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Facile synthesis of triazine-triphenylamine-based microporous covalent polymer adsorbent for flue gas CO_2 capture

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ABSTRACT

The sustainable capture and sequestration of CO_2 from flue gas emission is an important and unavoidable challenge to control greenhouse gas release and climate change. In this report, we describe a triazine-triphenylamine-based microporous covalent organic polymer under mild synthetic conditions. ^{13}C and ^{15}N solid-state NMR and FTIR analyses confirm the linkage of the triazine and triphenylamine components in the porous polymer skeleton. The material is composed of spherical particles 1.0 to 2.0 μm in size and possesses a high surface area (1104 m^2/g). The material exhibits superb chemical robustness under acidic and basic conditions and high thermal stability. Single-component gas adsorption exhibits an enhanced CO_2 uptake of 3.12 mmol/g coupled with high sorption selectivity for CO_2/N_2 of 64 at 273 K and 1 bar, whereas the binary gas mixture breakthrough study using a model flue gas composition at 298 K shows a high CO_2/N_2 selectivity of 58. The enhanced performance is attributed to the high Lewis basicity of the framework, as it favors the interaction with CO_2.

1. Introduction

Over the past several decades, significant research effort has been devoted to carbon capture and sequestration (CCS) due to widespread concerns of the rapid increase in the CO_2 level in the atmosphere, which creates adverse effects such as global climate change and ocean acidification [1–5]. Aqueous amine scrubbing is a commercialized CO_2 capture process, but it is corrosive and energy intensive and thus economically unfeasible for large-scale CCS applications [6,7]. To date, various CCS technologies have been developed, such as cryogenic distillation, membrane separation and adsorption [4]. Adsorption by porous solid adsorbents (PSAs) has been proposed as one of the most feasible alternatives [7–9]. The process, in principle, incurs a lower energy penalty than amine scrubbing, but the synthesis of high-performance PSAs that meet all practical requirements remains a large challenge [8,10]. A number of porous materials are under intensive investigation, including activated carbons [11,12], functionalized silicas [13,14], metal organic frameworks (MOFs) [15,16], covalent organic frameworks (COFs) [17,18], and molecular organic solids [19,20]. A special group of triazine-based microporous covalent organic polymer (TMCOP) materials developed recently have attracted much interest because these materials have shown promising gas adsorption performances and superb chemical robustness and thermal stability [21–28]. However, most TMCOPs are synthesized under harsh reaction conditions such as high temperature above 673 K and high pressure [21–24]. Herein, we report the synthesis of a novel TMCOP from cyanuric chloride and triphenylamine in the presence of the Lewis acid $AlCl_3$. A similar TMCOP made from the same starting materials has been reported by Xiong and coworkers [29]. However, their synthesis required a strong acid, CH_3SO_3H, in large excess (14 times excess), which requires careful handling. Our synthetic conditions are much milder, the synthetic procedure is facile and easy to scale-up, and more importantly, our product has a larger surface area, enhanced gas selectivity and superb chemical and thermal robustness.

2. Experimental section

2.1. Materials

Cyanuric chloride (99%), triphenylamine (Reagent Plus, 99%), *o*-dichlorobenzene (DCB; anhydrous, 99%), anhydrous aluminum chloride ($AlCl_3$) and hydrochloric acid (HCl) were all purchased

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from Sigma-Aldrich. Solvents such as tetrahydrofuran (THF), 1,4-dioxane, chloroform ($CHCl_3$), ethanol (EtOH), methanol (MeOH) and acetone were also purchased from Sigma-Aldrich. All of the chemicals were used as received without further purification.

2.2. Solvothermal synthesis

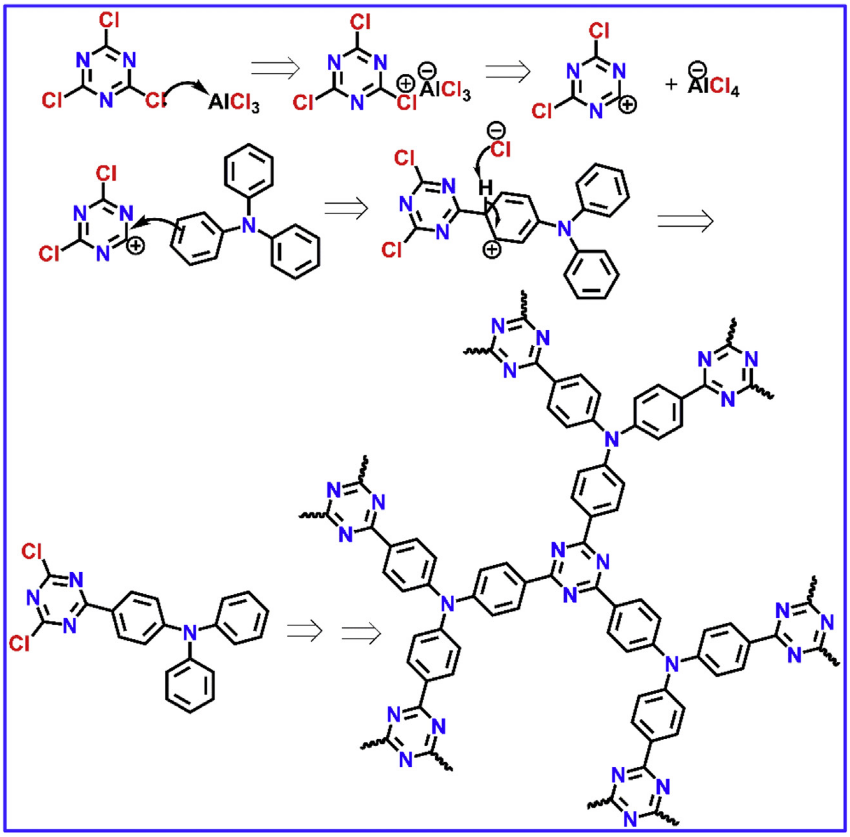
In a typical synthetic procedure, anhydrous aluminum chloride (480 mg, 3.0 mmol) was first dissolved in 10 mL of DCB in a flame-dried Schleck tube under sonication. Next, cyanuric chloride (184 mg, 1.0 mmol) was dispersed in 5 mL of degassed DCB through sonication and then added to the first solution. Triphenylamine (245 mg, 1.0 mmol) was quickly dissolved in 5 mL of degassed DCB and added to the first solution in a dropwise fashion using a syringe under vigorous stirring. The mixture was allowed to stir at room temperature for 6 h. The whole process was carried out under an argon environment. The solution was then refluxed at 463 K for 36 h under an argon environment. After cooling to room temperature, the reddish precipitate was collected by filtration, washed sequentially with dry DCB, methanol, ethanol, acetone, THF and dichloromethane, and finally dried in a drying oven. The sample was purified by Soxhlet extraction using methanol and then treated with 1 M HCl-ethanol solution.

2.3. Characterization techniques

Transmission electron microscopy (TEM) images were taken on an FEI Tecnai twin microscope operated at 120 kV. The samples were first ground into a fine powder and dispersed in ethanol. The solvent was evaporated, leaving the sample deposited on a 400-mesh copper TEM grid. Scanning electron microscopy (SEM) images were obtained using an FEI Nova Nano630 SEM and an FEI Helios NanoLab™ 600 DualBeam operated at 10 kV. The Brunauer-Emmett-Teller (BET) specific surface area was measured on an ASAP 2420 system (Micromeritics) using nitrogen at 77 K. Prior to all gas adsorption measurements, the samples were degassed at 453 K for 24 h under high vacuum. The pore size distribution was derived from the adsorption branch using nonlinear density functional theory (NLDFT). The total pore volume was estimated from the amount of nitrogen adsorbed at a relative pressure of 0.99. Single-component CO_2 and N_2 adsorption isotherms were measured on an ASAP 2050 sorption analyzer (Micromeritics). ^{13}C and ^{15}N NMR measurements were performed on a Bruker 400 M MAS system, and adamantine was used as the internal reference. The rotation frequency was set to 5 kHz. Fourier transform infrared spectroscopy (FTIR) was performed on a Nicolet iS10 smart FTIR spectrometer (Thermo Scientific, USA) equipped with a smart OMNI transmission over a range of 4000 cm^{-1} to 400 cm^{-1}. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on a thermal analyzer TG 209 (Netzsch) under N_2 flow (20 mL/min). The binary gas mixture breakthrough experiments were carried out at 298 K. Detailed information on the breakthrough setup, as well as descriptions of the calculation of the Henry selectivity, IAST selectivity and isosteric heat of adsorption (Q_{st}), are all available in our previous publications [30,31].

3. Results and discussion

Scheme 1 illustrates the formation of the TMCOP structure through a possible Friedel-Craft reaction mechanism in presence of a Lewis acid catalyst, $AlCl_3$ [32,33]. Briefly, $AlCl_3$ first interacts with cyanuric chloride to generate a carbocation complex. Then, the



Scheme 1. Schematic representation of the redox mechanism for the formation of TMCOP through a polymerization reaction in the presence of a Lewis acid catalyst, $AlCl_3$.