



# Microwave-assisted synthesis of amine functionalized mesoporous polydivinylbenzene for CO<sub>2</sub> adsorption



Tahereh Jafari<sup>a</sup>, Ehsan Moharreri<sup>a</sup>, Panteha Toloueinia<sup>a</sup>, Alireza Shirazi Amin<sup>b</sup>, Sanjubala Sahoo<sup>a,c</sup>, Nasser Khakpash<sup>a,c</sup>, Iman Noshadi<sup>d,e,f</sup>, S. Pamir Alpay<sup>a,c</sup>, Steven L. Suib<sup>a,b,c,\*</sup>

<sup>a</sup> Institute of Materials Science, University of Connecticut, 97 North Eagleville Road, Storrs, CT, 06269-3136, United States

<sup>b</sup> Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, CT, 06269-3060, United States

<sup>c</sup> Department of Materials Science and Engineering, University of Connecticut, 97 North Eagleville Road, Storrs, CT, 06269-5233, United States

<sup>d</sup> Department of Chemical and Biomolecular Engineering, University of Connecticut, U-3222, 191 Auditorium Road, Storrs, CT, 06269-3222, United States

<sup>e</sup> Department of Chemical Engineering, Rowan University, Glassboro, NJ, United States

<sup>f</sup> Harvard-MIT Health Science and Technology, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, 02139, United States

## ARTICLE INFO

### Article history:

Received 25 October 2016

Received in revised form 25 February 2017

Accepted 5 March 2017

Available online 24 March 2017

### Keywords:

Microwave synthesis  
Mesoporous polymers  
PDVB  
Amine functionalized  
CO<sub>2</sub>  
adsorption  
Post-combustion  
DFT modelling

## ABSTRACT

We report microwave assisted synthesis of a series of highly hydrophobic porous organic polymers of poly divinylbenzene (PDVB), for the first time, which were modified by amine-rich co-monomers of vinyl imidazole (VI) and vinyl triazole (VT) resulting in PDVB-VI and PDVB-VT adsorbents. There is an optimum amount of incorporated co-monomer and initiator which led to high adsorptive activity of the material towards CO<sub>2</sub>. Atmospheric CO<sub>2</sub> adsorption was enhanced by the addition of amine moieties while maintaining an optimum surface area and pore volume. A certain amount of initiator led to better incorporation of VT monomer while surface area and pores remain accessible. A maximum CO<sub>2</sub> adsorption of 2.65 mmol g<sup>-1</sup> at 273 K/1 bar was achieved for triazole based adsorbent (PDVB-VT) with 0.7 g of VT and 0.07 g of initiator. In comparison with a non-functionalized material (PDVB) with 1.2 mmol g<sup>-1</sup> CO<sub>2</sub> uptake, the adsorption efficiency was enhanced more than twice. The adsorbent maintained its efficiency up to seven cycles. Theoretical modeling confirms the active site is nitrogen on the imidazole/triazole ring and that incorporation of VT to the polymeric networks enhanced the adsorptive properties better than vinyl imidazole (VI) due to more active sites.

© 2017 Elsevier Ltd. All rights reserved.

## 1. Introduction

Adversely contributing to climate changes, greenhouse gases (GHG) emission has been a serious environmental concern. Carbon dioxide (CO<sub>2</sub>) being the predominant part of GHG, primarily comes from fossil fuel consumption in the transportation, energy generation, and industrial sectors [1,2]. GHG emission results in increasing the earth surface temperature which is predicted to be as high as 3 °C by the year 2100 (according to IPCC report) [3,4]. Mitigation of CO<sub>2</sub> emission by an alternative source of energy [5] needs significant changes to the current infrastructure of carbon based power plants. Therefore, CO<sub>2</sub> capture and storage techniques (CCS) could be applied to the current fossil-fuelled power plants to

tackle the problem in the short term [6]. Among various approaches in CCS techniques [7] the post-combustion methodology shows advantages over the others [8].

While absorption by amine-solution has drawbacks of corrosion, considerable energy loss, and inefficient regeneration, this has been the most widely adopted strategy [9]. Adsorption by solids provides some advantages such as (i) high CO<sub>2</sub> capture capacity, (ii) low energy requirement of adsorbent regeneration, (iii) adsorbent stability, (iv) fast kinetics, (v) easy handling, and (vi) efficiency under flue gas moisture [10,11]. On the atomic scale, polarizability or the quadrupole moment of the adsorbent functional site plays a significant role in the selective capture of CO<sub>2</sub> during physisorption [12,13]. However, for chemisorptive adsorption, selectivity is obtained based on chemical interactions between individual components of the gas mixture and surface functionalities of the adsorbent [14]. A regeneration step should follow the adsorption to recover the solid adsorbent. To regenerate the adsorbents a pressure/vacuum swing adsorption (PSA/VSA)

\* Corresponding author at: Department of Chemistry, University of Connecticut, 55 North Eagleville Road, Storrs, CT, 06269-3060, United States.

E-mail address: [steven.suib@uconn.edu](mailto:steven.suib@uconn.edu) (S.L. Suib).

and temperature swing adsorption (TSA) procedure could be employed [15,16].

An efficient solid CO<sub>2</sub> adsorbent needs high adsorption capacity and selectivity, high stability, scalability, low moisture sensitivity, and low energy of regeneration [17]. Several porous adsorbents have been evaluated for CO<sub>2</sub> capture including alkaline earth metal oxides [18], porous carbons [19], silica [20,21], zeolites [22], metal organic frameworks (MOFs) [23], porous organic frameworks (POFs) [24], and nanoporous organic polymers (NOPs) [25]. Chemical adsorption of CO<sub>2</sub> by alkaline earth metal oxides and metal salts at high temperatures requires high energy for regeneration [26–28]. Physical adsorbents like activated carbons (ACs) with advantages of prevalent precursor materials, hydrophobicity, and low heat of adsorption, still have the challenges of low selectivity and capacity [1]. Moreover, silicas and zeolites have been widely used as adsorbents to capture many impurities [29,30] especially CO<sub>2</sub> [22,31]. Zeolites capture the CO<sub>2</sub> molecules very rapidly with high chemical and thermal stability [32]. However, the moisture sensitivity, the low selectivity and high energy of regeneration has limited their application [33–35]. MOFs of M<sub>2</sub>(dobdc) have shown the highest CO<sub>2</sub> capacities of 5–8 mmol g<sup>-1</sup> (M = Mg/Co/Ni/Zn) [36], though M<sub>2</sub>(dobdc) is highly sensitive toward moisture resulting in much lower capacity (16–85% drop in capacity) in the presence of moisture [37]. Recently, a perfluorinated covalent triazine-based framework (FCTF-1) has been designed for selective CO<sub>2</sub> capture which is a moisture resistant adsorbent [38]. However, synthesis of fluorinated compounds is expensive and dangerous. To address low selectivity of widely used adsorbents of ACs and zeolites, different functionalities such as carboxylic, sulfonic, and amine groups have been applied to enhance CO<sub>2</sub> adsorption [39,40]. Based on loading methods of functional groups which mainly involve amines, there are two categories of adsorbents; amine-impregnated [41,42] and amine-grafted [43,44] materials. Impregnated adsorbents are easy to synthesize and provide high capacity. However, such materials have several drawbacks like blockage of support surface area and pores by increasing amine-loading, decomposition of loaded amines upon heating during CO<sub>2</sub> capture, and high diffusion resistivity [45]. Amine grafting by chemical reaction provides higher thermal stability for the adsorbent [43,46]. Recently, functional groups like N-donor Lewis base sites such as in organic amines have more tendency to adsorb CO<sub>2</sub> molecules [47]. Amine functionality provides Lewis base sites with lone pair electrons which coordinate favourably with CO<sub>2</sub> molecules [48] with several triazine-based polymeric adsorbents being developed for CO<sub>2</sub> adsorption [49–51]. Amine functionalized silicas have been shown to experimentally and theoretically influence the CO<sub>2</sub> adsorption mechanism [52] by the formation of intermolecular ammonium carbamates with primary amines, while being stabilized with secondary amines by forming carbamic acid.

Porous polymers provide several advantages of (i) clear design of the high surface area and well-defined porosity, (ii) easy processing, (iii) and light elemental composition which provide weight advantages [53]. Recently, several porous polymers (mesoporous or microporous) have been developed for CO<sub>2</sub> capture [54,55]. Amine modified porous polymers have also been drawn up to adsorb CO<sub>2</sub> more efficiently [56,57]. The new class of triazine-based microporous frameworks with high thermal and chemical stability have been developed through the Sonogashira-Hagihara reaction using Pd-based catalysts to improve CO<sub>2</sub> adsorption of polymeric materials [51]. In 2013, Liebl and Senker synthesized a series of triazine-based porous polyimide polymers via condensation reactions which resulted in microporous polymeric networks with the highest CO<sub>2</sub> uptake of 2.45 mmol g<sup>-1</sup> at 273 K and 1 bar [49]. Later on, Wang et al. developed ultramicropores and nitrogen-rich covalent triazine-based

frameworks for CO<sub>2</sub> capture with the capacity of 2.61 mmol g<sup>-1</sup> at 298 K for the adsorbent with 27.64% amine loading [24].

Previously, PDVB based polymers have been synthesized with various morphologies and textural properties including mono-dispersed microspheres [58], macroporous [59], nanoporous sheets [60] and as mesoporous materials [61]. Biogas purification from siloxane impurities has been conducted by highly hydrophobic mesoporous PDVB based materials [61,62]. The effect of synthesis parameters such as various solvent effects (type and ratio of solvent mixture) [63], synthesis temperature [64], and initiator amount [65] have also been studied on textural properties of PDVB-based materials. Feng et al. have synthesized mesoporous poly-ionic liquids of divinylbenzene copolymerized with alkylvinylimidazolium (P(DVB-IL)) [65], for which decreasing the amount of initiator enhanced the textural properties (higher surface area). Recently, PDVB-based materials which were modified by ionic liquids (ILs) [65] or amine rich monomers [66,67] for CO<sub>2</sub> adsorption. PDVB functionalized with ionic liquids of alkylvinylimidazolium salt showed CO<sub>2</sub> uptake of 0.5 mmol g<sup>-1</sup> at 298 K/1 bar [65]. PDVB was also functionalized with co-monomer of tartardiamide under long hydrothermal reaction which resulted in porous polymers with CO<sub>2</sub> adsorption capacity of 8.76 mmol g<sup>-1</sup> at 273 K under high pressure of 3 bar [66]. Copolymerization of divinylbenzene and triallylamine under solvothermal conditions, also resulted in amine modified porous polymers with CO<sub>2</sub> uptake of 19.5 mmol g<sup>-1</sup> at 273 K and high pressure of 3 bar [67]. However, there are no reported works on CO<sub>2</sub> adsorption by non-functionalized PDVB. Therefore, the roles of functional groups were not clearly understood.

All previously reported synthesis procedures of PDVB-based materials have been obtained by long hydrothermal reactions. However, microwave assisted synthesis of polymeric materials provides several advantages such as a uniform and fast heating process, non-contact, and highly specific heating [68,69]. Very recently a comparative study on thermal- and microwave assisted synthesis has been reported by Raj et al. in which higher molecular weight polymers were obtained in shorter reaction time by a microwave approach [70]. Hoogenboom et al. [71] have reported batch mode microwave-assisted polymerization with up to 250 fold scale up. Recent advances in flow mode microwave-assisted polymerization [72,73] have proved that the process will become less challenging from a commercial production perspective. Herein we study CO<sub>2</sub> uptake performance both experimentally and theoretically for non-functionalized and amine functionalized hydrophobic mesoporous poly divinylbenzene (PDVB) which were synthesized for the first time by microwave heating. The effect of amine type and amount of incorporation into the porous structure of the polymer and the effect of initiator amount were studied on the textural and adsorptive properties of the developed adsorbents. Theoretical calculations were conducted to enhance the understanding of the nature of the interactions between substrate and the adsorbates.

## 2. Experimental

### 2.1. Materials

Divinylbenzene (technical grade, 80%) 1-vinylimidazole (VI), 1-Vinyl-1,2,4-triazole (VT), 2,2'-azobis(2-methylpropionitrile) (AIBN), and dimethylformamide (DMF) were purchased from Sigma-Aldrich. Solvents and materials were used as received.

### 2.2. Synthetic procedures

In a typical run, non-functionalized PDVB was obtained through a microwave assisted procedure as follows. A Biotage initiator

Download English Version:

<https://daneshyari.com/en/article/4757695>

Download Persian Version:

<https://daneshyari.com/article/4757695>

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