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The Compatibility of Compositional and Structural Features of Aluminous Large Pore Zeolites with Sorption Characteristics

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Abstract. The parent NaX and KL samples were prepared by hydrothermal crystallization and their corresponding K- and Na-exchanged forms were obtained by post-synthesis modification by conventional ion-exchange technique. NaX, NaKX, KL and NaKL samples were characterized by powder XRD, IR, low temperature nitrogen adsorption and chemical analyses. Their sorption uptake behaviour has been investigated by gravimetric method. The kinetics of sorption using different sorbate probe molecules such as water, benzene and n-hexane was measured at 298 K, at $P/P_0 = 0.5$ for 90 minutes. All the results obtained were discussed in terms of the compositional and structural variations of the adsorbents. Lack of high dimensionality of the pore system, less openness in structure, low average framework oxygen charge and less number of accessible nonframework cations are some of the prominent factors which has resulted in reduced hydro- and organo-philicity in LTL type zeolites as compared to X-type. The size and concentration of the accessible nonframework cations were also found to influence the sorptive properties of these aluminous large pore zeolites. Among all the probe molecules, n-hexane was found to be as a promising probe for differentiating the structural peculiarities especially dimensionality of the pore system.

Keywords: sorption, zeolite X, zeolite LTL, exchangeable cations, structural features

1. Introduction

Zeolites, which are unique class of solids, are finding extensive application in adsorption and separation processes and as a catalysts for many chemical reactions due to their structural and compositional peculiarities coupled with a large internal surface area accessible to molecules of comparable size via diffusion through the pores (Naber et al., 1994; Rao et al., 1989; Csisery and Rabo, 1976; Maxwell and Stork, 1991; Zicovich-Wilson et al., 1994). The structures of these solids are based on an infinitely extending three-dimensional network of SiO_4 and AlO_4 tetrahedra sharing all the oxygen (Breck, 1974). Each AlO_4 tetrahedron creates a negative charge on the framework of the zeolite which is balanced by the cations. These charge balancing cations occupy non-framework/exchangeable sites. Numerous attempts were made to classify various zeolites on the basis of their morphology (Zicovich-Wilson et al., 1994; Breck, 1974; Milton et al., 1968; Szostak, 1989), crystal structure (Zicovich-Wilson et al., 1994; Breck, 1974), framework Si/Al ratios (Zicovich-Wilson et al., 1994; Breck, 1965, 1974), pore topology (Zicovich-Wilson et al., 1994; Vaughan, 1985) and their natural occurrence (Zicovich-Wilson et al., 1994).

According to the classification based on effective pore diameters, zeolite X: a aluminium rich end member of faujasite family and a synthetic zeolite LTL belong to a class of large pore variety of zeolites

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(pore diameter > 7 Å, 12-membered pore openings). The framework structures of both the zeolites are characterized by the double 6-ring, D6R, as the secondary building unit in their structural frameworks. The unit cells of zeolite X are cubic with large cell dimension of nearly 25 Å and contain 192 tetrahedra, whereas zeolite LTL has hexagonal unit cells and contains 36 tetrahedra. In X zeolite the β cages are connected tetrahedrally at six-rings by bridging oxygens, to give double six-rings (D6R's, hexagonal prisms) and concomitantly to give an interconnected set of even larger cavities (supercages) accessible in three dimensions through 12-ring windows. The aluminosilicate framework of zeolite LTL, is based on polyhedral cages formed by five six-membered and six four-membered rings (Zicovich-Wilson et al., 1994). The main channels consisting of alternate cancrinite (or ϵ) cages and hexagonal prisms form columns that run parallel to the c-axis.

These zeolites can be distinguished on the basis of dimensionality of the channel system (unidimensional for LTL and three dimensional for X), framework Si/Al ratios and different number of nonframework cations and their location at different sites.

To understand the extent of compatibility of physical structure alongwith their compositional component with the sorption properties of the zeolites, knowledge is required not only of the chemical composition, surface area and the pore size of the zeolites but also of the characteristics of the adsorbate such as molecular volume and configuration, polarization and the degree of unsaturation for organic molecules. In order to establish and control key materials and process parameters for wide range of application in selective molecular sieving and catalysis, the knowledge of extent of sorbate-sorbent and sorbate-sorbate interactions is also very essential. Although the temperature (Zikanova and Derewinski, 1995), crystal size and morphology (Shiralkar et al., 1991; Foger et al., 1984; Karsli and Yucel, 1992; Choudhary et al., 1990), the nature and concentration of the framework (Choudhary et al., 1990; Rao et al., 1990; Shaikh et al., 1998; Joshi and Shiralkar, 1993; Joshi et al., 1993, 1994) and the extra-framework (Joshi and Shiralkar, 1993; Kasture et al., 1998) cations have been shown to influence the sorption properties of various fully crystalline zeolites and related molecular sieves, less attention has been paid on investigating the influence of structural and compositional peculiarities of the zeolites which belong to large pore variety on their sorption behaviour.

In view of this, we are reporting the comparison of the sorption characteristics of X and LTL zeolites as a function of their structure and chemical composition in the present communication. Various sorbate probes such as N_2, water, benzene and n-hexane were used for the evaluation of the sorptive properties of these zeolites to confirm the compatibility with their compositional and structural features.

2. Experimental

2.1. Materials

Zeolites of type X and LTL have been prepared by hydrothermal crystallization at autogeneous pressure. Pure and highly crystalline Zeolite NaX was obtained from the reaction mixture having oxide mole composition $3.6Na_2O : 3SiO_2 : Al_2O_3 : 144H_2O$ by subjecting it to hydrothermal treatment at 368 K for 8 hrs. The raw materials used for the preparation of homogeneous reaction mixture were water glass solution (28.5% SiO_2, 8.5% Na_2O, 63.0% H_2O), sodium aluminate (43.65% Al_2O_3, 39% Na_2O, 17.35% H_2O), sodium hydroxide (AR grade, LOBA) and distilled water. The solid product was separated and thoroughly washed with hot water till free from excess alkali. The product was then dried for 8 hrs in an air oven maintained at 383 K. Zeolite LTL in potassium form (KL) was obtained by following the procedure described elsewhere (Joshi et al., 1990).

The ion exchange was accomplished by following the conventional cation-exchange method. The NaX sample was modified into K-exchanged form (NaKX) and KL sample was modified into Na- exchanged form (NaKL) by exchanges with 5% aqueous solution of chloride salts of the respective alkali metal species. The required degree of exchange was achieved by number of repetitions at 368 K. The aqueous salt solution was taken in the proportion of 15 ml/gm of zeolite, for each exchange experiment. The solid was separated by suction filtration, washed with distilled water till effluent showed negative chloride test. The solid was then dried in an air oven maintained at 383 K for 8 hrs.

Hydrocarbons (99.9% purity) such as benzene and n-hexane were used after further purification over activated 3 A molecular sieves. Double distilled water and high purity nitrogen was used for sorption measurements.

2.2. Methods

The phase purity and crystallinity of the as-synthesized and exchanged forms were examined by powder XRD. The XRD patterns were collected over 2θ range of 5° to 40° using Ni filtered Cu K_α ($\lambda = 1.54041$ Å) radiation using a Rigaku D Max-III VC X-ray diffractometer. The relative intensity (I/I_0) of each peak was evaluated by comparing the intensity of a peak (I) with the intensity of the most intense peak (I_0) in the XRD profile of a sample under investigation.

The framework IR spectra were recorded on a Pye-Unicam SP-300 spectrometer using a Nujol mull technique.

The chemical composition of samples was established by conventional wet chemical methods and using atomic absorption (Hitach Z—8000, Japan) spectrometer. In case of exchanged samples, the amount of sodium/potassium was also estimated from the filtrate collected after ion-exchanged treatment by atomic absorption spectrometer to cross-check the extent of exchange.

The low temperature (78 K) nitrogen adsorption measurements were carried out using a BET volumetric apparatus following the procedure described elsewhere (Shiralkar, 1980). The sorption uptake of water and different hydrocarbons was measured on all-glass gravimetric, McBain-Baker type apparatus using silica spring balance (with sensitivity = 50 cm/g) at 298 K and at $P/P_0 = 0.5$ following the procedure described elsewhere (Joshi et al., 1999). The kinetics of sorption of various sorbates at 298 K and at $P/P_0 = 0.5$ on different sorbents was carried out by measuring the extent of sorption uptake at different stages in the process. The time at which the activated sample is exposed to the sorbate vapours was referred as zeroeth minute and then progressive gain in weight as a function of time over the period of 90 minutes was recorded. The amount of weight gain (g/g) was then further converted into molecules sorbed per unit cell. Powder X-ray diffractograms were recorded for each sample after completion of sorption measurement to confirm whether any structural damage had occurred.

3. Results and Discussion

3.1. Characterization

The sample designation, unit cell composition, number of unit cells/g , intermediate electronegativity (S_{int}) and the framework oxygen charge (δ_{O}) are summarized in Table 1 for the samples selected for the present studies. The S_{int} and δ_{O} values were calculated by the equations reported elsewhere (Mortier, 1978). For comparison purpose, NaKX and NaKL samples are selected from different modified samples in a respective series such that in both the samples, K/(Na + K) ratio is almost identical (0.52 for NaKX and 0.53 for NaKL). The chemical analyses revealed that the number of exchanged nonframework cations estimated in solid was in close agreement with that of number of sodium (in case of X type zeolite) and potassium (in case of LTL zeolite) cations estimated from the effluent collected after ion-exchange followed by the sufficient washing. It is clearly evident from Table 1, that depending upon the total number of tetrahedra in each unit cell of different topology and the nature and concentration of nonframework cations in the same topology, the number of unit cell in unit mass was found to vary accordingly. It is interesting to note that, at identical level of nonframework cation composition [i.e. K/(Na + K) ratio], NaKX has exhibited 5.4% decrease, whereas NaKL has shown 2.7% increase in number of unit cells/g as compared to number of unit cells/g of their respective parent sample. The decrease in NaKX is due to the exchange of lighter Na by heavier K cations and increase in NaKL is associated with the exchange of heavier K by lighter Na cations. The unmatched extent of decrease in NaKX

Table 1. Unit cell composition (on unhydrous basis) and related details of cation exchanged type X and L zeolite.

Sample designation	Unit cell composition	Unit Cell/g $\times 10^{-19}$	S_{int}	$^{-}\delta_{\mathrm{O}}$
NaX	$Na_{89.4}[(AlO_2)_{89.4}(SiO_2)_{102.6}]$	4.46	3.230	0.417
NaKX	$Na_{42.02}K_{47.38}[(AlO_2)_{89.4}(SiO_2)_{102.6}]$	4.22	3.115	0.441
KL	$K_{8.70}[(AlO_2)_{8.70}(SiO_2)_{27.30}]$	24.14	3.516	0.357
NaKL	$K_{5.26}Na_{3.47}[(AlO_2)_{8.70}(SiO_2)_{27.30}]$	24.80	3.579	0.343

with that of the extent of increase in NaKL can also be attributed to the differences in number of framework Al and Si tetrahedra. Thus, the number of unit cells/g of zeolites X and LTL has shown the dependence on the number and nature of framework and nonframework cations.

Since Sanderson's electronegativity scale allows a prediction of sorptive characteristics of complicated chemical systems such as zeolites with the use of only the unit cell composition; an attempt was made to investigate the trends within the class of large pore in the present studies. It is clearly evident from Table 1, that intermediate electronegativity follows the trend: NaKL > KL > NaX > NaKX. Thus, in spite of having less number of total tetrahedra, zeolite of type LTL has shown higher intermediate electronegativity due partly to lower Al/(Si + Al) ratio as compared to X type zeolites. Since the acid strength of the individual site can be directly correlated with the electronegativity, NaKL has shown higher acid strength as compared to rest of the samples. Thus, the acid strength seems to be related not only to the compositional component but also to the structural peculiarities of zeolites. Since the pores or cavities of the zeolites are surrounded by the crystal lattice of the zeolites and are influenced by the crystal field, the rate of adsorption and extent of sorbate-sorbent interaction of the basic sorbate molecules may decrease in the order NaKL > KL > NaX > NaKX. Considering the coexistence of conjugated acid-base pair, the reverse trend was expected for the basic strength in these zeolites. The framework oxygen charge bearing the negative charge of the lattice is considered as the structural basic site. The oxygen charge that characterizes the intrinsic framework basicity was calculated and tabulated in Table 1. It is clearly evident from the Table 1 that basicity follows the trend NaKX > NaX > KL > NaKL. The higher basicity in X type zeolite may be associated with the more open structure, higher Al content yielding higher density of charges and low intermediate electronegativity. It is interesting to note that, at identical level of nonframework cation composition [i.e. K/(Na + K) ratio], NaKX has exhibited 5.8% increase, whereas NaKL has shown 3.9% decrease in charge on oxygen as compared to charge on oxygen in their respective parent sample. Thus, nature and concentration of the nonframework species are also found to contribute for the variation in the basic character of the given structure.

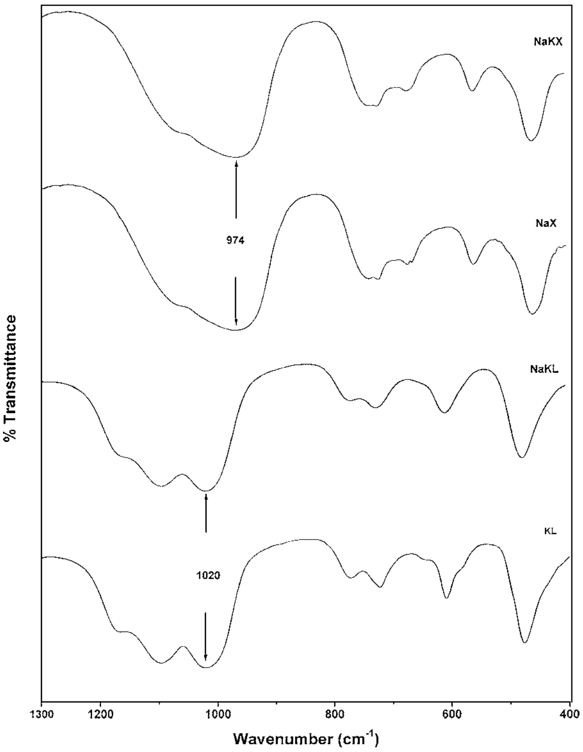

Figure 1. The framework IR spectra of parent and their modified forms.

The IR spectrum in the 400–1300 cm^{-1} region provides a useful structural information as it contains the fundamental vibrations of the framework Si(Al)O$_4$ groupings. The parent samples have shown a typical mid-infrared IR pattern in close agreement with the reported-one (Flanigen et al., 1971; Joshi et al., 1990). Figure 1 illustrates the comparison of framework IR spectra of modified forms with their parent sample. The framework IR spectra of the modified samples revealed that no shift was observed in the band at 974 cm^{-1} in X zeolite and 1020 cm^{-1} in LTL zeolite assigned (Flanigen et al., 1971) to stretching mode, which are sensitive to framework Si/Al composition. Thus, it seems that no dealumination has occurred during ion-exchange procedure. It was therefore concluded that framework composition (Si/Al ratio) remained unaltered during cation exchange modification. The chemical analysis data in relation to the framework composition are also found to be in support of these observations.

The powder XRD profile of parent and modified samples essentially showed the characteristics peaks of particular type of zeolite are in close agreement with the reported (Breck, 1974) data. The absence of impurity peaks and amorphous halo (Joshi et al., 1999)

Table 2. Powder XRD data for parent and modified samples.

L-type zeolite				X-type zeolite			
		$(I/I_0) \times 100$				$(I/I_0) \times 100$	
hkl	*d* (Å)	KL	NaKL	hkl	*d* (Å)	NaX	NaKX
100	15.92	100	100	111	14.51	100	84
200	7.98	7	5	220	8.92	25	27
001	7.53	35	14	311	7.60	24	18
201	6.01	29	30	331	5.77	54	47
111	5.82	18	9	333	4.74	17	24
220	4.60	30	37	440	4.43	30	30
310	4.41	13	12	620	3.96	15	20
301	4.34	13	14	533	3.82	78	100
221	3.92	52	39	444	3.61	11	31
311	3.78	5	5	642	3.35	81	82
320	3.66	38	19	733	3.05	20	27
410	3.48	44	22	822	2.95	39	49
321	3.28	19	16	555	2.88	95	85
212	3.18	48	48	840	2.80	41	76
330	3.07	43	14				
420	3.02	9	23				
222	2.91	50	34				
600	2.65	20	15				

region indicated highly pure and crystalline nature of all the phases under investigation. Table 2 summarizes the powder XRD data of the samples under present investigations. It is clearly evident from this data that, upon modification, only relative intensities were found to be changed without any shift in the respective peak positions. The variation in the charge to size ratio of the extraframework cationic species and framework distortion to some extent may be responsible for the observed change in the relative intensities.

Chemical analysis, framework IR and powder XRD results clearly indicated that in the present studies, the modification by ion-exchange technique has not resulted into any change as far as framework composition (Si/Al ratio), phase purity and crystallinity of X and LTL type zeolites are concerned.

3.2. *Sorptive Characteristics*

A unit cell is a unique unit at microscopic level representing the three dimensional structure of atoms. Crystalline zeolites have repetition of these unit cells. The number of unit cells/g was found to vary with the composition and the structure of zeolites in the samples under present investigation. It was thought to examine the sorptive properties of these samples on the basis of amount sorbed at unit cell level instead of at unit weight. Therefore, the amount sorbed per unit weight was converted into number of molecules sorbed per unit cell and then attempt was made to correlate the sorptive characteristic as a function of compositional and structural variations.

3.2.1. Low Temperature Nitrogen Adsorption. Nitrogen possesses quadrupole moment and hence is capable of having electrostatic interaction with the zeolite surface. The extent of such interactions and uptake were studied as a function of chemical composition and structural peculiarities of X and LTL type zeolites. The families of nitrogen adsorption isotherms for parent NaX, NaKX, KL, and NaKL are shown in the Fig. 2. At low-pressure region, all the samples exhibited rapid uptake followed by nearly tapered region at increased pressure. It may be due to negligible or no amorphous contribution in the microporous samples under investigation. It is very clear from the figure that, the number of N_2 molecules adsorbed per unit cell are quite high in X as compared to LTL type zeolite. Furthermore, at identical level of nonframework cation composition, the NaKX sample has exhibited almost 8.7 fold increase in the number of N_2 molecules adsorbed per unit cell when compared with NaKL. This can be explained on the basis of higher population of Al—O (1.75 Å) and Si—O (1.60 Å) bonds that has rendered more openness in the structure. If it is assumed that LTL has the same number of these bonds, it should have

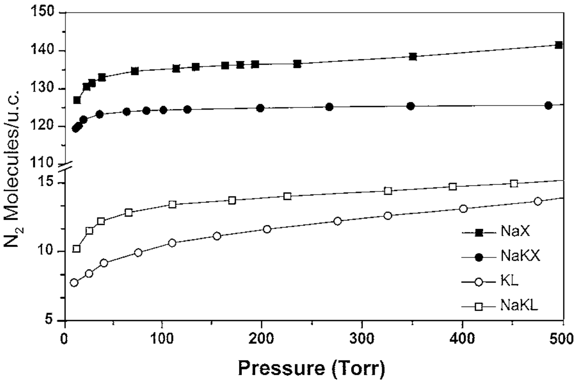

Figure 2. The families of nitrogen adsorption isotherms for parent NaX, KL and their exchanged forms NaKX, NaKL.

yielded 5.44 times higher uptake of nitrogen molecules as compared to that has shown in the present studies. Thus nitrogen uptake capacity of X has not increased just because of the higher number of unit cell tetrahedra but also due to crystallographic cubic symmetry of unit cell that enhances the packing efficiency. In addition to this, higher number and accessibility of adsorption centers, greater extent of surface-nitrogen interactions seems to be operative for higher uptake of nitrogen in X type zeolite. In order to gain some insight about the extent of surface-nitrogen interactions, the chemical affinity of nitrogen sorption was estimated as a function of amount sorbed in each zeolite by using the equation $\Delta\mu = RT\ln(P/P_0)$. The variation in the chemical affinity of the nitrogen sorbed has been estimated by using—$\Delta\mu$ as a quantitative measure. Since, the influence of compositional and structural features of the sorbents was thought to manifest itself through the affinity factor, the plots of chemical potential (expressed in kJ/mole) as a function of N_2 molecules adsorbed /u.c. were considered for representing the chemical affinity profiles of the sorption system. The comparison of affinity profiles for N_2 adsorption on NaX, NaKX, KL and NaKL are made in Fig. 3. It is seen from this figure that, in accordance with the thermodynamic expectation, there is a continuous increase in the amount sorbed with the decrease in chemical potential. Thus, the chemical affinity has exhibited an inverse trend with respect to amount sorbed, indicating dependence of free energy change on the affinity factor. The salient feature of this figure is that for constant coverage ca. 12.6 N_2 molecules/u.c., the chemical potential of the order of 0.6 and 1.6 kJ/mole was found to be required for KL and NaKL forms respectively. However, the magnitude of the chemical potential of the order 0.6 and 3.35 kJ/mole was exhibited for the identical uptake of ca. 126.0 N_2 molecules/u.c., in case of NaKX and NaX forms respectively. It can be also seen from the figure that, if extrapolated, the affinity plot for NaKX will cut X axis at higher value as compared to that for NaKL. Thus, from the above discussion it can be stated that both the parameters (composition and structure) influence the chemical affinity for nitrogen adsorption.

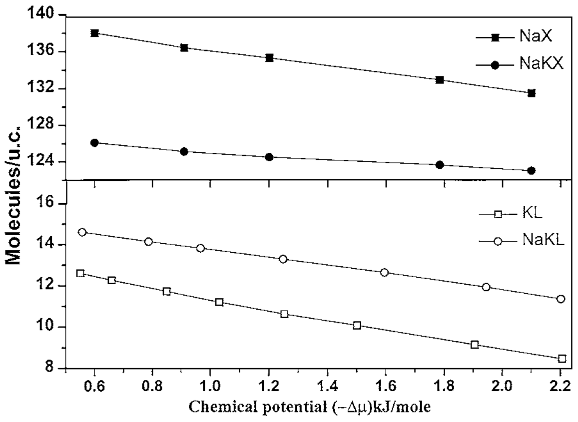

Figure 3. The comparison of affinity profiles for N_2 adsorption on NaX, NaKX, KL and NaKL.

Another interesting feature of Fig. 2 is that in a given structure, the extent of nitrogen uptake also has shown the dependence on the nature of nonframework cations. NaX has shown higher number of N_2 molecules adsorbed per unit cell than its modified analogue NaKX. NaKL exchanged form has however shown more number of N_2 molecules adsorbed per unit cell as compared to its parent (KL) sample. As the size of K^+ ions is larger than that of Na^+ ions and former cannot bury itself in the framework to the same extent as latter, lower adsorption of N_2 molecules per unit cell was observed in case of KNaX and KL. This indicates that electrostatic interaction energy with the nitrogen molecule decreases with increase in the nonframework cationic size. Thus, the dispersion and polarization energy components in given structure and the differences in the structural engineering of zeolites are responsible for the extent of electrostatic interaction with N_2 molecules and hence uptake. Neglecting any experimental error, at 325 Torr pressure (beyond inflexion point of each isotherm), the overall trend observed for the uptake of N_2 molecules/u.c. was as: NaX (138.3 molecules/u.c.) $>$ NaKX (125.0 molecules/u.c.) $\gg$ NaKL (14.4 molecules/u.c.) $>$ KL (12.6 molecules/u.c.).

The nitrogen sorption data were further analyzed to estimate the specific surface area and micropore volume by applying the conventional BET, Langmuir and Dubinin Radushkevich equations. The data obtained for the surface area and micropore volume of the X and LTL zeolites are summarized in Table 3. The specific surface areas for all the samples were greater when calculated using Langmuir approach than those by the BET approach. However, the BET approach probably gives more realistic estimate for the surface area responsible for the sorptive properties. It is interesting to note that, the BET specific area and Dubinin micropore volume for NaKX are approximately double than that for NaKL zeolite as against almost 8.68 times

Table 3. Surface area and void volume of zeolite NaX and KL.

Sample designation	Surface area (m^2/g) BET	Surface area (m^2/g) Lang.	Dubinin void volume (mL/g)
NaX	925	998	0.350
NaKX	834	912	0.321
KL	351	474	0.168
NaKL	421	579	0.172

higher adsorption of N_2 molecules/unit cell of former than latter. This tremendous difference can be partly attributed to the significant variation in the number of unit cells per gram of the samples. This, in turn, can be correlated to the nature and concentration of framework tetrahedral cations and their special arrangement in a given structure. Furthermore, in a given structure, at the identical degree of ion-exchange, the extent of variation in specific BET surface area and Dubinin micropore volume has shown the dependence on the structural peculiarity. NaKX has exhibited a drop of 9.8% in specific BET surface area and 8.2% in Dubinin micropore volume when compared with the parent NaX. On the contrary, NaKL has exhibited an increase of 20% in specific BET surface area and 2.3% in Dubinin micropore volume when compared with the parent KL.

3.2.2. Equilibrium Uptake of Water. In the investigation of influence of the compositional and structural features on sorption properties, it is of interest to study the differences in the extent of filling the zeolite cavities by the smallest water molecules capable of strong specific interaction with the zeolite and the mutual association of hydrogen bonds. Figure 4 represents the kinetics of water sorption in parent and modified forms of X and LTL zeolites at $P/P_O = 0.5$ and at 298 K for 90 minutes. It is seen from the figure that, both the sorption rate and the equilibrium sorption uptake have shown the dependence on the compositional and structural peculiarities. The overall trend in the equilibrium sorption uptakes in these samples was observed as: NaX > NaKX ≫ NaKL > KL. If the number of water molecules sorbed per unit cell was considered as a measure of hydrophilicity character, the same trend may be looked upon as the order of decreasing hydrophilic character in these sorbents. The lower hydrophilic character in LTL zeolites as compared with that of X-type zeolites may be partly attributed to the lower micropore volume and the polarizing ability of the zeolite cage. Beside these structural features, the extent of sorbent-sorbate and sorbate-sorbate interactions also may be responsible for the observed variations in the water sorption.

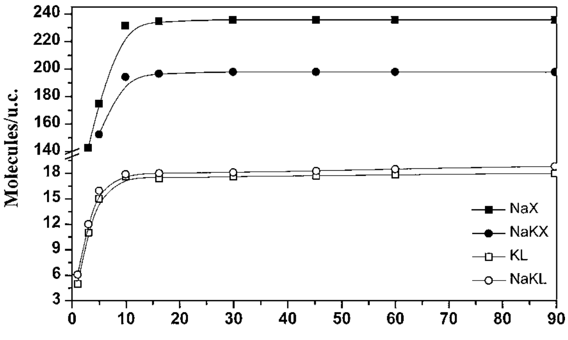

Figure 4. The kinetics of water sorption in parent and modified forms of NaX and KL zeolites.

The successive association of the adsorbed water molecules bound to the cations, to oxygen ions of zeolite and to each other has been well demonstrated by calorimetric measurements of the heat capacity of the KNaX + water system (Berezin et al., 1973). Thus, higher amount of water uptake in case of X type zeolites seems to be associated with the higher number of nonframework cations that are acting as adsorption centers and higher extent of water-framework oxygen and water-water interactions. As each accessible nonframework cation interacts with the unshared electron pair of water oxygen atom, certainly number of such centers may enhance the uptake capacity. The higher extent of water-framework oxygen interactions may be explained on the basis of higher charge on framework oxygen from the lattice of X type zeolite (refer Table 1) which favours the formation of strong hydrogen bond between proton of water molecule and the nearest framework oxygen. Thirdly, the higher extent water-water interaction may be partly associated with the favourable distance between the water molecules adsorbed on the cations for forming strong hydrogen bonds with already adsorbed water molecules (Kiselev et al., 1972). Thus, putting all the aspects together, it can be concluded that the formation of more regular network of water molecules connected with each other, with framework oxygen and with nonframework cations seems to be responsible for higher hydrophilic character of X type zeolite as compared to LTL.

It can be also seen from the Fig. 4, that upon exchanging the nonframework cations in a given structure, the hydrophilic character was found to alter in accordance with the concentration, size and polarizability of the cations. Therefore, the dispersion intermolecular interaction of water molecules with the zeolite seems to be operative in case of water uptake. The water-zeolite intermolecular interactions were found stronger in the samples containing more concentration of Na^+ cations in aluminous large pore X and LTL zeolites.

The micropore volume occupied by water in different samples was calculated using the equilibrium uptake of water. NaX and NaKX samples have shown the micropore volume occupancy of the order of 0.314 and 0.273 mL/g respectively, whereas 0.13 and 0.14 mL/g occupancy was exhibited by KL and NaKL samples respectively. None of these values are in close agreement with those of Dubinin micropore volume calculated using nitrogen adsorption data. However, it is interesting to note that, inspite of having the differences in structuro-compositional features such as number of unit cell/g, the simultaneous presence of two different types of cations due to incomplete degree of exchange, location and population of accessible adsorption sites, both the NaKX and NaKL samples have exhibited $83 \pm 2\%$ occupancy of micropore volume by the water molecules with respect to the total Dubinin micropore volume calculated using nitrogen adsorption data.

3.2.3. Equilibrium Uptake of Hydrocarbons

3.2.3.1. Benzene. Benzene was selected from aromatics probes since a large part of catalytic or adsorption processes involve aromatics. The accessible nonframework cations acting as Lewis acids are some of the possible adsorption sites that interact with the π electrons of benzene. Similarly, an interaction of the CH groups of the benzene with the framework oxygen atoms of the large aperture (12 R window) forms a basis for adsorption of benzene in yet another site i.e. 12 R window. Both, Zeolite X and LTL have 12 R windows and certain sets of accessible adsorption sites, the influence of the structure and composition on the mode of interaction and uptake of benzene was investigated. Figure 5 represents the kinetics of benzene sorption in parent and modified forms of X and LTL zeolites at $P/P_0 = 0.5$ and at 298 K for 90 minutes. The overall trend in the equilibrium sorption uptakes in these samples was observed as: NaX > NaKX ≫ NaKL > KL. The micropore volume occupied by benzene molecules in each sample was estimated using the equilibrium uptake values to shed some light on packing mechanism and hence on the mode of interactions. NaX and NaKX samples have shown the micropore volume occupancy of the order of 0.292 and 0.245 mL/g respectively, whereas 0.102 and 0.107 mL/g occupancy was exhibited by KL and NaKL samples respectively. None of these values are in close agreement with those of Dubinin micropore volume calculated using nitrogen adsorption data. This can be partly attributed to the steric hindrance experienced by the benzene molecule due to its larger dimension (5.85 Å).

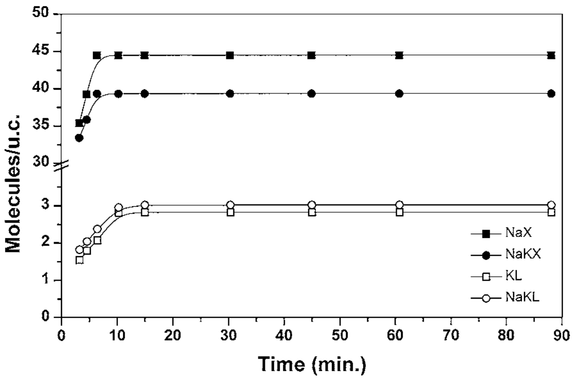

Figure 5. The kinetics of benzene sorption in parent and modified forms of NaX and KL zeolites.

Higher uptake of benzene at unit cell level and higher micropore volume occupancy in X type zeolites may be associated with the formation of benzene clusters on account of the adsorption on cations and 12 R windows (Jobic et al., 1987). The high selectivity of LTL zeolites in dehydrocyclization reaction as compared to faujasite (Besoukhanova et al., 1981) suggest the high diffusivity of benzene in LTL structure. From the above discussion, it can be concluded that the formation of clusters that restrict the mobility and hence diffusion of benzene molecules may not be occurring in the LTL zeolites due to unidimensional and nonintersecting channels and greater extent of deviation of true residual charge density of oxygen atoms in 12 R window from the average intrinsic framework basicity. It is also clearly evident from the figure that, the uptake of ~3 benzene molecules per unit cell in LTL framework matches closely with the number of nonframework cations occupied in site D located on the wall of main channel. This indicates that a ratio of number of adsorbed benzene molecules to number of cations in site D of the order of ≤1 confirm the fact that there is only interaction between the benzene molecules and cations.

Thus, eventhough, as evident from the figure, the nature and concentration of the nonframework cations have exhibited an influence on the benzene sorption behaviour, the dimensionality of the pore system has found a controlling factor as far as energetics and dynamics of benzene sorption in these aluminous large pore zeolites are concerned.

3.2.3.2. n-Hexane. The differences in the characteristics such as molecular volume and configuration, polarization and the degree of unsaturation have been considered to investigate the sorption properties as a function of compositional and structural components in aluminous large pore X and LTL zeolites. Figure 6 represents the kinetics of n-hexane sorption in parent and modified forms of X and LTL zeolites at $P/P_0 = 0.5$ and at 298 K for 90 minutes. The overall sequence in the equilibrium sorption uptakes in these samples was observed as: NaX $>$ NaKX $\gg$ NaKL $>$ KL. Eventhough, this sequence is identical with that of the benzene uptake, the lower amount of n-hexane sorbed was observed in all the samples. The difference in the uptake capacity may be partly associated with the comparatively lower packing efficiency with the cylindrical shape of n-hexane (4.2 Å) as compared to that with spherical (5.85 Å) benzene molecule and the differences in the energetics of the sorption. The structural and compositional components seem to be operative in the change in the electric field strength in the interior of the zeolites and hence in the extent of energy of dispersion of intermolecular interactions of the sorbate molecules. The higher heat of adsorption of benzene (10–12 kJ/mole) as compared to n-hexane (Zhdanov et al., 1990) also forms the basis for the explanation of higher uptake of benzene.

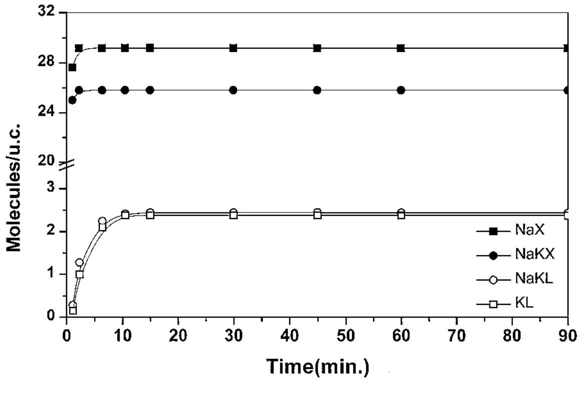

Figure 6. The kinetics of n-hexane sorption in parent and modified forms of NaX and KL zeolites.

It is interesting to note that the rate of n-hexane sorption is much higher in X type zeolites as compared to LTL. In addition to this, the time needed to reach equilibrium was also found to be shorter in case of X type zeolites. Another salient feature concerned with n-hexane uptake was that, the X type zeolites have exhibited capability of accommodating $>75\%$ of the total Dubinin micropore volume calculated using nitrogen adsorption data, whereas LTL type zeolites have exhibited their capability of accommodating $<50\%$ of total Dubinin micropore volume.

The energy of adsorption of saturated hydrocarbons mainly depends on the dispersion component. In X and LTL types zeolites, number of extraframework cations are several times less than the lattice oxygen atoms, the contribution of the oxygen atoms to the adsorption energy may be predominating. In other words, the specific interactions of n-hexane hydrogen atoms with the free electron pairs of zeolitic oxygen contribute appreciably in the energy of adsorption. Thus, it seems that interaction of the cylindrical n-hexane molecules with the lattice oxygen atoms may be operative in screening the adjacent nonframework cations. The framework of Zeolite X contains 384 lattice oxygen atoms located at 4 different sites whereas zeolite LTL has only 72 lattice oxygen atoms located at 6 different sites. If it is assumed that LTL contains the same number of lattice oxygen atoms as that of zeolite X, the n-hexane uptake in the former could have increased by 5.3 times. However, in the present studies, it is revealed that, around 10-fold increased uptake has been exhibited in X type zeolites as compared to that in LTL zeolites. This suggests that the higher dimensionality of the channel system, a yet another structural parameter, play a dominant role for enhancing the n-hexane uptake capacity in the X type zeolite, which favours sorbate-sorbate interactions. Thus, the higher dimensionality of pore system enables each of the subsequent n-hexane molecule to make contact not just with one but with several CH_2 groups of previously sorbed molecules.

Figure 7 depicts the corelationship between extent of occupancy of total micropore volume by various sorbents under identical set of measurement conditions with the compositionally and structurally different zeolites. It can be clearly seen from the figure that the population of the nonframework cations with smaller size was found to enhance the uptake in a given structure irrespective of nature of sorbate molecules. However, the extent of increase has shown the dependence on the characteristics of the probe molecule. The striking

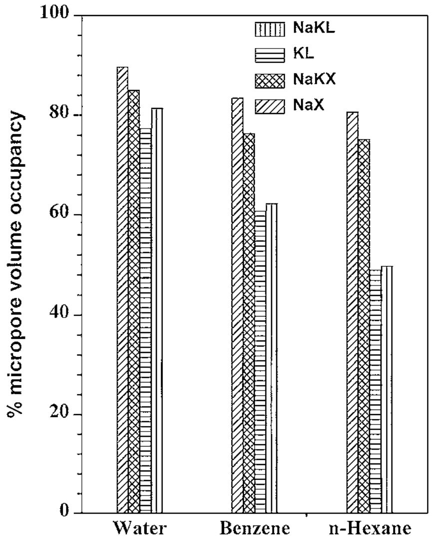

Figure 7. The corelationship between the % micropore volume occupancy by Water, Benzene and n-hexane in parent NaX, KL and their exchanged forms.

difference in the extent of micropore occupancy by n-Hexane molecules in structurally different zeolites was found to demonstrate its suitability to use n-hexane as a promising probe for differentiating the structural peculiarities especially dimensionality of the pore system. Thus, it can be concluded that the limiting amount of sorbate uptake is not only dependent on the characteristics such as molecular volume and configuration, polarization and the degree of unsaturation of sorbate molecules, but also on the structural and compositional components in the zeolitic adsorbents.

4. Conclusions

Zeolites NaX and KL were prepared by hydrothermal crystallization and were further modified by conventional ion-exchange technique. All the samples exhibited excellent purity and the crystallinity. The number of unit cells/g of these samples have shown the dependence on both the number and concentration of framework and nonframework cations. The acid strength of individual acid site in LTL zeolites was found to be higher than that of X type zeolites. The structural parameters such as number of T atoms, T—O bond length and bond angles and compositional components were found to control the acidity and basicity of the large pore zeolitic structures. The low temperature nitrogen adsorption behaviour revealed that due to higher number of T atoms, cubic symmetry of unit cell, greater extent of surface-nitrogen interactions are responsible for the higher rate and uptake of nitrogen in zeolite X as compared to zeolite LTL. The inverse chemical affinity trend with respect to nitrogen amount sorbed indicated the dependence of free energy change on the affinity factor. The lower hydrophilic character in LTL zeolites as compared to that of X type zeolites may be associated with the lower micropore volume and polarizing ability of the zeolite cages. The overall trend in the hydrophilic character was observed as: NaX $>$ NaKX $\gg$ NaKL $>$ KL. In spite of having the difference in the hydrophilic character, NaKX and NaKL samples have exhibited almost same $83 \pm 2\%$ occupancy of micropore volume by water molecules with respect to the total Dubinin micropore volume calculated using nitrogen adsorption data. The benzene uptake behaviour in X and LTL type zeolites suggested that the formation of clusters may not be occuring in LTL zeolits due to unidimensional and nonintersecting channels. The nature and concentration of the nonframework cations also have shown the influence on the energetics and dynamics of benzene sorption in these aluminous large pore zeolites. The striking difference in the extent of micropore occupancy by n-hexane molecules in structurally different zeolites demonstrated its suitability to use n-hexane as a promising probe for differentiating the dimensionality of the pore system in aluminous large pore zeolites.

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