Facile synthesis of nitrogen-enriched mesoporous carbon for carbon dioxide capture

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ABSTRACT

To investigate carbon dioxide adsorption behaviors, we prepared mesoporous carbon (MC) materials that incorporated framework nitrogen functional groups *via* a facile polymerization-induced colloid aggregation (PICA) procedure, where the nitrogen content varied as a function of carbonization temperature. The prepared MCs had high specific surface areas (*e.g.*, 974 m^2/g) with well-developed mesopores. The highest carbon dioxide adsorption capacity of 106 mg/g at 25 °C was achieved with the MCs-800 sample (carbonization temperature of 800 °C). We found that the materials prepared in this study were highly effective for carbon dioxide capture, because the nitrogenous functional groups in the MCs enhanced their affinities for acidic carbon dioxide.

Introduction

The increasing atmospheric concentration of anthropogenic carbon dioxide, substantially generated by the combustion of fossil fuels, is the primary factor contributing to global climate change [1]. Globally, human activities release several million tons of carbon dioxide into the atmosphere each year [2]. Currently, extensive research efforts are being devoted to limiting the emissions of greenhouse gases into the environment [3].

A transition to renewable energies, nuclear power, and biofuels may yet mitigate the perceived calamities of global climate change. In the meantime, the worldwide abundance of accessible, inexpensive coal, combined with increasing pressure for economic growth among developed and developing nations, will ensure that present-day investments in fossil energy are not casually abandoned. Many more gigatons of carbon dioxide are thus slated for discharge into the atmosphere in the coming decades [4].

Consequentially, urgent technological solutions are needed to control increasing carbon dioxide emissions. Accordingly, carbon dioxide capture and storage (CCS) technologies have become increasingly important areas of research to solve many problems resulting from environmental pollution [5]. Generally, CCS technologies comprise three steps: separation, transportation, and sequestration. Among these, the important step for controlling carbon dioxide emissions is the capture of carbon dioxide from flue gases using a gas separation process. The costs of carbon dioxide separation from flue gases account for approximately

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70−80% of the total expense of CCS [6]. For that reason, it is important to develop an efficient, economical synthesis method for a sorbent with high selectivity for the removal of carbon dioxide from various industrial waste streams.

Available technologies for carbon dioxide capture from flue gases include wet absorption, membrane-based separation, and dry adsorption. Wet absorption is good for treating large emission volumes from combustion and is very useful for changing the density of carbon dioxide. Though this absorption process is extensively applied today, it requires high energy for absorbent regeneration and is also plagued by corrosion problems [7]. Membrane technologies require a high-cost module, are not suitable for treating large emission volumes, and are not very durable.

Regenerable solid adsorbents for a dry adsorption offer promise as alternatives for carbon dioxide capture. Physical adsorbents based on activated carbons (AC) and zeolites are able to reversibly adsorb large quantities of carbon dioxide at room temperature [8].

The dry adsorption process has advantages over other processes, including low investment, low energy cost for regeneration, and excellent environmental effects. For carbon dioxide adsorption, many researches [9−13] are in progress using various adsorbents, which includes both naturally occurring materials such as coals and zeolites and synthetic materials such as ACs, activated carbon fibers, carbon molecular sieves, and carbon replicas. These dry solid sorbents can potentially offer several advantages over liquid amine systems for carbon dioxide capture.

Among the various sorbents, ACs are considered promising for gas adsorption and storage due to their large surface areas and porosities [14,15]. They have been widely used in separation, purification, and catalytic processes. However, though ACs can reversibly adsorb large quantities of carbon dioxide at room temperature, their capacities diminish quickly at elevated temperatures and their selectivity for carbon dioxide in the presence of water and other gases is poor. To prevent these negative phenomena, there have been several studies of adsorbents modified by amines that can enhance carbon dioxide solid interactions [16−18].
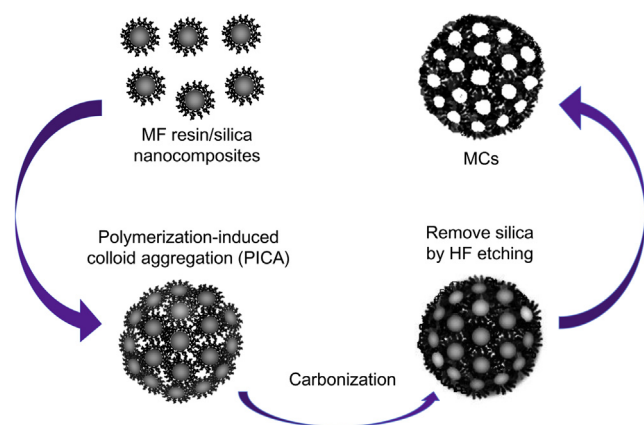
Nitrogenous functional groups incorporated into adsorbent materials have been evaluated as potential sources of basic sites for acidic carbon dioxide gas adsorption. They offer the benefits of typical adsorption processes, in that they are easy to handle and do not give rise to corrosion problems. However, excess amine treatment can block the pores of an adsorbent, decreasing its specific surface area and carbon dioxide adsorption capacity.

In this work, we prepared mesoporous nitrogen-enriched AC materials using a facile polymerization-induced colloid aggregation (PICA) procedure. We investigated the carbon dioxide adsorption behaviors of these ACs as a function of carbonization temperature.

Experimental

Materials and sample preparation

The fumed silica used as a hard template was purchased from Aldrich. Formaldehyde and hydrofluoric acid were obtained from Duksan Pure Chemicals Co., Ltd. and used as received. The mesoporous carbons (MC) materials were prepared by the carbonization of a melamine/formaldehyde (MF) resin/silica composite, followed by an etching process with hydrofluoric acid to remove silica [19].

For the preparation of the MCs, melamine (25 mmol) and formaldehyde solution (66 mmol) were added into deionized water (12.4 mL) and stirred at 85 °C. After 20 min, the resulting precursor solution was cooled to 40 °C and poured into a silica colloid solution (30 mL) while stirring at 40 °C. The mixtures were kept in a static condition for 3 h to obtain the MF/silica composite. The composite was filtered, washed with water and ethanol, and dried at 60 °C. The MF/silica composite was cured at 180 °C for 24 h in air, and then carbonized at 600, 700, 800, or 900 °C for 2 h to obtain the carbon/silica composite. Then, 20 wt% hydrofluoric acid was used to etch the silica template at room temperature and produce the mesoporous carbon materials. The samples were designated MCs-600, MCs-700, MCs-800, and MCs-900, depending on their respective carbonization temperature.

Characterization

The nitrogen content in the prepared sorbents was quantified by X-ray photoelectron spectroscopy (XPS) using an ESCA LAB MK-II (V.G. Scientific Co., UK) with monochromatic Al Kα radiation ($h\nu = 1486.6$ eV), operated in the constant analyzer

Fig. 1 − Schematic diagram of the polymerization-induced aggregation (PICA) process for the preparation of mesoporous carbon materials.

Table 1 − Chemical compositions of the prepared mesoporous carbons surface from XPS analysis.			
Specimens	Atomic amount (at.%)		
	C	N	O
MCs-600	63.2	28.0	8.3
MCs-700	64.0	31.6	4.3
MCs-800	70.5	24.2	5.3
MCs-900	78.6	16.3	5.0