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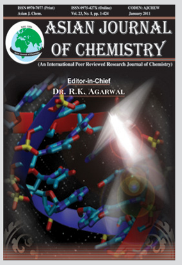

CO_2 Adsorption over Zinc Oxide Impregnated NaZSM-5 Synthesized Using Rice Husk Ash

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Zinc oxide (5, 10 and 15 wt %) impregnated NaZSM-5 zeolite synthesized using rice husk ash as silica source was tested for CO_2 adsorption. The materials were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive X-ray analysis, CO_2-temperature programmed desorption and Brunauer-Emmett-Teller techniques. The heat of the reaction (ΔH_r) derived from differential scanning calorimetry analysis for NaZSM-5 (10 %) to be 495 Btu/Lb. The maximum CO_2 adsorption capacity of NaZSM-5 (10 %) is 140 mg/g of sorbent. Extraction of silica from the agricultural waste, rice husk and its use in the zeolite synthesis is an added advantage in this study. Hence, from the study it is concluded that zinc oxide impregnated NaZSM-5 could be treated as novel material for CO_2 adsorption as they were found to be regenerable, selective and recyclable.

Key Words: NaZSM-5, Zinc oxide, Rice husk ash, CO_2 adsorption.

INTRODUCTION

Recently research has been focused to develop various solid sorbent for CO_2 capture process[1] as the emission of this gas results in increase in global warming. The increased usage of fossil fuel has contributed to the increase in CO_2 levels[2,3]. In this regard, CO_2 adsorption on oxides and mixed oxides[4-6], high surface area porous materials including zeolites[7-12], carbon[13], metal-organic frameworks (MOFs)[14], amine dendrimers and amine functionalized mesoporous silicas[15,16] are currently being studied. For large-scale CO_2 capture, some basic metal oxides were also identified to be efficient for high temperature CO_2 adsorption, however, they require severe energy penalties for desorption[1,17,18]. Alkali and alkaline earth metal oxides supported porous materials and carbons have also been examined for the same purpose as they readily form carbonates with CO_2[19-22]. In addition to alkali and alkaline metal oxides, CO_2 adsorption over transition metal oxides like TiO_2[23], Cr_2O_3[24], ZnO[25,26], Cu on ZnO[27] and Cu on porous carbon[28] have also been studied.

Carbon dioxide, by virtue of its relatively high polarizability and quadrupole energy[29] gets readily adsorbed on zeolites at room temperature, hence zeolites are widely used as solid supports for metal oxide impregnation. Among the zeolite, the microporous ZSM-5 and cation exchanged ZSM-5 are studied for CO_2 adsorption[30-32]. Even though different silicon sources have been employed in the synthesis of ZSM-5, silica obtained by extraction from rice husk (an agricultural waste) ash (RHA) by suitable alkali solution has been found to be low cost and highly reactive for the synthesis[33,34]. Until now no reports are available in literature for CO_2 adsorption on zinc oxide impregnated NaZSM-5 synthesized from rice husk ash. Taking into consideration the importance of zinc oxide in the adsorption of CO_2 and rice husk ash, in the present study we synthesized ZSM-5 using rice husk ash silicate solution (RHASS) as the silica source and subsequently impregnated zinc oxide using wet method.

EXPERIMENTAL

Tetrapropyl ammonium bromide (TPABr, Aldrich 98 %), aluminum sulphate ($Al_2(SO_4)_3\cdot 18H_2O$, Duksan 54-57 % Al_2O_3), sodium hydroxide (NaOH, Merck 99 %) and zinc acetate dihydrate ($Zn(O_2CCH_3)_2\cdot 2H_2O$, Aldrich 99 %) were used in the synthesis. Rice husk was obtained from a local farm, milled and heated to 700 °C for 24 h to obtain RHA. RHASS was extracted by refluxing rice husk ash (93 % SiO_2) in 2 M NaOH in H_2O at 70 °C for 24 h, as per previous report[35].

Synthesis of NaZSM-5 and zinc oxide impregnated NaZSM-5: The Na form of ZSM-5 was synthesized by the reported procedure[34]. The zinc oxide impregnated ZSM-5's with varying zinc oxide loadings were prepared by wet impregnation of 5 g of NaZSM-5 with an ethanolic solution of $Zn(O_2CCH_3)_2 \cdot 2H_2O$. The mixture was stirred and vacuum dried to remove the ethanol. The obtained material is finally calcined in air at 550 °C for 12 h and designated NaZSM-5(X) where X = 5, 10 and 15 wt %.

Catalyst characterization: Powder X-ray diffraction pattern (XRD) were recorded on Rigaku Miniflex diffractometer using a Cu-K_α radiation ($\lambda = 0.154$ nm). The diffraction data were recorded in the 2θ range 5 to 40° with a steps size of 0.02° and a step time of 1 s. The nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2010 volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 100 °C under vacuum ($p < 10^{-5}$ mbar) in the degas port. The surface area was determined from the linear part of the Brunauer-Emmett-Teller (BET) equation. The pore volume was calculated using the BET plot from the amount of nitrogen gas adsorbed at the last adsorption point ($p/p_0 = 0.95$). The thermogravimetric analysis (TGA) was carried out in a N_2 atmosphere at a flow rate of 20 mL/min on a SCINCO N-1000 thermogravimetric analyzer, by heating *ca.* 10 mg of the sample from 25 to 700 °C in steps of 10 °C/min. The morphologies of the samples were studied using a JEOL JSM 5600 scanning electron microscope (SEM) with an energy dispersive X-ray analysis (EDS) detector.

CO_2-temperature-programmed desorption (CO_2-TPD) and differential scanning calorimetry (DSC): The CO_2-TPD study was performed on a BELCAT-M catalyst analyzer. The sample cell was loaded with *ca.* 200 mg of the synthesized material and then heated in flowing helium at 500 °C for 2 h. After it was cooled to 25 °C, CO_2 (diluted in helium gas) at a flow rate of 30 mL/min was introduced to the sample cell for CO_2 adsorption for 1 h. Afterwards, the temperature-programmed desorption experiment was carried out by purging with helium at a rate of 80 mL/min from 25 to 500 °C with a temperature ramp of 283.6, 288.8, 296.8 K min^{-1}.

A thermal cycle for zinc oxide impregnated NaZSM-5 (10 %) was recorded using a Scinco DSC N 650 differential scanning calorimeter. Approximately 10 mg of sample was heated at 5 °C/min from 25 to 150 °C in dry helium and the sample was maintained isothermally at 150 °C for 1 h for pre-activation. The sample was then cooled to 25 °C at 5 °C/min and held isothermally for 1 h and the purge gas was then switched from dry helium to CO_2 (15.21 %) in helium. A plot of the resultant heat flux *versus* temperature or time directly gives the heat of reaction (ΔH_r) for the sample. The above experiments were repeated thrice and the average value was taken as ΔH_r.

CO_2 adsorption: CO_2 adsorption-desorption measurements for NaZSM-5 and zinc oxide impregnated samples were performed using thermogravimetric studies. A sample weight of *ca.* 10 mg was loaded into an alumina sample pan in a TG unit and tested for CO_2 adsorption-desorption performances. The initial activation of the samples was carried out at 200 °C for 1 h under N_2 atmosphere. The adsorption-desorption runs were conducted using high purity CO_2 (99.99 %) gas and N_2 flow, respectively. The adsorption runs were conducted at 25, 50 and 75 °C under atmospheric condition and desorption at 200 °C. Both the gases, CO_2 and N_2, were passed through an automatic valve, assisted with a timer for continuous adsorption and desorption profile.

RESULTS AND DISCUSSION

X-Ray diffraction: In our previous report[35], the XRD patterns of the rice husk, heat-treated at 500, 600, 700 and 800 °C for 12 h were shown to contain the crystalline, cristobalite form of silica at 800 °C and retain the amorphous form at 700 °C. As solubilization of rice husk ash in the crystalline form is difficult, the rice husk was heat-treated only up to 650 °C for 24 h in order to retain its amorphous phase for the effective extraction of the silica in NaOH solution. Fig. 1 depicts the XRD patterns of NaZSM-5 and the zinc oxide impregnated NaZSM-5's. In addition to the characteristic patterns of ZSM-5, additional peaks are observed for the impregnated samples in the 2θ value 31.6, 34.2, 36.1, pertaining to the hexagonal ZnO with wurtzite structure (JCPDS 89-7102). This indicates the dispersion of the zinc species in the zeolite.

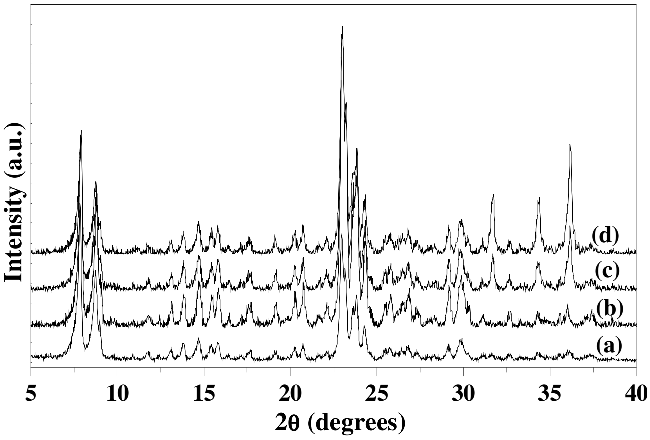

Fig. 1. XRD patterns of (a) NaZSM-5, (b) NaZSM-5(5%), (c) NaZSM-5(10%) and (d) NaZSM-5(15%)

Thermogravimetric analysis: Two stages of weight losses were observed in the thermogram of as-synthesized NaZSM-5 (figure not shown) attributing to physisorbed water (below 150 °C) and decomposition of the occluded template at around 400-450 °C. In the thermograms of the zinc oxide impregnated NaZSM-5 (figure not shown) the weight loss of dehydration was observed initially followed by the decomposition of zinc acetate to zinc oxide near 200 °C and completion of the decomposition process[36] before 300 °C. While the temperature reaches 500 °C almost the process completes and only the metal oxide remains in the zeolite crystals.

Brunauer-Emmett-Teller: The N_2 adsorption-desorption isotherms of the synthesized materials depicted in Fig. 2 exhibit isotherms of type I which is a characteristics of microporous materials. The surface area and the pore volume are tabulated in Table-1. The surface area and pore volume decrease with increasing zinc loading. Hence, zinc oxide might be impregnated within the pores of ZSM-5. This is also verified from SEM analysis.

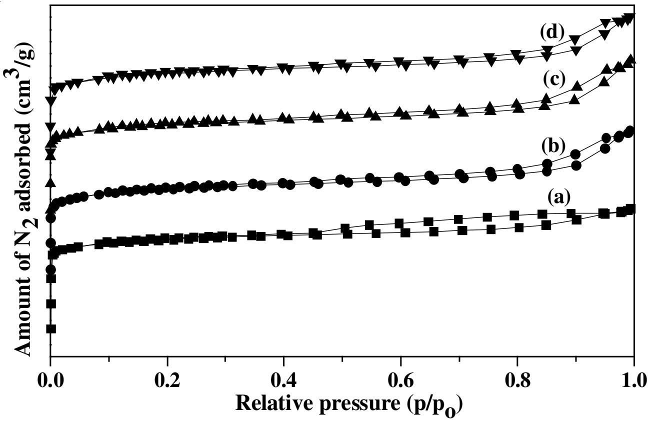

Fig. 2. Nitrogen adsorption-desorption isotherms of (a) NaZSM-5, (b) NaZSM-5 (5 %), (c) NaZSM-5 (10 %) and (d) NaZSM-5 (15 %)

TABLE-1
SURFACE AREA AND TOTAL PORE VOLUME OF NaZSM-5 AND ZINC OXIDE IMPREGNATED NaZSM-5

Catalysts	Surface area (m^2/g)	Pore volume (cm^3/g)
NaZSM-5	377.20	0.219
NaZSM-5 (5 %)	315.51	0.213
NaZSM-5 (10 %)	310.07	0.209
NaZSM-5 (15 %)	308.45	0.208

Scanning electron microscopy: Fig. 3 shows the scanning electron micrographs of NaZSM-5 and zinc impregnated ZSM-5s. Small cuboid particles assemble to form the zeolite crystals. The SEM did not show any evidence for separate crystals for zinc at lower loading while it's presence is evidenced at higher loadings. The EDS analysis (figure not shown) further confirmed the presence of zinc in the zeolite crystal.

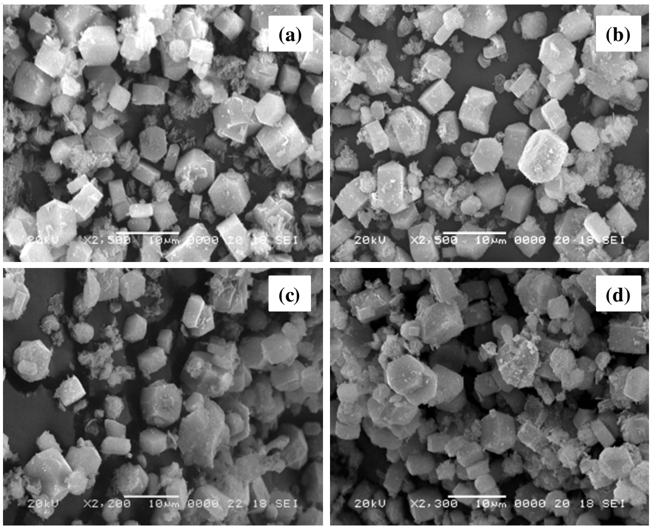

Fig. 3. SEM images of (a) NaZSM-5, (b) NaZSM-5 (5 %), (c) NaZSM-5 (10 %) and (d) NaZSM-5 (15 %)

CO_2-TGA: CO_2 adsorption/desorption profiles of NaZSM-5 and NaZSM-5(5, 10 and 15 %) at 25, 50 and 75 °C) are depicted in Fig. 4. CO_2 adsorption-desorption profiles illustrate the initial weight loss of *ca.* 4 and 8 wt % after preliminary activation at 200 °C in N_2 atmosphere, this weight loss is due to loss of moisture content and physisorbed CO_2 on exposure to the atmosphere. The maximum adsorption capacity of NaZSM-5 (10 %) was found to be 140 mg/g of sorbent. The adsorption capacity increased in the order NaZSM-5 < NaZSM-5 (5 %) < NaZSM-5 (10 %) while a decrease in adsorption capacity was observed for NaZSM-5 (15 %). The decrease in CO_2 adsorption is due to reduced diffusivity of CO_2 into the pores, as it is confirmed by a decrease in the pore volume.

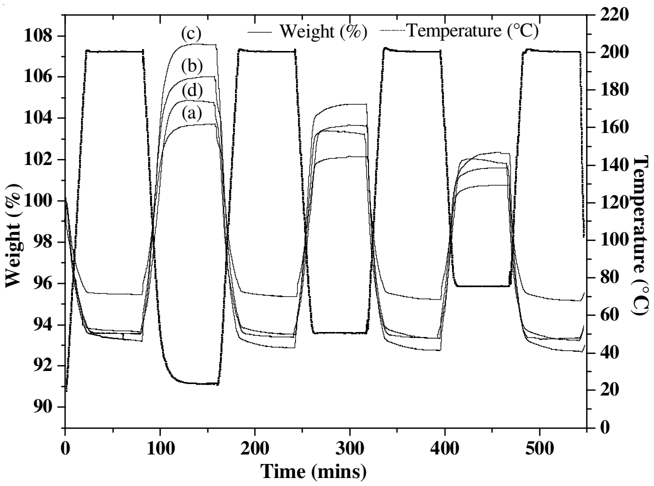

Fig. 4. CO_2 adsorption/desorption profiles of (a) NaZSM-5, (b) NaZSM-5 (5 %), (c) NaZSM-5 (10 %) and (d) NaZSM-5 (15 %) at 25, 50 and 75 ºC

Xu *et al.*[37] reported a maximum CO_2 storage capacity of 246 mg/g-PEI with 50 % polyethylenimine (PEA) loading in MCM-41. Blanco *et al.*[38] studied the adsorption of CO_2 over series of La_2O_3/SiO_2 samples and from the volumetric adsorption measurements they observed a high CO_2 adsorption capability of 2.5-2.8 mol nm^{-2} with 37.5 and 75 wt % La_2O_3 loadings on silica. The result of present study shows that an optimal 10 wt % loading of zinc oxide can be highly dispersed on the surface of NaZSM-5, thus maintaining its high surface area and providing maximum CO_2 storage capacity. The CO_2 adsorption over all zinc oxide impregnated NaZSM-5 decreases at 50 and 75 °C due to the reduced reactivity between CO_2 and the zinc oxide sites. The kinetic energy of CO_2 molecules increases at 50 and 75 °C and hence CO_2 molecules are not available for reaction. As the adsorption of CO_2 is rapid[25] at 25 °C and capacity is high, further adsorption studies were carried out at 25 °C.

The energy of desorption (E_d) was also calculated from CO_2-TPD by varying the heating rate (β = 283.6, 288.8, 296.8 K min^{-1}), using the following equation:

$$\log\left(\frac{T_P^2}{\beta}\right) = \frac{E_d}{2.303RT_P} + \log\left(\frac{E_d A_0}{RC}\right)$$

where T_P represents the desorption peak temperature (K), β the heating rate (K min^{-1}), E_d the energy of desorption (kJ mol^{-1}), A_0 the quantity adsorbed (mmol g^{-1}) and C a constant (related to desorption rate). E_d was calculated to be 22.9 kJ/mol from the slope by plotting log (T_P^2/β) *vs.* $1/T_P$. Furthermore, the heat of reaction (ΔH_r) was calculated from the DSC analysis. A maximum benchmark value of ΔH_r of CO_2 sorbent is 580 Btu/lb[39]. The ΔH_r value of NaZSM-5 (10 %) was determined to be 495 Btu/lb; this meets the energy requirements of a CO_2 sorbent.

The reusability of NaZSM-5 (10 %) was confirmed by four consecutive CO_2 adsorption (25 °C)/desorption (200 °C) runs (Fig. 5). There was no significant change in adsorption capacity. The XRD patterns of NaZSM-5 (10 %) (figure not shown) after 20 cycles are similar to those of the original NaZSM-5 (10 %). In addition, the selectivity of NaZSM-5 (10 %) was studied by conducting CO_2 adsorption/desorption experiments with diluted (15.21 % of CO_2 in N_2) and pure CO_2 (99.99 %) feed gases, as reported[35]. The absence of any significant change in adsorption capacity (Table-2) illustrates no co-adsorption of N_2 and high CO_2 selectivity of NaZSM-5 (10 %). Furthermore, the influence of desorption temperature on CO_2 adsorption over NaZSM-5 (10 %) at 300, 350 and 400 °C is presented in Table-2. The CO_2 adsorption capacity at 25 °C and desorption at 300, 350 and 400 °C were similar, which substantiated that CO_2 adsorption over NaZSM-5 (10 %) was not physisorption. Hence, NaZSM-5 (10 %) was found to be regenerable, reusable, thermally stable and a selective CO_2 sorbent.

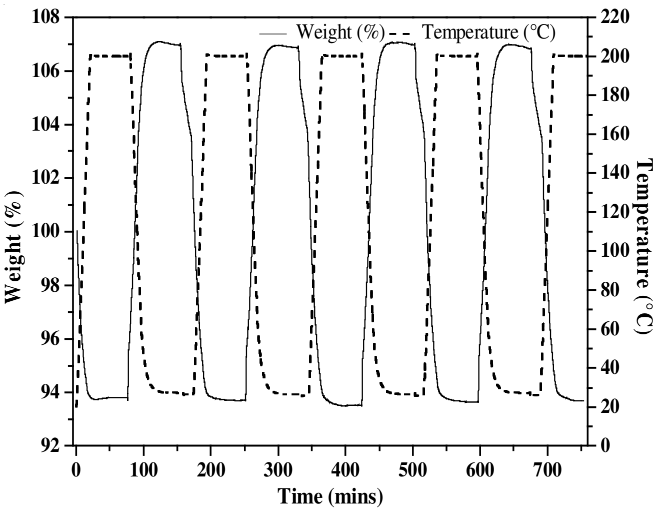

Fig. 5. Recycles of CO_2 adsorption (at 25 °C)/desorption (200 °C) profile for NaZSM-5 (10 %)

TABLE-2
EFFECT OF ADSORPTION AND DESORPTION TEMPERATURE, FEED GAS CONCENTRATION ON THE ZINC OXIDE IMPREGNATED NaZSM-5s

Catalysts	CO_2 adsorption temperature (ºC)	Desorption temperature (nitrogen) (ºC)	Adsorption capacity (mg/g)	CO_2 feed gas concentration (%)
NaZSM-5 (5 %)	25	200	120	99.99
	50	200	100	99.99
	75	200	80	99.99
NaZSM-5 (10 %)	25	200	140	99.99
	50	200	110	99.99
	75	200	85	99.99
	25	200	138	15.21
	25	300	138	99.99
	25	350	136	99.99
	25	400	133	99.99
NaZSM-5 (15 %)	25	200	114	99.99
	50	200	102	99.99
	75	200	82	99.99

Conclusion

NaZSM-5 zeolite was synthesized using rice husk ash as the silica source and impregnated by wet method with zinc oxide. The XRD patterns revealed the high crystallinity of the synthesized samples and carried the characteristic patterns of zinc oxide at higher loadings. Nitrogen adsorption-desorption isotherms of the synthesized samples were type-I, confirming the formation of micropores. The energy of desorption and heat of reaction obtained from CO_2-TPD and DSC results are 22.9 kJ/mol and 495 Btu/lb, respectively. NaZSM-5 (10 %) when subjected to CO_2 adsorption showed a maximum adsorption capacity of 140 mg/g of the sorbent. As the ZSM-5 zeolite was synthesized using rice husk ash, the process is said to be green and the zinc oxide impregnated ZSM-5s were found to be regenerable, reusable, thermally stable and a selective CO_2 sorbent.

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