Enhancing the Adsorption Capacity of CO_2 over Modified Microporous Nano-crystalline Zeolite Structure

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Abstract: **CO_2 is chosen as a probe molecule for adsorption over microporous zeolites like zeolite-13X, zeolite-NaX & BaX, FAU-X & Y, which as it creates a greenhouse gas effect and global warming. Synthetic Na form of zeolite-MFI with various Si/Al ratios (5, 30, 100, 200) are modified with HCl to enhance the porosity and screened there adsorption capacities of CO_2. Modification with HCl shows promising adsorption activity without damaging the crystal structure. All the modified zeolite-MFI Si/Al ratios are characterized with XRD and BET for crystallinity, pore volume, BET surface area is related with physorbtion of CO_2. After the HCl treatment of zeolites pore volume, BET surface area are improved promisingly indeed influenced the capacity of adsorption due to their interaction with the electric field.**

Index Terms: **Adsorption capacity, CO_2 adsorption, Modification, Zeolites.**

I. INTRODUCTION

Carbon dioxide (CO_2), methane, water, nitrous oxide and chlorofluorocarbons are the crucial greenhouse gases. The CO_2 produced and released from industries by the scorching of fossil fuel, which increased from 1 billion tons to 8 billion tons per year (Yang et al. 2008). Molecular sieves like Zeolites have high porosity and can be good CO_2 adsorbents (Triebe and Tezel 1995; Krishna et al. 2006). The adsorption of CO_2 under dry conditions over gamma alumina has been comprehensively studied (Maurin et al. 2005) before by Busca and Lorenzelli suggest the formation of carbonates, bicarbonates adsorbed over metal oxide catalyst surfaces during the hydroxylated reaction, and formats as well as bent CO_2 species (Garcia-Perez et al. 2006; Frenkel et al. 2009).

The force field precisely replicates the CO_2 adsorption is depend on zeolite structures (MFI, FAU and MOR) and also depends with varying aluminum percentage with sodium. The insertion of an AlO_4 tetrahedron in the structure channels and pores leads negative charge and SiO_4 tetrahedron is balanced through cation exchange (Amber et al. 2013; Garcia-Sanchez et al. 2009; Jaramillo et al. 2004). These cations exchange in structure leads an actual imperative role to estimate the gas-separation and adsorption properties of zeolites. These applications are purely be subject to the density of charge, size and dissemination of cations in the porous channel structure. The Si/Al ratio ranging from 3 to 5 are found to be well substituted of cations (natural minerals) (Zukal et al. 2011). Recent studies of CO_2 adsorption on Zinc oxide catalyst surface have results an uncommon tridentate carbonate species may be due to the interaction of two O atoms of the CO_2 molecule is bounded with two Zinc surface atoms (Duren and Snurr 2004). MgO catalyst is similarly reflected as a significant sorbent for CO_2 chemisorption. The catalyst MgO with stoichiometric ratio with CO_2 may be carried out rendering the reaction as $MgO + CO_2 \rightarrow MgCO_3$. Moreover alkaline earth based metal oxide materials as catalysts for adsorbents for CO_2 is well established the attention (Kwak et al. 2019).

This work is aimed to identify and efficiently characterize promising materials to be applied to carbon dioxide separation processes using adsorption method. This research is focused on CO_2 sorption capacities on microporous zeolite like NaZSM-5. The influence of porosity of zeolite and Si/Al ratio of NaZSM-5 for CO_2 sorption was investigated.

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II. EXPERIMENTAL

A. Chemicals Used

Sodium form of commercial zeolite-MFI (ZSM-5 with Si/Al=5, 12.5, 100, 200) was supplied by United Catalyst India Ltd., India. Hydrochloric acid from Central Drug House, AR grade and demineralised water.

B. Catalysts preparation

All the commercial zeolites are treated with concentrated HCl for 3h at room temperature. Treated catalysts are washed precisely with demineralised water filtered with suction. The filtrate cake is dried in oven at 120°C for 6h. Powered forms of dried zeolites are calcined at 500°C for 2h to remove the impurities.

C. Calorimetric Studies for Adsorption Studies

Microcalorimetry is used to study for gas-solid interactions (Garcia-Perez et al. 2007). To screen the adsorption features of the gases quantitatively with the Micromeritics (ASAP 2010) is used to accomplish the adsorption tests for CO_2 gases at 6°C and 26°C. To achieve stability in experiment and allowing the temperature in constant mode for optimising the adsorption rate the water bath is used to circulate and insulated with polymeric material. All the zeolite catalysts were outgassed for 24h at 350°C prior to adsorption experiments, under 5μmHg vacuum.

Before each experiment the zeolites are out gassed under heating of 26°C to 270°C with 1°C/min ramping rate. The sample was retained for 5h, after reaching the 270°C, then sample is attend to room temperature by gradually cooled down with the rate of 1°C/min.

The process diagram of the experiment was revealed in Fig. 1. As shown in setup of experiment the 10g of zeolite is filled in middle of tubular reactor with the support of quartz wool on both sides to avoid catalyst flush out by gas flow and pressure. The tubular reactor input flow is mixed with CO_2, N_2 and passed through treated zeolite. The zeolite adsorption rate is measure interms of entire quantity of gas adsorbed.

Fig. 1 The flow diagram of CO_2 adsorption setup

III. CHARACTERIZATION OF CATALYSTS

The modified catalytic zeolites are characterized by XRD and BET techniques.

A. Powdered X-ray diffraction

The phase purity of zeolite-MFI samples were analyzed over Ni filtered Rigaku powdered X-ray diffractometer with the 2θ scanning array of stuck between 5 and 60°. In Fig. 2, the XRD patterns of delaminated zeolites Na-ZSM-5, Na-ZSM-30, Na-ZSM-100 and Na-ZSM-200 are represented, respectively.

B. Surface area

For any studies of nanoporous materials the quantification of material pore volume and surface area is significant. To evaluate the adsorption studies the zeolites were subjected to Sorptomatic 1990 CE Instrument for the BET- pore volume and surface area technique by consuming adsorbent as a N_2 at the temperature of liquid nitrogen. The samples were outgassed for 15h at 473K in prior to adsorption studies and carrier gas as helium with detector TCD was used. The software (Sorptomatic 1990) was used to calculate the surface area from nitrogen adsorption isotherm.

IV. RESULT AND DISCUSSION

A. Effect of Porosity

The physical properties of commercial and modified microporous zeolite samples used are summarized in Table 1. Modified zeolites show considerable decrease in pore volume and surface area with increasing Si/Al ratio (Si/Al=5, Si/Al=30, Si/Al=100, Si/Al=200). Particularly the ones with high amounts of porosity in zeolite channels and surface area, may play a substantial role in this context (McGlashan 1971). The Fig. 2 shows crystallinity is stable and does not effect by modification with HCl. This is because they are stable under a broad range of conditions, commercially available and relatively inexpensive, they show high adsorption capacity and highly reproducible adsorption behaviour, and they are relatively easy to regenerate. Their high adsorption capacity could make them excellent candidates for storage applications involving high pressure and despite their relatively low affinity for CO_2 (Dzyaloshinskii et al. 1961).

Table 1. Effect of HCl treatment on physical properties of ZSM zeolite.

Zeolite-Si/Al ratio	Treatment with HCl	Surface area (m^2/g)		Average volume (cm^3/g)	
		Before	After	Before	After
Na-ZSM-5	2h	304	311	0.262	0.273
Na-ZSM-30	2h	297	306	0.236	0.251
Na-ZSM-100	2h	295	302	0.194	0.205
Na-ZSM-200	2h	296	299	0.178	0.183

The report of CO_2 adsorption capacity at atmospheric pressure is found about 4.0mmol/g over adsorbent NaY and about 5mmol/g over zeolite-13X to account of CO_2 intake at 273K temperature (Shao et al. 2009; Cheung et al. 2012). The CO_2 adsorption capacity over zeolite-β (adsorbent) will be drops with rising temperature may due to exothermic nature of adsorbents are mainly due to intermolecular interaction. Physisorption rate among the sorbent and the sorbate is principally found on intermolecular interactions. These synergetic effects of interactions may read between the sorbent and the sorbate may due to repulsive/ attractive interactions that

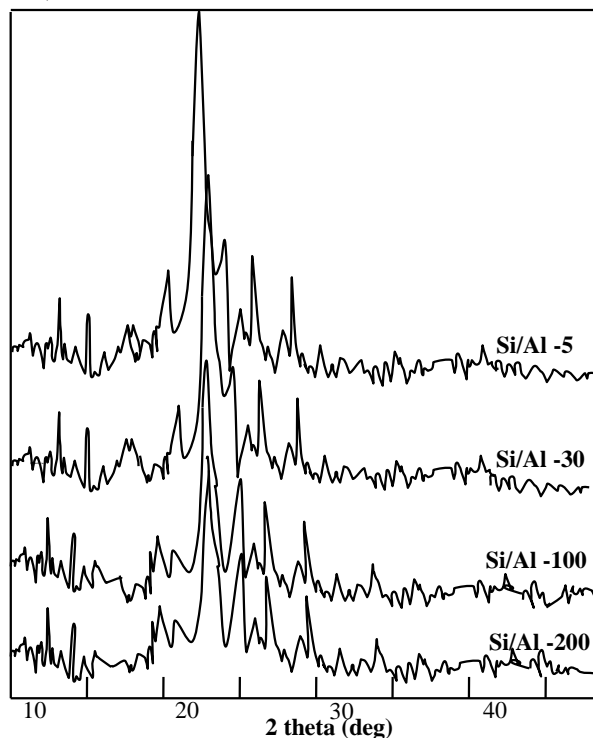comprise the definite mixture of dipole, quadrupole (Huesca et al. 1999).

Fig. 2 XRD pattern of modified catalysts

B. *Effect of Si/Al ratio of zeolites*

Table 2 shows zeolite-MFI with Si/Al ratios adsorption capacities at 6°C. Experimental data reveals the Si/Al ratio increases the adsorption decreases at 6°C. It seems that treatment with HCl for 2h significantly changes the framework structure. The framework structure endures physisorption and chemisorption of CO_2 adsorption by interactions of carbon dioxide molecules with the cations of extra framework and the oxygen of framework zeolite due to acid treatment (Jayaraman and Yang, 2002).

The low Si/Al ratio 5 shows unresolved impact of adsorption by cation in extra framework and cage nature result the topological and composition differences are shown in the Table 2. The inconsistency is may be due to the development of bridged adsorption complexes in the form of bent and/or linear conformations by various alkali-metal cations (Cheung et al. 2012; Li and Handan Tezel 2007; Huesca et al. 1999). The alkali-metal cations basicity credits the adsorption of carbon intermediates (Jayaraman and Yang, 2002) over NaX zeolite with respective to Al content. A report on Si/Al ratio varying the 1-1.5 and >1.5 of zeolite type X, LTA and FAU, respectively analysed the composition alterations and topological changes alters the physical and chemical properties, extra framework cations of zeolites that to determine adsorption capacities (Szostak 1997).

Table 2 shows considerable improvement in adsorption of CO_2 gas compared to commercial and dealuminated zeolites. Si/Al=5 show promising adsorption capacity increases from

Table 2. Adsorption capacities of zeolite-ZSM at 6°C and 26°C

Zeolite Si/Al ratio	Temper-ature	Pressure (kPa)	Absorption capacity	
			Before	After
Na-ZSM-5	6°C	81.05	2.81mmol/g	4.49mmol/g
	26°C	90.67	2.01mmol/g	3.79mmol/g
Na-ZSM-30	6°C	88.04	2.05mmol/g	3.01mmol/g
	26°C	82.06	1.09mmol/g	2.93mmol/g
Na-ZSM-100	6°C	82.01	0.76mmol/g	2.86mmol/g
	26°C	85.34	0.37mmol/g	2.53mmol/g
Na-ZSM-200	6°C	89.16	0.26mmol/g	1.96mmol/g
	26°C	86.90	0.07mmol/g	1.64mmol/g

2.81mmol/g to 4.49mmol/g by dealumination. Si/Al=100 and 200 shows decrease in adsorption capacities of 2.86mmol/g and 1.96mmol/g confirms the zeolite is gradual dealumination decreases the electrostatic field in the zeolite voids (Jayaraman and Yang, 2002). The report (Szostak 1997) suggests the zeolite with Si/Al=1 leads the robust interactions inside cages due to increasing the framework polarity and may also effects the distresses the Si-O-Al bonds. The zeolite dealumination increase in Si/Al ratio from 5 to 200 leads to, by the electrostatic field on the surface is decreased and become further hydrophobic. The hydrophobic is created in surface and inside the zeolite channels due to electrostatic field. The dominant strong interaction between higher Al content zeolite surface and CO_2 molecule makes to lower and weaker forces, which may leads lower adsorption capacity even lower pressures. The low Al content in zeolite surface shows higher hydrophobicity favours the adsorption equilibrium develops more homogeneous and CO_2 molecule-surface interactions increasing the adsorption capacity (Triebe and Tezel, 1995).

CONCLUSION

Porous zeolites are well practiced as an absorbent. CO_2 was chosen as a probe molecule for adsorption as it creates global warming and greenhouse gases. Zeolite-MFI with different Si/Al ratios and pore volume are used to screen on adsorption capacities. Commercial MFI samples are modified with HCl to enhance the adsorption capacities. Experimental data confirms the high Si/Al ratio with pore volume leads high adsorption capacity due to the tailoring the framework leads and strong Si-O-Al bonds interactions.

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