CO₂ Capture Using Amine-impregnated Mesoporous Silica

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Introduction

Several research groups had reported excellent performances of mesoporous silica materials incorporated with an amine-type capturing agent for CO₂ removal by sorption processes. Depending on the sample preparation methods, these materials can be classified either as grafting of diverse aminosilanes or impregnation of amine species such as PEI (polyethyleneimine) or TEPA (tetraethylenepentamine) [1-4]. We had previously investigated the influence of the physical properties of different kinds of mesoporous silica materials to the CO₂ adsorption capacity in the PEI-impregnated system [4], and it was pointed out that 3-D structured materials having large pore volumes are more effective as a support, since higher loading of a capturing agent and better distribution of it at the same loading level can be achieved.

In this work, we report the CO_2 capturing performances of HMS (hexagonal mesoporous silica) impregnated with either PEI or TEPA. The effectiveness of PEI and TEPA as a CO_2 capturing agent was compared in terms of adsorption capacity and operational stability. After demonstrating the merit of the textural mesoporosity in HMS for enhanced CO_2 capture, a silica monolith having a multimodal hierarchical pore structure was suggested and tested as a support material for amine impregnation.

Materials and Methods.

HMS and silica monolith were synthesized according to the recipes given in literature [5-7]. PEI and TEPA impregnation was conducted following the protocol suggested by Song et al. [2] and Yue et al.[3], respectively. The materials before and after impregnation were characterized by XRD, N_2 adsorption, TG, and SEM/TEM. CO_2 adsorption capacity was measured gravimetrically using a TGA unit connected to a flow panel under different conditions of temperature, PEI or TEPA loading levels, and CO_2 partial pressures. The adsorption run was carried out using high purity (99.999%) and 5% CO_2 gas, and desorption was conducted in a N_2 flow at the same temperature as in adsorption. Feed flow rate to the sample chamber (30 ml/min) was controlled with a MFC. Durability tests were also conducted for selected samples.

Results and Discussion

As-syn HMS alone demonstrated a CO_2 adsorption capacity of 34 mg/g at room temperature. When HMS was impregnated with either PEI or TEPA after removing the surfactant inside the pores, TEPA/HMS consistently exhibited higher CO_2 adsorption capacities than those of the PEI/HMS samples at the same loading levels. PEI/HMS maintained a stable performance in the prolonged cyclic operation at 75 $^{\circ}$ C, but TEPA/HMS suffered a leaching problem. CO_2 adsorption capacity was remarkably increased after PEI was loaded onto HMS samples with complementary textural mesoporosity; 60 wt% PEI loaded onto HMS synthesized at 90 $^{\circ}$ C exhibited a CO_2 adsorption capacity of 184 mg/g. With a silica monolith

support material, 210 and 165 mg CO_2/g -adsorbent were measured at 65 wt% PEI loading level (65PEI/monolith) at 75 °C using pure and 5 % CO_2 source, which belong to the highest amounts of adsorbed CO_2 reported so far among the PEI-impregnated systems (Fig.1). The 65PEI/monolith also exhibited very stable performance during a 10-repeated adsorption-desorption cycle (Fig.2).

Having high pore volumes with textural mesoporosity resulted in higher CO₂ adsorption capacities in PEI/HMS; high pore volume enables to accommodate a larger amount of PEI whilst textural mesoporosity can facilitate the CO₂ diffusion inside the 3-D channel system. Even higher CO₂ adsorption capacity was achieved by PEI/silica monolith due to exceptionally large pore volume, which is made of macropores as well as textural mesopores as confirmed by Hg-porosimetry.

Significance

HMS with textural mesoporosity and silica monolith in hierarchical pore structure exhibited significantly enhanced CO₂ capturing capacity than other mesoporous silica support materials reported so far.

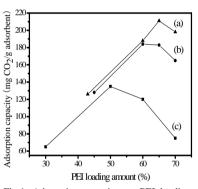


Fig.1. Adsorption capacity vs. PEI loading : (a) silica monolith, (b) HMS, and (c) KIT-6.

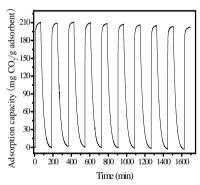


Fig. 2. CO₂ adsorption-desorption recycle runs using PEI/silica monolith (65% wt loading).

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