

## Adsorption of Aqueous Solutions of Carboxylic Acids on Montmorillonite, Silicalite, H-ZSM-5 and their Na<sup>+</sup>- and Li<sup>+</sup>- Exchanged Forms

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**Summary:** The adsorption of binary carboxylic acid-water solutions on montmorillonite clay, silicalite, H-ZSM-5 zeolites and Li-exchanged montmorillonite, Na- and Li-exchanged ZSM-5 has been studied. The purity, morphology and textural properties were characterized by XRD and SEM techniques. Liquid phase adsorption experiments were carried out at room temperature in screwed cap septum 14 mL round bottom vials. The mole fractions before and after adsorption were determined refractometrically. Montmorillonite clays swelled to jell-form in aqueous carboxylic acid solutions indicating no significant separation selectivity for water or carboxylic acid. The zeolites showed hydrophobicity in the order: silicalite > H-ZSM-5 > Na- ZSM-5 > Li- ZSM-5. The uptake of carboxylic acid was found in the order: C<sub>2</sub>H<sub>3</sub>COOH > CH<sub>3</sub>COOH > HCOOH. At higher concentration the adsorption of carboxylic acids decreased.

### Introduction

Montmorillonite is the best known member of the smectite group of clays [1]. Clays are Phyllosilicates (or sheet silicates) that consist of one (or two) sheets of polymerized silicon oxygen tetrahedral (T), and one sheet of polymerized aluminium or magnesium oxygen-hydroxyl octahedral (O). Smectite belongs to the 2:1 dioctahedral clay minerals species, characterized by an element block (cell unit) that consists of two tetrahedral sheets separated by one octahedral sheet. Thus, the thickness of the triple sheet (TOT) is 9.3 to 9.6 Å [2-4]. The distance between the montmorillonite layers is 14 Å, including the thickness of one of the layers. The height between the layers is obtained by subtracting 9.6 Å (corresponding to the sheet thickness) from the 14 Å which is equal to 3.4 Å.

Silicalite and H-ZSM-5 are synthetic zeolites which have inorganic crystalline structures, molecular size pores, and high mechanical, thermal and chemical stability. The silicalite (all silica) and H-ZSM-5 (H is the extraframework cation and ZSM-5 stands for Zeolite Socony Mobil Five) zeolites have MFI (Mobil Five) framework structure [5-7]. The crystal structure of MFI zeolite is characterized by a framework of linked tetrahedrals, each consisting of SiO<sub>4</sub> or AlO<sub>4</sub> units. These zeolites are highly porous materials and throughout their structures have

intersecting two dimensional pore structures. A set of straight channels run in the y-direction and zigzag channels run in the x-direction. The ZSM-5 has two types of pores, both formed by 10-membered oxygen rings. The first of these pores is straight and elliptical in cross-section (5.1 x 5.6 Å) the second pores intersect the straight pores at right angles, in a zigzag pattern and are circular in cross-section (5.4 x 5.6 Å). Maximum crystallographic pore diameter of ZSM-5 is 5.6 Å. The intersection of the two sets of channels creates a supercage cavity with a diameter about 9 Å [8].

Clays and zeolites, both natural and synthetic, are important industrial raw materials and their roles in many important processes have been studied. In addition to many other applications, they are used as adsorbents, ion exchangers, supports and as catalysts [9-14]. Recent work has revived interest in the use of clays, particularly smectite clays, as catalysts. Large pillars such as those made up of polynuclear inorganic cations are used to hold the clay layers apart and allow the entry of large molecules found in the heaviest fractions of petroleum residues which are otherwise too large to enter zeolite pores. Thus they form an intriguing alternative to zeolites [15, 16].

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In this paper we report the adsorption of carboxylic acids (HCOOH, CH<sub>3</sub>COOH, C<sub>2</sub>H<sub>3</sub>COOH) from water at 20°C on purified and Li-exchanged montmorillonite, Na- and Li-exchanged ZSM-5, H-ZSM-5 and silicalite. The materials were characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques, while adsorption study was measured refractometrically. Acetic acid is one of the most important intermediates in the chemical and food industries, for example, in the synthesis of vinyl acetate, terephthalic acid, cellulose ester and other esters [17, 18]. Azeotropic distillation and extractive distillation have been developed for acetic acid recovery, but distillation is very energy-intensive because of the small difference in the volatilities of water and acetic acid in dilute aqueous solution [19]. A zeolite membrane is a porous layer that can separate mixtures by adsorption and diffusion differences and in some cases by molecular sieving [20]. Zeolite membranes have been used for pervaporation, mainly

for the removal of organics from water, water from organics and for organic/ organic separation [18, 21, 22]. Pervaporation has advantages over distillation including reduced energy demands (only a fraction of the liquid is removed) and relatively inexpensive equipment (only a small vacuum pump is needed to create a driving force) [17, 23].

## Results and Discussion

The XRD pattern of Fig. 1a indicates that parent (commercial) montmorillonite has some peaks of impurities like quartz, micas, calcites, feldspars and cristobalite [15, 24]. The XRD patterns of Li-exchanged montmorillonite are shown in (Fig. 1b). The intensity of XRD patterns (Fig. 1b) confirm the purity and retention of crystallinity of the montmorillonite structure after purification and Li-exchange. Colin *et al.* reported [24] that the basal d (001) peak around  $2\theta = 7.2^\circ$  (Fig. 1b) is characteristic of montmorillonite according to the

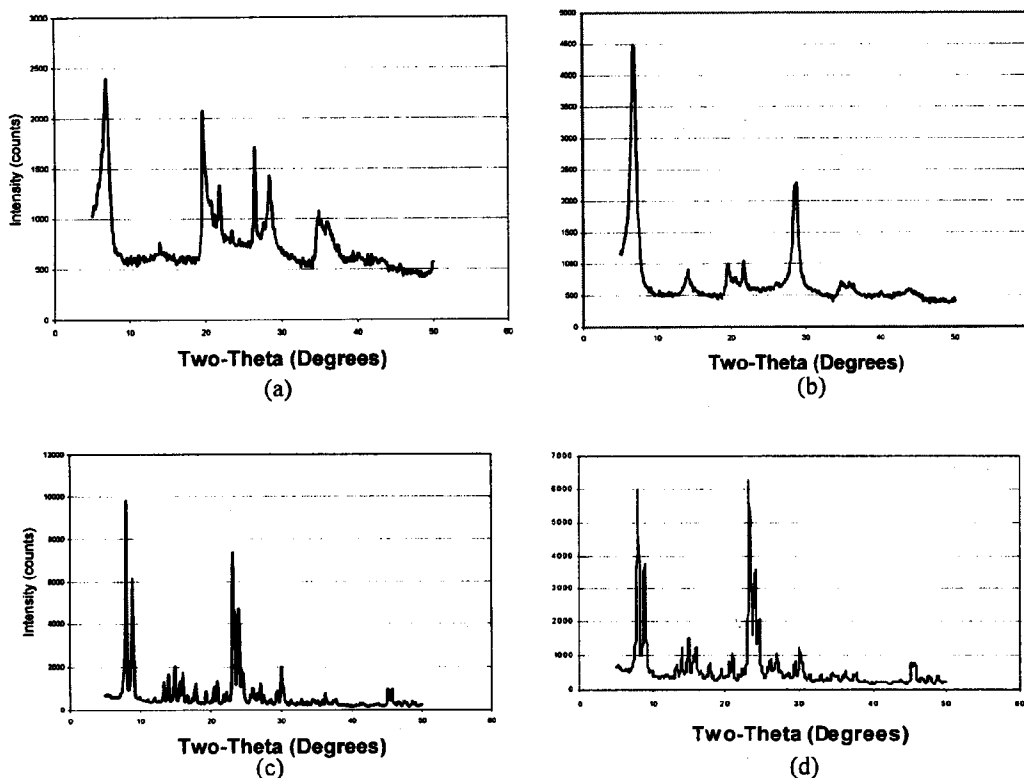


Fig. 1: XRD Patterns of dry powders of (a) Parent (commercial) montmorillonite, (b) Li-Montmorillonite, (c) Silicate, (d) H-ZSM-5.

JCPDS index crystallographic card, is very intense and thin. As silicalite and H-ZSM-5 both have MFI framework structure, therefore, their XRD patterns are almost identical. Furthermore  $\text{Na}^+$  and  $\text{Li}^+$  exchanged ZSM-5 also showed XRD patterns like H-ZSM-5, because the exchangeable cations are extraframework cations and do not have any significant effect on the structure of zeolites. The typical XRD patterns of silicalite and H-ZSM-5 are displayed in Fig. 1c and d respectively. All peaks for the silicalite/ H-ZSM-5 powders match those of zeolites reported previously [17, 25-28] with respect to the positions and intensities of the observed reflections, and no additional peaks were observed. The high intensity of XRD lines and the low

background intensity indicate high degrees of crystallinity for the powders.

The SEM images of parent and Li-exchanged montmorillonite are shown in Figs. 2(a, b) respectively. The particles of clays are essentially crystalline (either platy or fibrous) with a layered structure. Odom [3] showed that smectite crystals may be as large as  $2 \mu\text{m}$  and as small as  $0.2 \mu\text{m}$  with an average size of about  $0.5 \mu\text{m}$ . Individual crystal morphologies range from rhombic to hexagonal, lamellar to lath, and even to fiber shapes. Odom described a classification of aggregates including globular, mossy, lamellar, foliated, compact, and reticulated. The various aggregate types are

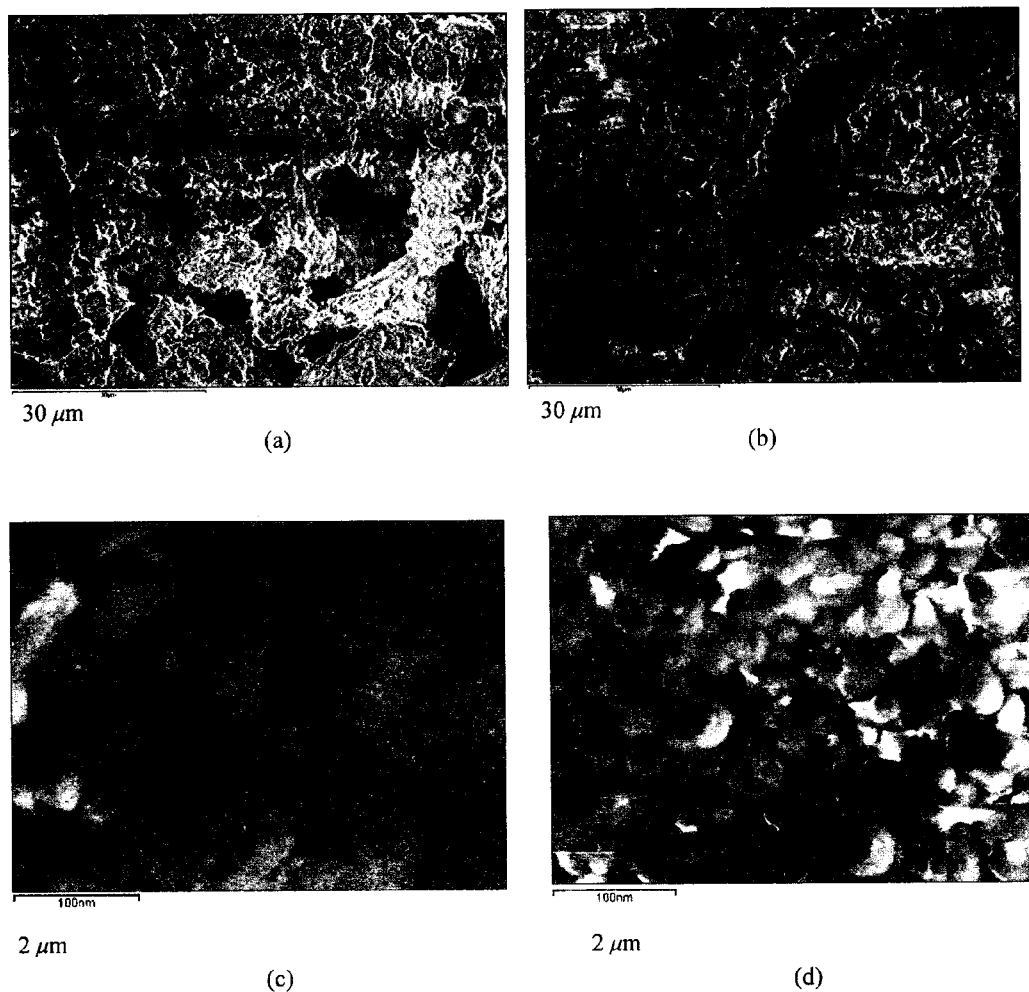


Fig. 2: SEM images of dry powders of (a) Parent Montmorillonite, (b) Li-Montmorillonite (magnification 1000 x), (c) Silicalite, (d) H-ZSM-5 (magnification 15000 x).

determined by the nature or shape of individual crystallites and by their arrangement in the aggregate. Crystal shape and aggregate characteristics can have an important influence on physical and rheological properties. The SEM image of Fig. 2a shows that parent montmorillonite contains crystalline impurities as mentioned above. The SEM image of Fig. 2b has resemblance to those reported by Odom [3]. Figs. 2c and d show SEM results of silicalite and H-ZSM zeolites respectively. As the SEM image of Na<sup>+</sup> and Li<sup>+</sup>-exchanged ZSM-5 resembled image of H-ZSM-5, therefore they are not displayed. It has been reported [28-31] that the morphologies of silicalite and ZSM-5 depend on the microemulsion composition, conditions and the Si/Al ratio under which they are synthesized. Furthermore, the morphology of ZSM-5 zeolite crystals largely depends on the impurity in the synthesis mixture [32]. The SEM images of Fig. 4c show that the crystals of silicalite are polyhedron, which agree with the results reported previously [28, 31, 33]. The SEM images of Fig. 4d show that the crystals of H-ZSM-5 are round shaped with intergrowths, similar SEM images have been reported by Schweiger *et al.* [31]. Thus, the samples of the clays and zeolites proved to be crystalline when the results of SEM images were examined.

The values of refractive indices of aqueous carboxylic acids (20 %, v/v) on adsorbents at 20°C are given in Table 1. The values of refractive indices of montmorillonite clays are not given, because the values of blank and supernatant solution, were same, indicating purified and Li-exchanged montmorillonite have about equal hydrophilic - hydrophobic character. The hydrophilic nature of montmorillonite clays is due to the presence of strongly hydrated interlayer cations i.e.; Na<sup>+</sup>, Ca<sup>2+</sup>, and Li<sup>+</sup> which act both as water sorption and transport sites [34]. As water is highly polar in nature, it is expected to interact strongly with the ionic sites in the interlayer. The montmorillonite clays swelled and formed nice cylindrical shaped jells in aqueous solutions of carboxylic acids in the vials. Probably the most important attractive and repulsive forces involved in expansion are the forces due to attraction of interlayer cations to the silicate layer and repulsion due to cation hydration [35, 36]. All the carboxylic acids used in aqueous solution for sorption can penetrate the pores of montmorillonite clays because the kinetic diameters of HCOOH, CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>5</sub>COOH in aqueous solution are 3.5, 4.5 and 5.5 Å respectively [37], while the pore openings of

montmorillonite are > 40 Å in distilled water [38]. The lamellar surfaces of montmorillonite clays and carboxylic acids can be linked through the formation of covalent bonds, or the interlayers and the carboxylic acid molecules can become associated through ion interactions, hydrogen bonding, van der Waal's dipole forces or dispersion forces [39, 40]. Thus, the spaces between the layers of montmorillonite in jell-form are accessible even to large molecules, the incorporation being referred to as intercalation [38].

Table 1 shows that the values of refractive indices of supernatants have decreased from blank solutions indicating that silicalite, H-ZSM-5, Na-ZSM-5 and Li-ZSM-5 are hydrophobic adsorbents. The adsorption isotherms at 20°C of 20% (v/v) aqueous solutions of HCOOH, CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>5</sub>COOH on zeolites are compared in Fig 3, Silicalite > H-ZSM-5 > Na-ZSM-5 > Li-ZSM-5

Table-1: Adsorption at 20 °C of 5mL of 20 % (v/v) of Aqueous HCOOH, CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>5</sub>COOH in 1.0 g of silicalite, H-ZSM-5, Na-ZSM-5 and Li-ZSM-5 Zeolites.

Aq. Acid n <sub>p</sub>	Silicalite n <sub>p</sub>	H-ZSM-5 n <sub>p</sub>	Na-ZSM-5 n <sub>p</sub>	Li-ZSM-5 n <sub>p</sub>
HCOOH 1.3466	1.3462	1.3462	1.3462	1.3465
C <sub>2</sub> H <sub>5</sub> COOH 1.3496	1.3481	1.3482	1.3481	1.3482
CH <sub>3</sub> CH <sub>2</sub> COOH 1.3508	1.3438	1.3501	1.3501	1.3500

The reason for the most hydrophobic character of silicalite is its all silica framework and its structure consists of only homopolar (hydrophobic) ≡Si-O-Si≡ bonds which adsorb organic molecules [41, 42]. While other zeolites have 1.185 Al per unit cell, consequently the framework increases in the number of partially ionic hydrophilic centers associated with the tetrahedrally coordinated aluminum ≡Al-OH-Si≡ [42-44]. Adsorption of water occurs on external surface silanol (SiOH) groups or cations associated with the framework aluminum and on centers ascribed to intracrystalline defects created as charge balancing centers for the charge template. The extraframework cations are usually located at the channels of the framework. Dedecek *et al.*, reported [45] that ZSM-5 has three sites of cations i.e.; α, β and γ. The site α is located in straight channel, while sites β and γ are located in sinusoidal channel of ZSM-5. Cations in all three sites are accessible for

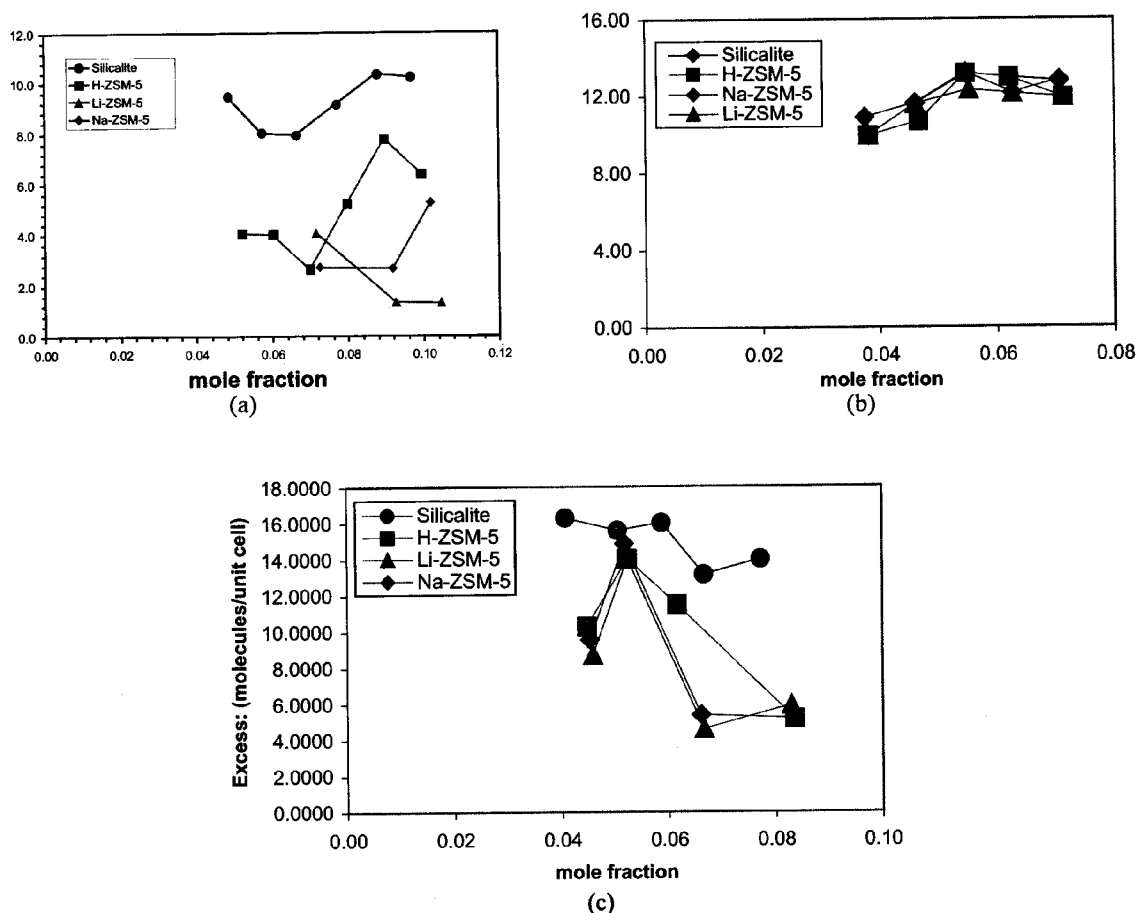


Fig. 3: Comparison of adsorption isotherms of 20 % (v/v) aqueous solutions of (a) Formic acid, (b) Acetic acid, (c) Propionic acid at 20°C.

small molecules and the accessibility for larger molecules is limited only by the size of the pore openings (10-rings). Thus, H-ZSM-5, Na-ZSM-5 and Li-ZSM-5 have two kinds of adsorption sites:

Silicalite like (1)  $\equiv \text{Si-O-Si} \equiv$   
Cationic Sites (2) ionic or polar

Santen and Kramer [46] and Matsuura *et al.*, [47] reported that H-ZSM-5 has (Si(OH)Al) acidic entity *i.e.*; Bronsted acid sites with which water molecules strongly interact. Sano *et al.*, reported [48] that every H(Al) adsorbs five H<sub>2</sub>O molecules, therefore according to the above formula of H-ZSM-5 zeolite contains about six H<sub>2</sub>O molecules per unit cell. The water transport through pores is

more likely favored because of a combination of favorable diffusion, due to small size (radius 2.8 Å) of water molecules, and favorable solubility due to the hydrophilic ionic species, H<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup> [49]. Furthermore, another reason for less adsorption of carboxylic acids into H-ZSM-5, Na-ZSM-5 and Li-ZSM-5 is due to the polarity of these acids. As the acids become less polar (dielectric constant: formic, 58; acetic, 6.2; propionic, 3.3) [37], their interactions with the cations *i.e.*; H<sup>+</sup>, Na<sup>+</sup> and Li<sup>+</sup> are reduced. Thus, the larger the size and the smaller the polarity of carboxylic acid, the better it is separated from water by hydrophobic zeolites. Thus all the above mentioned facts proved the more hydrophobic nature of silicalite than other zeolites investigated. The less hydrophobicity of Na-ZSM-5 and Li-ZSM-5 zeolites

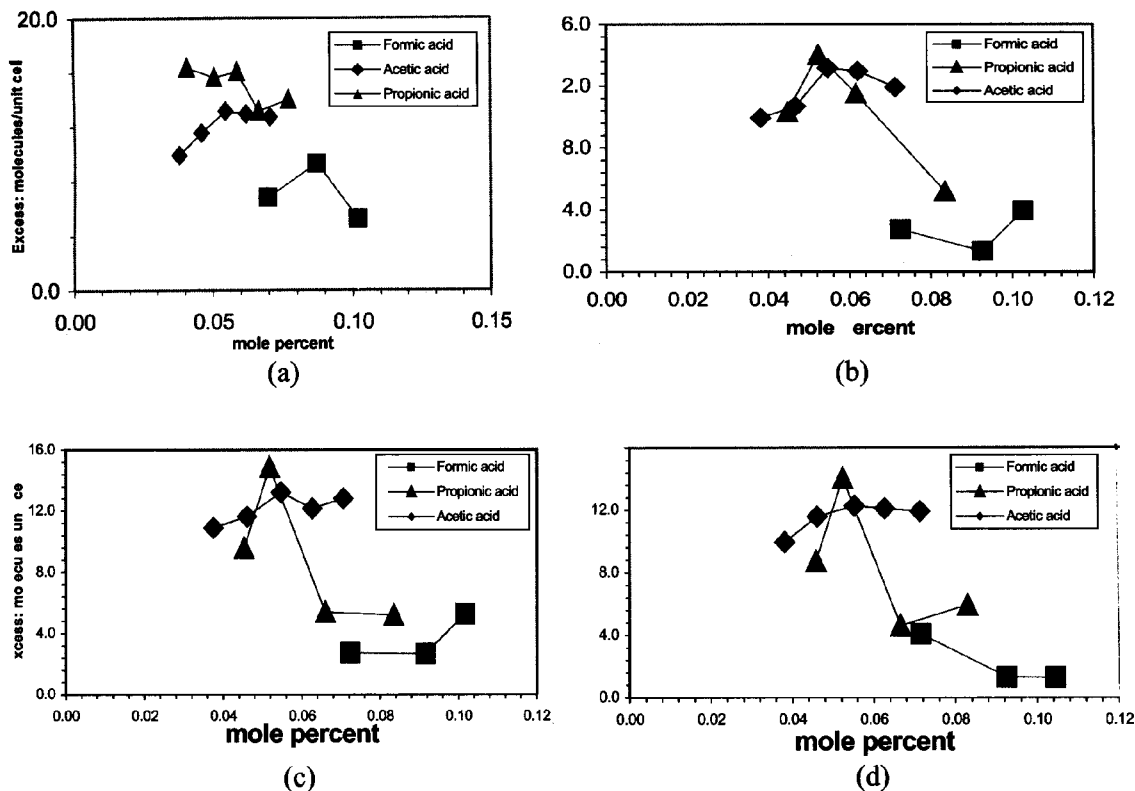


Fig. 4: Comparison of adsorption isotherms of 20% (v/v) of aqueous carboxylic acids solutions on (a) Silicalite, (b) H-ZSM-5, (c) Na-ZSM-5, (d) Li-ZSM-5 at 20°C.

than H-ZSM-5 and more hydrophobicity of Na-ZSM-5 than Li-ZSM-5 is due to strongly hydrated extra-framework cations,  $\text{Na}^+$  and  $\text{Li}^+$ . When  $\text{H}^+$  ion is replaced by  $\text{Na}^+$  and  $\text{Li}^+$  ions, the zeolite becomes more hydrophilic. Li-ZSM-5 is more hydrophilic than Na-ZSM-5 because  $\text{Li}^+$  has smaller ionic radius (0.60 Å) than  $\text{Na}^+$  (0.95 Å) and  $\text{Li}^+$  interacts more strongly with water than  $\text{Na}^+$  (hydrated radius of  $\text{Li}^+$ , 3.58 and  $\text{Na}^+$ , 3.41 Å) [49]. Thus, Li-ZSM-5 zeolite pores contain more water molecules than H-ZSM-5 and Na-ZSM-5, indicating  $\text{Li}^+$  ions made ZSM-5 zeolite framework less hydrophobic than other zeolites investigated.

The adsorption isotherms in Fig. 4 show that the uptakes of carboxylic acids from aqueous solutions on zeolites were found in the order:



One reason of this sequence of adsorption is the more organic character of the larger molecule

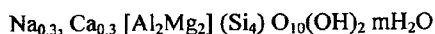
(bigger alkyl group) of propionic acid. HCOOH adsorbs the least because it has no alkyl group. Another reason, as mentioned above is the polarity of carboxylic acids. As  $\text{C}_2\text{H}_5\text{COOH}$  is less polar than  $\text{CH}_3\text{COOH}$  and HCOOH therefore its interaction with hydrophobic sites will be more. The zeolites investigated here have MFI framework structure and they are more siliceous samples, therefore they have more hydrophobic  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  centers where adsorption of organics occurs. In addition, the above results confirm that molecular sizes of the carboxylic acids *i.e.* propionic ( $\sim 5.6$  Å diameter in aqueous solution) > acetic ( $\sim 4.5$  Å) > formic ( $\sim 3.5$  Å) has no effect on adsorption because they are smaller than the MFI zeolite pores as confirmed by XRD ( $5.3 \times 5.6$  Å) or estimated from theoretical calculations ( $6.2$  Å) [49]. It suggests that adsorption of carboxylic acids is taking place only in pores on  $\equiv\text{Si}-\text{O}-\text{Si}\equiv$  sites and not on cation sites ( $\text{H}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ), because if adsorptions were taking place on cations then it would have been less on silicalite which has no extra-framework cations. The least adsorption of

HCOOH (the smallest acid) and highest adsorption of CH<sub>3</sub>CH<sub>2</sub>COOH (the biggest acid) suggests that the pore openings are not partially blocked by the extra-framework cations.

A general trend is also observed in adsorption isotherms (Figs. 3 and 4) that in the beginning the adsorption of acids increases with concentration but after higher concentration it starts declining. The possible reason for this trend is that the carboxyl group (<sup>δ-</sup>COOH<sup>δ+</sup>, partially polar) of acid molecules adsorbed into the intrinsic zeolite pores seems to change the surface property of the pores from silicalite grains to slightly hydrophilic [50]; consequently, the adsorption of carboxylic acid decreases after covering the hydrophobic sites on pore surface and starts adsorbing H<sub>2</sub>O molecules.

### Experimental

Montmorillonite in powder form of olive green color, was purchased from WARD's (lot # 46 E 0435) having unit cell formula:



Cations enclosed in square brackets, occupy octahedral sites and in parentheses occupy tetrahedral sites. The cations preceding the square bracket are exchangeable and are attached to the surfaces of the clay particles and do not normally penetrate the structure. In the formula m denotes number of water molecules which vary with relative humidity and with the size and nature of the exchangeable cations present [2, 51, 52]. Silicalite (lot # 2066000004) and H-ZSM-5 (Si/Al = 80) (lot # 8020-01-TC) white powdered forms were provided by the UOP and Zeolyst International respectively. Their most probable unit cell compositions are [53, 54]:

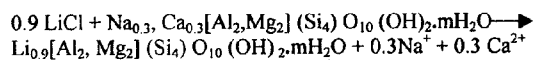
Silicalite: Si<sub>96</sub>O<sub>192</sub>

H-ZSM-5: H<sub>1.185</sub> [Al<sub>1.185</sub> Si<sub>94.815</sub> O<sub>192</sub>].6 H<sub>2</sub>O

The montmorillonite was purified (particle size < 2 μm) by using a sedimentation procedure [52, 55]. 12 grams of the clay was sprinkled over 1L of deionized water in a beaker with rapid stirring to prevent clumping of the clay. Vigorous stirring was achieved with a magnetic stir bar at room temperature on a magnetic stirrer / hot plate. The pH of the slurry was noted by using a digital pH-meter (JENCO Model 608). The dispersion was left for 24

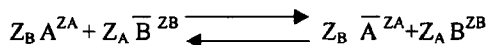
h to allow impurities and heavy mineral fractions to settle. The clear clay suspension was poured into a graduated beaker and the residual heavy mineral fractions were discarded. The suspension was centrifuged at 13000 RPM for 30 minutes at room temperature using refrigerated super speed centrifuge (Du Pont Instruments, Servall Rc-5B) and rotor GSA, radius 14.56 cm. The supernatant was discarded and the swelled jelly-like clay was transferred to a porcelain evaporating dish for drying in air at room temperature for several days. The dried sample of pure montmorillonite shrank considerably and stuck with the porcelain dish and formed thin flakes and laths. The montmorillonite was scratched and removed from the porcelain dish and ground by using a mortar and pestle and stored in glass vial for further investigations.

Li-exchanged montmorillonite was prepared by saturating the suspensions of particles < 2 μm montmorillonite with Li<sup>+</sup> cations by adding sufficient 1 M solution of LiCl (EMD Chemicals Inc. Lot # 1034B45). The LiCl solution was added at intervals of time in order to avoid the salt imbibe [56-58]. After adding 1 M LiCl solution to the stirring purified suspension of montmorillonite, it was left for overnight stirring at 50°C. The suspension was centrifuged, the supernatant was discarded and the sediment (swelled jelly-like) was washed several times with deionized water. Again 1 M LiCl solution was added to the stirring partially exchanged lithium montmorillonite suspension at 50°C and left for many hours for complete replacement of exchangeable cations by Li<sup>+</sup> ions and then it was centrifuged to separate the Li<sup>+</sup>-exchanged montmorillonite. The Li-exchanged clay was washed several times with deionized water and then resuspended in the deionized water and stirred for about 1 h and it was recentrifuged to recover the Li-exchanged clay. The clay was repeatedly washed, centrifuged and separated till the supernatant showed no Cl<sup>-</sup> ions (AgNO<sub>3</sub> solution test) [59, 60]. Finally Li-exchanged montmorillonite was dried and ground and placed in glass vial for further experiments. Li<sup>+</sup> exchange reaction in montmorillonite can be written as follows:



As silicalite is an all silica zeolite, it has no extraframework cation and therefore Na<sup>+</sup> and Li<sup>+</sup> ions could not be introduced into it. Na<sup>+</sup> and Li<sup>+</sup> ions were

introduced into H-ZSM-5 zeolite by conventional cation exchange method [61, 62]. The hydrated cations within zeolite pores are loosely bound and they will readily exchange with other cations in surrounding aqueous media. Exchange between cation  $A^{Z_A}$ , initially in solution, and  $B^{Z_B}$ , initially in a zeolite, can be written as follows:



where  $Z_{A,B}$  are the valencies of the ions and the characters with a bar relate to a cation inside the zeolite crystal.

8 grams of H-ZSM-5 zeolite were stirred with 250 mL of deionized water on a magnetic stirrer/hot plate at 25 °C and the pH of slurry was recorded by a digital pH-meter. 1 M / 750 mL, MCl ( $M = Na^+, Li^+$ ) solution was added in parts and the temperature of the slurry was increased to 65°C. The slurry (~ 900mL) was left for overnight stirring at 65 °C. The ion exchanged slurry was filtered by using buckner filtration and water suction pump. The partially cation exchanged sample was washed several times with hot (65 °C) deionized water and then the sample was stirred with 250 mL deionized water. Again 1 M/ 250 mL of MCl solution was added to the stirring slurry at 65 °C. After 3 h, the pH of the cation exchanged zeolite slurry was recorded, the slurry was filtered and the sample was washed several times with hot deionized water until the washings indicated no white precipitate with  $AgNO_3$  solution and the cation exchanged sample of ZSM-5 became free of  $Cl^-$  ions. The cation exchanged sample was then shifted to a porcelain evaporating dish for drying at room temperature (25 °C) for several days.

The powder X-ray diffraction (XRD) measurements were performed by using Rigaku Dmax-A diffractometer with a Ni filtered  $CuK\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) and the detector NaI scintillation with a photo-multiplier tube inside tight light capsule. Scanning electron microscopy (SEM) measurements were performed using a Hitachi S-4500 CFEG SEM instrument operated at 5 kV, current 10  $\mu A$ , condenser lens 1-5 mm, working distance 10 mm and aperture 2.

Adsorption experiments were carried out in screw cap septum vials, 14 mL (LxDia. 72 x 18mm)

at room temperature ( $25 \pm 0.5 \text{ }^\circ C$ ). A known weight of the adsorbents 1.0 g for zeolites and 0.05 g for clay (less weight due to swelling) without activation was introduced into 5 mL (for zeolites) and 10 mL (for clays) binary solution of carboxylic acid and water. The mixture was stirred with an egg-shaped stir bar (L x Dia; 19 x 9.5 mm) teflon coated on magnetic stirrer / hot plate for about 1 h. Then it was left for about 24 h for settling the suspension until transparent supernatant appeared. The blank solutions were also stirred similarly but without adsorbents. 100  $\mu L$  of the transparent solution was removed by a micro liter syringe and placed on the prism of a refractometer (Reichert AR 200 Digital Refractometer, Germany). The refractive indices of the aqueous solution of carboxylic acids and also of blank solutions were recorded. As refractive indices are very sensitive to temperature, therefore they were converted to

20 °C by using the formula below:  
 $n_D^{20} = n_D^{obs} + (T-20) 0.00045$

## Conclusions

We conclude that the adsorption selectivity of carboxylic acid from water by zeolites having high silica MFI type framework structures depends on polarity (dielectric constant) of the acid, the larger the alkyl group of the acid, lower the polarity, higher will be adsorption. The hydrophobicity of the zeolites depends on the homopolar,  $\equiv Si-O-Si \equiv$  bonds, more the homopolar bonds, more will be hydrophobic-character. The hydrophobicity of H-ZSM-5 zeolite decreased after exchange by  $Na^+$  and  $Li^+$  ions due to increase in the hydrophilic sites (ionic) in the framework pores. In addition, the exchanged cations ( $Na^+$ ,  $Li^+$ ) do not partially block the pore openings indicated by the higher adsorption of the biggest acid ( $C_2H_5COOH$ ) and the lower adsorption of the smallest acid ( $HCOOH$ ). Furthermore, the uptake of carboxylic acid decreased at high concentration after covering the homopolar bonds, perhaps due to hydrophilic nature of the carboxyl group (partially polar). The montmorillonite clays showed intermediate hydrophobic-hydrophilic behavior due to the presence of hydrophobic interlamellars (interfaces) and hydrophilic interlayer cations.

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