



Amine-based CO₂ capture sorbents: A potential CO₂ hydrogenation catalyst

Srikanth Chakravartula Srivatsa*, Sankar Bhattacharya

Chemical Engineering Department, Monash University, Wellington Road, Clayton, VIC-3800, Australia

ARTICLE INFO

Keywords:

FTIR
CO₂ capture
Amine coverage
Carbamate
Carbamic acid

ABSTRACT

Mechanism of CO₂ adsorption on amine loaded SBA-15 sorbents with varying amine coverage has been assessed using thermogravimetric analysis (TGA) and in-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS). TGA study showed that sorbent adsorption capacities increased by 122–153% with CO₂ concentrations (5–80%) in the gas at 50/75 °C. The DRIFTS studies indicate that low amine loaded sorbents exhibit higher uptakes with an increase in CO₂ concentrations which is attributed to the mode of CO₂ adsorption i.e. 1:1 CO₂ to amine forming carbamic acid. At higher amine loadings CO₂ is adsorbed following the 1:2 CO₂ to amine forming carbamate-ammonium ions pair resulting in lower adsorption capacities per amine site. The studies also showed an increase in carbamic acid formation with pressure from 100 to 500 kPa at low amine loadings and both carbamic acid and carbamates at higher amine loadings. The paper provides insights into the mechanistic understanding of CO₂ adsorption behaviour of the varyingly covered amines on the SBA-15 support with a change in concentration and pressure of CO₂. The current work presents the conditions to alter the CO₂ adsorption mechanism on amine sites with potential application in CO₂ conversion to chemicals.

1. Introduction

Selective removal of CO₂ from industrial gas streams have been reported to be carried out by physical adsorption of CO₂ on materials like zeolites [1,2], metal-organic frameworks (MOF) [3,4], chemical absorption on to solvents [5–7], adsorption on solid amines [8–15] and membrane separations [16–18]. During the past decade, adsorption of CO₂ using amines immobilised on solid supports gained prominence to capture the CO₂ emission from coal-fired power plants. Amines immobilized on solid supports like Santa Barbara Amorphous, SBA-15 [19,20], Mobil Composition of Matter MCM-41 [21–23], SiO₂ [12,24,25], hierarchically porous silica HPS [26,27], ion-exchange based resin [28] and carbonaceous materials [11,13,29] are promising candidates with high adsorption capacities. Although many amine-based sorbents were identified as potential sorbents for CO₂ capture they either suffer from inferior CO₂ adsorption efficiency, lack of long-term cyclic stability in the long term or high final cost of the sorbent to capture CO₂. All the sorbents are tested for only for few cycles which does not give a true picture of the sorbent stability though might have high adsorption capacities. A recent work by Gadipelli *et al.* on amine loaded hyperporous graphene networks showed enormous promise with very high capture capacity of 7.5 mmol/g-sorbent [30]. The sorbents suffer degradation over long cyclic times due to the formation of urea in CO₂ environment or formation of N=O due to degradation of primary amine in the air [28].

However, the present work is focused on understanding the nature of CO₂ adsorption mechanism under varying adsorption conditions such as gas concentration and pressure and amine loading. The amine efficiencies (CO₂/N ratio) only remained < 0.4 in the majority of the sorbents suggesting the amine sites present in the sorbent remained significantly underutilized. Hence, it is important to identify possibilities which can allow these amine sites to participate in the CO₂ adsorption process and achieve higher adsorption [31] capacities and open opportunities for chemical production by CO₂ as reactant and amine site as an active site for CO₂ activation.

It is accepted that CO₂ is adsorbed on amines and produce carbamates which require two amine sites for its adsorption and stabilisation resulting in only 50% capture efficiency. However, the nature of adsorbed species can be varied depending on the amine loading, type of amine, density of amine sites and the molecular size of amine immobilised on the solid support and importantly the concentration of CO₂ or pressure used for the CO₂ capture. In our previous studies [32] the effect of Tetraethylenepentamine (TEPA) loading on the CO₂ adsorption on fresh and oxidative degraded TEPA/PEG/SiO₂ sorbents by FTIR revealed the presence of weakly and strongly adsorbed CO₂ and that their fractions depend on the amine loadings. At lower amine loadings, a higher amount of weakly adsorbed CO₂ was present and was removed easily by the flow of inert gas. At higher loadings, the adsorbed CO₂ was stabilised by the hydrogen bonding with adjacent amine molecules, thus producing a higher fraction of strongly adsorbed

* Corresponding author.

E-mail address: srikanth.chakravartula.srivatsa@monash.edu (S. Chakravartula Srivatsa).

CO₂ [32]. CO₂ adsorption on degraded oxidative sorbents showed an increase in the carbamic acid formation due to the isolation of amine sites and physisorption of CO₂ onto surface silanol groups [32]. When CO₂ is adsorbed as a carbamic acid, it requires only one amine site per CO₂ adsorption, which suggest that we can double the adsorption capacity of the sorbents by forming carbamic acid rather than carbamates. Hence, if the adsorption conditions are such that CO₂ is adsorbed on single amine site as carbamic acid, the adsorption capacities of the amine-based sorbents can be increased to two folds. The adsorption of CO₂ as carbamic acid on amine sites provides an opportunity to convert CO₂ to value-added chemicals such as formic acid or methanol in presence of H₂. To this extent, different amines sorbents were prepared and the adsorption conditions are varied to change the of adsorbed CO₂ species.

In the present work, we prepared four different amines with varying amine density are loaded onto the SBA-15 support. The sorbents were tested with varying CO₂ concentrations in the flue gas and different pressures to investigate the adsorbed species using in situ FTIR studies. The work highlights how the adsorbed CO₂ species on solid sorbents can be adjusted with varying amine loadings or change in the CO₂ concentrations or pressures to increase the adsorption capacity of sorbents.

2. Experimental

The following procedure was used to prepare the SBA-15 support used for the sorbent preparation. In a typical preparation, 7.8 g of Pluronic 123 surfactant (poly (ethylene glycol)-block-poly (propylene glycol)-block-poly (ethylene glycol) average MW ~5800, Aldrich Chemicals) was dissolved in 146 ml water and 6.2 ml anhydrous acetic acid solution (Aldrich Chemicals). The solution was stirred until all P123 had dissolved and a consistent, translucent appearance was achieved. 24.5 g of tetraethoxysilane (TEOS, Aldrich Chemicals) was added dropwise, and the solution stirred continuously at 40 °C for 20 h. This mixture was then transferred into a reagent bottle capable of withstanding pressure and was heated in an oven at 105 °C for 24 h. The solution was then centrifuged, the solid product extracted and washed with ethanol and water and dried in the oven at 105 °C overnight. The P123 template was removed by calcining the material at 500 °C for 5 h in the air.

The amines used in this study are 3-(aminopropyl) trimethoxysilane (APTS, Aldrich Chemicals), N-(3-Trimethoxysilylpropyl) diethylentriamine (Triamine, Aldrich Chemicals), and polyethyleneimine (PEI, 50 wt% in water, MW = 1200 Aldrich Chemicals).

Two grams of SBA-15 sample was treated in an oven at 100 °C for 12 h to remove moisture. The dehydrated sample was dispersed in a mixture of 3 mL of APTS or Triamine and 60 mL isopropanol and refluxed at 95 °C for 3 h. After refluxing, the suspended solid product was filtered and washed with anhydrous ethanol three times and then dried at 70 °C for two h in air to give APTS/SBA-15 and Triamine/SBA-15 sorbents. Sorbents with 10 and 25 wt% content of amine (PEI) on SBA-15 support were prepared by mixing SBA-15 with 10 mL of an ethanol solution containing the requisite amount of PEI. The mixtures were dried in an oven at 100 °C until all the ethanol was evaporated. In specific for PEI₁₀ sorbent 1.9 g of SBA-15 and 0.2 g of 50 wt% PEI in water was mixed with 10 ml of ethanol to disperse the amine on to the support and the excess ethanol and water was evaporated.

2.1. Characterization

N₂ adsorption/desorption isotherms on the SBA-15 and amine loaded sorbents were performed using the ASAP 2020 (Micromeritics USA). 100 mg of the sample was loaded into the sample tube and pretreated at 80 °C for 2 h. Low-temperature pretreatment was chosen to prevent the loss of amine under high vacuum treatment. The N₂ adsorption was performed at liquid nitrogen temperatures up to relative

P/P₀ of 0.995. Brunauer-Emmett-Teller (BET) surface area was measured by 0-0.3 P/P₀ and total pore volume by at 0.995 from the amount of liquid nitrogen adsorbed.

Amine loading on the sorbents was measured following an established procedure [33] by using Thermogravimetric analysis (TGA) (Model STA 449 F3 Jupiter, NETZSCH-Geratebau GmbH, Germany). 10 mg of the sample was pretreated at 105 °C for 30 min in the N₂ atmosphere to remove any pre-adsorbed CO₂ and water from the sample. The sample was then heated to 200 °C and 600 °C and held for 30 min respectively followed by heating to 900 °C where the N₂ gas is switched to Air for 30 min. The weight loss from 105 °C is considered as the amine loading on the sample. Elemental analysis was performed using Perkin Elmer-2400 series to determine % N content in the sorbents by combusting the sample at 950 °C.

Fourier Transform Infrared (FTIR) spectrum of the SBA-15 and sorbents was collected using Perkin Elmer Frontier FTIR with Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) accessory capable of high temperatures up to 850 °C and 34 bar pressure. The spectra were collected from 4000–1000 cm⁻¹ with 16 co-added scans at a spectral resolution of 4 cm⁻¹.

2.2. CO₂ adsorption/desorption

2.2.1. Thermogravimetric analysis

Measurement of the CO₂ adsorption capacity of various sorbents was carried out by taking 20 mg of the sample in the ceramic crucible. The sample was pretreated at 130 °C for 15 min in 100 ml N₂ flow and allowed to cool down to 50 °C in the same N₂ atmosphere. Varying concentrations of 5, 15, 30, 50 and 80% CO₂ balanced in N₂ at a flow rate of 100 ml/min for 30 min for the saturation of the sample. The samples were then purged for 15 min using N₂ flow at 100 ml/min, and Temperature programmed desorption (TPD) was performed by heating the sample from 50 °C to 130 °C at 5 °C/min and held at 130 °C for 15 min in N₂ flow 100 ml/min to completely regenerate the sorbent.

2.2.2. In-situ FTIR studies

In-situ FTIR studies using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) mode is performed to investigate the mechanism of CO₂ adsorption on various amine sorbent. FTIR is an analytical technique used to measure absorption of infrared radiation by the sample versus wavelength. FTIR give characteristics peaks for each chemical bond in the molecule when they are polar without overlapping. The vibrations bands can be observed simultaneously and continuously giving us a real-time understanding the mechanism involved in the adsorption-desorption process

The sorbents were pretreated by heating the sample from room temperature to 130 °C in the N₂ flow of 100 ml/min and held for 15 min before cooling down to 50 °C to conduct CO₂ adsorption/desorption cycles. The varying concentrations of CO₂ gas were achieved by controlling the flow rates of CO₂ and N₂ using mass flow controllers. Similar to TGA profiles CO₂ adsorption/desorption was carried out in FTIR-DRIFTS mode, except the CO₂ adsorption time was kept for only 10 min while N₂ purge for 5 min. The changes in the spectral features of the sorbent throughout the experiment were monitored in a continuous series scan single beam mode using Perkin Elmer Frontier FTIR with ten co-added scans at a resolution of 4 cm⁻¹. The single beam spectra are normalized according to the procedure reported before proceeding to absorbance spectra to observe the spectral changes in the sample during CO₂ adsorption [32]. Once all the spectra are normalized and absorbance spectra are obtained, the intensities against the desired wavenumbers with time can be plotted against to obtain the profile at each wavenumber.

To study the effect of pressure on CO₂ adsorption, the sorbents were initially saturated with 15% CO₂ for 10 min. The chamber was then set to batch mode closing the inlet and outlet valves. The pressure of the chamber was maintained using a back-pressure regulator to the desired

Download English Version:

<https://daneshyari.com/en/article/6528504>

Download Persian Version:

<https://daneshyari.com/article/6528504>

[Daneshyari.com](https://daneshyari.com)