MONOLITHIC CARBON-SUPPORTED ZEOLITE BETA WITH HIGHLY PERFORMABLE POST-COMBUSTION CO_2 CAPTURE PROPERTIES

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ABSTRACT

Herein, we describe new facile approach to design zeolite Beta@carbon monoliths by controlled carbonization of zeolite-embedded macroporous polyHIPE (high-internal phase emulsion polymer) matrix. Highly accessible zeolite nanoparticles immobilized within macroporous N-doped carbon walls enables efficient CO_2 capture performances with excellent selectivity towards N_2 even in the humid post-combustion conditions. Carbonized walls with electric conductivity of 3 S/m have large thermo-response at 6-7 V boosting the heating up to 150 °C with rate of 50 °C/min. Fast diffusion of the accessible nanosized zeolites together with the efficient electric-induced heating properties of the carbon walls makes the developed material exceptional in the electric-swing adsorption regeneration processes with durability over many cycles.

Keywords: zeolite/carbon composite, post combustion CO_2 capture, electric swing adsorption.

INTRODUCTION

One of the most promising strategies to steady the growth rate of CO_2 in the atmosphere is its capture, storage and utilization for production of chemicals that could contribute to the sustainable growth and close the carbon cycle. Three routes are generally used in CO_2 capture technology namely, post-combustion (PC), pre-combustion and oxy-fuel combustion. Among these, post-combustion capture is most attractive since it enables retrofitting in the existing power-plants and thus sustainability of fossil fuel combustion process [1]. The conventional post-combustion CO_2 capture method which is based on chemisorption on aqueous solutions of alkanolamines (wet-scrubbing) suffers several important drawbacks such as large energy penalty for sorbent regeneration, corrosiveness, health and environmental issues of the used amines. Therefore, the alternative technology based on physisorption on solid sorbents, that in major extent surpasses the above mentioned drawbacks, is intensively studied. The main challenge for the efficient CO_2 adsorption-based capture is to develop material with: (1) high adsorption capacity at low partial pressures (p/po = 0.1 – 0.2) and high selectivity towards accompanying gases in the post-combustion processes; (2) fast adsorption/desorption kinetics; (3) mild conditions for regeneration either by temperature, pressure or vacuum swing processes; (4) performance durability enabling the constant adsorption-desorption process through numerous cycles; (5) structure and performance resistance towards moisture and other impurities present in the exhaustion system [2]. Essentially, three classes of porous materials are considered to be most promising for tackling the above enlisted criteria: (1) metal-organic frameworks; (2) zeolites; (3) carbon-based materials. However each group of material holds its own disatvantages. Briefly, general disadvantage of MOF materials is their moisture sensitivity, while zeolites suffer of too high adsorption enthalpies at low surface coverages and severe reduction of CO_2 capture performances in humid environment due to the high hydrophilic nature [3].The chemical inertness or limited microporosity of the carbon-based materials on the other hand causes typically lower CO_2 uptakes and selectivity against N_2 compared to MOFs or zeolites [4].

In the light of searching an optimal adsorbent which would fulfil the requirements for efficient post-combustion CO_2 capture, the development of integrated system containing different types of adsorbents can be one of the most obvious strategies to overcome the capture property disadvantages of the individual components. Different approaches of carbon-supported zeolite composites design are well investigated but rarely evaluated for CO_2 capture applications[5]. Main challenges in the design of zeolite@carbon systems is to find a facile synthesis strategy that would assure high accessibility of the involved components synergistically affecting to each other and thus boosting the overall CO_2 capture performance properties. Herein we introduced innovative approach of zeolite@carbon design by controlled carbonization of zeolite nanoparticles immobilized on emulsion-templated polymers (polyHIPE) substrate.

EXPERIMENTAL

Al-free Ti-Beta nanoparticles synthesized according to our previous research [6] was further used as a precursor for zeolite@carbon material for several reasons: (*i*) 3-D intersected pore channel system with the dimensions of the approximately doubled size of CO_2 kinetic diameter (0.66 x 0.56 nm) could provide an optimal CO_2-to-framework interactions; (*ii*) Al-free zeolitic framework provides higher hydrophobicity which could positively affect CO_2 capture performance in humid environment. Oil-in-water HIPEs with 80 vol % toluene as the internal phase was prepared by dissolving acryl amide and methylene bisacrylamide in aqueous phase. Afterwards, 20 wt% of zeolites was added together with the surfactant and dispersed in the above acryl amide via sonication. At last, initiator, ammonium persulfate was added and HIPE mixture was emulsified with stirrer. The as-obtained HIPE was transferred in an appropriate mould and polymerised. Polymeric composite denoted as **Beta@polyHIPE** was carbonized in the tubular oven using optimized heating protocol first in air flow up to 450 °C in order to allow oxidation of polyHIPE matrix. At this stage the flow was switched to argon and the heating was further processed up to 900°Cto produce Ti-Beta@carbon monolithic material denoted as **Beta@C**.

RESULTS AND DISCUSSION

Structural properties. Beta@C composite shows highly macroporous morphology of the carbon matrix possessing large spherical cavities with the average size of 50 μm which are interconnected through smaller windows with dimensions of approximately 1 μm (Figure1a). Zeolite Beta nanoparticles are located on the surface as well within the walls of the carbon matrix (Figure1b and 1c). The presence of zeolite Beta nanoparticles immobilized into both Beta@PAAM and Beta@C materials was confirmed by XRD and the mass contributionof zeolite Beta within the composite Beta@C deduced from TG analysis can be estimated to be 50 wt%.
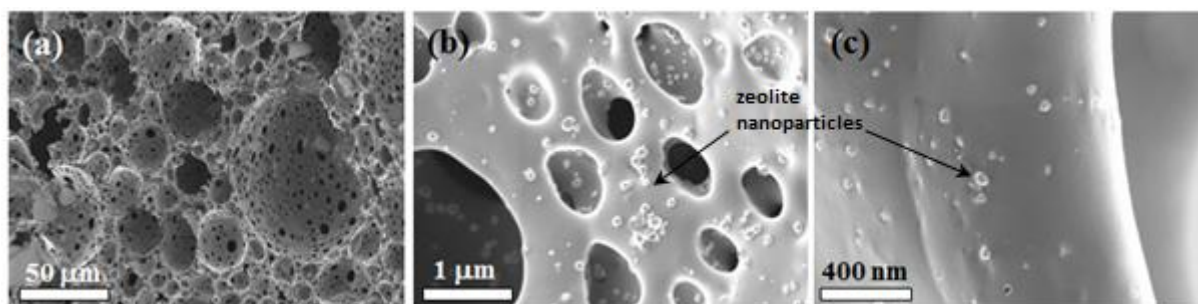

Figure 1. SEM micrographs of (a-c) as-prepared Beta@PAAM and (d-f) Beta@C composite materials observed at different magnifications. Arrows indicate zeolite Beta nanoparticles.

As-prepared Beta/PAAM composite does not possess any significant microporosity due to the substantial blocking of the zeolitic micropores with polymer PAAM phase (S_{BET} = 21 m^2/g). However, the carbonization significantly improves micropore accessibility reflecting in significant increase in S_{BET} to 258 m^2/g for Beta@C material. TEM analysis of as-prepared Beta@PAAM composite reveal the presence of zeolite Beta crystallites with the average size of 100 nm which seem to be completely covered and clogged with the polymer phase (Figure 2 a,b). On the other hand, carbonization process apparently causes certain degree of matrix shrinkage due to the loss of matter during the heating. This causes formation of cavities around zeolite crystallites and the access to the cavities seems to be provided through the micropores of the carbon walls.
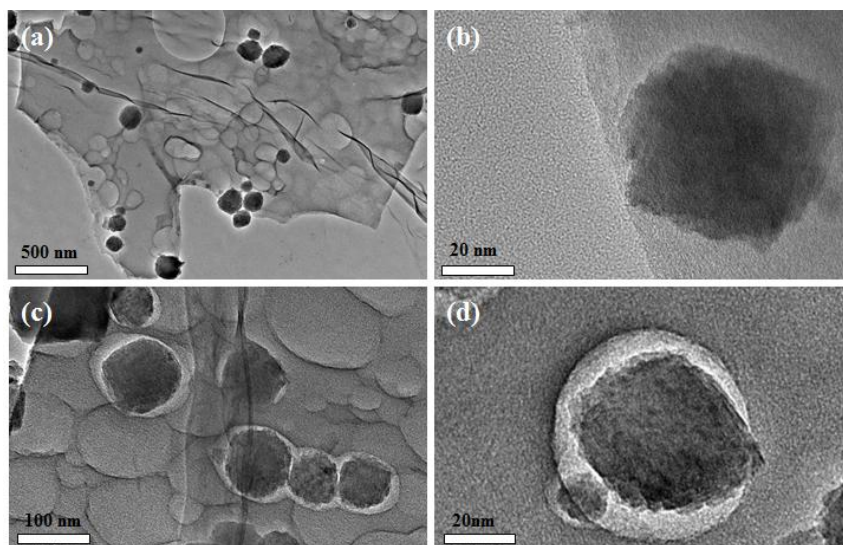

Figure 2. TEM micrographs of as-prepared Beta@PAAM (a,b) and Beta@C composite (c,d) observed at different magnifications.

CO$_2$ capture performances. Adsorption equilibrium capacities for CO$_2$ at working conditions of zeolite Beta, pure carbonized matrix and Beta@C composite are represented on Figure 3a. CO$_2$ adsorption capacity of the composite increases for 50 % compared to the zeolite Beta powder ending up at 3 mmol/g at 25 °C and 1 bar. Moreover, the composite's CO$_2$ selectivity against N$_2$ at above mentioned conditions is even more significantly improved compared to the pristine materials (Figure 3b). Whereas pure zeolite Beta exhibit CO$_2$/N$_2$ selectivity below 30, the separation capabilities of zeolite Beta@Cmonolith boosts to approximately 80. Such pronounced improvement can be assigned to the ultramicroporosity of the carbon walls and relatively high content of nitrogen atoms doped within carbon matrix, which together with high zeolite micropore accessibility synergistically contribute to the high affinity toward CO$_2$ adsorption.

The newly described method of Beta@C composite design affords the shaping in any kind of form. Moreover, heating of carbonization step at sufficiently high temperature (900 °C) makes the carbon walls conductive. Notable electrical conductivity properties of Beta@C composite (3 S/m) affords regeneration step via electrical swing adsorption (ESA), where heat is produced upon employment of certain voltage on the material. Figure 3c shows thermoelectrical response when discrete voltage is employed to the composite. First notable thermal respond occurs at 3 V and it increases in exponential trend up to 7 V. Due to the low heat capacity even at high temperatures (1.2 J/gK at 200 °C) the cooling of composite process is rapid accomplishing the room temperature from 200 °C at approximately 5 minutes. High heating and cooling ramps can enable fast adsorption/desorption cycling allowing many regeneration steps in short period of time. Last but not least, hydrophobic nature of the carbon

matrix also contributes to the lower affinity toward water, making its adsorption on the developed composite less competitive with CO_2, therefore the composite can be applied for the CO_2 capture directly from post-combustion system containing typically 5-7 % of water.
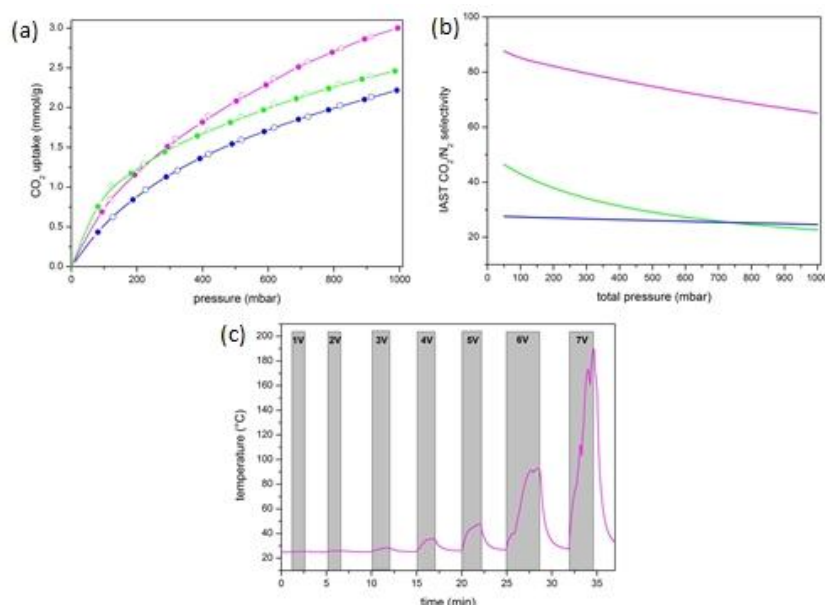

Figure 3. (a) CO_2 isotherms of investigated materials measured at 20 °C; (b) CO_2/N_2 selectivity vs. total pressure at CO_2/N_2 = 15/85 binary mixture; (c) thermoelectrical response as a function of employed voltage (indicated by the gray square areas) on the Beta@C composite monolith. Pristine calcined zeolite Beta – blue lines; Beta@C composite – purple lines; pure carbonized polyHIPE matrix – green lines.

CONCLUSION

Specific structural properties of zeolite@carbon composite material are resulted in boosting all important CO_2 capture performance parameters compared to the pristine powdered zeolite making the newly developed material promising for post-combustion CO_2 capture applications.

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