Chemical Engineering Journal 306 (2016) 214–225

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Production of spherical mesoporous molecularly imprinted polymer particles containing tunable amine decorated nanocavities with CO_2 molecule recognition properties

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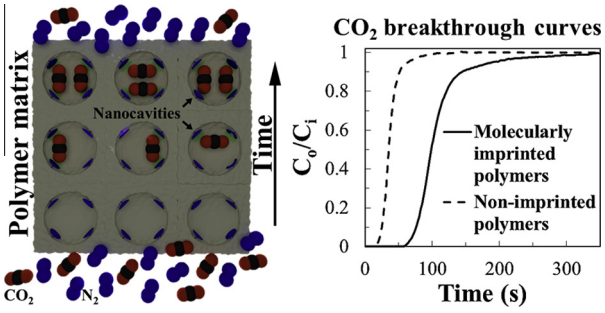
HIGHLIGHTS

- Spherical poly(AAm-co-EGDMA) particles with CO_2 recognition cavities were synthesized.
- Optimum ratio of acetonitrile to toluene in the organic phase was 30:70.
- Particles were thermally stable up to 240 °C as revealed by thermogravimetric analysis.
- CO_2 capture capacity reached 0.62 mmol/g at 25 °C and 0.15 bar CO_2 partial pressure.
- CO_2 capture capacity increased by increasing the density of CO_2-philic NH_2 groups.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 11 March 2016
Received in revised form 29 June 2016
Accepted 14 July 2016
Available online 16 July 2016

Keywords:
CO_2 recognition property
Molecularly imprinted polymer adsorbents
Amide decorated cavities
Post combustion carbon capture
Suspension polymerization
Dynamic CO_2 adsorption isotherms

ABSTRACT

Novel spherical molecularly imprinted polymer (MIP) particles containing amide-decorated nanocavities with CO_2 recognition properties in the poly[acrylamide-co-(ethyleneglycol dimethacrylate)] mesoporous matrix were synthesized by suspension polymerization using oxalic acid and acetonitrile/toluene as dummy template and porogen mixture, respectively. The particles had a maximum BET surface area, S_{BET}, of 457 m^2/g and a total mesopore volume of 0.92 cm^3/g created by phase separation between the copolymer and porogenic solvents. The total volume of the micropores (d < 2 nm) was 0.1 cm^3/g with two sharp peaks at 0.84 and 0.85 nm that have not been detected in non-imprinted polymer material. The degradation temperature at 5% weight loss was 240–255 °C and the maximum equilibrium CO_2 adsorption capacity was 0.56 and 0.62 mmol/g at 40 and 25 °C, respectively, and 0.15 bar CO_2 partial pressure. The CO_2 adsorption capacity was mainly affected by the density of CO_2-philic NH_2 groups in the polymer network and the number of nanocavities. Increasing the content of low-polar solvent (toluene) in the organic phase prior to polymerization led to higher CO_2 capture capacity due to stronger hydrogen bonds between the template and the monomer during complex formation. Under the same conditions, molecularly imprinted particles showed much higher CO_2 capture capacity compared to their non-imprinted counterparts. The volume median diameter (73–211 μm) and density (1.3 g/cm^3) of the produced particles were within the range suitable for CO_2 capture in fixed and fluidized bed systems.

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http://dx.doi.org/10.1016/j.cej.2016.07.054
1385-8947/

1. Introduction

Excessive concentration of atmospheric CO_2, mainly because of extensive utilization of fossil fuels, has significantly contributed to global warming and requires immediate remedies [1,2]. Carbon capture and storage is the most viable short- to medium-term approach for decreasing the amount of CO_2 released into the atmosphere [3,4]. Carbon capture technologies can be classified into three main groups: oxy-fuel combustion, pre-combustion, and post-combustion carbon capture [5–9], the latter being the most practical approach to retrofit carbon capture onto existing power generation systems [4,9]. Post-combustion carbon capture by amine scrubbing is the most established technique for CO_2 capture from flue gases [10]. However, amines are corrosive and undergoes degradation on exposure to CO_2, O_2, SO_2, and heat, leading to increased costs and generation of products that are harmful to human health and the environment [1,11–15]. In addition, amine-based scrubbing systems require large volume, because of their low interfacial area per unit volume and high energy consumption for the solvent regeneration, decreasing the power output typically by 20–25% [16,17].

Solid CO_2 adsorbents are more efficient and environmentally friendly than amine solutions, because of their lower regeneration energy, high surface area per unit volume, and low volatility and corrosivity [16,18]. Zeolites are the most explored sorbents for post-combustion CO_2 capture with a very high CO_2 uptake and selectivity in some cases [19–21]. However, the presence of moisture in flue gases dramatically reduces their adsorption capacity and the desorption step must be carried out at higher temperatures [22,23].

Silica-based porous materials are associated with low CO_2 uptake, because of the low affinity of silica towards CO_2, but can readily be functionalized with amine groups [20,24–26], which exhibit a high affinity towards the molecules with a high quadrupole moment and polarizability. Amongst all the molecules present in post-combustion flue gases, CO_2 has the largest quadrupole moment and polarizability, which results in much higher CO_2 adsorption capacity of amine-functionalized adsorbents compared to their unmodified counterparts [27]. Amine groups can be incorporated into the silica surface through physical impregnation or covalent tethering [28–31]. Although impregnated silica materials exhibit lower cyclic stability than adsorbents with covalently tethered amines, both methods lead to a significant increase in CO_2 capture capacity, especially in the presence of moisture [15,32,33].

Metal organic frameworks (MOFs) have gained a lot of interest because of their high specific surface area, ease of structural tuning, narrow pore size distribution, and high CO_2 adsorption at elevated pressures [34]. However, they mostly suffer from low CO_2 adsorption at low pressures [35,36], low CO_2 selectivity, and significant deterioration in the presence of moisture, NO_x and SO_x [20,37]. Carbonaceous materials are another attractive type of adsorbents, because of their high surface area, tunable pore structure, low heat of adsorption, and low sensitivity to moisture and gas impurities [7,38]. Since CO_2 is adsorbed by physisorption, they suffer from a low CO_2 adsorption capacity under low pressure [2], which can be improved by potassium intercalation [39–41] and introduction of nitrogen functional groups [42,43]. The main disadvantage of highly porous materials, such as activated carbon and some MOFs is their low density, which can limit their application in fluidized bed reactors [7,39].

Polymer-based materials such as porous aromatic frameworks (PAFs), hyper cross-linked polymers (HCPs), and covalent organic polymers (COPs) [44–46] are a new class of CO_2 sorbents characterized by high selectivity and CO_2 uptake, hydrothermal stability and ease of structural modification. Polymeric adsorbents are usually produced as very fine particles that pack too tightly and can easily be entrained out of the bed. Therefore, they must be pelletized to be used in fluidized bed systems, which can block their reactive sites and reduce CO_2 adsorption capacity. Recently, molecularly imprinted polymer (MIP) particles for CO_2 capture with a separation factor of up to 340, insensitive to moisture, SO_2, NO, and O_2, have been synthesized by bulk polymerization [47,48]. Molecular imprinting creates template-shaped cavities within the polymer matrix with molecular recognition properties towards a specific target molecule [49]. However, bulk polymerization is not suitable for large-scale production. After polymerization, the bulk polymer is crushed, ground and sieved to obtain particles of the desired size range, which is time consuming, laborious, and only 30–40% of the ground polymer can be recovered. In addition, the particles produced by this method are susceptible to mechanical attrition because of their irregular shape and broad size distribution [49].

In suspension polymerization each monomer droplet acts as a tiny batch reactor, which facilitates heat transfer and thus, the polymerization occurs faster and the final conversion of the monomer can reach higher values [50]. Due to their spherical shape, the particles have a lower tendency to break down and their size can be finely tuned by controlling the operating conditions and phase compositions during emulsification [50]. In addition, the process is scalable and higher particle yields can be achieved due to the smaller amount of waste (off-specification) material.

In this work, novel spherical acrylamide-based MIP particles for CO_2 capture were fabricated by suspension polymerization in an oil-in-water (O/W) emulsion. Amide-decorated nanocavities were created by crosslinking acrylamide in the presence of oxalic acid, followed by extraction of the dummy template to expose nanocavities. The particles were inherently amide-functionalized and there was no need for amine grafting to increase CO_2 adsorption capacity. Due to CO_2-philic moieties on the walls of the cavities and their shape that is complementary to CO_2 molecules, the particles are highly selective to CO_2. They are suitable for use in fluidized bed reactors, because of their tunable diameter greater than 100 μm and relatively high density. The emulsion formulation and operating conditions were optimized to maximize CO_2 adsorption capacity of the particles in realistic post-combustion CO_2 capture situations.

2. Experimental section

2.1. Materials

Oxalic acid (OA), acrylamide (AAm), acetonitrile (AN), toluene (TL), methanol, and 0.1 M hydrochloric acid were supplied by Fisher Scientific, UK. Ethylene glycol dimethacrylate (EGDMA), azobisisobutyronitrile (AIBN), and polyvinyl alcohol (PVA, M_w = 13,000–23,000, 87–89% hydrolyzed) were purchased from Sigma Aldrich, UK. All the reagents were of analytical grade. Pure water was supplied using a Millipore Milli-Q Plus 185 water purification system. All the gases were supplied by BOC, UK with a purity higher than 99.999%.

2.2. Particle synthesis

O/W emulsions were prepared using the dispersed phase composed of OA (template), AAm (functional monomer), EGDMA (crosslinker), and AIBN (initiator) dissolved in a mixture of TL and AN (porogenic solvents). The continuous phase was a 0.1–1 wt% aqueous solution of PVA. Formulation parameters and polymerization conditions are shown in Table 1 and in the caption of Fig. 7. The particle synthesis involved four major steps, as follows: