

CO₂ capture by amine-modified materials, tailored for enhanced adsorption capacity and selectivity

Khalil Ahmad¹, Eric M. Kennedy¹, Bogdan Z. Dlugogorski², John C. Mackie¹ and Michael Stockenhuber¹

¹PRCfE, Chemical Engineering, School of Engineering, The University of Newcastle, Callaghan, NSW 2308, Australia

²School of Engineering and IT, Murdoch University (WA 6150) Australia

E-mail: Michael.Stockenhuber@newcastle.edu.

Abstract

We have modified zeolite Na-Y (Si/Al = 2.55) with triethylenetetramine (TETA), using a wet-impregnation method, with the aim of synthesising a hybrid material with enhanced CO₂ adsorption capacity and selectivity, in the presence of water vapour. The dynamic adsorption capacity of CO₂ on NaY-TETA, prepared with varying loadings of amine, was examined. Following modification, the surface properties of the adsorbent were changed, as evident by examining the adsorption and desorption isotherms of CO₂ from wet gas streams. The modified materials display excellent CO₂ uptake under humid conditions. A mechanism describing the interaction of CO₂ on the surface suggests a transformation from a mainly physical to chemical bonding due to modification of the surface functional groups on TETA. In addition, multicyclic use of NaY-TETA suggests that it could be an ideal sorbent for CO₂ capture from flue gases.

Keywords: *CO₂ capture, Na-Y, triethylenetetramine, breakthrough*

Introduction

A promising approach to reduce CO₂ emissions from the point sources such as fossil-fuel-power plants is through the adoption of carbon capture and storage (CCS) technologies, which require binding (capture) of CO₂. Post-combustion capture (PCC) is an end-of-the pipe technology, considered to be the most effective approach to enable CO₂ capture, as it can be applied to existing as well as new power plants. The objective of the present work is to develop new adsorbents which readily adsorb and release CO₂ with minimal energy requirements. Amines, tethered on to solids like zeolites, are potential candidates for this purpose.

The partial pressure of CO₂ in flue gases is typically 0.10 to 0.15 bars (McDonald, D'Alessandro et al. 2011; Figueroa 2008), and therefore (in case of post-combustion CO₂ capture) it is challenging to develop high adsorption capacities at these low pressures, especially where the CO₂ is in the presence of significant quantities of water vapour. Among the separation technologies available today, adsorption on solids is one of a number of effective methods for the separation of emitted CO₂. A variety of solid adsorbents such as zeolites (Lee, Kim et al. 2002; Siriwardane, Shen et al. 2003; Walton, Abney et al. 2006; Stevens, Siriwardane et al. 2008; Xu, Zhao et al. 2009; Seung-Tae Yang (2010)), ZIFs (Phan 2010), MOFs (C.J. Kepert 2006; Hao, Li et al. 2011), activated carbon (Burchell, Judkins et al. 1997; Siriwardane, Shen et al. 2001; Lee, Kim et al. 2002; Grande and Rodrigues 2008; Zhang, Zhang et al. 2010), metal oxides (Jaenicke, Chuah et al. 2000) have been explored for capture of carbon dioxide. In spite of displaying high CO₂ adsorption capacity at room temperature, their capacities decrease with increasing temperature and in the presence of water vapour. Moreover, they have poor selectivity due to the physical rather than chemical nature of the interaction.

Absorption in aqueous alkanolamine (MEA, DEA) is the most mature post-combustion technology for removal of carbon dioxide from flue gas. However, due to thermal and oxidative degradation of the amine resulting in the formation of corrosive by-products, large energy requirements for solvent regeneration, and fouling of equipment, new ways to remove carbon dioxide still being explored. Compared to those in the liquid phase, solid phase adsorbents, in general, have the advantage that they are non-corrosive, exhibit better stability and offer ready separation. The combination of high capacity amine absorbers with solids is thus an attractive strategy to develop new, high capacity reusable adsorbents.

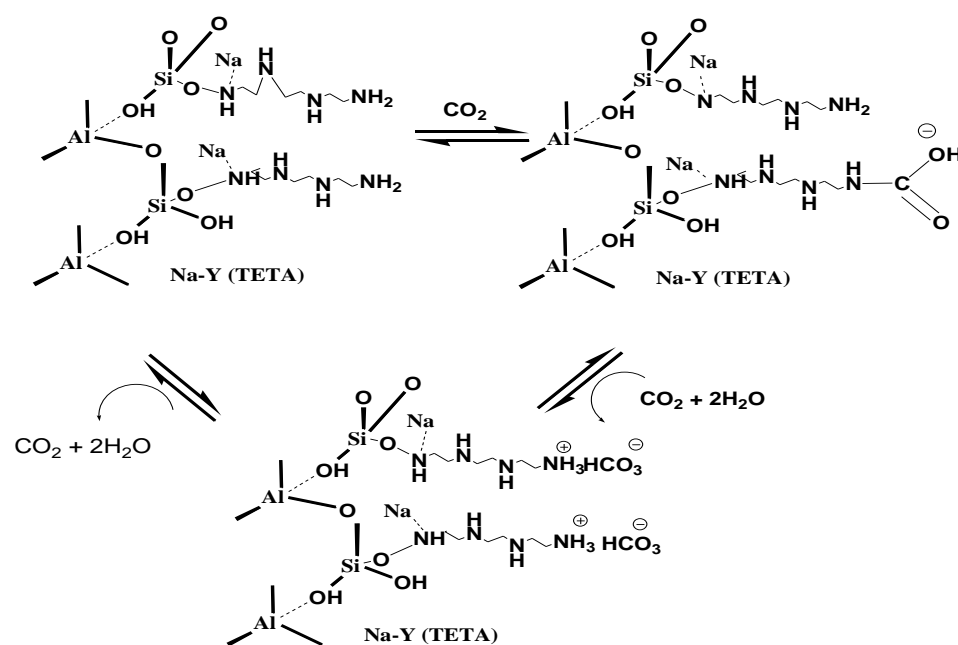
A number of technologies exist to graft functional groups onto the surface of porous materials such as porous silicas, carbons and zeolites, have yielded the development of promising new adsorbents (Aaron and Tsouris 2005; Breuninger 2006; Chatti, Bansawal et al. 2009; Bollini, Didas et al. 2011; Ahmad, Mowla et al. 2013). The binding of organic amines onto porous structures is considered an attractive option to enhance carbon dioxide capacity and selectivity at moderate temperatures and pressures. These modified adsorbent offer reversible attachment of CO₂ in the form of ammonium carbamate and carbonates through the basic surface and acidic CO₂ interaction (Yang, Xu et al. 2008). They also eliminate the slip and corrosion (Veawab 2003) problems associated with the use of liquid amines because of direct binding of the amine to the support which not only increases their thermal stability but also enhances the selectivity for CO₂ in the presence of water and is less corrosive nature compared to the liquid amines.

Chatti et al (Jadhav, Chatti et al. 2007; Chatti, Bansawal et al. 2009) immobilized primary (MEA) and secondary (ED, IPA) amines on zeolite 13X and investigated the effect of factors such as different temperatures, solvent, shaking time, synthesis temperature, and wetting of pellets. More recently, Su et al (Su, Lu et al. 2010) modified Y-type zeolite with triethylenetetramine (TEPA); they found enhancement in capacity up to 4.27 mmol g^{-1} in the presence of moisture. Liu et al (Liu, Shi et al. 2010) modified KIT-6 type mesoporous silica with tetraethylenepentamine (TEPA) using post-synthesis impregnation, the dynamic adsorption capacity increased from 1.5 mmol g^{-1} to 2.9 mmol g^{-1} with complete desorption at 373 K. Xu et al (Xu, Zhao et al. 2009) recently, modified β -zeolite with monoethanol amine (MEA) for the adsorption and separation of CO_2 , CH_4 and N_2 , they found that the modified material shows very high selectivity for CO_2 over N_2 in the ratio of 25:67. SBA-15 was modified with ethylenediamine by Zheng et al (Zheng, Tran et al. 2005) with adsorption capacity of 86 mg g^{-1} at 25°C and 1 atm pressure from 15% CO_2 stream. Chang et al (Chang, Chuang et al. 2003) investigated the adsorption/desorption process of CO_2 on SBA-15 modified by γ -(Aminopropyl) triethoxysilane. Zelenak et al (Zelenak, Halamova et al. 2008) modified SBA-12 mesoporous silica by 3-(aminopropyl) (AP), 3-(methylamino)propyl (MAP) and 3-(phenylamino)propyl (PAP) ligands. Sorption capacities of 1.04 mmol g^{-1} , 0.98 mmol g^{-1} and 0.68 mmol g^{-1} were obtained by SBA-12/AP, SBA-12/MAP and SBA-12/PAP respectively, with complete regeneration using an inert gas without heating. Recently, Li et al (Li, Zhang et al. 2008) reported polyethyleneimine containing fibrous adsorbents which could adsorb 276.96 mg of $\text{CO}_2 \text{ g}^{-1}$ of PEI at 30°C . This material adsorbs 19 times more CO_2 under humid conditions compared to dry with complete regeneration at 120°C . Xu et al (Xu, Song et al. 2002) modified mesoporous molecular sieve MCM-41 with polyethyleneimine and obtained a novel "Molecular Basket" adsorbent, where it was claimed that modified MCM-41-PEI could adsorb 24 times more than un-modified and 2 times that of pure PEI. Yue et al (Yue, Sun et al. 2008) fabricated MCM-41 modified with tetraethylenepentamine (TEPA) and found that 50 wt.% was optimum loading to give an adsorption capacity of 183 mg g^{-1} in 5% CO_2 concentration. Recently, Knowel et al (Knowles, Graham et al. 2005) reported functionalization of different mesoporous structures with 3-aminopropyltrimethoxysilane and describes the effect of pore geometry, pore spacing, pore volume, surface area and surface silanol concentration on the extent of functionalization. The resulting materials were tested for adsorption in the presence of moisture which enhanced the adsorption capacity, however it was noticed that desorption capacity was reduced.

Y-type zeolite belongs to the FAU (Beaumont and Barthomeuf 1972) which has been intensively investigated for CO_2 adsorption. These materials possess pore sizes comparable to a CO_2 molecule with well-defined pore structure. In the past few years, a number of researchers (Xu, Song et al.

2002; Zheng, Tran et al. 2005; Yue, Chun et al. 2006; Jadhav, Chatti et al. 2007; Yang, Xu et al. 2008; Zelenak, Halamova et al. 2008; Liu, Shi et al. 2010; Gerhard D. Pirngruber (2009)) have been focused on the development of new solid sorbents for CO₂ capture from flue gas with superior adsorption. However, there have been few studies (Su, Lu et al. 2010) undertaken on the modification of NaY with amines.

In the present study, we demonstrate the direct capture of CO₂ using supported amine adsorbent, prepared by the modification of NaY zeolite with triethylenetetramine (TETA). To achieve this, a comprehensive set of experiments were conducted to examine the working capacity, regenerability, structural integrity and thermal stability. A plausible mode of adsorption and desorption of CO₂ on these materials is shown in scheme 1.



Scheme 1: Suggested surface reaction mechanism of CO₂ without and with moisture for adsorption onto NaY-TETA

Materials and Methods

Adsorbent preparation: NaY (Si/Al = 2.55) adsorbent with different triethylenetetramine (TETA) loadings were prepared. Details of the loading, adsorption capacity, pore volume and Langmuir surface area are given in Table 1. Specifically, a 3.0 g charge of NaY and TETA (40%) was mixed, corresponding to the molar Al content in NaY. 100 ml deionized water was added and the mixture was stirred overnight at 60-80°C. Subsequently, the solid hybrid material was collected by filtration and washed with ample deionized water followed by drying in over at 110 °C before further performing any analyses.

Before starting adsorption experiments; the crystal phases of the hybrid materials were characterized through X-ray diffraction (XRD), liquid N₂ adsorption isotherms, surface area analysis, and the thermal stability of sorbents was determined by the thermogravimetric analysis (TGA).

The regenerability of the materials was assessed by heating the CO₂ saturated material after the adsorption test. The adsorbent was placed in a furnace (Ward, Australia) equipped with a temperature controller (Eurotherm) where the sample was heated at 5 °C min⁻¹ under nitrogen flow rate 40 mL min⁻¹ and subsequently cooled to room temperature for the next cycle.

Adsorption experiments

The dynamic adsorption capacity test of the original (NaY) and surface modified material (NaY-TETA) was carried out in a continuous tubular flow packed bed reactor. The inflow and outflow gases were analysed online with a Varian CP-4900 micro gas chromatograph (GC) equipped with thermal conductivity detectors (TCD), Molsieve 5A and PoraPlot Q columns and using He as carrier gas. Before each experiment, the adsorbents were regenerated at 150 °C for 3-4 h under nitrogen flow. For inlet gas, a mixture of CO₂ (15%) balance with N₂ with a flow rate of 30 mLmin⁻¹ was used. The dynamic adsorption capacity was determined for dry and humid conditions. A moisture saturated feed gas mixture was obtained by passing the N₂/CO₂ through a water bubbler which was maintained at a fixed temperature 5-20°C. The amount of captured carbon dioxide was estimated by measuring the CO₂ concentration at the outlet using a micro gas chromatograph (GC). The CO₂ dynamic capacity (q , mmol/g) at a breakthrough time (t_b , min) was calculated as:

$$q = \frac{1}{m} \int_0^{t_b} [Q_{in}C_{in} - Q_{eff}C_{eff}]dt \quad (1)$$

Where m is the dry weight of virgin sorbent (g), Q_{eff} is the effluent gas flow rate (Lmin⁻¹), and C_{in} and C_{eff} are the influent and effluent CO₂ concentration (ppm), expressed in volume percentage. The final capacity was worked out using ideal gas law at the working temperature and pressure.

A typical adsorption and desorption curve is shown in figure 4 and results are shown in Table 1. As a result of modification of NaY with TETA, the adsorption capacity was significantly enhanced with optimum amount of amine. The preferential adsorption of moisture over CO₂ has been reported by Stumpf et al(Gallei and Stumpf 1976) using CaY and NiY, Ruthven et al(Brandani and Ruthven 2004) using FAU type zeolites, and Yang et al(Rege and Yang 2001) with NaX who employed FTIR to study the effect of moisture along with CO₂. Adding moisture to the feed results in a decreased adsorption capacity for NaY as shown in Table 1, where in case modified NaY result in higher capacity under humid conditions. Hence suggesting that the modified adsorbent could be ideal for

real situation of flue gas purification. We have studied the effect of loading on the NaY zeolite by using different concentrations of TETA (tetraethylenetetramine) with respect to aluminum content of the zeolite. The zeolite framework charge localized at the tetrahedral aluminium provides the active site for CO₂ adsorption in the parent zeolite. Due to the stoichiometry of the amine, the concentration of sites is increased in the amine modified zeolite. The adsorption of CO₂ on amine functionalized solid adsorbents works similar to the liquid amine process where CO₂ is chemically attached by the formation of carbamate and bicarbonates with primary and secondary amines(Choi, Drese et al. 2009).

Results and Discussion

Material Characterization

X-ray diffraction patterns of NaY together with modified NaY before and after cyclic adsorption were performed using Philips X'Pert Pro MPD diffractometer using Cu K α radiation ($\lambda = 0.1541$ nm) 1.54 in the range of 5-70° with a step size of 0.02° and collection time of 1s step. The patterns were matched to the International Centre for Diffraction Data[®] (ICCD) with X'Pert Highscore[®]. As shown in figure 1, the intensity of the characteristic peaks changed while the position of the peaks remain the same after the loading of the organic molecules into the pores. Similar results are seen for the characteristic peaks of modified NaY, showing that the structure of the parent material is intact on incorporating amines via wet impregnation.

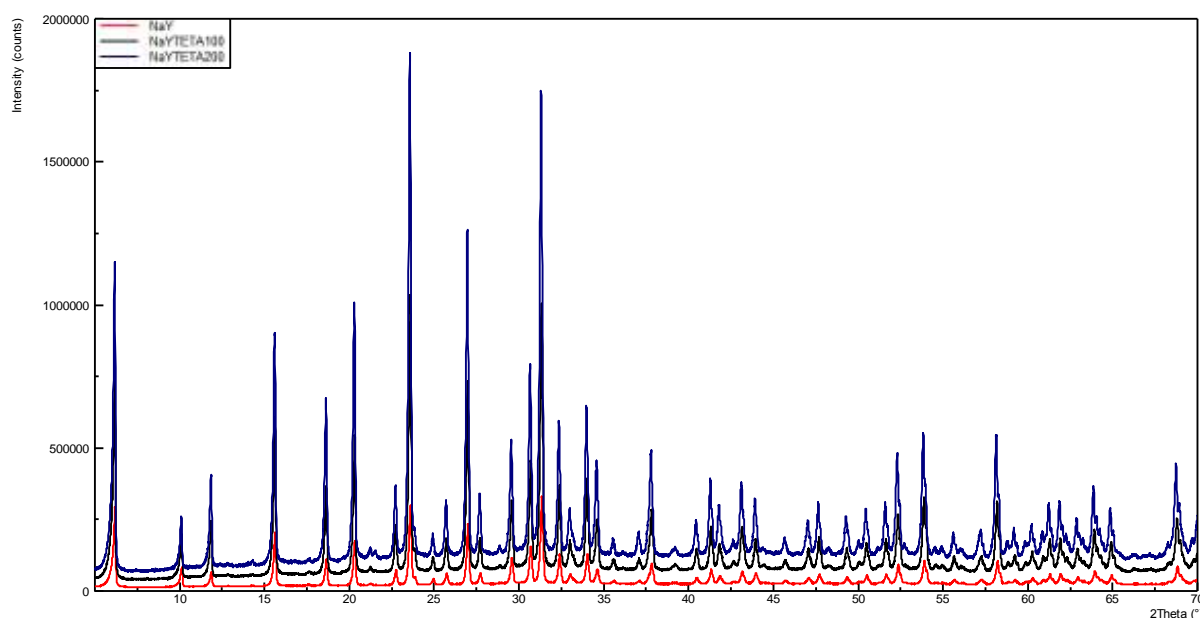


Figure 1: X-Ray diffraction of different samples

The original and modified materials were analyzed by liquid nitrogen gas sorption. A Gemini II 2370 surface area analyzer from Micromeritics was used for obtaining the Adsorption/desorption isotherms at 77 K as shown in Figure 2. The Langmuir surface areas were evaluated adsorption of the liquid nitrogen isotherms over a relative pressure range of $P/P^{\circ} = 0.05-0.95$ and micropore volumes were evaluated using the t-plot method. The surface areas and pore volumes along with the dynamic adsorption capacity of each sample is presented in Table 1.

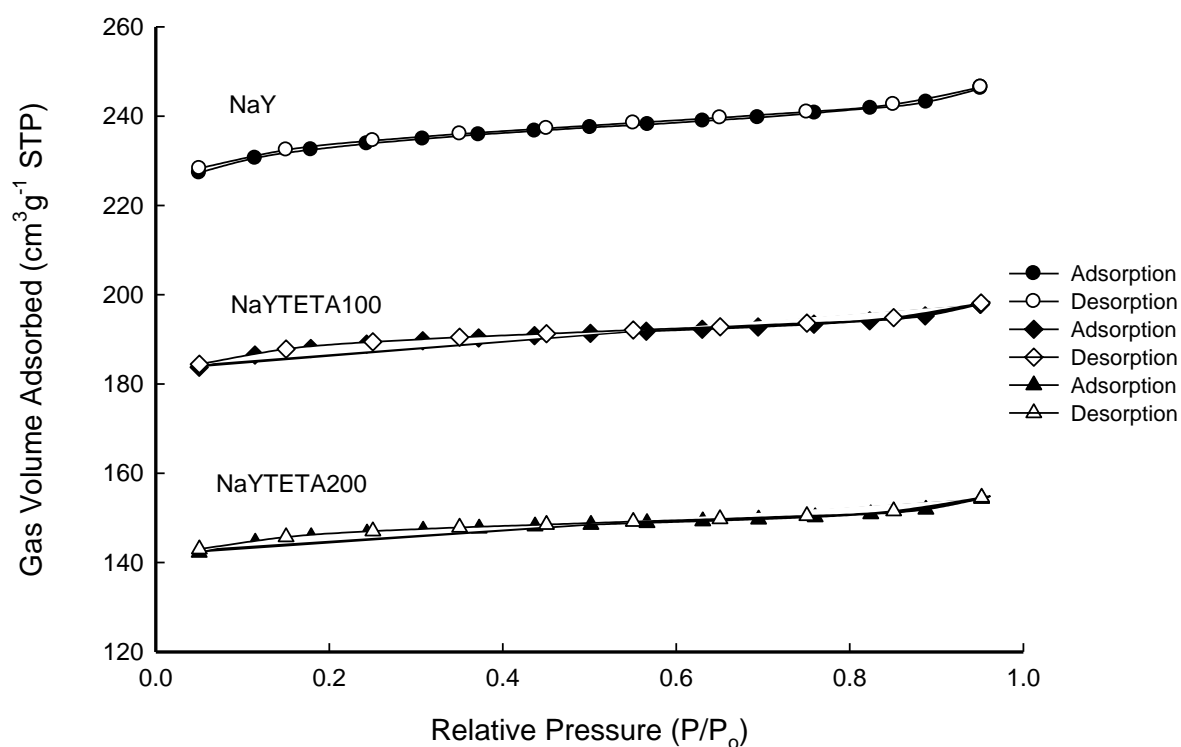


Figure 2: N₂ adsorption-desorption isotherms for different materials

Figure 3 depicts the TGA profiles and the corresponding differential thermogravimetry (DTA) profiles of NaY-TETA100. It is observed in the TGA profile of NaY-TETA100 that the mass loss below 100 °C, which could be due to loss of adsorbed water. The weight loss between 200-400°C may be attributed to the Hofmann elimination of amine in NaY-TETA100. The NaY-TETA100 show thermal stability up to 200-250°C, suggesting that the regeneration should be done at temperatures less than 200°C. The outgoing gases were sent to Thermostat Quadruple Mass Spectrometer via a heated capillary line coupled with the TGA. It is found that outgoing gases are moisture and amines (NH₂)

resulting from breakage of organic species as shown by the mass spectrometric results.

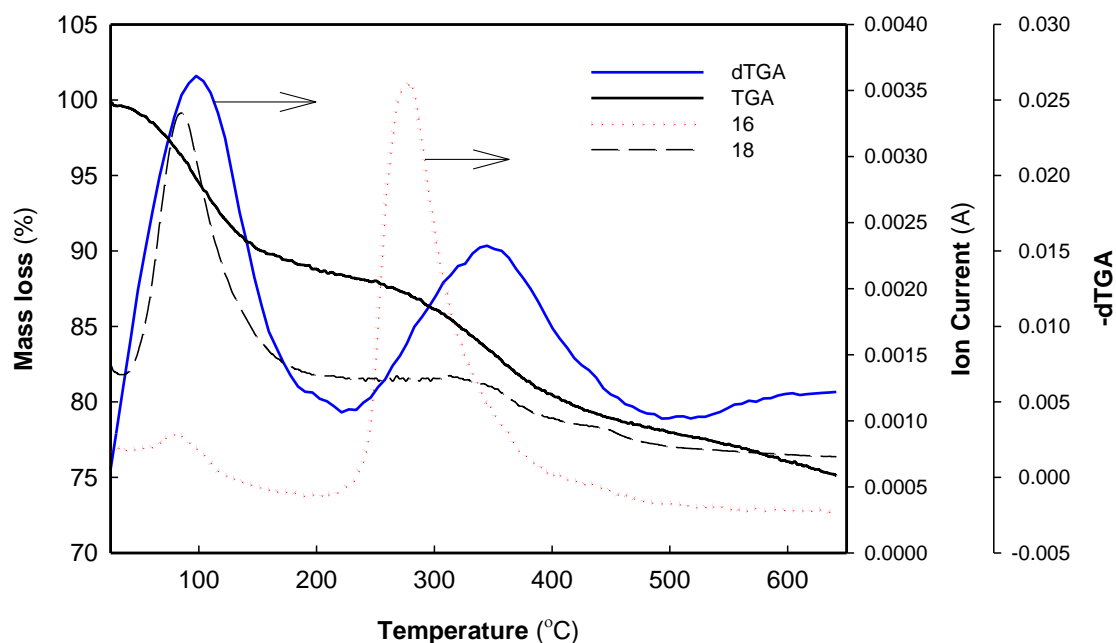


Figure 3: TGA / DTG and MS curves for NaY-TETA100

The performance of amine groups attached on the zeolite surface can be assessed by the method described in the US patent (Leal 1992). A saturated cupric sulphate aqueous solution was prepared which on mixing with the NaY-TETA100 changed the blue colour of cupric sulphate into greenish. The resulting material was dried in oven overnight. As shown in Table 1, the dynamic adsorption capacity after treatment with cupric sulphate solution was reduced to a great extent due to the complex formation by Cu^{+2} ions with the surface amino groups. This confirms the contribution of amine groups for the enhancement of carbon dioxide capture.

The dynamic adsorption capacity of different samples was performed and results are presented in table 1. The experiments were conducted in dry and wet environment. Number of cycles was completed with each sample to confirm the working capacities and average values are reported in the table below. A typical adsorption breakthrough curve of different sample in wet condition is shown in Figure 4, which also highlights the importance of the presence of the amine in the sample. In figure 5 and 6, the adsorption capacity of the modified adsorbents is compared for the wet and the dry feed. A significant increase of the adsorption capacity was observed when the zeolite was modified with TETA in equimolar amounts to tetrahedral aluminium (NaY-TETA100). If the zeolite was modified with additional quantities of TETA (2:1 TETA/Al, NaY-TETA200) a decrease in the adsorption capacity under wet conditions was observed. Excess amounts of amine result in the loss of active sites hence an optimum amount of amine is essential to obtain high adsorption capacity from the modified adsorbent. Reduced accessibility of the sites is expected to be the origin of the reduced adsorption capacity.

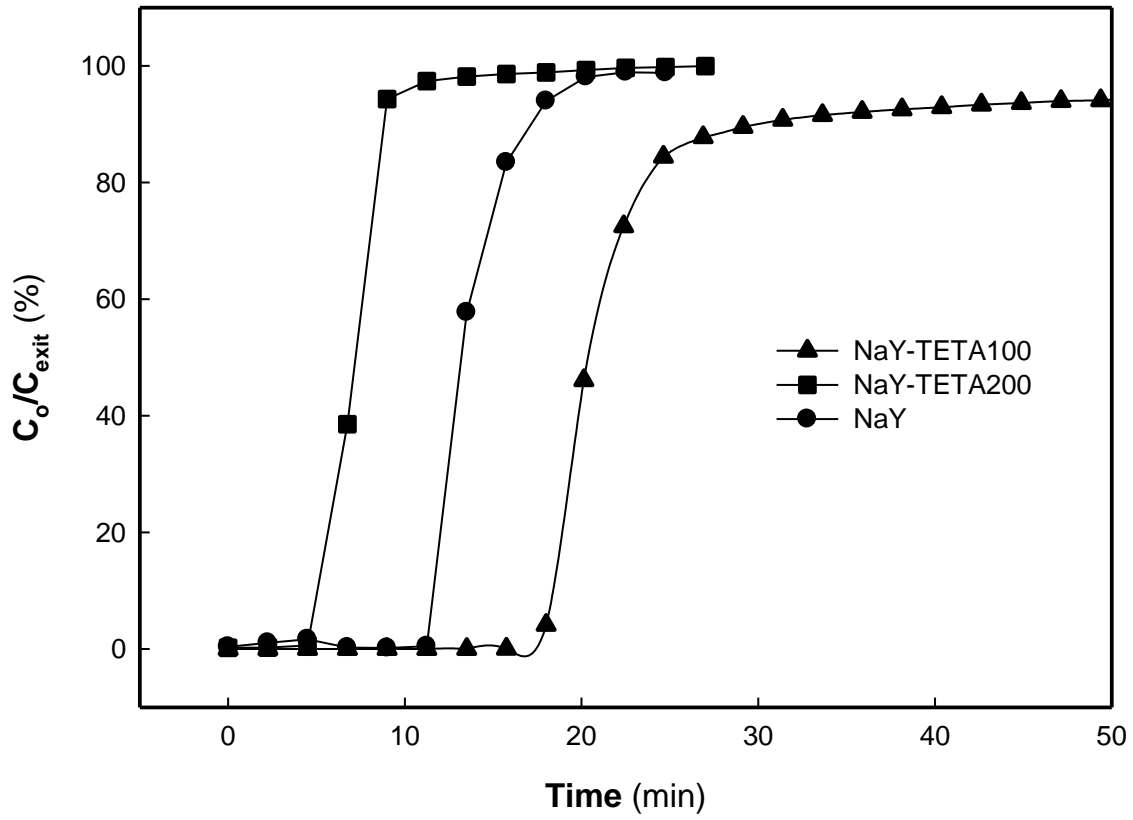


Figure 4 : Breakthrough curves of different samples at 30°C and 101.3 kPa in wet conditions

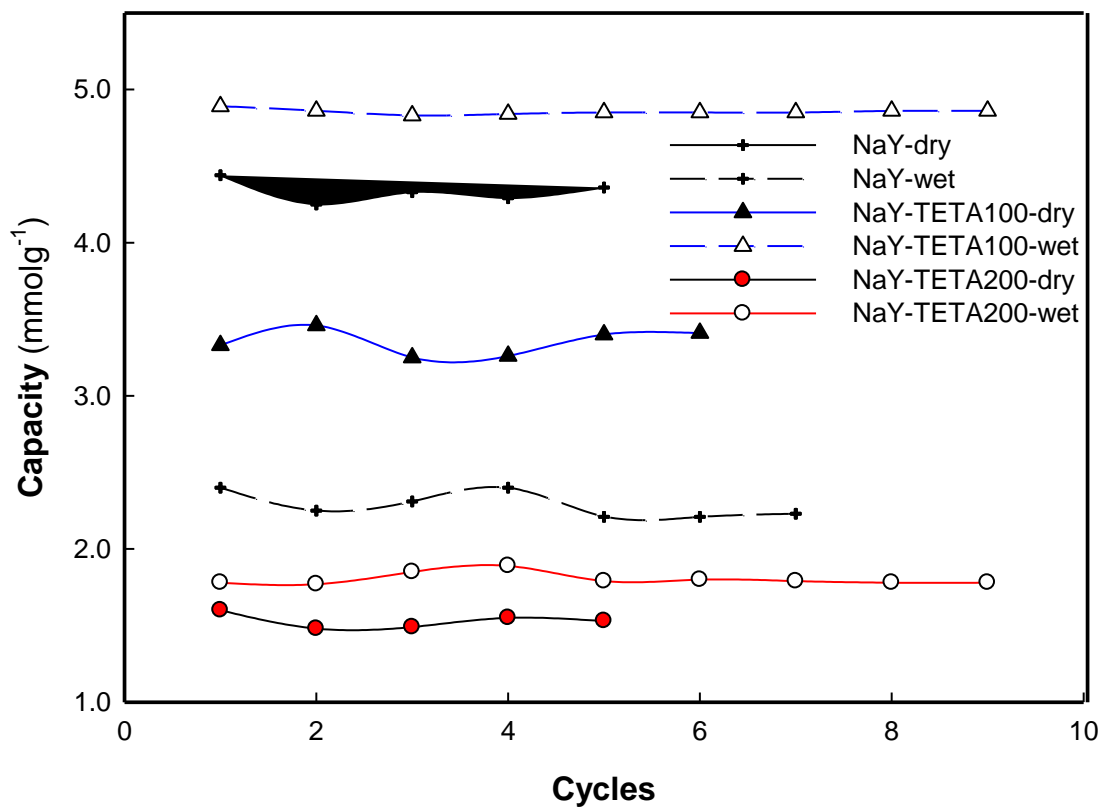


Figure 5: CO₂ adsorption capacity, as a function of adsorption cycle for NaY/NaYTETA100 and NaYTETA200 in dry and wet conditions

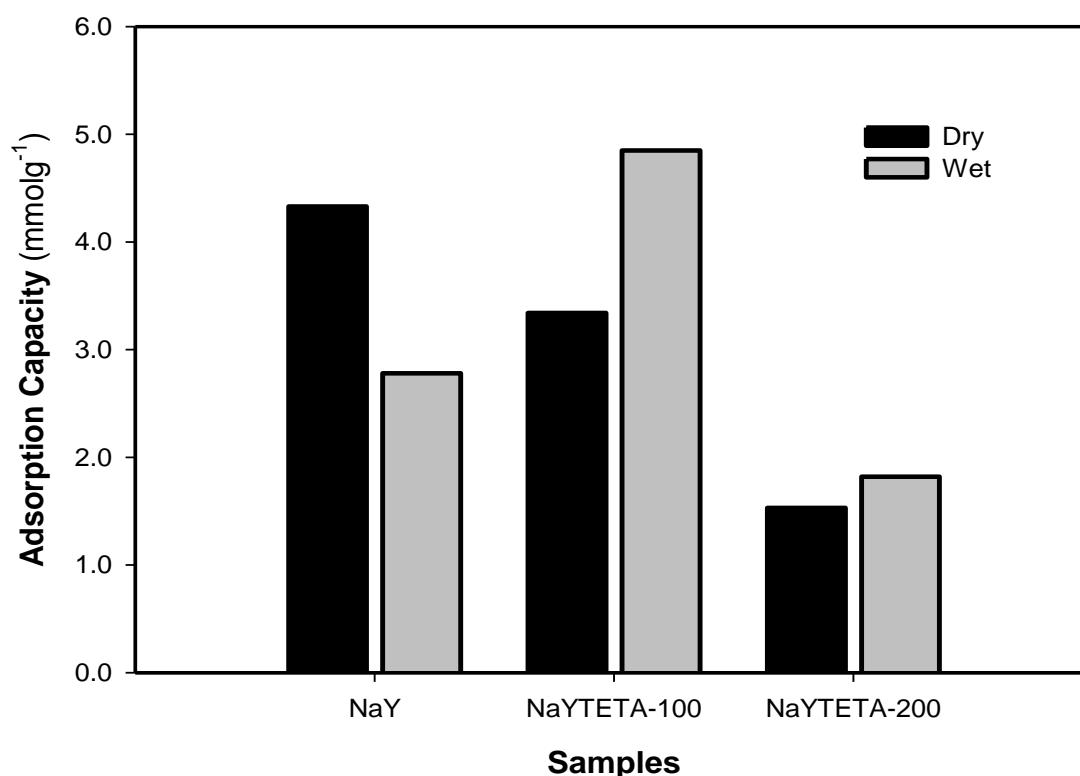


Figure 6: Capacity comparison of NaY and modified samples at 30°C, 101.3 kPa under moist conditions

Table 1: Basic characteristic details for substrate and product materials

Sample	$q_{dry}^{[a]}$ mmole CO ₂ g ⁻¹	$q_{humid}^{[b]}$ mmole CO ₂ g ⁻¹	$S_{Langmuir}^{[c]}$ [m ² /g]	$V_p^{[d]}$ [cm ³ /g]
NaY (Si/Al= 2.5)	4.33	2.28	694	0.33
NaY-TETA100	3.34	4.85	560	0.27
NaY-TETA200	1.53	1.82	435	0.21
NaY-TETA100+CuSO ₄	0.72	-	-	-

[a] Dynamic Capacity dry conditions [b] Dynamic Capacity humid conditions [c] Langmuir surface area [d] Pore volume

Conclusions

A modified adsorbent provides an increase in the capacity of CO₂ adsorption in the presence of water vapour, while showing excellent regenerability in cyclic use due to the attachment of amine groups onto the support via covalent tethering. Owing to its easy preparation, adsorption capacity, muticycle performance and excellent stability in moist gas streams, we suggest that NaY-TETA adsorbent may be considered as a practical CO₂ capture medium. It can be concluded from this study of finding CO₂ capture material that: the incorporation of amines onto solid support results in higher CO₂ uptakes in humid conditions anticipated for practical situation of separating CO₂ from flue gases.

There is clear relationship between the extent of CO₂ uptake and amine loading as well as the textural characteristics of the modified material.

Acknowledgment

The financial support for this research provided through the University of Newcastle International Postgraduate Research Scholarships (UNIPRS) and University of Newcastle Research Scholarship External (UNRSE) for this research is gratefully acknowledged.

Biography



Khalil Ahmad (Presenter)

Khalil Ahmad completed his Bachelor degree in Chemical Engineering at The University of the Punjab, Lahore (Pakistan). He commenced his Master's studies at the University of Newcastle in 2009. Currently, he is pursuing his research on Carbon Dioxide (CO₂) Capture from Point Sources Using Amine-Anchored Zeolites, under the supervision of Prof Eric Kennedy, Prof Bogdan Dlugogorski, Dr Michael Stockenhuber and Prof John Mackie.

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