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Research Paper

Polyethyleneimine (PEI) loaded MgO-SiO_2 nanofibers from sepiolite minerals for reusable CO_2 capture/release applications

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ABSTRACT

CO_2 capture and storage (CCS) by advanced materials and technologies will play a significant role in reducing industrial or human caused CO_2 emissions. In this article, a clay mineral based CO_2 absorbent was prepared by impregnating polyethyleneimine (PEI) onto acid modified fibrous sepiolite. X-ray diffraction (XRD), Fourier transform microscopy (FTIR), thermogravimetric analysis (TGA), and N_2 adsorption - desorption isotherms accompanied BET (Brunauer-Emmett-Teller) analysis were used to characterize the raw mineral and the prepared absorbents as well as their CO_2 adsorption performances. After the acid treatment, the raw sepiolite changed into amorphous silica (SiO_2) containing a small amount of MgO, but maintained their nanowire morphology, the S_{BET} value of acid treated Sep was 4 times larger and pore volume was about 2 times higher than the raw mineral. The MgO-SiO_2 nanowires and polyethyleneimine (PEI) successfully formed an organic-inorganic hybrid composite. A maximized adsorption capacity of 2.48 mmol/g at 75 °C was reached in CO_2 adsorption/desorption measurement when the composite contained 50 wt% PEI. The product also showed an excellent adsorption repeatability, above 98% of the optimized CO_2 adsorption capacity could be maintained after 10 circles tests, which confirmed that the fibrous MgO-SiO_2 assembly optimal amount of PEI is a promising solid absorbent in CO_2 gases controlling fields.

1. Introduction

Carbon dioxide (CO_2) is a primary greenhouse gas, its excessively emission would cause global warming and catastrophic climate change (Wang et al., 2014). The urgent requirements in reducing the CO_2 emissions have attracted many researchers to design an efficient capture and consolidation techniques to CO_2. Three main technologies, including liquid, solid and membranes adsorption methods, have been used in recent years to capture gaseous CO_2 (Barelli et al., 2016; Fan et al., 2016; Hasib-ur-Rahman et al., 2010; Li et al., 2013; Sanglard et al., 2013; Sherman and Rochelle, 2017; Sreedhar et al., 2017; Wang et al., 2014, 2012; Yu et al., 2012; Zhang et al., 2016a; Zhao et al., 2012; Zhou et al., 2011, 2016a). Among these methods, the solid state adsorption technique, which is often the combination of a porous solid inorganic matter (as the matrix) and certain kinds of organic amine radicals assembled on the matrix to facilitate the large scale and environment friendly fixation of CO_2 gas, has been recognized as a very promising avenue. The organic amine loaded solid adsorbents have attracted intense attentions from both academic and industrial aspects in the last decade due to the lower energy requirement, higher CO_2 capacity, and higher stability compare to liquid absorbents (Dutcher et al., 2015; Li et al., 2013; Yu et al., 2012), although they still don't have high enough resistance to contaminant gases. This kind of absorbents has been proposed to be suitable for capturing CO_2 from power plants (Roth et al., 2013), space vehicles, and air cleaning (Dutcher et al., 2015; Li et al., 2013; Wang et al., 2011; Yu et al., 2012) etc.

For sufficient application of CO_2 capturing material, a stable matrix with high specific surface area and some organic amine radicals are often required to take full advantage of the designed adsorbent. The matrix for CO_2 capturing plays the role of supporter for the amine species to keep the product in a stable and solid state (to facilitate the storage, transportation, reduce corrosivity and volatility). The amine

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Table 1
Type of matrix and CO_2 adsorption capacity of different solid absorbents in literatures.

Matrix materials	Surface modification	Capacity	Ref.
Nanoporous carbon	PEI	1.09 mmol/g at 75 °C, 1 bar	(Tang et al., 2013)
Mesoporous carbon	PEI	4.7 mmol/g at 60 °C, 1 bar	(Wang et al., 2013)
Hierarchical porous carbons	nitrogen-doped	3.96 mmol/g at 0 °C, 1 bar	(Bing et al., 2017)
CNTs/ACF	PEI	2.75 mmol/g at 60 °C, 1 bar	(Kong et al., 2013)
MWCNTs	APTES	1.7 mmol/g at 60 °C, 1 bar	(Gui et al., 2013)
Graphite	APTS	1.16 mmol/g at 30 °C, 1 bar	(Tang et al., 2013)
MOF-5/graphite oxide	–	1.1 mmol/g at 25 °C, 4 bar	(Zhao et al., 2013)
Silica fume	Amino-modified	1.3 mmol/g at 30 °C, 1 bar	(Liu and Lin, 2013)
Mesoporous silica	TEPA	3.5 mmol/g at 75 °C, 0.1 bar	(Zhao et al., 2013)
Kaolin	H_2SO_4	0.08 mmol/g at 25 °C, 1 bar	(Chen and Lu, 2015)
Smectite	PEI and APTMS	1.7 mmol/g at 75–85 °C, 1 bar	(Stevens et al., 2013)
Bentonite	PEI	1.07 mmol/g at 75 °C, 1 bar	(Chen et al., 2013)
Bentonite	Monoethanol-ammonium cations	0.79 mmol/g at 25 °C, 1 bar	(Chen et al., 2013)
Sepiolite	TEPA	3.8 mmol/g at 85 °C, 1% H_2O	(Irani et al., 2015)
Halloysite	(3-aminopropyl) triethoxysilane	0.13 mmol/g at 85 °C, 1 bar	(Jana et al., 2015)
Halloysite	PEI	2.75 mmol/g at 85 °C, 0.2 bar	(Niu et al., 2016)

species stand for the active centers to adsorb and react with CO_2 gas and then consolidate them through chemical bonds. From another point of view, the textural structures of the inorganic matrix determine the effective contacting area of the absorbents, which will assembly the organic amines, and thus will determine the reaction probability of the CO_2 with amine radicals. But, in fact, the influence of the textural structure on adsorption performances is still a matter of debate.

Many kinds of porous materials in this field have been investigated for the solid adsorbent matrix, including graphite/graphene, carbon, zeolites, silica, polymers, metal organic frameworks (MOF), TiO_2 nanotubes, natural clay, etc. Detailed information of the various matrices is summarized in Table 1. Some key factors such as the working temperature, absorption capacity, durability, and the costs should be considered and optimized for practical applications. Among the above cited literature, clay mineral has attracted much attention in recent years, as they were recognized as a kind of promising matrix material for CO_2 capturing adsorbents. Traditionally, clay minerals have been extensively used to develop functional nanomaterials due to their versatility in resources and fairly good ability to assemble many kinds of active species at the nano scale (Li et al., 2016; Li and Tang, 2016; Niu et al., 2016; Ouyang et al., 2016; Peng et al., 2016; Yang et al., 2016; Zhang et al., 2016b; Zhou et al., 2016b). Clay minerals may play the ideal supporting materials for CO_2 adsorbents because of their advantages such as easy mining, high chemical and mechanical stability, great abundance and commercial cost. Recently, several kinds of clay or clay minerals, such as kaolin (Chen and Lu, 2015), bentonite and smectite (Chen et al., 2013; Elkhalifah et al., 2015; Michels et al., 2015; Stevens et al., 2013; Yang and Zaoui, 2016), halloysite (Jana et al., 2015; Niu et al., 2016), and sepiolite (Irani et al., 2015) were explored to apply as matrix for CO_2 capturing. Based on the results presented in Table 1, it can be supposed that the clay based adsorbents could reach relatively higher capacity than the other ones.

Sepiolite (abbreviated as Sep) is a porous and fibrous hydrated magnesium silicate composed of blocks of two tetrahedral silica sheets sandwiching an octahedral sheet of magnesium oxide hydroxide. The Sep is different with montmorillonite due to the discontinuous silica tetrahedral sheets, where the bridging oxygen is inverted periodically to yield discontinuous octahedral sheets through the [010] direction, and two tetrahedra through the [001] direction, showing the channels parallel to the *c*-axis and a fibrous morphologies (Garcia-Romero and Suarez, 2013). It may be one of the suitable clays for supporting matrix due to its large specific surface area and abundant silanol groups. In addition, the sepiolite resource is abundant (Pozo et al., 2016), which may contribute to its application at an industry scale. Sepiolite has been applied to various adsorbents for hydrogen (Ruiz-García et al., 2013), arsenite (Öztel et al., 2014), Cd(II) and U(VI) (Huang et al., 2015), Cd (VI) and Pb (II) (Fu et al., 2015), safranin dye (Fayazi et al., 2015) etc. These applications verified that the sepiolite shows a strong physicochemical adsorption performance, and thus may be a potential candidate matrix for CO_2 capturing. Recently, Irani et al. (2015) modified sepiolite with acid and then immobilized tetraethylenepentamine (TEPA), the CO_2 sorption capacity reached 3.8 mmol/g in moist gases (1% CO_2 and 1% H_2O in N_2) at 60 °C. However, the capacity reduced to 92% of its highest level at the tenth cycle due to the evaporation of TEPA, and the capacity in dry circumstances (which is often required in medicine and aerospace conditions) was not reported.

In order to synthesis CO_2 adsorbents with high stability, particular emphasis needs to be focused not only on the modified porous matrixes, but also on the selection of proper kinds of amines. As shown in Table 1, the polyethyleneimine (PEI) and TEPA are commonly used organic amine resources because they have relatively high CO_2 adsorption capacities per molecule. But the molecule weight (MW) of PEI (varying in the range 300–3000 g/mol according to the condensation degree, a MW ~ 600 g/mol PEI was used in this experiment) is larger than TEPA (189.31 g/mol), as a result, PEI is less volatile and less prone to temperature induced evaporation. And most importantly, PEI is of high biological safety and high stability, thus the PEI for CO_2 condensation may provide promising prospects in real applications.

The aim of this work is to take advantage of the adsorption properties of fibrous sepiolite, and to develop a low-cost mineral based polyamine adsorbent with high CO_2 capturing capacity, good repeatability and high-stability. Because relatively larger pore size and suitable larger specific surface area (SSA) have been verified to be more feasible for CO_2 diffusion (Zhao et al., 2016), hot acid leaching was adapted firstly to improve textural properties and surface activity of the natural sepiolite. PEI was selected as the amine contents, then a series of acid treated sepiolite (and untreated sepiolite) supported PEI solid adsorbents with different loading contents were synthesized and characterized. Thermogravimetric analysis (TGA) was applied to study the influence of PEI loading content and adsorption temperature on the CO_2 adsorption properties. Finally, multi-cycle tests were conducted to demonstrate the stability of the composites.

2. Experimental

2.1. Materials synthesis

Pristine sepiolite was obtained from Shijiazhuang, Hebei Province, PR China. The ideal chemical formula is $Mg_8(OH)_4Si_{12}O_{30}(H_2O)_{12}$. Chemical compositions of the pristine mineral were: SiO_2 62.28%, MgO 28.51%, and the impurities were CaO 4.73% (probably be the interstitial ions or substitute the position of MgO and act as the