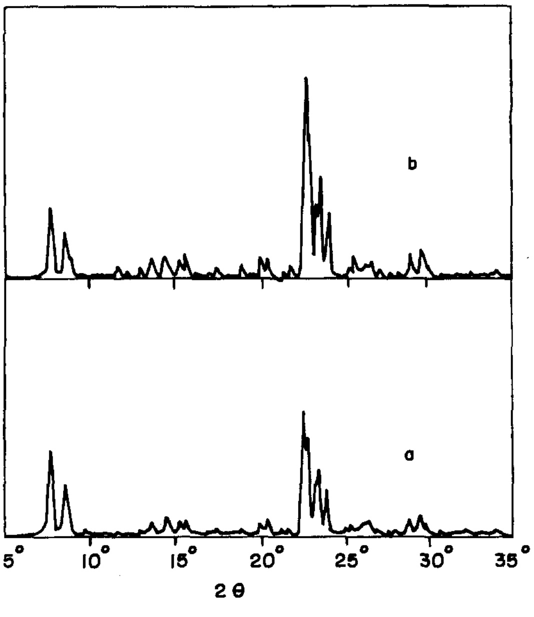


Fig. 1. X-ray diffractogram of zeolite ZSM-5 prepared (a) without organic template and (b) with organic template.

Table 1
Surface area and crystallinity of the templated and non-templated HZSM-5

Designation	Amount of seed (wt %)	Surface area (m^2/g)	XRD crystallinity (%)
catalyst			
HZSM-5 without template	10	295	85
	2	250	80
	–	170	62
HZSM-5 with template	–	380	100

increased from 62 to 85%. For all further studies, the sample prepared with the addition of 10 wt% of the seed material was used.

The diffuse reflectance infrared spectrum in the framework region (400–1200 cm^{-1}) of the zeolite sample is shown in fig. 2. The absorption bands at 434, 550, 800 and 1000–1200 cm^{-1} are assigned to external linkages. The absorption around 450 cm^{-1} is assigned to distorted double five-membered ring present in the zeolite framework and is characteristic of the pentasil family of zeolites. The spectrum is in agreement with that reported in published literature [7].

The thermogram of the zeolite sample showed only a single step of 3.2 wt% loss till 390°C due to removal of water (fig. 3). In the case of the templated sample additional weight loss around 410°C is because of removal of the organic template. The zeolite sample shows the same X-ray crystallinity even after calcination at 800°C.

Scanning electron microscopic studies of the as-synthesised zeolite sample prepared in the presence of seed material revealed the formation of crystals of size in the wide range of 0.5–10 μm, while the crystal size of the seed material was 2–3 μm. The micrograph in fig. 4a shows the presence of a large crystal having a size of 5 μm, while fig. 4b shows the formation of a new hexagonal prismatic crystal on

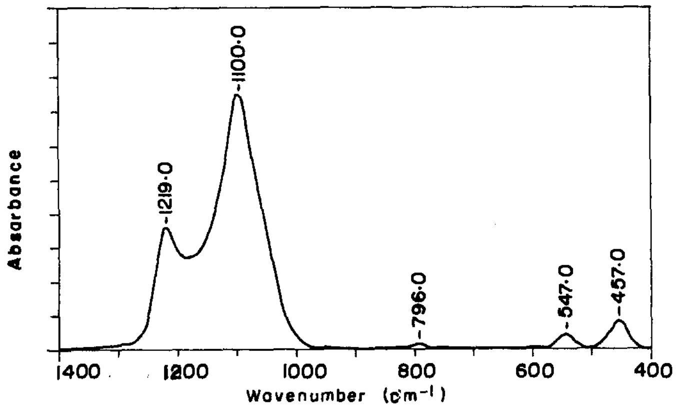


Fig. 2. Framework IR spectra of zeolite ZSM-5 prepared without organic template.

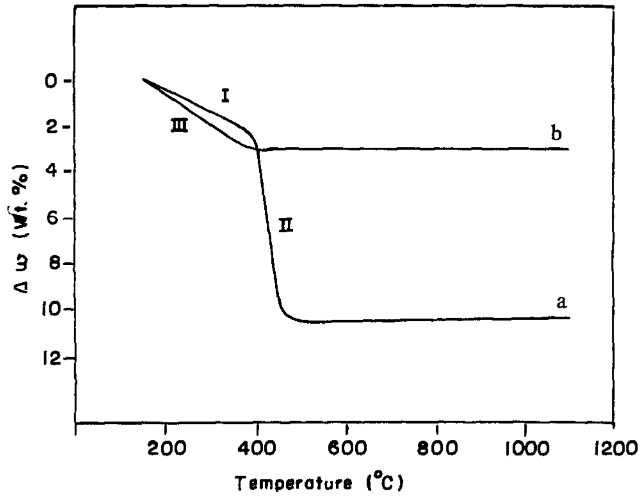


Fig. 3. Thermograms of zeolite samples prepared (a) with organic template, (b) without organic template.

the surface of the seed material. This indicates that crystallisation of ZSM-5 zeolite takes place in two modes: (i) formation of small new crystals on the surface of the seed material and (ii) growth of seeds into large crystals.

3.2. HEPTANE REACTION STUDIES

Conversion of normal and singly-branched paraffins selectively into aromatics can boost the octane number of gasoline [8]. The reaction can also be used for the preparation of high-value aromatics, like benzene, toluene and xylenes from low-value petroleum feed stocks, e.g. natural gasoline [9]. In the present investigation *n*-heptane was used as a probe molecule to study the aromatisation reaction. As presented in scheme 1, *n*-heptane is cracked over H-ZSM-5 zeolite forming both lower olefin and paraffin molecules [10]. Olefins ultimately are converted to aromatics via oligomerisation and hydrogen transfer reactions. Lower paraffins can also form by hydrogen transfer reaction of olefins. Such paraffins are mainly in the LPG range. In the absence of any dehydrogenating metal function in the zeolite catalyst, aromatics are limited to lower yield [11]. The product distribution over zeolite samples prepared with and without the aid of the organic template is presented in table 2. The activity of both the samples is comparable as revealed by similar *n*-heptane conversion and selectivity to aromatics. The data presented in table 2 also shows that activity of the catalyst is completely restored by the regeneration of catalyst, thus the catalyst is completely regenerable. Reduction in the formation of benzene and toluene along with a corresponding increase in the formation of C_{9+} aromatics was observed over the non-templated zeolite sample. This difference in aromatics distribution over the non-templated zeolite may be

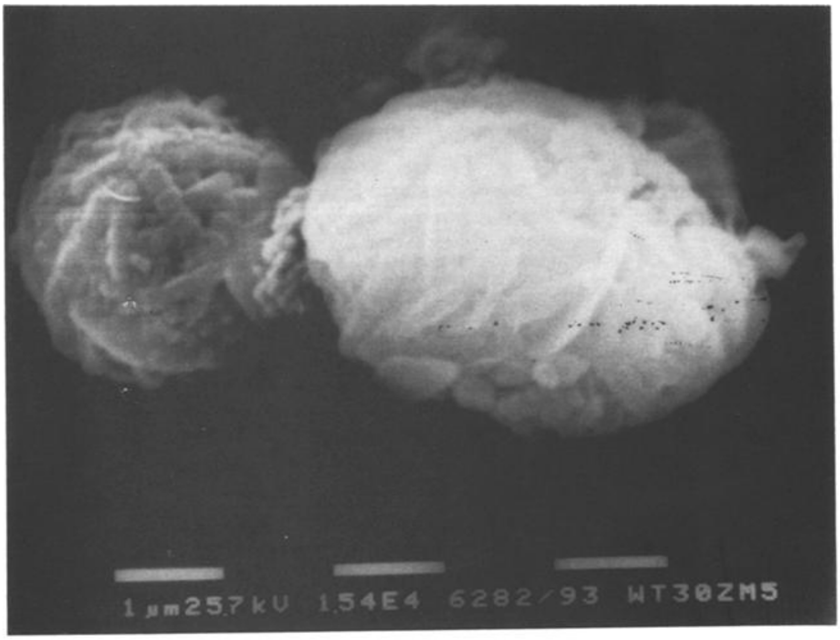
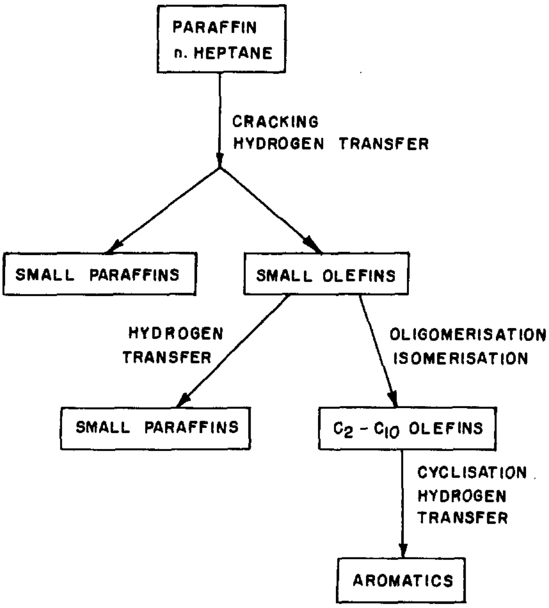


Fig. 4. Scanning electron micrographs of zeolite ZSM-5 prepared without organic template; amount of seed added 10 wt%.



Scheme 1.

due to the presence of some amorphous silica–alumina, formed along with the crystalline phase [4]. The presence of amorphous material catalyses non-shape-selective reactions resulting in the formation of C_{9+} aromatics. Similar observations were made by Stander et al. [12] in the catalytic conversion of methanol to hydrocarbons over amorphous silica–alumina prepared in presence of tetrapropylammonium ions. The cut-off at C_{12}, which is mainly due to non-shape-selective

Table 2
Comparison of catalytic activity [a]

Catalyst	HZSM-5 with template	HZSM-5 without template	
		fresh catalyst	after regeneration of deactivated catalyst
conversion (wt%)	96.0	93.3	91.9
selectivity (wt%)			
methane	0.1	–	0.1
ethane + ethylene	0.6	1.4	1.2
LPG	83.0	74.2	76.6
n-pentane + isopentane	3.8	13.0	12.0
benzene	0.8	0.4	0.4
toluene	4.0	2.6	2.2
C_8 aromatics	6.8	5.5	4.9
C_{9+} aromatics	0.9	2.9	2.6

[a] Reaction conditions: temperature = 400°C, pressure = 10 kg/cm^{-2}, LHSV = 2 h^{-1}.

reactions has been described as an inherent feature of amorphous catalysts. In any event, the non-templated synthesis produces a ZSM-5 zeolite with good catalytic activity.

4. Conclusion

(1) Highly crystalline zeolite ZSM-5 could be prepared without the aid of an organic template using silica gel as a silica source.

(2) Addition of seed material increased the crystallinity of the sample.

(3) Scanning electron microscopic studies revealed that crystallisation of zeolites takes place on the surface of the seed material to form small crystals, as well as by their growth into larger crystals.

(4) Catalytic activity of the non-templated zeolite in aromatisation of *n*-heptane has been found comparable to that of the templated zeolite.

(5) Formation of more C_{9+} aromatics over non-templated zeolite could be attributed to non-shape-selective reactions on amorphous silica alumina.

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