



Enhanced adsorption of carbon dioxide on surface-modified mesoporous silica-supported tetraethylenepentamine: Role of surface chemical structure



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ABSTRACT

Amine-impregnated mesoporous silica materials were prepared using surface-modified silica supports for CO₂ capture, and the effects of the surface chemical structure of the support on the CO₂ adsorption performance of surface-modified silica-supported amines were investigated systematically. The thermal stability and CO₂ adsorption characteristics of amine-impregnated materials were determined experimentally. The surface modification of mesoporous silicas by particular functional groups leads to increases in thermal stability of loaded amine and CO₂ adsorption capacity. In particular, the CO₂ adsorption performance in the presence of water vapor was remarkably enhanced by surface modification of the silica support. Computational analyses indicated that increases in the thermal stability of loaded amine and CO₂ adsorption capacity were due to the hydrophilicity and electron donativity (nucleophilicity) of introduced functional groups. Compared to non-modified support, CO₂ adsorption capacities for surface-modified silica supported amines were increased up to 118% in the absence of water vapor and 182% in the presence of water vapor. It is suggested that the surface structure of supports for amine-impregnated mesoporous silica materials plays an important role in CO₂ adsorption performance.

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1. Introduction

Global warming has become a major concern in recent decades, and the increase in the atmospheric concentration of CO₂ is considered one of the major causes of global warming [1–5]. The CO₂ capture and sequestration (CCS) from flue gases at large point sources such as coal-fired power plants contribute to the reduction of CO₂ emissions. For separation and recovery of CO₂, many techniques including liquid amine absorption, adsorption and membrane separation have been studied [1–7]. Liquid amine scrubbing processes are a commercially available technology for CO₂ separation but highly energy consuming [8–10]. Furthermore, they have other drawbacks such as solvent evaporation, equipment corrosion and large equipment sizes [3,4]. Therefore, more efficient techniques to overcome these drawbacks are required for the practical application of CCS.

A prospective technique for overcoming these drawbacks is adsorptive separation. To date, many adsorbents have been studied for CO₂ capture, including zeolites, carbonaceous materials, silica materials, nanocomposites, metal organic frameworks (MOFs) and covalent organic frameworks (COFs) [3–6]. Even now the novel materials for CO₂ capture synthesized with various approaches are continuously proposed [11–14]. In particular, amine functionalization of porous supports is considered one of the most promising approaches for CO₂ capture because of high CO₂ adsorption capacity, fast CO₂ adsorption/desorption, water tolerance, and easy regeneration [2–5,8–10].

Because of their feasibility, a large number of reports on amine-functionalized materials for CO₂ capture have been produced [15–25]. The key factors for designing amine-modified materials are adsorption capacity (working capacity), adsorption-desorption kinetics and material stability because they directly affect the separation process, operation and equipment size (i.e., separation cost) for actual applications. In an effort to improve these factors, many reports focused on the properties of loaded amines [15,20,26–31], the pore properties of supports [24,32–35] and CO₂ adsorption mechanisms [36–40]. However, the surface properties

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of supports have been disregarded. To enhance the adsorption performance of amine-impregnated materials, tuning the surface properties of supports may be another key approach.

At relatively low temperatures, amine-impregnated materials exhibit an appreciable decrease in CO₂ adsorption capacity because CO₂ adsorption is restricted by the diffusion in loaded amines. In some literature [41–47], the surface modification of porous supports showed positive effects for enhancing adsorption performance at ambient conditions. Yue et al. reported as-prepared SBA-15 supported tetraethylenepentamine (TEPA) for CO₂ capture, and concluded that the remaining silica template enabled the dispersion of amine species within pore channels, which are then highly accessible to CO₂ molecules [41]. Heydari-Gorji et al. also reported that long alkyl chains on the support surface improve the dispersion of loaded amine and decrease the diffusion resistance, thereby leading to enhanced CO₂ adsorption [42,43]. Our group has reported on mesoporous silica adsorbents, which are prepared by the combination of amine grafting and the amine impregnation method [25]. These materials showed higher CO₂ adsorption capacity and amine efficiency because of higher amine density. Another group has also reported a similar attempt (i.e., double-functionalization method of grafting and impregnation) to improve the dispersion of amine molecules in the silica support [44,45]. Attempts to modify the support surface with propanesulfonic acid and tetrapropyl orthotitanate to enhance CO₂ diffusion were also studied [46,47]. More recently, the effectiveness of heteroatom loading on mesoporous silica-supported amines was reported [48,49]. It was suggested that both acid and base sites created by incorporated Ce, Ti and Zr may stabilize and/or activate loaded amines, leading to enhanced CO₂ adsorption performance.

It is clear that the surface properties of supports affect CO₂ adsorption performance. However, no systematic investigation on the effect of the chemical structure of surface functional groups on enhanced performance has been conducted. The main focus of this study is to reveal the effects of the surface properties of supports on CO₂ adsorption. The surfaces of mesoporous silica supports were modified by various silane-coupling agents, and then CO₂ adsorption characteristics were evaluated for amine-impregnated sorbents using these surface-modified mesoporous silicas. Furthermore, computational studies, such as density functional theory (DFT) calculations, were performed to elucidate the enhanced sorbent ability owing to the surface modification of the support.

2. Experimental

2.1. Materials

All chemicals and reagents were used without any further purification. Pluronic P-123 (triblock copolymer, EO₂₀PO₇₀EO₂₀) and TEPA were purchased from Sigma-Aldrich. Methanol (MeOH), ethanol, toluene and acetic acid were obtained from Wako Pure Chemical Industries. Sodium silicate solution (29% SiO₂, 10% Na₂O) was obtained from Kishida Chemical. All silane-coupling agents for the surface modification of mesoporous silica materials were purchased from Gelest Inc.

2.2. Synthesis of mesoporous MSU-H silica

The mesoporous MSU-H silica was prepared using a previously reported method [50,51]. Sodium silicate solution (29% SiO₂, 10% Na₂O) was added to a mixture of Pluronic P123, acetic acid, and distilled water under vigorous stirring at 303 K. The molar ratio of SiO₂/NaOH/P123/CH₃COOH/H₂O was 1.0:0.78:0.017:0.83:230. The

mixture was heated under gentle stirring at 320 K for 20 h, and then the reaction temperature was increased to 373 K for an additional 20 h under static conditions. The solid product was filtered and washed with 0.5 L of distilled water followed by 0.5 L of a 1:1 ethanol-water mixture before drying at 353 K overnight. The dried product was calcined in air at 773 K for 8 h to remove the structure-directing surfactant.

2.3. Surface modification of mesoporous MSU-H silica

In this study, silane-coupling agents including n-propyltrimethoxysilane (nPS), isobutyltrimethoxysilane (IBS), cyclohexyltrimethoxysilane (CHS), 2-phenylethyltrimethoxysilane (PES), 3-aminopropyltrimethoxysilane (APS), 3-(2-imidazolyl)propyltriethoxysilane (IMPS), cyanopropyltrimethoxysilane (CPS) and (3,3,3-trifluoropropyl)trimethoxysilane (TFPS) were used for the modification of silica surfaces (see Fig. 1). Properties of the silane-coupling agents were listed in Table S1 of Supporting Information.

For the surface modification, excess amount of silane-coupling agents was reacted with MSU-H silica. Typically, approximately 10 g (10 cm³) of silane-coupling agent was added to 1 g of MSU-H dispersed in 50 cm³ of anhydrous toluene. The reaction was carried out at 393 K for 24 h under reflux with gentle stirring. The product was filtered, washed several times with toluene and MeOH, and then dried at 353 K. The obtained mesoporous MSU-H silicas modified by nPS, IBS, CHS, PES, APS, IMPS, CPS and TFPS are denoted nPS/MSU-H, IBS/MSU-H, CHS/MSU-H, PES/MSU-H, APS/MSU-H, IMPS/MSU-H, CPS/MSU-H and TFPS/MSU-H, respectively.

2.4. Preparation of amine-impregnated silica materials

Amine-impregnated mesoporous silica materials were prepared by a wet impregnation method. In a typical preparation, after a specific amount of silica material was dispersed in MeOH, the given amount of TEPA was added and the mixture was well agitated by ultrasonic mixing for 10 min. To obtain the products, the MeOH solvent was removed using a rotary evaporator. All samples were prepared as 50 wt% amine-loaded materials and denoted as T50-Support (e.g., T50-nPS/MSU-H).

2.5. Material characterization

The pore structure of synthesized mesoporous silica was analyzed by X-ray diffraction (XRD) measurements using a RINT2200 X-ray diffractometer (Rigaku Co.). The transmission electron microscopy (TEM) images of mesoporous silica were obtained on a JEM-3100FEF (JEOL Ltd.) microscope. All materials were characterized by N₂ adsorption-desorption at 77 K on an ASAP 2420 automatic adsorption system (Micromeritics Instrument Co.). The specific surface area (S_{BET}) and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively. The S_{BET} was evaluated from adsorption data ranging from 0.05 to 0.3, and the total pore volume was calculated from the amount of adsorbed N₂ at P/P₀ = 0.99. Fourier transform infrared (FT-IR) spectra of MSU-H and surface-modified MSU-H silicas were measured using the KBr pellet method on an IRPrestige-21 FT-IR spectrometer (Shimadzu Co. Ltd.). The nitrogen content (N content) of prepared materials and the thermal stability of the loaded amine were determined by thermogravimetric (TG) analysis on a Thermo plus TG 8120 (Rigaku Co.). Samples were heated from approximately 303 to 1273 K in an air stream at a rate of 5 K/min.

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