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Mechanism of CO₂ capture in nanostructured sodium amide encapsulated in porous silica

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ABSTRACT

Nanostructured sodium amide encapsulated in a porous silica gel matrix (“NaNH₂-SG”) was investigated for CO₂ capture and storage by in-situ gravimetric gas sorption. Exposure of NaNH₂-SG to CO₂ at 25 °C and 1 bar pressure resulted in ~ 3.6 wt. % CO₂ uptake over eight sorption/desorption cycles. Over 90% of the CO₂ uptake was non-reversible due to reaction between CO₂ and NaNH₂ to form sodium carbamate, as confirmed by ¹³C and ²³Na solid-state NMR. Electronic structure calculations suggest a two-stage reaction process involving initial formation and subsequent rearrangement of the carbamate product. **This research confirms the feasibility of sequential reactions of nanoparticles in a porous substrate (Na-SG to NaNH₂-SG to Na-carbamate-SG), and of CO₂ capture by NaNH₂-SG nanoparticles stabilised by encapsulation within the porous substrate.** This encapsulation method could allow further hygroscopic or reactive starting reagents or compounds to be explored for CO₂ capture and long-term storage.

1. INTRODUCTION

Concern over the serious environmental and economic implications of climate change have prompted many countries to commit to lowering of CO₂ emissions.[1, 2] Currently, the majority of anthropogenic atmospheric CO₂ emissions originate from transportation and fossil fuel based power generation. A range of CO₂ capture and storage techniques such as chemical absorption, physical adsorption, cryogenic distillation, and membrane technologies have been explored,[3] for industrial post-combustion CO₂ capture (also known as flue gas scrubbing). Recently, use of alternative solid amine adsorbents have shown promise for CO₂ capture. These materials are prepared through the physical or chemical immobilisation of amines onto solid supports such as activated carbon,[4, 5] zeolites[6, 7] and porous silica.[8-11] As well as amines, solid sodium-based sorbents such as sodium hydroxide and sodium carbonates have been investigated for CO₂ capture.[12, 13] The use of more strongly reactive compounds such as sodium amide has also been proposed, but their chemical instability limits their usefulness. The reactivity of sodium amide with CO₂ opens up possibilities for accessing long-term CO₂ storage, such as is used in mineralisation[14], provided the drawbacks associated with the chemical instability and pyrophoric nature of such compounds can be overcome.

This work examines the interaction of CO₂ with crystalline sodium amide nanoparticles that have been encapsulated in a porous silica matrix. This material, hereafter called NaNH₂-SG, enabled the stabilization of the highly reactive sodium amide compound, potentially making it useful as a solid CO₂ sorbent. The feasibility of CO₂ capture and storage using this NaNH₂-SG material was then investigated using experimental and computational approaches. This work demonstrates the feasibility of successive reactions (Na-SG to

NaNH₂-SG to Na-carbamate-SG) in nanoparticles encapsulated within a porous silica matrix.

2. EXPERIMENTAL METHODS

2.1. Preparation of the NaNH₂-SG

NaNH₂-SG was prepared[15] by saturating a commercially available sodium-loaded silica gel material (Na-SG) with ammonia.[16] The commercially-available starting material (sodium encapsulated in a porous silica gel, denoted as Na-SG, 37 wt. % Na),[16-18] is produced by agitation of a mixture of molten sodium and silica gel. As synthesized, the Na-SG is a coarse black powder with nano-sized sodium particles dispersed within the pores of a silica matrix, the pore diameters being up to 150 nm[17]. ~ 0.5g Na-SG was exposed to gaseous anhydrous ammonia in a differential tubular reactor at 338 K for over 20 h, upon which the material changed colour from black to brown due to the *in-situ* formation of a sodium amide contained in the pores of the silica matrix; this material is henceforth denoted as NaNH₂-SG.[15] The degree of conversion of Na to NaNH₂ was calculated using *Equation 1* and *Equation 2* to be approximately 24 ± 3 % by mole, the variance being estimated from five separately produced samples.

$$w_{Na} = w_{Na-SG} \times 37 \% \quad \text{Equation 1}$$

$$\text{Conversion} = \frac{\frac{w_t - w_{Na-SG}}{M_{NH_2}}}{\frac{w_{Na}}{M_{Na}}} \times 100 \% \quad \text{Equation 2}$$

where w_{Na} is the weight of Na in the Na-SG, w_{Na-SG} is the total weight of Na-SG starting material, w_t is the weight of the synthesized sample of $NaNH_2$ -SG, M_{Na} is the molar mass of Na and M_{NH_2} is the molar mass of NH_2 .

A similar process (using hydrogen as the reactant gas) was used in previously by the authors to synthesize an encapsulated sodium hydride, NaH-SG.[19] The resulting encapsulated $NaNH_2$ -SG, as with the NaH-SG[19], did not display any pyrophoricity. Furthermore, it can be observed visually that the encapsulated $NaNH_2$ -SG material oxidises/hydrolyses at a lower rate compared to the bulk Na amide, which would burst into flames in air. The oxidation of the $NaNH_2$ -SG occurs more slowly (over several minutes) and is characterized by an irreversible colour change from brown to white.

2.2. Structural characterization

Scanning Electron Microscopy (SEM) backscattered imaging and Energy Dispersive X-ray Spectroscopic (EDS) analyses were carried out with a JSM-7600F field emission scanning electron microscope (FESEM). High Resolution Transmission Electron Microscopy (HRTEM) analysis was carried out on a JEOL JEM-2100F equipped with a 200 kV field emission gun and integrated with Energy Dispersive X-ray Spectrometry (EDS) on samples suspended in ethanol and deposited on holey-carbon grids. Particle size distributions were determined from TEM images using ImageJ software.

The specific surface areas of the SG and $NaNH_2$ -SG after CO_2 sorption were obtained using multipoint BET analysis applied to N_2 sorption data collected on a Micromeritics 3Flex volumetric gas sorption analyser at 77 K in the relative pressure (P/P_0) range 0.05 - 0.3. The samples were dried at 60 °C for 8 h in the vacuum oven and then outgassed *in situ* under

dynamic vacuum (10^{-7} mbar) at 60 °C for 8 h on the 3Flex prior to N₂ gas sorption measurement at 77 K. Since the pore structure of the silica gel has been well-characterized previously, full N₂ adsorption-desorption isotherms were not collected in this study.

Solid-state NMR spectra (¹³C and ²³Na) were obtained at the EPSRC UK National Solid-State NMR Service at Durham, on ~100 mg samples of NaNH₂-SG after exposure to 1 bar CO₂. Measurements were taken on a VNMRS 400 for both nuclei. For the ¹³C-NMR, frequencies of 100.562 MHz and 50.32 MHz were used for cross polarized (CP) and magic angle spinning (MAS) respectively. Neat trimethylsilane was used as a reference. The ²³Na-NMR was recorded with a frequency of 105.784 MHz using MAS, in direct excitation mode without ¹H decoupling. For a reference, 1 mole of aqueous sodium chloride was used.

¹H NMR and ¹³C NMR were also used to identify the reactant products after exposure of the NaNH₂-SG to CO₂. The NaNH₂-SG after CO₂ cycling was analysed by fully quenching the sample with D₂O, and analysing the supernatant by NMR.

2.3.CO₂ sorption procedures

In-situ CO₂ sorption experiments were performed on a Hiden Isochema Intelligent Gravimetric Analyser (IGA). All sample handling was done under an inert N₂ atmosphere (BOC 99.998 % purity). ~100 mg of NaNH₂-SG was degassed prior to analysis under high (3×10^{-6} mbar) vacuum at 80 °C until a stable dry weight was reached (~12 h). The temperature of the reactor chamber was controlled by a R4 refrigerated bath, Grant Instruments at 25 °C. CO₂ gas (BOC, 99.998 % purity) was subsequently introduced at 25 °C at a rate of 30 mbar min⁻¹ to a pressure of 1 bar, with the final pressure maintained for a minimum of 720

minutes to allow the system to reach equilibrium. To study the behaviour of the system under cycling, the adsorbent was exposed to high vacuum in situ at 25 °C after every sorption cycle, until no further decrease in weight was observed (approx. 600 mins), before starting the sorption step of the next cycle. Sorption was expressed in weight %, using the initial weight of the dry material (after degassing) as the basis.

Control experiments were performed using a ~100 mg sample of pure silica gel (SG) (Sigma Aldrich, Davisil®, Grade 646, size 150 Å, 35-60 mesh), in order to distinguish between CO₂ adsorption onto the silica framework and reactions with the contained nanoparticles of sodium amide. The SG control sample was dried overnight in a vacuum oven at 150 °C prior to loading onto the IGA microbalance under inert conditions. The CO₂ adsorption and desorption isotherm of the pure SG was measured on the IGA up to a pressure of 1 bar at 25 °C. The reaction of CO₂ with pure NaNH₂ was not performed in this study due to the known risk of producing explosive compounds.

2.4.Molecular simulation

Density Functional Theory (DFT) calculations to investigate a proposed reaction pathway between CO₂ and sodium amide were carried out in the gas phase, with a default pressure (1 bar) and temperature (298.15 K), using the M06-2X functional and the 6-311++G(d,p) split-valence triple ζ basis set with polarisation and diffuse functions. The basis set was selected to account for potential anions and non-bonding interactions. The M06-2X functional is one of the hybrid meta-generalised-gradient-approximation (hybrid meta-GGAs) exchange-correlation functionals developed by Truhlar *et al.*[20] M06-2X includes 54% of

Hartree-Fock exchange, and has been parameterised for non-metals and is recommended for application in main group thermochemistry, kinetics and the study of non-covalent interactions.²¹ All geometries were fully optimised without symmetry or geometry constraints, but only the most stable conformational isomers are reported for all intermediates. The nature of all the stationary points as minima or transition states was verified by calculations of the vibrational frequency spectrum: local minima are characterised by the absence of an imaginary mode, whereas transition states were characterized by precisely one imaginary mode corresponding to the intended reaction. These were augmented by an intrinsic reaction coordinate (IRC) calculation to confirm reaction identity. [21-23] Free energies were calculated within the harmonic approximation for vibrational frequencies. All modelling was carried out using the Gaussian09 suite of codes.[24] Full coordinates for all stationary points, together with computed free enthalpies and vibrational frequency data, are available via the corresponding Gaussian 09 output files, stored in the digital repository DOI: [10.6084/m9.figshare.3081643](https://doi.org/10.6084/m9.figshare.3081643).

3. RESULTS AND DISCUSSION

3.1. Sorption of CO₂ in NaNH₂-SG-CO₂ and SG-CO₂ systems

The interactions of CO₂ with the SG and the synthesised NaNH₂-SG material were investigated via gravimetric gas sorption analysis and showed noticeably different sorption behaviours. Adsorption of CO₂ at

25 °C and 1 bar on the bare SG material

resulted in an almost linear CO₂ sorption isotherm characteristic of weak physical adsorption, with a CO₂ loading of ~1.7 wt. %. This adsorption was almost fully reversible, with the adsorbed gas quickly removed under high vacuum at 25 °C (**Figure 1**). The corresponding measurement of CO₂ on NaNH₂-SG at 25 °C resulted in a Type I isotherm with a maximum uptake of ~ 2.7 wt. % at 1 bar and incomplete desorption, showing a much stronger interaction with the CO₂ as a result of the encapsulated NaNH₂.

Figure 2: (left) Kinetics of CO₂ adsorption on the pure SG at 25 °C up to 1.2 bar as measured by gravimetric gas sorption; (right) Gravimetric CO₂ sorption at 1 bar at 25 °C on NaNH₂-SG, and desorption under vacuum. showing high CO₂ retention even upon application of high vacuum (at ~720 mins). The black lines in each plot represent weight change (wt%) and the red lines indicate CO₂ pressure in mbar.

The CO₂ sorption on the NaNH₂-SG as a function of time was investigated to determine adsorption kinetics. Figure 2 shows the kinetics of CO₂ adsorption on the SG at 25 °C up to 1.1 bar, indicating that the entire isotherm took ~260 min over 13 steps and equilibrated over 20 min for each dosing step. The CO₂ loading of ~ 2.7 wt. % on NaNH₂-SG at 1 bar agreed with the equilibrium adsorption capacity shown in Figure 1 but illustrates the significant difference in equilibration times between the SG and NaNH₂-SG materials. The CO₂ uptake in the NaNH₂-SG was largely irreversible under high vacuum at 25 °C and characteristic of strong-

er sorption interactions compared to the SG substrate which showed almost complete reversibility with decreased CO₂ gas pressure (see Figure 1). Indeed, only 0.3 wt. % reversibly desorbed over 600 min in the NaNH₂-SG at high vacuum (Figure 2). This largely irreversible uptake demonstrates that the dominant mechanism in the case of the NaNH₂-SG was not pure physisorption onto the porous silica, but either the result of strong binding (chemisorption) of molecular CO₂ to the sodium amide in the pores of the silica matrix, or a chemical reaction between the amide and the CO₂, as would be expected for a non-encapsulated amine/amide. In the case of the NaNH₂-SG the CO₂ uptake had not reached a plateau even after 720 minutes, even though the equilibration times used here would typically be ample for physical adsorption of CO₂ (as exemplified by the isotherm of CO₂ on SG in Figure 2).

To examine the stability and further investigate the CO₂ saturation of NaNH₂-SG, the material was cycled between 1 bar CO₂ pressure and high vacuum over 8 cycles at 25 °C. This cycling resulted in an irreversible weight increase after each sorption cycle, accompanied by a smaller reversible component, to a saturation limit of ~3.6 wt. % by the 8th cycle (Figure 3). The total weight increase was concluded to result from two effects: ~3.3 wt. % weight gain from the irreversible interaction between CO₂ and NaNH₂ (the dotted line in Figure 3) and ~0.3 wt. % from the reversible physisorption of CO₂ onto the porous silica. The irreversibility of the strong binding would prevent the use of the solid material for pressure-swing adsorption/desorption, but is a valuable feature for long-term CO₂ capture and storage.

During cycling, the NaNH₂-SG changed colour from dark brown to light pink while retaining its granular morphology, indicating a reaction between the CO₂ and the encapsulated sodium amide (see Figure 3).

**Figure 3: CO₂ capture
25°C under CO₂ pres-**

tween 1 bar and high vacuum.

**cycles of NaNH₂-SG at
sure, alternating be-**

Srivastava *et al.* described the reaction (1),²⁶

as an intermediate during the formation of ammonium carbamate from ammonia and carbon dioxide (reaction 2):

The colour change accompanying the conversion of NaNH₂ to sodium carbamate encapsulated in the silica matrix can be attributed to the reaction (3):

Figure 5 (a) Na-SG (black powder), (b) NaNH₂-SG, and (c) sodium carbamate in SG.

From Figure 3, the amount of weakly adsorbed and partially reversible CO₂ uptake for the NaNH₂-SG remained relatively constant (~0.3 wt. %) during cycling at 25 °C, while the differential weight gains due to the irreversible component gradually decreased with number of cycles as the NaNH₂ became saturated with CO₂.

After the 8th cycle, the sample was heated under vacuum to 80 °C for 120 min, and showed removal of ~0.6 wt. % of the weakly bonded CO₂.

TEM images of the NaNH₂-SG after eight CO₂ sorption cycles showed the persistence of distinct, isolated nanoparticles dispersed within the silica matrix (*Figure 5*). In addition, ImageJ analysis of the TEM images showed a normal distribution of particle sizes over the range of 10 – 90 nm with mean diameter of 46 ± 0.8 nm, consistent with previous

reports.[15, 19] Scanning electron microscopy (SEM) after CO₂ uptake showed large openings or cavities on the surface of the porous silica (*Figure 5 c and d*). Taken together, these results confirm that nanostructured crystalline sodium compounds were encapsulated within the porous silica. The morphological similarity observed in this case to those seen during the formation of NaH-SG and NaNH₂-SG[15, 19] indicates CO₂ capture proceeds without disrupting the silica matrix.

The rapid CO₂ uptake in each cycle is consistent with initial adsorption between CO₂ and NaNH₂-SG prior to the irreversible strong interaction. However, the observed weight gain of 3.3 wt. % seen for the NaNH₂-SG is much lower than the theoretical weight gain predicted for carbamate formation (15.2 wt. %, based on the 24 % conversion of Na to NaNH₂, as measured gravimetrically). The presence of the Na-NH₂ groups already coordinated to CO₂ groups could be responsible for hindering the diffusion and further conversion of CO₂ into the pores. Thus, the formation of the stronger interactions between the Na-NH₂ and the CO₂ may be diffusion limited once the NaNH₂ at the entrance of the pores is saturated. The larger measured BET surface area of the pure SG (330 m² g⁻¹), compared to the NaNH₂-SG (228 m² g⁻¹) accounts for the slightly higher wt. % of reversible physisorption of CO₂ on the SG substrate while the smaller surface area of the sodium carbamate-SG can be attributed to occlusion of pores by the nanostructured sodium compounds. To investigate this further, NMR and molecular modelling were employed to identify potential reaction products.

3.2.Molecular simulations of reaction pathway

DFT calculations in the gas phase are able to provide information about the potential reaction products, although it is important to note that it does not model the effect of the encapsulation in NaNH₂-SG. The complex nanostructure of the material and the amorphous SG structure make it impractical to carry out solid-phase calculations using a periodic unit cell.

The Gibbs free energy profile of the most favourable reaction shows the reaction of CO₂ + NaNH₂ proceeds in two thermodynamically favoured steps (*Figure 6*). The first step is the nucleophilic attack of the nitrogen atom of NaNH₂ on the electrophilic carbon atom of carbon dioxide ($\Delta G = -25.6 \text{ kcal mol}^{-1}$), *Figure 6*. The second step is the transfer of the sodium atom from nitrogen to the oxygen of the newly formed carbamate species ($\Delta G = -15.8 \text{ kcal mol}^{-1}$). Limiting energy barriers of $\Delta G = +2.3$ and $+3.0 \text{ kcal mol}^{-1}$ for the nucleophilic attack and the sodium transfer steps respectively are low enough for the reaction to proceed readily at 25 °C. All transition states were characterised by normal coordinate analyses, revealing precisely one imaginary mode corresponding to the intended reaction. In both cases, this was augmented by intrinsic reaction coordinate (IRC) calculations (for TS₁₋₂, the flat energy surface limited the exploration to one direction), which also confirmed the identity of the reaction (see *Figure 7* and *Figure 8*). The overall ΔG of the reaction is calculated to be $-41.4 \text{ kcal mol}^{-1}$ at 298 K. The formation of sodium carbamate from carbon dioxide and

sodium amide is therefore strongly thermodynamically favoured, and is consistent with the irreversible CO₂ uptake of the NaNH₂-SG observed experimentally. While the encapsulation effect is not considered in the calculations (*vide supra*), it is logical that, due to the effects of increased local reactant concentration resulting from CO₂ excess adsorption, encapsulation would likely further favour the reaction of sodium amide with CO₂ both kinetically and thermodynamically.

Figure 7: Computed intrinsic reaction coordinates for transition state TS₁₋₂ showing the nucleophilic attack of sodium amide on carbon dioxide.

Figure 8: Computed intrinsic reaction coordinate for transition state TS₂₋₃ showing rotation of the sodium atom from the nitrogen atom to the oxygen atoms of the carbamate 3.

3.3.NMR analysis of reaction products

To confirm the chemical conversion of CO₂ into carbamate, solid state ¹³C-NMR was carried out on a NaNH₂-SG sample exposed to 1 bar CO₂. A spectrum recorded in cross polarisation (CP) mode showed two distinct signals at 164.69 ppm and 170 ppm (*Figure 9 a*). Both of those signals lie in the carbamate region of the spectrum. To give a CP signal those species must have a reasonably close relationship to ¹H. The ²³Na SS NMR spectrum showed two signals at 4.63 ppm and 6.43 ppm (*Figure 9 b*), which can be assigned to two different environments of sodium in the vicinity of carbamate and could feasibly correspond to states 2 and 3 of the DFT calculations.

Figure 9: (a) CP Solid State ¹³C-NMR spectrum of NaNH₂-SG-CO₂ (Peak around 25ppm is contamination due to finger grease); (b) Solid State ²³Na-NMR spectrum of NaNH₂-SG-CO₂; (c) ¹³C NMR spectrum in D₂O of NaNH₂-SG-CO₂ after liquid extraction.

In order to further investigate the formation and persistence of carbamate species in our material after CO₂ exposure, the CO₂-loaded NaNH₂-SG was opened, fully quenched with D₂O, and the supernatant obtained analysed by NMR. The ¹H NMR spectrum is essentially featureless with no observable peaks. The ¹³C NMR spectrum displayed a sole singlet at 168.23 ppm (see *Figure 9 c*). The direct reaction of sodium amide with water would only produce sodium hydroxide and water with no carbon-containing species. The signal ob-

served could correspond to either a carbamate or a carbonate species. Gottlieb *et al.* [25] reported ^{13}C NMR chemical shifts of 168.88 ppm for sodium carbonate and 161.08 ppm for sodium hydrogen carbonate in D_2O , while 161.97 ppm has been reported for ammonium carbamate in D_2O .^[26] Based on ^{13}C NMR, the compound extracted with D_2O could be a carbamate or a mixed sodium/ammonium carbonate species, formed by hydration of sodium carbamate (see Scheme 1).

Scheme 1: Potential hydration reaction of sodium carbamate species leading to mixed sodium/ammonium carbonate species.

Preliminary DFT calculations to investigate the latter proposed reaction, using the same level of theory as before but augmented with a self-consistent-reaction-cavity continuum solvation model to account for the solvent water (protocol SCRF=(cpcm, solvent=water)) found in Scheme 1, is slightly unfavourable thermodynamically ($\Delta G = +3.1 \text{ kcal mol}^{-1}$ at 298 K). However, given the uncertainties involved in the calculation and the small ΔG , the reaction cannot be ruled out. While further work is needed to establish the exact nature of the species extracted from $\text{NaNH}_2\text{-SG-CO}_2$, it is apparent that $\text{NaNH}_2\text{-SG}$ does react with CO_2 , with the calculations supporting the evidence for formation of the carbamate species from the experimental measurements.

4. CONCLUSION

The interaction of carbon dioxide with a nanostructured sodium amide contained within silica gel was investigated as a potential method of carbon capture and storage. The materi-

al contained nano-sized particles of crystalline sodium compounds with an average particle size of 46 ± 0.8 nm dispersed within the porous silica matrix. The $\text{NaNH}_2\text{-SG}$ displayed the ability to capture up to 3.6 wt. % CO_2 at 25 °C. Cycling CO_2 uptake on $\text{NaNH}_2\text{-SG}$ showed that compared to SG, there is a small reversible physical CO_2 adsorption and a larger irreversible uptake of ~ 3.3 wt. % which was attributed to a chemical reaction of the CO_2 with $\text{NaNH}_2\text{-SG}$. The irreversible uptake, retained under high vacuum, would prevent the use of the solid material for pressure-swing adsorption/desorption, but is a potentially valuable feature for long-term CO_2 capture and storage.

The DFT modelling suggests conversion of NaNH_2 to sodium carbamate, with SSNMR providing experimental evidence for formation of a sodium carbamate species. The demonstration of successive reactions of a solid reagent within the porous silica gel framework ($\text{Na-SG} \rightarrow \text{NaNH}_2\text{-SG} \rightarrow \text{sodium carbamate-SG}$) opens up the possibility of encapsulating further highly reactive compounds into porous materials for solid CO_2 capture. In addition, it highlights the potential for the encapsulation of hygroscopic or reactive starting materials within frameworks to stabilise and enable otherwise unfavourable or unsafe reactions. The measured irreversible CO_2 uptake of ~ 3.3 wt% is notably less than what would be expected for a stoichiometric conversion to the carbamate. This indicates that while the encapsulation may allow use of these reactive NaNH_2 species, the pore sizes or distributions of the active species may need to be more closely controlled to manage steric factors limiting the access to the reactive sites. If the degree of uptake could be increased closer to the stoichiometric value (~ 15 wt. % for this material) and long term retention could be confirmed,

carbon capture in a porous reactive solid may be a useful complement to promising but geographically restricted approaches such as mineralization[14].

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Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9