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POST SYNTHESIS MODIFICATION OF RICE HUSK ASH RHA-SBA-16 BY ALUMINUM AND TITANIUM METAL IONS

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ABSTRACT :

Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. The diameter of the spherical particles can be controlled in the range of 0.5–8 μm by varying Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. It is suggested that this morphology transition is due to a change in hydrolysis and condensation rate of the silica source and as a result the assembly of F127 micelles will differ. The SBA-16 samples were characterized using powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Nitrogen adsorption techniques.

KEYWORDS: *SBA-16; Spherical particles; Synthesis temperature; Morphology; Pluronic F127.*

INTRODUCTION:

Spherical particles of mesoporous silica SBA-16 with cubic Im3m structure were synthesized at low pH using Pluronic F127 as template and RHA as silica source. The diameter of the spherical particles can be controlled in the range of 0.5–8 μm by varying[1] .The synthesis of mesoporous materials by a liquid-crystal template mechanism was reported The properties of these materials make them attractive for adsorption, catalysis, separation, chemical sensing, optical coating, drug delivery and electronic applications. For practical purposes, the overall morphology of a mesoporous material is a necessary requirement in combination with their internal structure. SBA-16 is a mesoporous material with 3D cubic pore arrangement corresponding to Im3m space group In this body-centred-cubic structure each mesoporous is connected with its eight nearest neighbours to form a multidirectional system of mesoporous network[2-4]Due to its large cage, high surface area and high thermal stability. This material appears to be one of the best candidates for catalytic support and packing materials for separation. Using F127 as a surfactant is the common way of synthesizing SBA-16.However, there are also reports on alternative surfactants such as F108,a blend of P123 and F127[5-8].

Micro porous zeolite are widely used as solid acid catalysts, but their applications are intrinsically limited by drawback of zeolite is that the small size of the channels (less than 0.8 nm) and cavities (<1.5 nm) imposes diffusion limitations on reactions that can cause high back pressure on flow systems. The dimensions of the zeolite micro pores (< 2 nm), mesoporous (2-50nm) and macro pores (> 50 nm) permit faster migration of guest molecules in the host frameworks. Since fast mass transfer of the reactants and products to and from the active sites is required for catalysts[9-11],the concept of infusing mesoporous into zeolite particles has attracted much attention. Recent progress involving this issued to ordered mesoporous materials such as MCM-41, SBA-16 and SBA-15[12-16]. These mesoporous materials have pore diameters of 3.0 nm– 8.0nm and exhibit catalytic properties for the catalytic conversion of bulky reactants, but unfortunately, when compared with micro porous zeolite[17-18],the catalytic activity and hydrothermal stability are relatively low, which can be attributed to the amorphous nature of the mesoporous walls. To overcome this problem, some recent research efforts have been concentrated on introducing mesoporous or macro pores linked to the zeolite micro pores.

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These materials called Hierarchical zeolite materials with combinations of micro/meso/macro pores would further extend the application of zeolite as solid acid[19].

POST MODIFICATION OF RHA-SBA-16 BY Al^{+++} and Ti^{++}:

So as to impart the catalytic and adsorptive activity to the chemically inert mesoporous silicate framework, substitution of Si^{4+} ions by other heteroatom in the prepared materials has been endeavored. This part describes the synthesis procedures used for post modification of RHA-SBA-16 by introducing heteroatoms such as Aluminum and Titanium into their meso-structures to improve their catalytic activity of reactions of bulky molecules and the adsorption activity significantly[20-22].The post modification synthesis of RHA-SBA-16 can be possible by various methodologies; among them we have followed the ion exchange method.In this method, the presence of Aluminum in the silica alumina mesoporous framework gives rise to anion, which attracts cations in the framework as they are loosely bounded. The replacement of cation held in the framework structure is possible by the ion present in the external solution. Hence ion exchange is possible[23]. Initially RHA-SBA-16 was converted in to their protonic forms. The 100% crystalline RHA-SBA-16 sample in its protonic form was selected and was further modified by using batch ion exchange method with metal ions like Al^{+++} and Ti^{++} with different metal ion concentrations. Introduction of metal ions such as Al, and Ti, creates new Lewis acid sites and Bronsted basic sites respectively within the RHA-SBA-16 host.

EXPERIMENTAL:

Post Synthesis Modification of RHA-SBA-16 with H^+:

Exchange of RHA-SBA-16 in to its protonic form was done by batch ion exchange method using subsequent acidic salt solutions. Ammonium nitrate 2.5wt % (2g) was taken in a 150 ml single neck round bottomed flask and 25 ml methanol was added into it as a solvent.

10g of the dried RHA-SBA-16 powder was also added and the blend was stirred under reflux condition for 3h at 80^{0}C. Then this mixture was allowed to cool to room temperature by natural convection followed by filtration. Further the filtrate was washed repeatedly with deionized water.The residue is NH_4-RHA-SBA-16. It is dried for overnight by heating at 100^{0}C in an oven. Later on, NH_4-RHA-SBA-16 is heated at 500^{0}C in automated muffle furnace for 3h, to exile ammonia and is converted in H^+ form i.e.H-RHA-SBA-16.

Post Synthesis Modification of H-RHA-SBA-16 by Al^{+++} metal ions:

To tune and enhance the acidic behavior of RHA-SBA-16, we have exchanged its protonic form into modified Al-RHA-SBA-16 using corresponding metal salt solutions of different molarities by ion exchange method as described earlier. The calculated quantity of concentrated salt solution of Al^{+++} [Al2(SO4)3.18 H2O] i.e.10.28g for 1M, 8.23g for 0.8M and 5.15g for 0.5M in 30g of methanol were taken in three different single neck round bottom flask (RBF) of 150 ml. Then 5g of the dried H-RHA-SBA-16 powder was added to it and was stirred under reflux condition for 6h at 100^{0}C. Later the mixture was brought to room temperature naturally and then the solvent was evaporated. The residue was dried in the oven at 100^{0}C, and calcined at 450^{0}C to500^{0}C for 4h.To ensure the ion exchange of the Al^{+++} in RHA-SBA-16 we have examined the elemental composition of the calcined samples by EDAX and came to know that their Si/Al ratio varies from 4-9. These modified forms were named as Al-RHA-SBA-16 (Si/Al = 4, 7 and 9).

Post Synthesis Modification of H-RHA-SBA-16 by Ti^{++} metal ions:

To tune and enhance the basic behavior of RHA-SBA-16, we have exchanged its protonic form into modified Ti-RHA-SBA-16 using corresponding metal salt solutions of different molarities by ion exchange method as described earlier. The calculated quantity of concentrated salt solution of TiO_2i.e.0.8g for 2wt%, 1.3g for 4wt%and 1.9g for 6wt% in 30g of methanol were taken in three different single neck round bottom flask (RBF) of 150 ml. Then 5g of the dried H-RHA-SBA-16 powder was added to it and was stirred under reflux condition for 6h at 90^{0}C. Later the mixture was brought to room temperature naturally and later the solvent was evaporated. The residue was dried in the oven at 100^{0}C, and calcined at 450^{0}C to500^{0}C for 4h.To ensure the ion exchange of the Ti^{++}in RHA-SBA-16 we have examined the elemental composition of the

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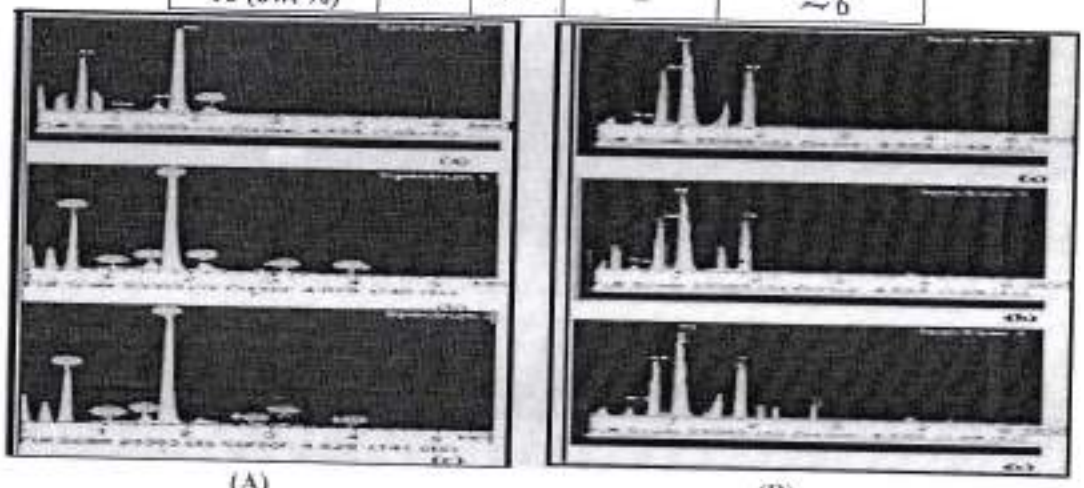
calcined samples by EDAX. These modified forms were named as Ti-RHA-SBA-16 (2wt%, 4wt% and 6wt%).

RESULTS AND DISCUSSION:

Energy Dispersive Analysis of X-ray (EDAX):

Table 1 Elemental Composition of the Samples Analyzed by EDAX

Sample name	Si	Al	Si/Al ratio	Ti Metal ion wt%
Al-RHA-SBA-16 (Si/Al=4)	56.81	14.68	Si/Al=3.87 ≈ 4	–
Al-RHA-SBA-16 (Si/Al=7)	64.62	9.42	Si/Al=6.86 ≈ 7	–
Al-RHA-SBA-16 (Si/Al=9)	69.30	7.83	Si/Al=8.85 ≈ 9	–
Ti-RHA-SBA-16 (2wt %)	68.47	1.74	–	Ti =1.91 ≈ 2
Ti-RHA-SBA-16 (4wt %)	63.71	1.78	–	Ti =3.83 ≈ 4
Ti-RHA-SBA-16 (6wt %)	64.11	1.81	–	Ti =5.76 ≈ 6



(A) (B)

Fig.1. (A) EDAX IMAGES OF (a) Al-RHA-SBA-16(Si/Al=5), (b) Al-RHA-SBA-16(Si/Al=9) and (c) Al-RHA-SBA-16(Si/Al=11).

(B) EDAX IMAGES OF (a)Ti-RHA-SBA-16 (2wt %), (b) Ti-RHA-SBA-16 (4wt %) and (c) Ti-RHA-SBA-16 (6wt %).

The observed EDAX spectra for all the modified samples analyzed are shown in Fig. 1.(A, B). In EDAX, X-ray photons emitted from the sample are dispersed by a crystal and plotted as a function of energy. The X-rays being analyzed came from the area being imaged, so elemental composition is determined as a function of location on the sample. Outstandingly it is observed that the atomic percentage of Si, Al, Ti and O in modified forms of the RHA-SBA-16 are almost uniform. Even the Si/Al ratio is observed to be within the range in case of modified RHA-SBA-16 which shows that, the elementary compositions in the modified samples are uniform. The observations made by using SEM-EDAX correlate well with the XRD data for all the analyzed samples. The amount of Ti- metal ions weight percentage in all the samples is found to be around 1.93–5.71wt%. The metal compositions after the modification with the RHA-SBA-16 samples are given in Table 1.

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APPLICATION IN CO_2 ADSORPTION OF SYNTHESISED ZEOLITE NAX AND ITS MODIFIED FORM

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Keywords: Synthesised Zeolite NaX, Cs^+ exchanged forms, Langmuir equation, Isosteric heats of sorption.

Abstract:

The carbon dioxide was chosen as sorbet due to the large linear quadruple moment as a probe in investigates the sway of the size and valance of the exchange cation upon the quadruple energy Acidic probe. The Carbon dioxide sorption was perform on a surface area analyzer NOVA- 1200 unit at 273 K, 303 K, 333 K and 363 K with pure CO_2 The sorption size were recorded with built-in microprocessor-based adsorption software series for 0 to 600 Torre pressure, at selected sample temperature. However, at constant temperature in the low-pressure region exhibit a very rapid uptake. While considering the effect of non-framework cations on carbon dioxide sorption.

It is also observed that sorption uptake decreases with increased in size of nonframework cation (Cs^+) at a constant temperature. In addition, the decrease in cation-specific CO_2 uptake, in Cs-exchanged NaX zeolite is due to reduce in charge density. The cations with lower charge density will have lower extent of electrostatic interface with the sorbet molecules. Even after their post alteration, no marginal changes are found in their structural morphology. The families of isotherms of carbon dioxide on parent NaX and Cs^+ cations exchanged samples is illustrated. The application of different isotherm equations are relevant.

INTRODUCTION:

The carbon dioxide was selected as sorbet due to its following factors:

1) The large linear quadruple moment

2) As a probe in investigating the influence of the size and valance of the exchange cation upon the quadruple energy

3) Acidic probe.

The effect of different Lewis acid-base character (cationic and framework oxygen charge densities) of these sorbents on the equilibrium sorption capacities[1], application of various isotherm equations, physical state of sorbet, free energies and isosteric heats of sorption will be discussed. The results on ammonia and carbon dioxide sorption in parent NaX and its modified form viz. The XRD pattern was also recorded for each sample after the sorption measurements to confirm the structural stability.

EXPERIMENTAL:

Carbon dioxide sorption was performed on a surface area analyzer NOVA-1200 (Quanta chrome Corporation U.S.A) unit at 273 K, 303 K, 333 K and 363 K with pure CO_2 (99.99%). The carbon dioxide used for sorption measurements was purified through a series of traps containing activated silica gel, activated molecular sieve (3A), copper fillings reduced in hydrogen atmosphere at 873 K and finally through a trap at 195 K. The sample was activated at 373 K for 10 h in a calibrated cell (6-mm) under the high vacuum. The activated sample was then loaded to analyzer station under the vacuum.

The sorption measurements were recorded with built-in microprocessor-based adsorption[2] software program for 0 to 600 Torre pressure, at selected sample temperature. The sample temperature was maintained either by

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using automated Dewar elevator or heating mantles. A fresh sample was subjected to the above procedure each time prior to the measurements at different temperature. The XRD pattern was also recorded for each sample after the sorption measurements to confirm the structural stability.

CARBON DIOXIDE SORPTION ISOTHERM IN NAX AND ITS CS^+ EXCHANGED FORMS:

The Fig.1.1& 1.2 illustrate the families of isotherms of carbon dioxide on parent NaX and Cs^+ cations exchanged samples. These isotherms were measured at an interval of 30 ^{O} in the range of 273 to 363 K up to 600 Torre. Since the number of unit cell per gram of selected zeolite samples vary with the cation exchange, the amount sorbed is expressed as molecules per unit cell for the true comparison on the basis of size and the nature of exchanged cations[2-4]. The shape of the isotherms approximates to the type I (Langmuir type) according to the Kiselev's classification. The uptake of CO_2 was found to depend on both, the size of the no framework cation and the temperature at which the isotherms were measured. It can clearly be seen from the Fig.1.1&1.2 that carbon dioxide sorption capacity in NaX and its exchanged forms decreases with the increase in temperature from 273 K to 363 K.

However, at constant temperature in the low-pressure region (< 100 Torre), samples exhibited a very rapid uptake. While considering the effect of non-framework cations on carbon dioxide sorption, it is also observed from the figure, that sorption uptake decreases with increased in size of no framework cation (Cs^+) at a constant temperature. For example the equilibrium uptake of carbon dioxide[5-7] above at 273 K, for pressure above100 Torre follows the trend NaX > NaCsX. Even though, the occupancy of the different exchange positions in the parent and modified forms is not known, it is believed that cations are distributed over the highest charged sites in such a way that the free energy of the structure is minimized. Since sites I, I' and II' are inaccessible to carbon dioxide molecules on account of the critical diameter of CO_2 molecule is 3.3 Å.

The cations with lower charge density will have lower extent of electrostatic interaction with the sorbet molecules. Since CO_2 has more linear quadrupole moment it interacts mainly with the extra framework cations and framework oxygen. The dispersion forces acting on the sorbet molecule will also be altered to different extents depending upon the charge density of the extra framework cations and framework oxygen as well. Similarly, when the zeolite in Na was exchanged with more electropositive cation, such as cesium, the polarizing effect of the cation plays an important role in the sorption of CO_2.

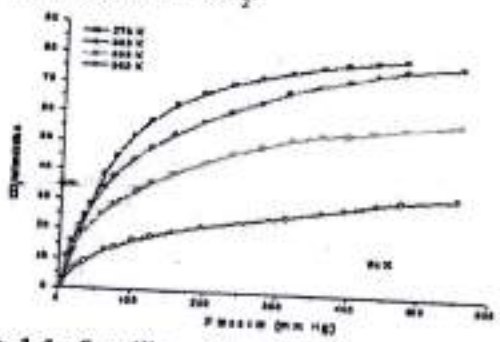

Fig. 1.1 : Families of isotherms of carbon dioxide on parent NaX sample

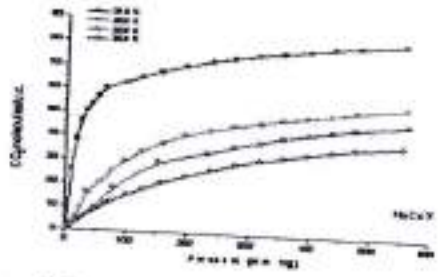

Figure 1.2 : Families of isotherms of carbon dioxide on Cs^+ cations exchanged sample

In case of Cs-exchanged sample the mean charge on framework oxygen is more than the rest of the NaX. This may be result in the lower uptake of CO_2 in NaCsX. From the Fig. 1.2 it is found that at constant temperature 273 K

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and pressure 600 Torre, in the NaCsX sample approximately 92 molecules of CO_2 are sorbed per unit cell, while 75 CO_2 molecules are sorbed per unit cell of parent NaX sample. But in low-pressure region this difference between amount sorbed is not significant.

APPLICATION OF ISOTHERM EQUATIONS:

Langmuir Sorption Model:

A Langmuir sorption isotherm equation has been derived on the assumption[8] of localized monolayer sorption on the sorption centers of equal energy and 1:1 correspondence between sorption centers and sorbate molecules. The Langmuir equation can be expressed as

$n = n_m kP/1+kP$

where n is the experimental amount of sorbate, n_m that sorbed at saturation, k is coefficient depending on temperature. When the Langmuir equation was applied to the CO_2 sorption[9-11] data in NaX and its identical degree of K, Rb and Cs -exchanged forms, the linear plots with varying intercept were obtained. Typical Langmuir plots are shown in the Fig.3 &4 samples over entire range of pressure and the temperature (273 to 363 K

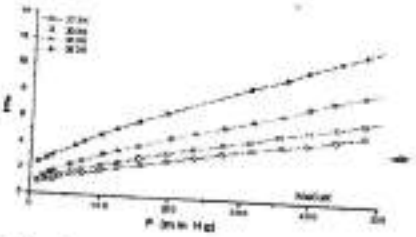

Fig. 1.3 : Langmuir plots for NaCsX sample

A silent feature of these Langmuir plots is the marginal increase in the intercept on Y axis in parent NaX sample with the increase in temperature as compared with its NaCsX and other exchanged forms. It can also be seen from the Fig.1.3 that the higher value of intercept was obtained in NaCsX than NaX sample with the increase in temperature. The intercept on Y-axis is usually related to the strength of the sorption centre. It may be noted that as the intercept decreases the contribution due to interaction involved in the sorption process increases[12]. Hence, it was reflected that NaX has more interaction than Na CsX.

Freundlich Isotherm:

Analysis of the CO_2 sorption data in different cationic form of NaX zeolites in terms of Freundlich isotherm model yielded nearly linear plots. Typical Freundlich plots for CO_2 sorption in the parent NaX and the exchange sample over the entire pressure (up to 600 Torr) and temperature (273 to 363 K in steps of 30 K) range are shown in Fig. 1.4 & 1.5

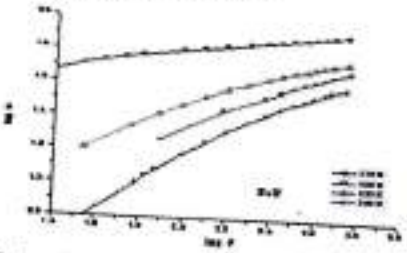

Fig. 1.4 : Freundlich Isotherm of NaX parent sample

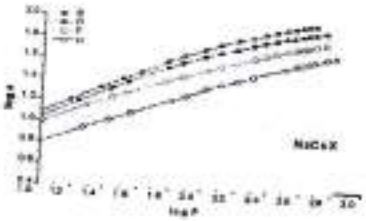

Fig. 1.5 : Freundlich Isotherm of NaCsX exchange sample

Application of Dubinin Equation:

The original Polanyi's potential theory, modified by Dubinin and co-workers for the sorption of gases and vapours in zeolites, has become increasingly empirical. In view of this an attempt has been made here to obtain characteristic curves by plotting $[\log P_o/P]^2$ against log P for CO_2 sorption data. The obtained Dubinin-Polanyi characteristic curves for CO_2 uptake[13-15] in NaX and its modified sample cation exchange are shown in the Fig. 1.6 and 1.7. From the Figure it can be seen that the characteristic curves are almost linear, indicating the carbon dioxide sorption data satisfactorily represent

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Dubinin-Radushkevich equation.

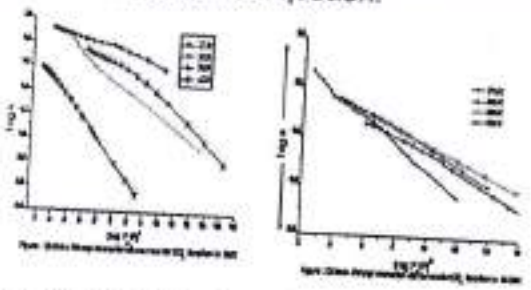

Fig. 1.6 : a) Polarity characteristic curves forCO_2 sorption in NaX,
b) Polarity characteristic curves forCO_2 sorption in NaCsX Chemical affinity and selectivity of the sorbed phase:

The chemical affinity of carbon dioxide for sorbents having the same topology but different chemical composition, especially differing in charge density and size of nonframework cations, is one of most significant parameters governing the extent of decrease in free energy which accompanies a given sorption process[16-18]. The plot -Dm against amount sorbed also serve as useful criteria for the comparison of sorption affinities of probe molecules in the lattices of Cs-exchanged NaX zeolite.

Typical chemical affinity plots for CO_2 sorption at 303 and 423 K shown in Fig.1.7. This figure, clearly demonstrate that in accordance with thermodynamic expectation, all the sorbents exhibited continuous increase in the CO_2 uptake with the decrease in chemical potential. The sorption affinity (-Dm) decreases with the increase in temperature for both the samples in the low coverage region. It can also be seen from the figure that chemical potential (-Dm) more gradually decreases with increase in the coverage for NaCsX than parent NaX..It indicates that the exchanged form NaCsX was offer more heterogeneous surface for CO_2 sorption, which is in agreement with reported data.

The replacement of monovalent extra framework cation by another monovalent but with larger size[17-20], may give rise rather more complicated sorption phenomenon on account of varying chemical affinity due to simultaneous but unequal variations in the contributions due to energy components such as dispersion and repulsion energies between carbon dioxide and the zeolite, polarization energy, field- dipole energy, field gradient - quadrupole energy and self potential.

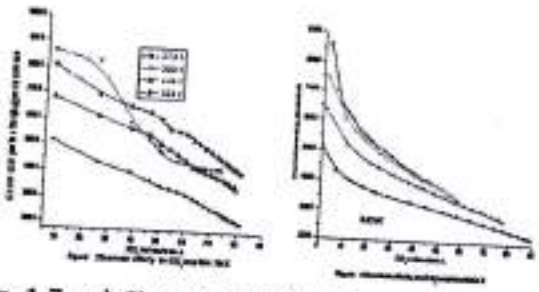

Fig. 1.7 : a) Chemical affinity for CO_2 sorption :NaX
b) Chemical affinity for CO_2 sorption:NaCsX

Isosteric heats of sorption (q_{st}):

The isosteric heat (q_{st}) of carbon dioxide sorption is derived from the shift of sorption equilibrium with temperature at constant sorbet loading by using the Clausius Clapeyron equation.

$$q_{st} = -(_1 = R[(T_2T_1) / (T_2-T_1)] \times \ln (P_2/P_1)$$

The plots of q_{st} as a function of amount sorbed in NaX and its cation exchanged form The small variation in the q_{st} values as a function of CO_2 uptake in NaX.This shows that isosteric heat of carbon dioxide in parent NaX was independent of coverage. It is observed that the marginal increase in the isosteric heat with the increase in loading, indicating the dominance of sorbate- sorbate interactions[21-23] and relatively homogeneous environment for gas-solid interaction.

The NaX show a flat heat profile with the increasing amount sorbed than that NaCsX indicating a balance between the strength of energetic heterogeneity of sorbate-sorbent interaction and sorbate-sorbate interaction. The qst value of NaX for the coverage of 20 molecules per unit cell is nearly equal to 26 kJ, mol^{-1}.This may be due to the difference in frame-

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