

Chapter 49

Surface Remodelling of Zeolite 4A Bodies for CO₂ Capture: A Case Study



Debashis Panda , Sanjay Kumar Singh  and E. Anil Kumar 

Abstract The effect of both physical and chemical modification of zeolite 4A bodies on CO₂ adsorption characteristics was critically investigated. The physical modification was done by milling using planetary ball mill and chemical modification was done by amine impregnation technique. The surface area decreased by 53% after milling which leads to 28% drop in CO₂ adsorption capacity in Zeo-12 (milled zeolite 4A bodies). Whereas, after the chemical modification via *isopropylamine* impregnation on Zeo-00 (un-milled zeolite 4A bodies) and Zeo-12, there was an increase in CO₂ adsorption capacity by 10.45% and 46.23%, respectively. Further, Henry constant was calculated from CO₂ adsorption isotherm data which was enhanced by 2.92% and 130.79% in Zeo-00 and Zeo-12-IPA, respectively. Such significant augmentation in adsorption capacity and Henry constant indicated that the chemical modification via amine impregnation is an efficient route for bulk CO₂ adsorption as compared to physical modification.

Keywords Zeolite 4A bodies · CO₂ adsorption · Amine impregnation · Ball milling · Isotherm model

D. Panda · E. Anil Kumar
Discipline of Mechanical Engineering, Indian Institute
of Technology Indore, Simrol, Indore 453552, India

S. K. Singh (✉)
Discipline of Chemistry, Indian Institute
of Technology Indore, Simrol, Indore 453552, India
e-mail: sksingh@iiti.ac.in

Discipline of Metallurgy Engineering and Materials Science, Indian Institute of Technology
Indore, Simrol, Indore 453552, India

E. Anil Kumar (✉)
Department of Mechanical Engineering, Indian Institute of Technology
Tirupati, Tirupati 517507, India
e-mail: anil@iittp.ac.in

49.1 Introduction

With an inimical contribution to climate change, anthropogenic greenhouse gases emission has been considered as an earnest environmental problem. The carbon dioxide, one of the vital parts of greenhouse gases comes from the combustion of fossil fuel, which not only causes serious human symptoms like headache and dry eyes but also increases the earth surface temperature, predicted to be as high as 6.4 °C by the year 2100 according to IPCC report [1]. Hence, the growing concerns of global climate imbalance have impelled researchers towards the development of sustainable, less energy-intensive methodology for carbon capture and sequestration on a larger scale. In this direction, various strategies (pre-combustion, post-combustion and oxyfuel combustion) and multifold technologies (absorption, adsorption, membrane separation and cryogenic distillation) are currently being explored, with primary focus on (i) separation of CO₂ from N₂ in flue gas for post-combustion (ii) separation of CO₂ from H₂ for pre-combustion and (iii) bifurcation of CO₂ from CH₄ for natural gas reserves [2, 3]. From the past decade, a number of microporous and mesoporous adsorbents namely zeolite, activated carbon, metal-organic framework (MOF) and so on have been synthesized and extensively investigated for CO₂ adsorption. Although adsorbents like MOF-177 show relatively high CO₂ adsorption capacities (54 mmol g⁻¹) at room temperature and super-ambient pressure (50 bar), their capacity decreases rapidly at atmospheric pressure (1 bar) [2]. Since post-combustion requires adsorption at the atmospheric and sub-atmospheric conditions, it is necessary to find adsorbents which should have high adsorption capacity, faster kinetics and resistant to moisture. Taking into account all the above-mentioned attributes, researchers found that the zeolite may be a suitable adsorbent due to its high adsorption capacity at low partial pressure, prolonged thermo-cyclic stability and low heat of regeneration. As on September 2016, 232 zeolite frameworks have been identified, among them, 40 are found naturally [4]. CO₂ adsorption on zeolite depends on both its textural properties and the surface heterogeneities caused by the presence of cations. Although natural zeolites are inexpensive, they show poor performance in CO₂ adsorption due to their non-uniform structural framework. Siriwardene et al. reported that, naturally found zeolites like herschelite-sodium chabazite, clintopile (sodium based), clintopile (potassium based) displayed only 0.8, 0.42 and 0.09 mmol g⁻¹ CO₂ adsorption capacity, respectively, whereas, synthesized zeolite 13X and 4A showed around 3.63 and 3.06 mmol g⁻¹, respectively, at room temperature and 1 bar CO₂ partial pressure conditions [5, 6]. In spite of the synthesized zeolites showed relatively high adsorption capacity at room temperature, their capacity rapidly decreases with a rise in temperature and in presence of moisture. Since moisture is the essential part of flue gas, surface modification of the zeolite is necessary to capture CO₂ from moist gas at both atmospheric and sub-atmospheric conditions. Physical and chemical surface modifications (such as impregnation or grafting) have been used for zeolite to increase its adsorption capacity [7]. Correa et al. have synthesized γ -Al₂O₃ adsorbents in a planetary ball mill for 10 h with urea and aluminium nitrate through solution combustion method,

which exhibited CO₂ adsorption capacity of 1.94 mmol g⁻¹ at 60 °C and 15 bar via chemisorption method [8]. Also, researchers impregnated various amines such as monoethanolamine (MEA), *isopropanol* amine, pentaethylenhexamine (PEHA), tetraethylenepentamine (TEPA) to chemically modify zeolite having larger pore such as 13X, Y and β [2]. Despite the overwhelming evidence supporting the CO₂ adsorption ability of modified adsorbents, there is no concrete comparative study on the effect of both physical and chemical modifications on adsorption properties of the same adsorbent. It is worth noticing that CO₂ adsorption mechanism on amine-implanted binder containing zeolite 4A or zeolite 4A bodies (in granule form) has not been extensively investigated so far. Since, binder is the primary constituent for zeolite in its commercial form, the intimate contact between the microporous zeolite and binder in zeolite bodies and their heterogeneous pore size distribution can produce remarkable consequences in its amine modification owing to better CO₂ capture. The objective of the present work is to modify zeolite 4A bodies physically via ball milling and chemically via impregnation of *isopropylamine* for investigation of its physiochemical properties and effect on CO₂ adsorption performance.

49.2 Experimental Methods

49.2.1 Materials

Commercial zeolite 4A bodies (Sigma Aldrich) was used as test adsorbent in this study. Anhydrous high purity (99.99%) ethanol and *isopropylamine* (Sigma Aldrich) were used as solvent and modifier, respectively. The procured materials were directly used without any purification. For physical modification, zeolite 4A bodies (0.1 g) were preheated under vacuum at 250 °C for 3 h. Further, it was continuously grounded with the ball-to-powder weight ratio of 5:1 (w/w) for 12 h in atmospheric condition by means of a planetary ball mill (Fritsch Pulverizer-5). The rotational speed was kept constant at 350 rpm while performing the experiment. The experiment was carried out in a 250 mL stainless steel jar with a protective jacket of zirconium oxide and different balls of size (5, 10 mm) made of zirconium oxide as milling media. The grinding jars were arranged eccentrically on the sun wheel of the planetary ball mill. The movement direction of sun wheel and grinding jars was opposite. After milling, the grounded samples were dried at 120 °C in a vacuum oven for a period of 3 h prior to characterization. For chemical modification, the preheated sample was treated with *isopropylamine* (IPA; 0.3 wt%) in ethanol under slight agitation for 20 min. The resultant slurry was continuously stirred for 24 h at room temperature. Finally, the mixture was filtered off, washed with ethanol and dried at 120 °C for 3 h under vacuum. The un-milled sample, sample after milling, un-milled sample after amine impregnation, milled sample after amine impregnation were designated as Zeo-00, Zeo-12, Zeo-00-IPA and Zeo-12-IPA, respectively. The gas adsorption

measurements were conducted using pure CO₂ and N₂ (99.99%) supplied by INOX Air product India.

49.2.2 Characterization

Powder X-ray diffraction patterns (P-XRD) of the studied adsorbents were recorded using a Rigaku SmartLab advanced diffractometer with monochromatic Cu K α radiation ($\lambda = 1.54 \text{ \AA}$) at a step size of 0.03° over a 2θ range of 5° – 80° . The surface morphology, pore structure and their distribution of studied adsorbents were examined using field emission scanning electron microscope, equipped with energy-dispersive X-ray spectroscopy (FESEM model ZEISS Supra-55) that operates at a voltage of 15 kV. The thermogravimetric study (TGA) was performed to analyse the thermal stability and dehydration characteristics of studied adsorbents using Mettler-Toledo TGA/SDTA851 thermal analyser. The textural properties of the adsorbent materials were determined using a Quantachrome Autosorb iQ₂ TPX automated gas sorption system. The variation in chemical property during modification was determined by Fourier transform infrared spectrometer (FTIR) equipped with an attenuated total reflectance (FTIR/ATR Model FTIR-SP-1 Spectrum one, Perkin-Elmer, MA, USA).

49.2.3 Adsorption Measurements

The gas adsorption measurements were carried out in Quantachrome Autosorb iQ₂ TPX automated gas sorption system equipped with highly accurate pressure transducers and thermostatic bath. Prior to the adsorption experiment, samples were degassed at a temperature of 120°C for 8 h. The CO₂ adsorption capacities of studied adsorbents were evaluated at a temperature of 25°C and pressure of 1 bar. Further, in order to evaluate the adsorption affinity between adsorbate and adsorbent, the adsorption data were fitted with Langmuir and virial isotherm models which are given below.

$$\frac{P}{q} = \left(\frac{P}{q_m} \right) + \frac{1}{b \times q_m} \quad (49.1)$$

$$P = \frac{q}{K_H} \exp(Aq + A_1q^2 + A_2q^3 + A_3q^3 + \dots) \quad (49.2)$$

where P is the equilibrium adsorbate pressure (bar), q is the CO₂ adsorption capacity (mmol g^{-1}) of the adsorbent and q_m is the maximum theoretical CO₂ adsorption capacity (mmol g^{-1}) at complete monolayer coverage. b is called affinity or Langmuir constant (bar^{-1}) [9]. A , A_1 and A_2 are the virial coefficients. K_H is called Henry constant deduced from the intercept $-\ln(K_H)$ at $q \rightarrow 0$ and Langmuir model ($q_m b$).

Fundamentally, the Langmuir models suggest the formation of a monolayer on the outer surface of adsorbent by balancing occupied and unoccupied sites on the surface.

49.3 Results and Discussion

The results obtained from physical and chemical modification studies and measurement of CO₂ adsorption characteristics are discussed in the following sections.

49.3.1 Physical and Chemical Modification of Zeolite 4A bodies

The physical and chemical modifications of zeolite 4A bodies were performed using ball milling and impregnation technique as illustrated in Fig. 49.1. Powder X-ray diffraction (P-XRD) studies (Fig. 49.2e) of Zeo-00, Zeo-12, Zeo-00-IPA and Zeo-12-IPA showed similar reflection pattern, suggesting that the crystalline framework of zeolite 4A bodies was well preserved after both physical and chemical modifications. Similarly, FESEM images of studied adsorbents showed that there was a drastic degradation in morphology after prolonged grinding. The particle size of Zeo-00 was reduced from 2.5 μm to ~ 500 nm and its shape changed from cubical to spherical with high irregularities. However, after amine impregnation, there were no visible structural changes suggesting that morphology remained intact (Fig. 49.2c–d).

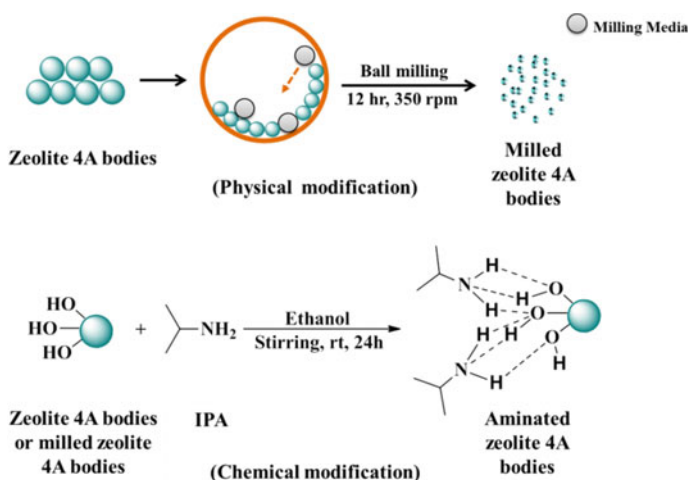


Fig. 49.1 Schematic representation of the modification of zeolite 4A

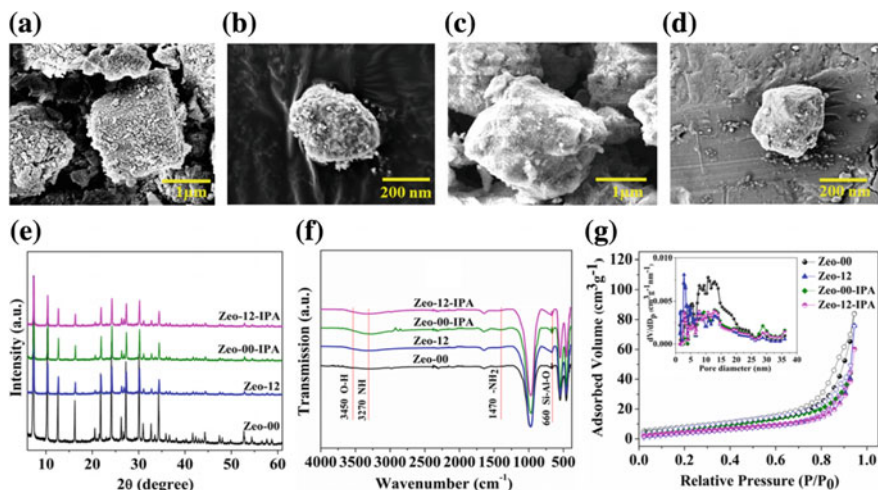


Fig. 49.2 a–d FESEM images of a Zeo-00, b Zeo-12, c Zeo-00-IPA and d Zeo-12-IPA, e P-XRD spectra, f FTIR spectra and g N₂ adsorption–desorption isotherm and pore size distribution (inset) of studied adsorbents

The observed FTIR results of physically and chemically modified zeolite 4A bodies showed that there was an increment in intensity as well as broadness of band range from 3600 cm^{-1} to 2800 cm^{-1} for Zeo-00-IPA and Zeo-12-IPA as compared to Zeo-00 and Zeo-12 (Fig. 49.2f). This was due to several overlapping bands in the single region [9].

All the adsorbents showed vibration bands at 3450 , 975 , 660 cm^{-1} for O–H asymmetric stretching vibrations of the hydrogen-bonded silanol group (Si–O(H)) and Si–Al–O symmetric stretching vibration, respectively. The broad band observed at *ca.* $3010\text{--}3500\text{ cm}^{-1}$ was attributed to NH (–NH₂ group) and O–H (Si–OH) stretching. Moreover, the increment in the intensity of peaks within the range $750\text{--}680\text{ cm}^{-1}$ for Zeo-00-IPA and Zeo-12-IPA was noticed due to various rotations and vibration of alkyl and aromatic C–H that confirmed the presence of amine molecule in zeolite 4A bodies [10].

Figure 49.2g displayed a typical type-IV nitrogen-sorption isotherm having a well-defined plateau with modest hysteresis for the studied adsorbents. Specific surface area (SA) of the studied adsorbents were determined from sub-critical nitrogen isotherms by using Brunauer–Emmett–Teller (BET) equation (at $P/P_0 = 0.05\text{--}0.3$); average pore diameter (APD) was analysed by Barrett–Joyner–Halenda (BJH) equation and pore volume (PV) was calculated from adsorption data (at $P/P_0 = 0.995$). Physicochemical properties of the adsorbents are listed in Table 49.1. The observation of inverse H3 type hysteresis in the P/P_0 range of $0.4\text{--}0.9$ indicates the presence of bigger and slit-shaped pores, characteristics of hierarchical porous materials may be due to presence of binder [11]. Presence of large mesopore and high specific surface area confirm the presence of binder which circumscribed the microporous zeolite 4A within it [12]. The average pore size of Zeo-00 was 15.33 nm , which can be

Table 49.1 Physicochemical properties and CO₂ adsorption performance of the adsorbents

Adsorbents	SA (m ² g ⁻¹)	PV (cm ³ g ⁻¹)	APD (nm)	q (mmol g ⁻¹)	q _m (mmol g ⁻¹)	b	R ²	k _H (mmol g ⁻¹ bar ⁻¹)
Zeo-00	27.11	0.13	15.33	2.20	3.01	2.84	0.97	^a 8.54/ ^b 9.78
Zeo-12	17.71	0.11	3.30	1.58	25.57	0.07	0.01	^a 1.78/ ^b 1.83
Zeo-00-IPA	24.43	0.06	3.12	2.43	3.37	2.61	0.99	^a 8.79/ ^b 10.35
Zeo-12-IPA	17.44	0.01	3.30	2.31	2.57	7.67	0.99	^a 19.71/ ^b 53.87

SA—Specific surface area; PV—pore volume; APD—average pore diameter; Q —the amount of CO₂ adsorption; Q_m —the amount of maximum theoretical CO₂ adsorbed; R^2 —the goodness of fit and k_H —Henry constant calculated from ^aLangmuir model, ^bVirial model

attributed to the mesoporous nature (Fig. 49.2g in the inset), and reduced after both physical and chemical modifications. The pronounced effect in Zeo-12 suggests that milling increases the defect in the crystal. However, the reduction in specific surface area and pore volume of the adsorbents (Zeo-00-IPA, Zeo-12-IPA) indicates the pore filling due to amine impregnation.

49.3.2 CO₂ Adsorption Studies of Modified Zeolite 4A bodies

The maximum amount of CO₂ adsorbed on the studied zeolite 4A bodies is listed in Table 49.1. It is obvious that CO₂ adsorption capacity depends upon both specific surface area and the type of chemical functionality anchored on zeolite surface. The hybrid adsorption mechanism due to physical adsorption and chemical interaction was observed in our studied adsorbents. As physisorption depends on the specific surface area, due to the reduction of surface area in Zeo-12 by 53%, there was a substantial drop in CO₂ adsorption capacity by 28% (from 2.20 to 1.58 mmol g⁻¹). On the other hand, in Zeo-00-IPA and Zeo-12-IPA, there was an increase in adsorption capacity by 10.45 and 46.23%, from respective Zeo-00 and Zeo-12 due to the dominant role of chemical interaction by amine impregnation (Fig. 49.3a). Because of amine impregnation, the basicity increased with the formation of extra adsorption sites by the presence of the free NH₂ group. The amine present inside the zeolite bodies meso pore binds CO₂ through lone pair electron on nitrogen atom to form Zwitterion intermediates followed by deprotonation of other free amine to form carbamate and ammonium species which augmented the adsorption capacity [2]. Encouraged with the increment in adsorption capacity, the CO₂ isotherm data on studied adsorbents was fitted with Langmuir and virial models, respectively. The goodness of fit of Langmuir model for Zeo-00-IPA and Zeo-12-IPA was about 0.99, which signified a better interaction between CO₂ and adsorbents, whereas it was least for Zeo-12.

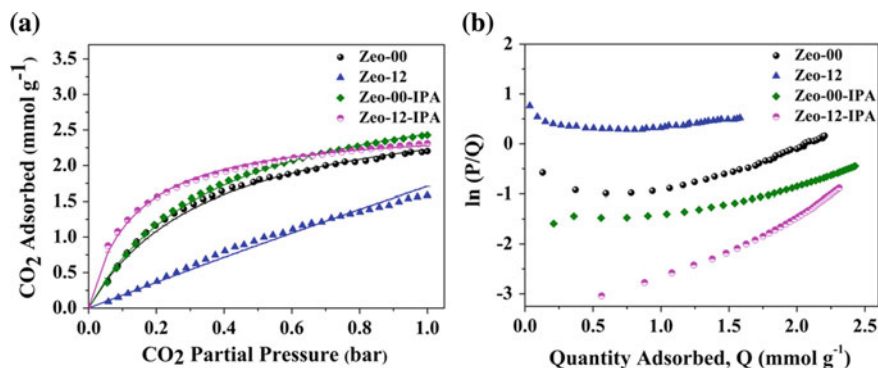


Fig. 49.3 **a** Adsorption isotherm of CO₂ on studied adsorbents at 1 bar and 25 °C. **b** Virial plot of CO₂ on studied adsorbents at 1 bar and 25 °C

Similarly, Henry constant (K_H) was also evaluated to determine adsorbate–adsorbent interaction at low pressure and room temperature, where adsorbate–adsorbent forces predominate. From the Table 49.1, it is clear that K_H is highest in Zeo-12-IPA and lowest in Zeo-12, which signifies the presence of an amine in zeolite bodies enhanced the CO₂ interaction. The values of Henry constant found from two models are slightly different due to variation in fitting reliability. Such high Henry constant for zeolites are matched with the earlier reported results [13].

49.4 Conclusions

In the present study, we have modified zeolite 4A bodies both physically and chemically. Surface area of zeolite 4A bodies was reduced after physical modification due to prolonged milling; hence, its CO₂ adsorption capacity also decreased. Whereas, chemical modification via amine impregnation enhanced the adsorbate–adsorbent interaction at low pressure and room temperature which was confirmed by their superior Henry constant. The hybrid adsorption mechanism due to both physisorption and chemical interaction augmented the CO₂ adsorption capacity of Zeo-00-IPA, which paves the way for further exciting research towards post-combustion CCS.

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