



Hydrotalcite/SBA15 composites for pre-combustion CO₂ capture: CO₂ adsorption characteristics

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ABSTRACT

Hydrotalcite-like compounds (HT) show potential as CO₂ adsorbent materials for pre-combustion CO₂ capture applications, but require improvements in stability, adsorption capacity and kinetics. In this study, HT/SBA15 hybrids (with different Mg/Al ratios varying from 0.3 to 3) have been synthesised using a two-stage grafting method to coat a mesoporous SBA15 with hydrotalcite layers. The HT/SBA15 hybrids showed significant improvement in intrinsic CO₂ uptake (per mass of HT), initial uptake rate, and multicycle stability compared to unsupported HT. Compared to previously reported nanostructured carbon supports (e.g. CNF, MWCNTs), the HT/SBA15 hybrids were found to be more thermally stable and exhibit comparable adsorption uptake and rates. In particular, the use of SBA15 as a support is shown to prevent the gradual loss in weight from thermal decomposition observed for HT/MWCNT or HT/GO composites over extended cycling.

1. Introduction

Over the last decades there has been widespread concern about the increasing concentration of carbon dioxide in the atmosphere due to anthropogenic activities, with fossil fuel combustion being the main CO₂ source [1]. There is, therefore, strong motivation in developing suitable processes for carbon dioxide capture and storage (CCS). Among a range of technologies suggested for this purpose, gas-solid adsorption appears as one of the most promising strategies for CO₂ capture applications. Unlike liquid sorbents, solid adsorbents can be used over a wide temperature range. Pre-combustion carbon capture is an attractive approach to CCS in which a developing technology is sorption-enhanced H₂ production, which operates between 573 and 773 K [2–4]. Numerous studies have proposed the use of hydrotalcite-like compounds for application as adsorbent materials in sorption-enhanced H₂ production [2–4].

Hydrotalcite-like compounds (HTs), also known as mixed-metal layered hydroxides or layered double hydroxides (LDHs), belong to a large class of anionic and basic clays. Their structure is composed of brucite Mg(OH)₂ layers, where Mg²⁺ is octahedrally coordinated by hydroxyl groups. These octahedra share adjacent edges to form sheets or layers. In HTs, some of the Mg²⁺ ions are replaced by Al³⁺ resulting in positive layers that are balanced by charge-compensating anions (e.g. Cl⁻, CO₃²⁻, SO₄²⁻) located in the interlayer region, where hydrating

water molecules are also accommodated. The general formula of HTs is: (M_{1-x}²⁺M_x³⁺(OH)₂)^{x+}(A_{x/m}^{m-}·nH₂O)^{x-} where M²⁺, M³⁺ and A^{m-} commonly represent Mg²⁺, Al³⁺ and CO₃²⁻ respectively. Compared to other adsorbents, HTs are competitive at temperatures between ~473 K and ~723 K, exhibiting fast adsorption-desorption kinetics and being positively influenced by the presence of water [2,5]. In addition, they require less energy to be regenerated and show better stability upon cycling than other potential CO₂ adsorbents (e.g. calcium oxides) [3]. However, a major drawback of HTs for commercial use is their relatively low CO₂ adsorption capacities. In order to alleviate this weakness and to improve their overall adsorption performance, many studies have focused on modifying the chemistry of HTs by exchanging their structural ions and/or by incorporating alkali dopants [4,6–8]. It has also been reported that the CO₂ performance of HTs can be improved by supporting them with forms of carbon such as nanofibers (CNF) [6], multi-walled nanotubes (MWCNT) [9] and graphene oxide (GO) [10–12]. Although significant enhancement in terms of intrinsic capacity and regenerability have been achieved by the use of these carbon materials, thermal degradation of the support was observed over extended multicycles [10–12]. Composite mixtures of hydrotalcite with a more thermally stable material such as alpha alumina did not result in as marked enhancement of the activity or the stability as the observed with the nanostructured carbon supports [10,11].

Mesoporous silicas have been widely investigated as support

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materials in CO₂ sorption applications due to their pore structure, high surface area and hydrothermal stability. They have been functionalised with amines/polyetheneimine for low temperature CO₂ adsorption [13–18] and used as support for high temperature CO₂ adsorption by CaO-based sorbents [19]. Recently, Pramod et al. [20] investigated the CO₂ adsorption performance of HT-SBA15 composites at low temperature (343 K). Composites with Mg/Al ratio = 2 and a range of HT contents up to 50% were prepared by co-precipitation in an aqueous suspension of SBA-15. The HT/SBA15 adsorbents showed enhanced adsorption capacities and adsorption kinetics over pure hydrotalcite. Multicycle stability was also demonstrated over five cycles of adsorption at 343 K and desorption at 413 K. Very recently, Yilmaz [21] assessed the CO₂ adsorption performance of an amine modified hollow mesoporous silica-Mg-Al HT composite which showed high CO₂ uptake at 348 K and was found to be stable over four adsorption-desorption cycles. These studies demonstrate the utility of mesoporous silicas, and SBA-15 in particular, as support material for HT in CO₂ adsorption processes. However, the adsorption temperatures have been much lower than would be used in pre-combustion CCS or in the sorption enhanced water gas shift reaction (SEWGS).

In this paper we report the synthesis of HT/SBA15 hybrids with different Mg/Al ratios and their CO₂ adsorption performance tested at the higher adsorption temperature relevant for pre-combustion CCS applications (573 K) in contrast to earlier work on this type of material. The present HT/SBA15 composites were prepared free from residual sodium following a methodology adapted from the grafting approach reported recently by Creasey et al. [22]. The two step preparation method allows easy adjustment of the Mg/Al ratio while keeping the Al constant, and in principle, should favour porosity and mass transport involving the underlying silica architecture. We show that the SBA15 support confers significant advantage in terms of enhanced intrinsic adsorption capacity and adsorption kinetics compared to unsupported HT and previously reported HT-MWCNTs adsorbents [9]. The composites have also been tested over extended adsorption-desorption cycles and show good relative thermal stability and exhibit no gradual loss in weight which is a feature of HT on carbon nanostructure supports.

2. Experimental section

2.1. Materials

A mesoporous SBA15 was purchased from ACS Chemicals Supplier; aluminium-*tri-sec*-butoxide, triethylamine, magnesium methoxide solution, methanol, toluene, ethanol, Mg(NO₃)₂·6H₂O (99%), Al(NO₃)₃·9H₂O (98%), NaOH and Na₂CO₃ were purchased from Sigma-Aldrich.

2.2. Alumina grafting onto SBA15 (Al-SBA15)

The Al-SBA15 framework was synthesised following a methodology adapted from Creasey et al. [22] Triethylamine (0.525 mL) and SBA15 (0.25 g dried at 373 K), were added to a solution of 0.59 M Aluminium-*tri-sec*-butoxide in toluene. The resulting suspension was heated at 358 K for 6 h under stirring (300 rpm). The resulting suspension was filtered under vacuum using 0.4 µm polycarbonate membranes and washed three times with 25 mL of toluene at 333 K. The alumina surface was then hydrolysed in a mixture of ethanol (79.5 mL) and water (0.4 mL) for 24 h at 298 K under stirring. The solid was filtered using 0.4 µm polycarbonate membranes and washed with 75 mL of ethanol. The sample was dried for 12 h at 353 K. To produce an alumina monolayer in the sample, a three-step calcination sequence was used: The material was first heated to 523 K for 1 h, then 673 K for 1 h and finally 773 K for 4 h (at 1 K min⁻¹). Four consecutive grafting cycles were carried out using the same procedure (using 1 g of Al-SBA15 solid produced in the previous cycle).

2.3. Synthesis of hydrotalcite-coated SBA15 (HT-SBA15)

The as-synthesised Al-SBA15 sample (100 mg) was dried for 1 h at 353 K and then promoted by incipient wetness impregnation with a magnesium methoxide solution (8–10 wt% in CH₃OH). The sample was then stirred for 15 min and dried at 353 K for 1 h to remove the excess methanol. The volume of magnesium methoxide was varied to produce samples with different Mg:Al atomic ratios. 2.7 mL were used for the sample with a Mg:Al ratio 1:1. Subsequently, the sample was calcined at 723 K at 1 K min⁻¹ for 15 h under 20 mL min⁻¹ O₂. The sample was then cooled down to 298 K flowing 20 mL min⁻¹ N₂. For every 75 mg powder, 12.5 mL of distilled water was added. The sample was then heated to 398 K and stirred overnight. Then, it was cooled down to room temperature, filtered, washed with 500 mL of water and dried in an oven for 24 h at 353 K. Four different HT-SBA15 hybrids were prepared with nominal Mg:Al ratios 0.3/1 (HT-SBA15-0.3), 1/1 (HT-SBA15-1), 2/1 (HT-SBA15-2) and 3/1 (HT-SBA15-3). A conventional hydrotalcite (HT) reference material with a Mg:Al ratio 2:1 was prepared via a coprecipitation technique (details are given elsewhere) [10].

2.4. Characterisation

The specific surface area and pore structure of the samples was determined by Brunauer–Emmett–Teller (BET), in which N₂ adsorption isotherms were measured at 77 K using a Tristar 3000 volumetric system. The samples were degassed at 393 K overnight under nitrogen. The phase composition of the samples was analysed by X-ray diffraction using a X'celerator detector (X'Pert PRO model), with a radiation source of Cu-Kα, a set voltage of 40 kV and set current of 20 mA. The morphology of the samples was investigated by STEM-EDS using a JEM-2100F instrument and Transmission electron microscopy using a JEOL 2000FX microscope. Thermogravimetric analysis (TGA), was performed in a TG209 F1 Libra NETZSCH coupled with mass spectroscopy. The sample (20 mg) was heated from 393 to 720 K at a heating rate of 10 K min⁻¹ in 60 ml min⁻¹ air. The elemental composition of the samples was determined by inductively coupled plasma-optical emission spectroscopy (ICP-OES) in a PerkinElmer Optima 2000DV instrument, and by energy dispersive spectroscopy (EDS) using an Oxford Instruments INCA energy dispersive X-ray spectrometer.

2.5. CO₂ adsorption measurements

The adsorption capacity, multicycle stability and kinetics of the samples were determined in a thermogravimetric analyser (PerkinElmer, TGA4000). The amount of adsorbent used in the CO₂-TGA experiments was relatively small varying from 5 to 20 mg and the samples were very fine particles in all cases. After the samples were pre-treated in situ by flowing 20 mL min⁻¹ of N₂ at 673 K for 4 h, they were cooled down to 573 K and held for 10 min. The feed was then switched to a 20% CO₂/Ar premixed gas and held typically for 1 h. The adsorption capacity of the solid was determined from the change in mass during the CO₂ flow. The regeneration and stability of the samples was assessed by multicycle tests in which the adsorption step was carried out at 673 K during 30 min flowing nitrogen. In both steps the flow rate was kept at 20 mL min⁻¹ during the experiment.

3. Results and discussion

3.1. Characterisation of the adsorbents

3.1.1. Chemical composition

The composition of the as-synthesised HT-SBA15 hybrids and the conventional unsupported HT are given in Table 1. The Mg/Al ratios of the adsorbents determined by ICP are close to the intended nominal ratios. Only traces of alkali impurities (Na and K) were detected in the

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