Influence of mild dealumination on physicochemical, acidic and catalytic properties of H-ZSM-5

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Abstract

Mild dealumination of ZSM-5 using HCl, acetylacetone and ammonium hexafluorosilicate resulted in a slight increase in the XRD crystallinity and overall surface area, but there was a marginal decrease in the micropore area and a considerable increase in mesopore area. ^{27}Al MAS–NMR spectra showed very weak signals due to octahedral aluminium for the samples treated with HCl and acetylacetone. FTIR spectra revealed small amounts of extra framework Al and four bands due to OH stretching vibration. The nature and intensity of the bands due to different hydroxyl groups varied depending on the treatment. Dealumination resulted in an increase in *m*-xylene conversion but a decrease in isomerization selectivity. The activity was maximum for HCl- and acetylacetone-treated samples that is attributed to the increase in the overall acidity (both Lewis and Bronsted) of samples as well as to the creation of mesoporosity. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The acidity of zeolites depends upon the framework Si/Al ratio [1]. Thus, the acid catalytic properties of zeolites can be controlled by manipulating the Si/Al ratio either during synthesis or by post-treatment dealumination methods. Dealumination by steaming, SiCl$_4$ treatment, reaction with chelating agents like EDTA, acetylacetone, ammonium hexafluorosilicate, oxalic acid, etc. and leaching with HCl are some of the post-synthesis methods used to control the acidity of the zeolites [2]. To date, steaming is the most common dealumination technique used to prepare industrially important catalysts of high activity, selectivity and stability [3].

Mild steaming is found to greatly enhance the acidity of H-ZSM-5-type zeolites [4]. The enhancement in acidity is manifested in reactions like paraffin isomerization, paraffin cracking, and toluene disproportionation. Lago et al. [5] reported the generation of sites with enhanced activity on mild steaming of H-ZSM-5 while severe steaming was found to reduce the activity. Infrared spectroscopy of ZSM-5 samples after mild treatment with aqueous HF

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showed a decrease in the number of strong Bronsted acid sites and an increase in the number of Lewis acid sites [6]. Two different types of Lewis acid sites were found; the intensity of the band associated with the stronger sites increased with mild HF treatment but more severe HF treatment eliminated all Lewis sites. Loeffler et al. [7] have studied the nature of different-OH groups in dealuminated H-ZSM-5 using diffuse reflectance IR spectroscopy. Depending upon the dealumination conditions they identified five different types of acid sites due to the formation of non-framework Al. Kornatowski et al. [8] have compared the effectiveness of various treatments on the dealumination of large crystals of ZSM-5 and their influence on the crystal structure. Dealumination of Pd/H-ZSM-5 by HCl treatment was found to increase the strong acid site density resulting in an increase in isobutane yield in *n*-butane isomerization but there was no clear change in surface area or pore volume on dealumination [9]. Similarily, the activity of H-ZSM-5 for phenol hydroxylation was found to increase after hydrothermal dealumination that was attributed to the creation of Lewis acid extra framework alumina [10]. The present work aims to compare the effectiveness of Al leaching reagents like HCl, acetylacetone and ammonium hexafluorosilicate in dealumination and the resulting influence on acidity and catalytic activity. The reaction of *m*-xylene, besides its industrial importance, is a commonly used test reaction not only to provide information on the geometry of the zeolite channels [11], but also to characterize acidic catalytic properties of solid acids. Hence, the transformation of *m*-xylene was carried out to examine the influence of dealumination on shape selectivity and acidity of the dealuminated samples.

2. Experimental

Synthesis of a ZSM-5 sample with $Si/Al = 40$ was carried out according to a reported procedure [12,13]. The synthesized sample was washed with distilled water, dried at 373 K (12 h) and calcined at 813 K in air for 7 h to burn off the organic template. It was then exchanged with 1 M of ammonium nitrate solution under reflux for 8 h thrice to convert it into the ammonium form, NH_4–ZSM-5. Subsequently, it was converted into H-ZSM-5 by calcining at 813 K for 6 h in flowing air. The sample was then characterized by XRD (Cu K_α radiation, Ni filter, Rigaku Model D-MAX-VC) for phase purity. Crystallinity, particle size and morphology were studied by scanning electron microscopy (SEM) (JEOL JSM-840A). Chemical composition was determined by wet chemical analysis and atomic absorption spectroscopy. BET surface area was determined by N_2 sorption (Omnisorb 100 CX; Coulter, USA). Dealumination of H-ZSM-5 [ZSM-5(a)] was carried out with ammonium hexafluorosilicate [ZSM-5(b)], dil. HCl (0.85 M) [ZSM-5(c)] and acetylacetone [ZSM-5(d)] for 18 h at 363–473 K thrice following earlier reported methods of dealumination [14–17]. The samples treated with different leaching agents were thoroughly washed, dried and calcined at 813 K and were characterized by XRD, SEM, IR, MAS–NMR, BET surface area measurement and wet chemical analysis.

FTIR investigations were carried out in absorbance mode in the range 3200–3800 cm^{-1} using a Nicolet 60 SXB instrument to study the nature of hydroxyl groups using self-supported wafers (~ 6 mg/cm^2). The samples were activated in vacuum (10^{-6} Torr) at 673 K for 5 h and cooled to 373 K before recording the spectra.

The parent and dealuminated ZSM-5 samples were pelletized and crushed to 22–25 mesh size and were used for *m*-xylene isomerization using a bench top reaction system (BTRS, Autoclave Engineers, USA) with a fixed bed continuous down-flow type stainless steel reactor (5 cc) under fixed reaction conditions: pressure (atm), 1.0; H_2/m-xylene (mol), 3:1; reaction temperature (K), 623–673; WHSV (h^{-1}), 2. *m*-Xylene

was fed through a HPLC liquid injection pump (Alcott, Model 760) and hydrogen was passed through using a mass flow controller (Brooks, Model 5896). The reactants were mixed and vaporized in a preheated oven maintained at 393 K and passed through the reactor (6 mm i.d.). The temperature around the reactor was maintained by a temperature-controlled furnace. The reaction products were analyzed on-line using a gas chromatograph (HP 5890; capillary column, HP1, 50 m × 0.2 mm; FID).

3. Results and discussion

Comparison of the powder XRD patterns of the parent and dealuminated samples showed that dealumination resulted in an increase in crystallinity in the order H-ZSM-5(a) < H-ZSM-5(b) < H-ZSM-5(c) < H-ZSM-5(d) that could be due to leaching of intraporous extra framework aluminium. This shows that acetylacetone [for H-ZSM-5(d)] is the most effective reagent while $(NH_4)_2SiF_6$ [for H-ZSM-5(b)] is the least effective for Al leaching. Such an increase in crystallinity after dealumination has been reported by earlier workers in the case of some zeolites [8,18]. Physicochemical properties of the untreated and dealuminated ZSM-5 samples are presented in Table 1. BET surface area measurement by nitrogen sorption showed an increase in the overall surface area after dealumination in the order H-ZSM-5(a) < H-ZSM-5(b) < H-ZSM-5(c) < H-ZSM-5(d). Even though there is only a slight change in overall area, the surface area of the mesopores (found

from *t*-plot analysis) was found to increase considerably in the same order, though the micropore area decreased slightly, the order of micropore areas being H-ZSM-5(a) > H-ZSM-5(b) > H-ZSM-5(c) ∼ H-ZSM-5(d). As the order of increase in overall surface area was same as that for the increase in XRD crystallinity, the increase in surface area could be attributed to Al leaching as well as to the creation of mesopores. There was no visible change in particle size and morphology as evidenced from SEM.

Si/Al ratio, as found from wet chemical analysis, showed that the Si/Al ratio is slightly larger for the dealuminated samples suggesting mild dealumination. ^{27}Al MAS–NMR of the parent, as well as the dealuminated sample, showed a single line at 54 ppm due to tetrahedrally coordinated aluminium. There was a very weak signal at 0 ppm for samples ZSM-5(c) and ZSM-5(d), that is almost absent in ZSM-5(a) and ZSM-5(b) and is attributed to octahedral extra framework Al species (Fig. 1). But earlier workers [19] have found from ^{27}Al MAS–NMR spectra the presence of a much stronger signal at 0 ppm due to octahedral aluminium in ZSM-5 samples after acid treatment, which was absent in the parent material. This difference in the two observations could be due to the difference in the synthesis methods adopted and the extent of dealumination.

The FTIR spectra of the parent and the dealuminated samples in the range of –OH stretching vibrations are shown in Fig. 2. Loeffler et al. [7] have identified up to five bands of varying intensities for dealuminated ZSM-5 samples depending on the dealumination conditions, while

Table 1
Physicochemical properties of different HZSM-5 samples

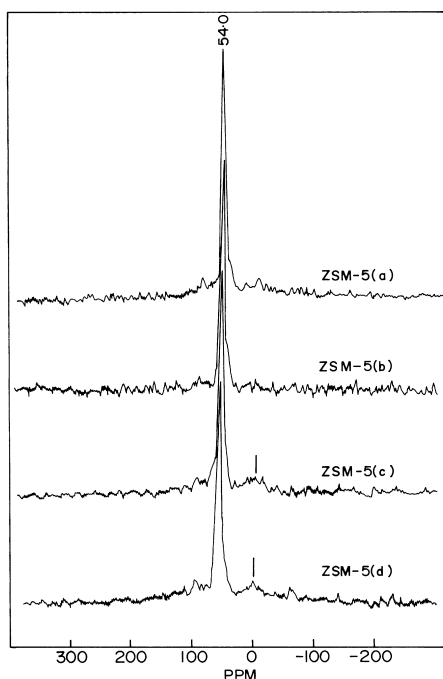| Catalyst	Extracting reagent	Si/Al ratio	Surface area (m²/g)		
			Overall	Micropore	Mesopore
ZSM-5(a)	untreated	29.5	357	346	10.69
ZSM-5(b)	$(NH_4)_2SiF_6$	38.2	374	337	36.89
ZSM-5(c)	HCl	35.9	381	310	70.61
ZSM-5(d)	Acetylacetone	32.6	388	309	79.40

Fig. 1. ^{27}Al MAS–NMR spectra of parent [ZSM-5(a)] and dealuminated [ZSM-5(b–d)] samples.

the parent ZSM-5 sample exhibited only three OH bands — an intense band due to a strongly acidic OH group at 3610 cm^{-1}, a less intense vibrational band of terminal SiOH groups at 3745 cm^{-1} and a broad band at about 3250 cm^{-1} ascribed to the bridged hydroxyl groups forming a strained intramolecular hydrogen bond with a neighboring oxygen atom of the framework. We could identify only four bands due to –OH stretching vibrations out of which only three peaks were well defined. These bands are assigned as follows: (I) 3735 cm^{-1}, terminal silanol groups; (II) 3710–3720 cm^{-1}, extra lattice Al-ions partially attached to the lattice; (III) 3665 cm^{-1}, extra lattice Al-ions in octahedral coordination; and (IV) 3610 cm^{-1}, bridging –OH groups [6,20,21]. The presence of small amounts of extra framework Al observed in the FTIR spectra of the samples (and not observed clearly in the ^{27}Al MAS–NMR spectra), particularly for ZSM-5(a) and ZSM-5(b) (Fig.1) could be due to their greater IR sensitivity or their

creation during pretreatment of the wafers in the IR cell at 673 K, though this is unlikely as the samples were already calcined at 813 K. Earlier workers have reported some Al species to be 'NMR invisible' [22,23]. In the case of dealuminated H-ZSM-5 samples, we found that the stretching vibration band at 3610 cm^{-1} due to bridging hydroxyl groups was very strong for the samples dealuminated with ammonium hexafluorosilicate of similar intensity for the untreated and HCl treated sample and of slightly lower intensity for the samples treated with acetylacetone. The band at 3665 cm^{-1}, which has been ascribed to –OH groups on non-framework aluminium species, is nearly absent in the samples treated with ammonium hexafluorosilicate (which also shows no signal in ^{27}Al MAS–NMR at 0 ppm due to extra framework Al, Fig. 1, ZSM-5(b)) but is present in all other samples but of lower intensity than that for the untreated sample. However, a peak at about 3800 cm^{-1} is noticed in the ammonium hexafluorosilicate treated sample. It is likely that this is also due to structurally different extra framework Al ions.

The results of *m*-xylene isomerization over the parent and treated H-ZSM-5 samples showed that treatment with dealuminating reagents re-
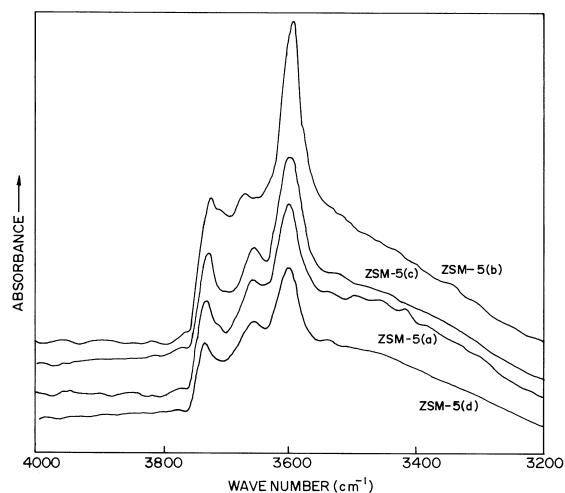

Fig. 2. FTIR spectra of −OH groups in parent [ZSM-5(a)] and dealuminated [ZSM-5(b–d)] samples.

sulted in a very significant increase in catalytic activity compared to the untreated sample with a simultaneous decrease in the isomerization selectivity. But ammonium-hexafluorosilicate-treated sample showed highest selectivity for isomerization and minimal disproportionation, which could be due to its higher Bronsted acidity, than all other samples, evidenced from a much stronger band at 3610 cm^{-1} due to bridging hydroxyl groups compared to all other samples. Treatment with acetylacetone and dil. HCl resulted in a similar increase in the catalytic activity but the selectivity for disproportionation was slightly more over the HCl-treated sample than that over the acetylacetone-treated sample. The order of overall activity for *m*-xylene reaction was H-ZSM-5(a) < H-ZSM-5(b) < H-ZSM-5(c) ∼ H-ZSM-5(d) and the order for disproportionation selectivity was H-ZSM-5(a) ≪ H-ZSM-5(b) < H-ZSM-5(d) < H-ZSM-5(c). Earlier reports provide ample evidence for the fact that even though both isomerization and disproportionation of *m*-xylene are catalyzed by Bronsted acid sites, disproportionation requires stronger acid sites (both Lewis and Bronsted) [24,25]. In earlier studies [5,26] over dealuminated H-ZSM-5 samples, an enhanced activity for *n*-hexane cracking has been found due to generation of acid sites of increased activity that

may involve synergism between framework Bronsted sites and dislodged Al species or it may involve generation of additional active sites unconnected with framework Bronsted sites. The large increase in disproportionation activity in the dealuminated samples suggests the creation of strong acidity on dealumination. Also, as dealumination is expected to decrease the number of Bronsted acid centers (bridging –OH groups), which is not clearly observed (Fig. 2), it appears that the increase in disproportionation activities is due to the extra framework Al ions that give rise to Lewis acid sites of strong activity. Also, lower activity for samples ZSM-5(a) and ZSM-5(b) that have almost no octahedral aluminium in ^{27}Al MAS–NMR spectra (Fig. 1) and weak bands for –OH group associated with non-framework aluminium (Fig. 2) shows that extra framework aluminium could be responsible for the enhancement of catalytic activity after dealumination. Furthermore, a decrease in diffusion constraints brought about by the creation of mesoporosity in the dealuminated samples (as seen from the enhancement of the mesopore area of the dealuminated samples) could also contribute partly to the enhancement in the activity. It is observed that for samples ZSM-5(c) and ZSM-5(d) (treated with HCl and acetylacetone respectively), which show maxi-

Table 2

Results of *m*-xylene conversion over different H-ZSM-5 samples (*p/o* = *p*-xylene/*o*-xylene; TMB = trimethyl benzene; *I/D* = isomerization/disproportionation ratio)

Catalyst	Temperature (K)	Conversion (wt.%)	Product distribution (wt.%)					*p/o*	*I/D*
			o-Xylene	*p*-Xylene	Toluene	Benzene	TMB		
ZSM-5(a)	623	4.6	1.3	3.3	–	–	–	2.5	–
	648	10.2	3.0	7.2	–	–	–	2.4	–
	673	20.2	6.3	13.8	–	–	–	2.2	–
ZSM-5(b)	623	38.6	15.2	21.1	1.1	0.4	–	1.4	24.0
	648	39.2	15.0	21.0	1.1	1.3	–	1.4	14.8
	673	40.3	15.4	20.9	1.1	0.7	–	1.4	19.5
ZSM-5(c)	623	47.7	20.0	22.2	2.6	–	2.7	1.1	7.8
	648	50.9	19.0	21.0	5.3	–	5.2	1.1	3.7
	673	52.3	17.9	20.5	9.3	–	4.7	1.1	2.7
ZSM-5(d)	623	47.8	20.7	22.3	2.2	–	2.4	1.1	9.2
	648	49.2	20.6	21.9	3.3	–	3.2	1.1	6.5
	673	52.0	20.2	20.7	5.3	–	5.7	1.0	3.7

mum enhancement in mesopore area, the *para/ortho* ratio of the isomerized product (1.1) is almost equal to thermodynamic equilibrium value (1.0) that could be due to decreased shape selectivity resulting from the generation of mesopores; samples ZSM-5(a) and ZSM-5(b) with much lower mesoporous area show a much higher value for *para/ortho* ratio (high shape selectivity) (Table 2).

4. Conclusions

Mild dealumination (with HCl, acetylacetone and ammonium hexafluorosilicate) increases the activity of H-ZSM-5 in the isomerization of *m*-xylene. Dealumination, however, decreases isomerization selectivity. It is suggested that the extra framework Al species are responsible for the larger activity of the dealuminated samples. $(NH_4)_2SiF_6$ could be the reagent most suited among the three reagents studied for dealumination of ZSM-5 to obtain maximum isomerization as well as *p*-xylene selectivity at optimum conversion.

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