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Highly selective adsorption of CO over CO_2 in a Cu(I)-chelated porous organic polymer

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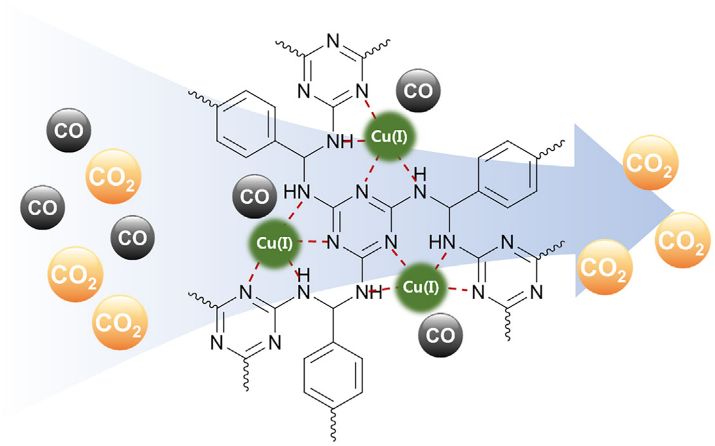
HIGHLIGHTS

- Cu(I) species were stably chelated to nitrogen atoms in SNW-1 by mixing with a CuCl solution.
- Cu(I)-chelated SNW-1 shows selective CO adsorption over CO_2 due to the π-complexation of CO with Cu(I).
- 1.3Cu(I)@SNW-1 exhibits good cyclic CO/CO_2 separation performances under dynamic mixture flow conditions.
- 1.3Cu(I)@SNW-1 exhibits a good stability under exposure to atmospheric air.

GRAPHICAL ABSTRACT



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ABSTRACT

Cu(I) species were successfully chelated to nitrogen atoms in a nitrogen-rich porous organic polymer (SNW-1) by mixing with a CuCl solution (Scheme 1). Although pristine SNW-1 adsorbs CO_2 better than CO, Cu(I)-incorporated SNW-1 (nCu(I)@SNW-1) shows selective CO adsorption over CO_2 because of the π-complexation of CO with Cu(I). To the best of our knowledge, this is the first CO/CO_2 selectivity observed for POP-based materials. 1.3Cu(I)@SNW-1 exhibits high CO/CO_2 selectivity (23) at 1 bar and a large CO working capacity (0.6 mmol/g) at 0.1–1 bar. Moreover, the breakthrough and thermogravimetric experiments show that 1.3Cu(I)@SNW-1 can effectively separate CO from CO_2 under dynamic mixture conditions and can be easily regenerated under mild regeneration conditions without heating the column. Furthermore, 1.3Cu(I)@SNW-1 exhibited a good stability under exposure to atmospheric air for 3 h or 9 h. These results suggest that chelating Cu(I) species to a nitrogen-rich porous organic polymer can be an efficient strategy to separate and recover CO from CO/CO_2 mixtures.

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1. Introduction

Carbon monoxide (CO) is a tasteless, odorless and notably toxic gas produced by the incomplete combustion of carbon-containing compounds. Simultaneously, it is an important raw material in chemical industrial applications, such as aldehyde synthesis from hydroformylation, methanol production from hydrogenation and acetic acid synthesis from the Monsanto process [1–3]. Therefore, it is important to separate and recover CO from various gaseous mixtures. There are several large-scale CO sources, such as off-gases from the steel industry and synthesis gas from steam reformation, and these gases typically contain CO_2, CH_4, N_2, H_2 and CO. Among the current CO separation methods, adsorption is a cost- and energy-effective option [4,5]. For adsorption-based separation, adsorbents play a vital role in determining the separation performance. If an adsorbent exhibits selective CO adsorption over CO_2, it may also have CO selectivity over other gases, such as CH_4, N_2 and H_2, because CO_2 has the highest polarizability of the gases in the mixture. Therefore, it is important to find an adsorbent with selective CO adsorption over CO_2.

Transition metal ions, such as Ag(I) and Cu(I), are known to form special π-complexations with molecules that have unsaturated π-orbitals such as CO [6]. Because of their low cost and availability, Cu(I) ions have been incorporated into various porous materials for CO separation [7,8]. There have been two types of Cu(I)-incorporated sorbents: 1) monolayer or near-monolayer salts dispersed in the pores of various supports such as zeolites and activated carbons; 2) Cu(I)-exchanged zeolites [8]. Since Cu(I) salts such as CuCl are water-insoluble, the Cu(I) salts have been typically dispersed in the supports through a two-step procedure including wetness impregnation of Cu(II) salts followed by reduction into Cu(I) salts using a reducing gas such as CO and H_2 [9–11]. Because Cu(I) salts are soluble in acid or base solutions, the Cu(I) salts have been also dispersed in the supports through a direct impregnation of Cu(I) salts by dissolving in acid or base solutions [12–14]. However, this method should involve thorough washing steps to remove the used acid or base solutions and typically results in poor dispersion of Cu(I) salts [8]. Due to the feasibility of cation-exchange in zeolites, Cu(I)-exchanged zeolites have been prepared by the ion exchange with Cu(II) followed by partial reduction of Cu(II) to Cu(I) [15–17]. However, this method requires a reducing gas such as CO and H_2 or a high-temperature heating and generally results in low Cu(I) concentration due to the limited sites for cation exchange and the incomplete reduction [8].

Due to the development of Cu(I) adsorbents, pressure swing adsorption (PSA) for CO separation has been commercialized since 1989. However, due to the strong interaction between Cu(I) and CO, the PSA processes have been operated at increased temperature (e.g. 70 °C) and vacuum desorption (typically at 0.1 ~ 0.3 atm) [8]. Furthermore, a partial oxidation of Cu(I) into Cu(II) during the separation process reduces the life of Cu(I) adsorbents. Therefore, there is a tremendous need for developing more efficient CO adsorbent with superior stability.

The recently reported CO adsorbents involve Cu(I)-loaded activated carbons [18–20], Cu(I)-loaded zeolites [21], metal-organic frameworks (MOFs) [22,23] and Cu(I)-loaded MOF [24]. Because of their high chemical and thermal stability, low cost and high specific surface area, porous organic polymers (POPs) have recently emerged as potential materials for various applications, such as gas storage [25,26], gas separation [27,28], heterogeneous catalysis [29–32] and supercapacitors [33,34]. However, to the best of our knowledge, there has been no report of using POPs for CO separation.

In this work, a nitrogen-rich POP, SNW-1 (Schiff-base Network-1), was prepared via Schiff base chemistry [35]. Then, Cu(I) species were incorporated into the pores of SNW-1 by mixing with a CuCl solution. Using different CuCl concentrations, the Cu(I) contents of the Cu(I)-incorporated SNW-1 materials (nCu(I)@SNW-1) were systematically controlled. The obtained nCu(I)@SNW-1 materials were rigorously characterized by various methods, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), elemental analysis, Fourier transform infrared (FTIR), field emission scanning electron microscope (FE-SEM), spherical aberration correction scanning transmission electron microscope – energy dispersive X-ray spectrometer (STEM-EDS), X-ray photoelectron spectroscopy (XPS) and N_2 adsorption/desorption. Moreover, the nCu(I)@SNW-1 adsorbent was applied for adsorptive CO/CO_2 separation by using its Cu(I) sites for π-complexation with CO molecules. Finally, the stability of 1.3Cu(I)@SNW-1 was evaluated by measuring the CO adsorption isotherms after exposure to atmospheric air for several hours.

2. Experiments

2.1. Materials

Melamine (99%), terephthalaldehyde (99%), CuCl (97%) and acetonitrile (≥99.9%) were obtained from Sigma-Aldrich (St. Louis, MO, USA). Dimethyl sulfoxide (anhydrous, 99.7%) was purchased from Fisher BioReagents. Acetone (99.5%), tetrahydrofuran (99%) and dichloromethane (99.5%) were provided by Daejung chemical Co., Korea. All chemicals and solvents were used without further purification.

2.2. Syntheses of SNW-1 and nCu(I)@SNW-1

SNW-1 was prepared following the reported procedures [36]. First, 156.5 mg of melamine, 250 mg of terephthalaldehyde and 7.65 ml of dimethyl sulfoxide were mixed and sonicated for 1 h. The mixture was loaded in a Teflon autoclave. The autoclave was heated to 180 °C for 10 h and slowly cooled to room temperature. The obtained product was filtered and washed with acetone until a white powder was obtained. To remove unreacted precursors, further purification was performed with acetone at 45 °C for 6 h, tetrahydrofuran at 55 °C for 3 h, and dichloromethane at 30 °C for 6 h. Finally, the synthesized SNW-1 was dried overnight at 45 °C in a vacuum oven.

nCu(I)@SNW-1 samples were prepared as follows: A certain amount of CuCl and 10 ml of acetonitrile were mixed and sonicated until fully dissolved. Then, 100 mg of SNW-1 was added to the CuCl solution. The obtained mixture was stirred at 25 °C for 72 h under a reflux condenser. The resulting CuCl-incorporated SNW-1 was filtered and washed with excess acetonitrile. Finally, the powder was dried at 100 °C for 6 h under vacuum. To prepare CuCl-incorporated SNW-1 samples with different Cu loadings, 100 mg of SNW-1 was mixed with different amounts of CuCl (30, 50, 70, 90, 110, 130 and 150 mg). The resulting samples were denoted as nCu(I)@SNW-1 (where n = 0.3, 0.5, 0.7, 0.9, 1.1, 1.3 and 1.5). Here, n indicates the amount (mg) of CuCl relative to 1 mg of SNW-1.

2.3. Characterizations

ICP-AES analyses were performed on an OPTIMA 8300 (Perkin-Elmer, USA). Elemental Analysis was measured using a 2400 Series II CHNS/O Elemental Analyzer (Perkin-Elmer, USA). ^{13}C cross-polarization total suppression of the spinning sidebands (CP/TOSS) NMR spectrum was obtained on an Advance II (Bruker, Germany) at 125.8 MHz with 4 mm probe. The FTIR spectra were measured using a Spectrum 100 (Perkin-Elmer, USA) in the range of 700–4000 cm^{-1}. The surface area and pore volume were obtained using a Tristar 3020 (Micromeritics, USA). The structure and copper mapping were characterized with a JSM-7800F FE-SEM (JEOL Ltd,