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Polyamine-Grafted Magadiite: High CO_2 Selectivity at Capture from CO_2/N_2 and CO_2/CH_4 Mixtures

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ABSTRACT

The organic-inorganic adsorbent composed of polyethylenimine (PEI) grafted within organosilane-magadiite layers has been synthesized using different alkoxysilanes with different PEI loadings as a novel adsorbent for CO_2 capture from postcombustion and natural gas. The synthesis was confirmed by XRD, ^{13}C and ^{29}Si NMR, TGA and elemental analysis. The increase of nitrogen concentration from PEI was proportional to the chloro- (CP) or glycidyloxypropyl (GM) pending groups' concentration. However, there was a negative effect in the glycidyloxypropyl-magadiite in high concentration due to the size of this pending group. PEI-xCP-MAG and PEI-xGM-MAG adsorbents were subjected to CO_2, N_2, CH_4, CO_2/N_2 (15/85 vol %) and CO_2/CH_4 (30/70 vol %) adsorption up to 20 bar at 75 °C. The experimental isotherms were fit using dual-site Sips (DSS) and Sips model. The parameters obtained from pure gases applied to the extended DSS and Sips model were able to predict the adsorbents selectivity. The selectivity presented expressive values which are comparable to MOF's, zeolites, porous polymers and carbon, even with a low CO_2 adsorption. The CO_2/N_2 and CO_2/CH_4 selectivities at 1 bar gas mixture were in the range of 111–279 and 10–83, respectively. The studied adsorbents are promising materials in CO_2 capture at postcombustion.

1. Introduction

There is a great appeal nowadays within the worldwide scientific community to propose methods to decrease/mitigate Greenhouse gases, specifically carbon dioxide (CO_2), which reached almost 409 ppm last June 2017 according National Oceanic & Atmospheric Administration (NOAA) [1]. This is *ca.* 46% increase when compared to emissions at the time of the Industrial Revolution [2,3]. One of paths to mitigate CO_2 is based on Carbon Capture and Storage (CCS), in which CO_2 is captured from different emission sources: at precombustion (CO_2/H_2) [4], postcombustion (CO_2/N_2) [5], oxycombustion (CO_2/H_2O) [4] and natural gas separation (CO_2/CH_4) [6].

The current technology for CO_2 separation uses aqueous liquid alkanolamines (monoethanolamine − MEA and diethanolamine − DEA) to absorb CO_2 in ammonia plants, in the manufacture of hydrogen, treatment of gas streams and thermal power stations to limit CO_2 in flue gas [7]. However, it is known that there are a lot of disadvantages in this process from the energetic and operational points of view, the most important being the need to replace aqueous amine that was degraded by a new batch, solvent loss by evaporation, corrosion of the equipment and high energetic demand to desorb CO_2 [2,5,8,9].

In the last decade, different adsorbents have been studied in an attempt to replace the current technology for a process without the drawbacks already known. In this sense, it is possible to find in the literature, several inorganic supports modified either physically [10,11] or chemically [12,13] with a multitude of amines and linear or branched polymeric amines (polyamines), among others.

Xu et al. [14] were the first to prepare a class of adsorbents that could chemically bond CO_2 using MCM-41 mesoporous silica as support and polyethylenimine (PEI) as an active adsorption site. PEI is a polymeric amine with a large concentration of primary, secondary and tertiary amines [15]. The MCM-41-PEI composite showed an adsorption

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capacity of 3.02 mmol g^{-1} (at 75 °C under pure CO_2) when compared with bare MCM-41 (0.19 mmol g^{-1}) and pure PEI (2.48 mmol g^{-1}) separately.

Li et al.[16] classified adsorbents with classes 1 (physically impregnated into/onto porous supports), 2 (covalently linked to the support) and 3 (polymerization *in situ* of a monomer on porous supports). Recently, Wilfong et al. [17] reported class 4 (class 1 and 2 combination) that has a superior resistance to degradation (H_2O vapor) and oxidation in air.

The use of a lamellar silicate as inorganic support can aid to decrease or even eliminate diffusion problems due to the fact that interlamellar spaces are expansible, that is, there is virtually no space restriction. Moura and Pastore [18] and Andrade Jr. and Pastore [19] synthesized talc phyllosilicates, which is a lamellar silicate, grafted with different aminosilanes and amines-based dendrons, respectively.

Moura and Pastore [20] synthesized Na-Magadiite, a lamellar silicate followed by CTA^+ ion-exchange and subjected it to grafting with 3-aminopropyltriethoxysilane (APTES) into the interlamellar space and onto pillared magadiite. The results revealed that the pillared magadiite grafted with APTES was the best adsorbent among the ones prepared having a CO_2 adsorption of 0.13 mmol g^{-1} (CO_2 5% vol., 50 °C). Vieira and Pastore [21] impregnated PEI into the Na-magadiite and CTA^+-magadiite lamellar silicates. The best adsorption capacity was 1.03 mmol g^{-1} and efficiency of 0.19 at 75 °C, after 3 h of adsorption.

Ogawa et al. [22–25], Kuroda et al.[26,27] and Yukutake et al.[28] reported the grafting of multifunctional units (phenyltrichlorosilane, glycidylpropyltrimethoxysilane, phenyltrimethoxysilane and trimethylsilane) on the layered materials, for example, magadiite, kenyaite, octosilicate and layered titanates.

There are only a few papers that describe the application of clays and lamellar silicates in CO_2 adsorption studies, more specifically amines physically or chemically bound to the lamella in an attempt to prevent blocking of the interlamellar space.

In this context, the aim of this work is to chemically attach PEI into magadiite lamellae following three steps: synthesize CTA^+-magadiite [29], graft CTA^+-magadiite with alkoxysilanes and covalently attach PEI into magadiite lamella through the anchoring points. The influence of loading and type of alkoxysilanes was investigated. The performance of these adsorbents was evaluated with CO_2, N_2 and CH_4 and mixtures (CO_2/N_2 and CO_2/CH_4) adsorption isotherms, simulating postcombustion and natural gas upgrading scenarios.

2. Materials And Methods

2.1. Organo-Magadiite

CTA^+-magadiite synthesis was carried out according to Pastore et al. [29] Briefly, cetyltrimethylammonium bromide (CTAB) was added deionized water to obtain a final concentration of 33 wt. % and left under magnetic stirring for 15 h. Sodium metasilicate pentahydrate ($Na_2SiO_3{\cdot}5H_2O$, 0.0555 mol SiO_2) was dissolved in distilled water (32 mL) to prepare a 1.5 mol L^{-1} silica solution. The CTAB aqueous gel was added to the silica solution to prepare a viscous gel with molar ratios CTA^+/Si = 200 or CTA^+/Na^+ = 25. After that, a certain volume of distilled water was added to obtain a final ratio H_2O/SiO_2 = 100. After 30 min under stirring at room temperature, the pH of the suspension was reduced from *ca.* 13.3 to 10.4–10.6 with concentrated HNO_3. The gel was aged for 4 h at 74–76 °C and transferred to Teflon® lined stainless steel autoclave for the hydrothermal treatment during 66 h at 150 °C. The solid was filtered, washed several times until pH 7.0 and dried in air. The materials were named 25CTA-MAG.

2.2. Organosilane-Magadiite

The grafting of silane groups was carried out according to the literature [30,31] with modifications. Approximately 1.0 g of 25CTA-MAG was previously dehydrated under vacuum ($5{\cdot}10^{-5}$ bar) using Schlenk apparatus during 3 h at 100 °C. Then, 50 mL of previously dried toluene (4A molecular sieve) was added and the mixture was maintained under stirring for 30 min under argon. After that, a certain volume of (3-chloropropyl)trimethoxysilane (CPTS) or (3-glycidyloxypropyl)trimethoxysilane (GPTS) ($Si_{silane}/Si_{Q3}{}^3$ = 0, 25, 50 and 100%) was added in the mixture and the reaction was processed duSring 72 h at 110 °C under argon atmosphere. The solid was then washed several times with toluene (4 × 40 mL), methanol (4 × 40 mL) and acetone (4 × 40 mL) to eliminate unreacted silane groups and the excess of CTA^+ salts followed by drying in air overnight. The final solid was named xCP-MAG and xGM-MAG for chloropropyl and glycidyloxypropyl groups, respectively.

2.3. Polyamine-Grafted-Magadiite

PEI was anchored to organosilane-magadiite also according to the literature [30,31] with some modifications.

2.4. Chloropropyl-magadiite

this solid was dehydrated under vacuum ($5{\cdot}10^{-5}$ bar) using Schlenk apparatus during 3 h at 150 °C. In order to ensure the maximum binding of chloropropyl groups, a PEI/chloropropyl = 10 molar ratio was used. The required amount of PEI was dispersed in 50 mL of methanol/THF (5:3 vol %) and stirred for 1 h under argon. Then, this solution was added to a Schlenk containing xCP-MAG followed by the addition of *N,N*-diisopropylethylamine (DIPEA) in molar ratio PEI/DIPEA = 2. The reaction was processed during 48 h at 60 °C under argon. After that, the solid was filtered and washed with methanol (5 × 40 mL) and dried in air overnight. The unreacted PEI was extracted with methanol using a Soxhlet during 24 h at 80 °C. Finally, the solid was dried in air overnight and then characterized. The solids were named as PEI-xCP-MAG.

2.5. Glycidyloxypropyl-magadiite

The procedure to prepare PEI-xGM-MAG was the same described above for chloropropyl-magadiite with the exception that only methanol was used as solvent and the addition of DIPEA was not necessary. All other reaction conditions were maintained as previously. The solid sorbents were named as PEI-xGM-MAG. Scheme 1 summarizes the experimental procedures.

2.6. Characterization

X-ray diffraction (XRD) was performed in a Shimadzu XRD7000 apparatus with Cu Kα = 1.5406 Å (40 kV, 30 mA) source. Slits of 5 mm were used for dispersion and convergence and 3° for exit. The measurements were obtained between 1.4 and 55° 2θ at room temperature at a scan rate of 2° 2θ min^{-1}. The basal spacing of the lamellar silicates was calculated by Bragg's law. Fourier transformed infrared spectroscopy (FTIR) using KBr pellets (0.25 wt %) was recorded with the use of a Thermo Nicolet 6700 FTIR spectrophotometer equipped with a DTGS detector (resolution 4 cm^{-1}). Spectra were collected from 400 to 4000 cm^{-1} by accumulating 128 scans. ^{13}C cross-polarization magic angle spinning nuclear magnetic resonance (^{13}C CP-MAS NMR) was measured in a Bruker 400 MHz Avance 400+ II spectrometer. The frequency used was 100.6 MHz with delay time of 1 s and contact time of 4000 μs. The samples were spun at 10 kHz in a zirconia rotor. More than 2000 scans were obtained and adamantane (38.2 ppm) was used as reference. ^{29}Si high-power decoupling magic angle spinning nuclear

[3] Q^3 are the silicon sites attributed to the silanol (Si-OH) and silanolate ($Si\text{-}O^-$) groups that can be functionalized (ion-exchange, grafting, for example).