Synthesis of ZSM-5 type zeolites with and without template and evaluation of physicochemical properties and aniline alkylation activity

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ZSM-5 zeolite containing $SiO_2/Al_2O_3 = 28$ was synthesised by hydrothermal process with and without template. Characterisation of the zeolites was done using XRD, IR, NMR, SEM and BET surface area measurements. Acidity of the zeolites was measured by ammonia adsorption–desorption. Catalytic activity of HZSM-5 zeolites was evaluated by aniline alkylation, cumene dealkylation, alkylation of benzene with ethylene and propylene and isomerisation of *m*-xylene. Catalytic activity is discussed from the point of view of zeolite acidity and morphology.

Keywords: synthesis of ZSM-5; template-free zeolites; zeolite morphology; aniline alkylation; catalytic evaluation

1. Introduction

MFI type zeolite ZSM-5 is conventionally synthesised using various kinds of organic bases as templating agents [1–4]. Very often the templating agents are changed to modify the structure and morphology of the zeolites. It is also understood that the use of template not only facilitates crystallisation but also helps orientation of crystal growth. Tetrapropyl ammonium bromide (TPABr) is a common template used in the synthesis of ZSM-5. The template is not usually recoverable, corrosive, expensive and requires high hydrothermal treatments for its decomposition and removal from the zeolite.

Attempts have been made to synthesise high silica pentasil zeolites without the aid of a template. In some cases seed crystals have been used to facilitate the crystal-

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lisation process [5–13]. In most of the cases the products obtained were of low crystallinity or contained crystallographic phases other than ZSM-5. In spite of some reported information on the synthesis of ZSM-5 zeolites without template, systematic effort on the synthesis, characterisation and the evaluation of catalytic properties still remains insufficiently examined [14,15]. In the present work the synthesis of ZSM-5 with and without template having $SiO_2/Al_2O_3 = 28$ is reported. The physicochemical properties of these catalysts as well as their catalytic properties are compared and correlated with the acidic function of the zeolites. We have chosen aniline alkylation for this purpose as it is an important industrial reaction. The other reactions used in this study to evaluate the behaviour of both the zeolites are (1) alkylation of benzene with ethylene and propylene, (2) dealkylation of cumene and isomerization of *m*-xylene.

2. Experimental

2.1. SYNTHESIS

NaZSM-5 with $SiO_2/Al_2O_3 = 28$ was synthesised with and without the use of TPABr as a template in an autoclave under autogeneous pressure at 443 K. The autoclave was maintained at this temperature for 48 and 168 h for zeolites with and without template. Ludox 30% silica, sodium aluminate, NaOH and water were used. The oxide mole compositions of the reactants used were $SiO_2 = 0.7523$, $Al_2O_3 = 0.02688$, $Na_2O = 0.06725$. After the specified crystallisation time, the autoclave was cooled and the crystalline product was separated by filtration. The product was washed thoroughly with de-ionised water, dried overnight at 373 K and calcined at 823 K for 16 h. NaZSM-5 thus obtained was ion-exchanged three times with 0.5 M ammonium nitrate solution at 343 K. The NH_4ZSM-5 thus obtained is dried overnight at 373 K and was then converted into its hydrogen form by calcination at 823 K for 7 h.

2.2. CHARACTERIZATION

The zeolite samples were checked for crystallinity by X-ray powder diffraction using a Philips diffractometer (PW 1710) and Cu Kα radiation ($\lambda = 1.54014$ Å). Infrared spectra of the samples were taken by means of the KBr pellet technique in the region 400–1400 cm^{-1} using a Fourier transform Bruker spectrometer.

The morphology and crystallite size of the samples were examined under a scanning electron microscope (SEM Hitachi S-800) with the sample coated with Au film. ^{29}Si and ^{27}Al MAS NMR of the zeolite samples were taken with a Bruker MSL-300 instrument. The conditions used for ^{29}Si are: frequency, 59.63; pulse width, 2 μs; recycle time, 20 s; spinning rate, 4 kHz. For ^{27}Al they are: frequency, 78.2; pulsewidth, 1 μs; recycle time, 1 s; spinning rate, 4 kHz.

Surface areas of the samples were measured in an all glass adsorption apparatus capable of achieving 1×10^{-5} Torr. Nitrogen was used as an adsorbate at 80 K. Surface acidity of HZSM-5 was measured by the ammonia adsorption–desorption technique using a Micromeritics pulse chemisorb 2700. The sample is activated before adsorption at 683 K for 3 h. Ammonia adsorption was carried out at 393 K and the desorption at 673 K.

2.3. CATALYSIS

Catalytic evaluation of the samples was carried out in a vertical down-flow reactor in which ca. 500 mg of the powdered sample is packed in between ceramic beads. The liquid reactants along with the carrier gas were fed from the top at a calibrated rate. For aniline alkylation the sample was pretreated at 723 K for 4 h in nitrogen flow. The reaction was carried out at 673 K by feeding an aniline–ethanol mixture of 1 : 10 mole ratio at a WHSV of 0.0133 mol of aniline h^{-1} g^{-1} of zeolite. The liquid products collected in a cold trap were analysed by a gas chromatograph with a 2 m long column of 10% Apiezon L treated with 2% KOH on chromosorb AW. For cumene dealkylation ca. 20–10 mg of zeolite was pretreated at 723 K for 4 h in nitrogen flow. The reaction was carried out at 623 K and WHSV $= 0.12$ mol h^{-1} g^{-1}. The products were analysed by a gas chromatograph with 2 m long Betone column, the major product was benzene due to dealkylation. For benzene alkylation by C_2H_4, 20 mg of the sample was used, partial pressure of C_6H_6 being equal to 14 kPa, partial pressure of $C_2H_4 = 9$ kPa. Isomerisation of *m*-xylene was performed at 623 K using 20 mg of sample at a total flow rate of 9 ℓ/h and the pressure of *m*-xylene being 1.1 kPa. For alkylation of benzene with propylene 10 mg of sample was used at 523 K at a total rate of 5 ℓ/h, the pressure of propylene and benzene being $C_3H_6 = 9$ kPa and $C_6H_6 = 18.6$ kPa. In all cases, before any measurements it has been checked that the rates measured were independent of the flow rates of the feeds.

3. Results and discussion

The X-ray diffraction patterns of the ZSM-5 samples with template (designated as IFC-19) and without template (designated as IFC-37) are given in fig. 1. Both the samples show crystallinity and possess peaks characteristic of ZSM-5. The template-free sample synthesised for 48 h shows poor crystallinity. The *d*-values and the corresponding peak intensity values (I/I_0 max) of both IFC-19 and IFC-37 are given in table 1. Comparison of these values confirms that the major characteristic peaks of ZSM-5 are present on both the samples.

Infrared spectra of the zeolites taken in the region 400–1400 cm^{-1} give a clue as to the structural characteristics of the zeolites. In fig. 2 IR spectra of IFC-19 and IFC-37 are given. Both the spectra appear to be similar with respect to their adsorption bands. Furthermore, the intensities of the bands are also matching. The char-

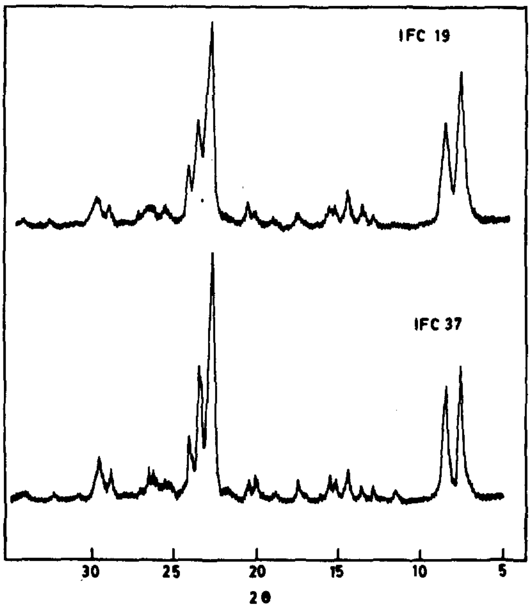


Fig. 1. XRD patterns of IFC-19 and IFC-37.

acteristic bands at 450 cm^{-1} (T–O band), 550 cm^{-1} (double ring) and 795 cm^{-1} (symmetric stretch) are all present in both samples confirming the ZSM-5 structural properties [16–18]. If there were any impurity like the presence of the mordenite phase, the intensity of the double ring band at 550 cm^{-1} would have been reduced [8]. The fact that there is no change in the intensity of the IR bands of the zeolites with and without template and the absence of any peak in the template-free sample lead us to believe that both the zeolite samples are of pure ZSM-5. In order to confirm further the purity of these two samples and the SiO_2/Al_2O_3 ratio ^{29}Si and ^{27}Al MAS NMR spectra were taken (figs. 3 and 4). The SiO_2/Al_2O_3 ratio as estimated from MAS NMR was found to be around 28. The analysis of ^{27}Al MAS NMR spectra shows a singlet around $\delta = 52.8$ ppm (IFC-19) and $\delta = 54.2$ ppm (IFC-37). It shows that aluminium is in tetrahedral coordination and there is no non-framework aluminium in the zeolites. This is further confirmed by the distinct signal of ^{29}Si MAS NMR of both the zeolites around $\delta = -111$ ppm. Since there is no baseline shift, the presence of invisible aluminium could be excluded.

BET surface area of IFC-19 is 352 m^2 g^{-1} and that of IFC-37 is 321 m^2 g^{-1}. The morphology of the two samples as seen from the SEM pictures is shown in figs. 5a and 5b. IFC-19 samples prepared with template for 48 h appear to have small particles when compared to IFC-50 and IFC-37 prepared with and without template for 168 h. The zeolite samples prepared with and without template (IFC-50 and IFC-37) for 168 h consist of large and elongated particles. One of the reasons for the large crystallite formation in both template and template-free zeolites synthesised for 168 h is the long crystallisation time [19].

Table 1
XRD data of NaZSM 5 with and without template

IFC-19		IFC-37	
d (Å)	$I/I_0 \times 100$	d (Å)	$I/I_0 \times 100$
11.0562	68.56	11.2317	53.14
9.9893	52.42	10.1033	44.93
7.5030	2.56	7.4999	4.36
6.7068	6.15	6.7271	6.57
6.3340	12.11	6.3841	6.57
5.9847	16.97	6.0191	14.79
5.7286	9.99	5.7397	7.96
5.5519	12.11	5.5973	10.16
4.9789	6.76	5.3924	1.74
4.5999	5.38	4.9942	8.16
4.3657	7.40	4.6308	3.63
4.2579	10.50	4.3753	10.39
4.0883	3.69	4.2864	8.37
3.8471	100.00	3.8653	100.00
3.7402	44.62	3.8251	74.10
3.6973	47.98	3.7612	45.43
3.6399	26.21	3.7309	49.98
3.4569	5.95	3.6590	25.18
3.3074	8.07	3.4974	6.02
3.2506	5.02	3.3171	9.69
3.0497	10.50	3.2611	3.09
2.9878	15.68	3.1504	1.64
2.8621	1.64	3.0594	10.16
2.7286	4.33	2.9986	15.65
2.6093	3.24	2.8778	2.48
2.4860	3.84	2.7461	2.48
2.3963	3.53	2.6208	2.72
2.3227	5.76	2.4960	5.86
2.2202	1.64	2.4097	2.84
2.1246	4.33	2.1075	9.24
2.0941	1.74	1.9954	9.92
2.0092	10.24	1.9460	3.22

Catalysis

The catalytic activity and the acidity of the samples are given in table 2. Aniline alkylation gives mainly NEA. NN′DEA, if present, was in small quantities under the experimental conditions. It is interesting to note that the template-free zeolite (IFC-37) shows higher aniline alkylation activity. This is in agreement with the acidity of the zeolites as measured by the ammonia adsorption–desorption method. Thus a correlation between the acidity and the alkylation activity can be envisaged.

Fig. 2. IR spectra of IFC-19 and IFC-37.

The presence of a larger number of Lewis acid sites in the template-free sample than in the templated sample may be responsible for its higher aniline alkylation activity, since aniline alkylation is a Friedel–Craft type of reaction and requires Lewis acid sites.

It is generally expected that small crystallites will have higher acidity and large crystallites lower acidity, especially, if the SiO_2/Al_2O_3 ratio is the same [19]. Interestingly, we found that the templated and template-free HZSM-5 synthesized for 168 h, although they have larger crystallites, have different acidity. The template-free sample was found to have more acidity than the templated sample. This probably explains the higher alkylation activity of IFC-37 than that of IFC-19 and IFC-50. The activity of the catalysts remained unaffected for 4 h, the total time of collection of the products (fig. 1). IFC-19 and IFC-37 were also evaluated by carrying out other model reactions, such as alkylation of benzene with ethylene and propylene, isomerization of *m*-xylene and dealkylation of cumene. The results of this study are given in table 3. Contrary to the observation on aniline alkylation, these catalysts behave differently. For example IFC-19 shows slightly higher activity for alkylation of benzene, isomerization of *m*-xylene and dealkylation of cumene

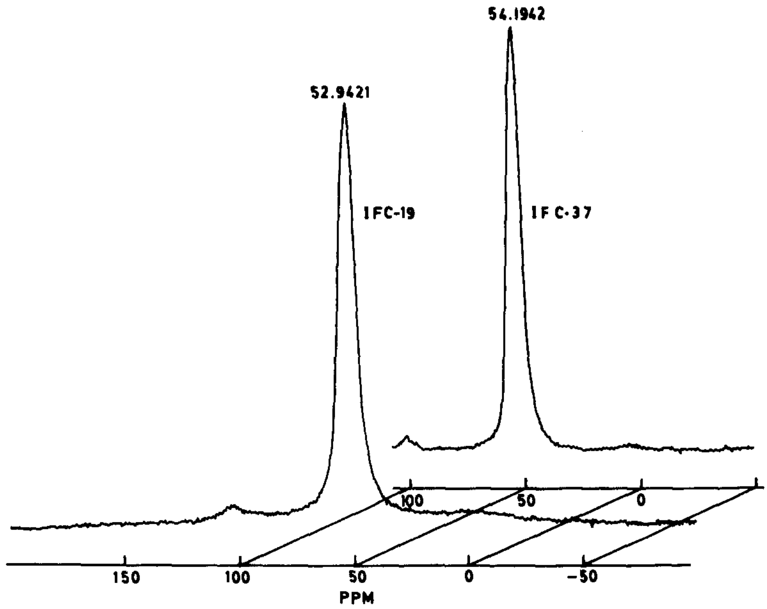


Fig. 3. ^{27}Al MAS NMR spectra of IFC-19 and IFC-37.

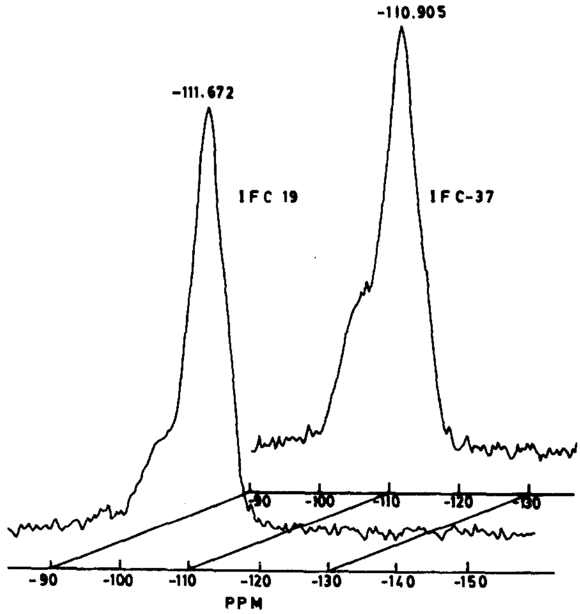
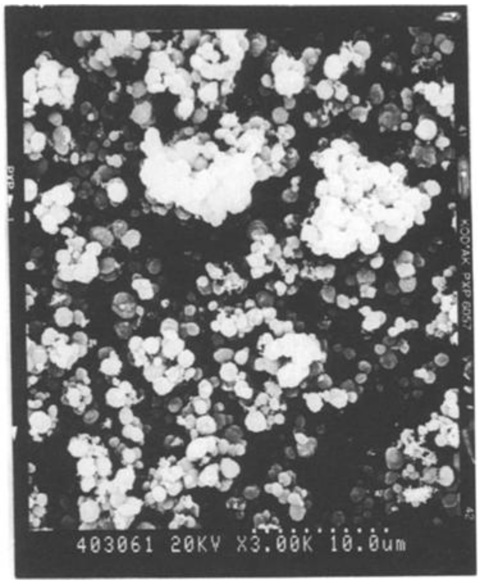


Fig. 4. ^{29}Si MAS NMR spectra of IFC-19 and IFC-37.

a



IFC-19

b

IFC-37 IFC-37

Fig. 5. SEM of IFC-19 and IFC-37.

Table 2
Acidity and catalytic activity of HZSM-5 zeolites

Sample	Synthesis time (h)	With/ without template	Ammonia desorption temp. (K)	Acidity (mmol g^{-1})	Total acidity	Aniline alkylation conv. (%)
IFC-19	48	TPABr	503	0.235		
			613	0.083	0.398	28
			723	0.080		
IFC-50	168	TPABr	503	0.220		
			613	0.066	0.367	23
			723	0.079		
IFC-37	168	–	503	0.400		
			613	0.160	0.705	41
			723	0.145		

when compared with IFC-37 [19]. In addition, the samples are compared at times on stream which are not close to the initial rate (fig. 6).

4. Conclusions

ZSM-5 zeolite with $SiO_2/Al_2O_3 = 28$ can be prepared with and without template. Acidity and aniline alkylation activity were found to be more on template-free sample. ZSM-5 with and without template are also evaluated with other model reactions such as alkylation of benzene, cumene dealkylation and isomerisation of *m*-xylene. More catalytic work involving template-free zeolite and their correlation with acidity will help us understand the differences from templated zeolites.

Table 3
Rate of formation [a]

Sample	Ethylbenzene [b,d]	Isomerization of *m*-xylene [b,d]	Dealkylation of cumene [b,d]	Isopropyl benzene [c,d]
IFC-19	188	24.8	16.1	8.1
IFC-37	151	18.8	14.8	4.8

[a] Rate in mmol h^{-1} cat.
[b] Temperature = 623 K.
[c] Temperature = 523 K.
[d] After 5 min on stream deactivation under these experimental conditions is low.

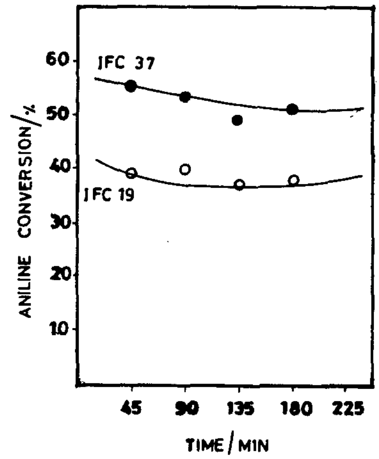


Fig. 6. Aniline alkylation activity with time on stream.

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