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Development of amine-impregnated solid sorbents for CO_2 capture

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Abstract

Based on insight into the amine-CO_2 chemistry from quantum chemical calculations, we designed and developed energy efficient amine solid sorbents for CO_2 capture. Novel amine absorbent were synthesized and used for the wet impregnation into mesoporous materials. The blending effect on the CO_2 capture was also investigated for various amine absorbents. The developed amine solid sorbents showed high performance in terms of adsorption capacity, desorption efficiency, and regeneration energy.

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Keywords: Adsorbent ; Amine ; Quantum chemical calcuculation

1. Introduction

Research Institute of Innovative Technology for the Earth (RITE) developed innovative chemical absorbents under the Cost Saving CO_2 Capture System by Utilizing Low-grade Waste Heat (COCS) project from 2004 to 2009. Under this project, various types of high-performance absorbents were fabricated for capturing and separating CO_2 from steel-making blast furnace gases. As a result, the CO_2 capture energy consumption of the developed absorbents (RITE solvents) was significantly reduced when compared with that of the conventional monoethanolamine (MEA) solvent as shown in Fig. 1 [1].

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A main drawback of the conventional amine scrubbing process is the energy cost associated with the presence of water solvent [1,2]. In addition, this process suffers from equipment corrosions and solvent losses. Alternatively, CO_2 capture using amine solid sorbents has been considered as one of the most promising techniques. RITE has studied aminosilane modified mesoporous silica prepared by grafting various aminosilanes [3-5]. Since mesoporous silica has uniform and large pores as well as high surface area, a large number of active sites or adsorption sites can be introduced uniformly on the pore walls by its surface modification. Furthermore, the amine-based silica sorbent preferably adsorbs CO_2 in the presence of water vapor unlike zeolite.

Based on the technologies of RITE solvents and porous adsorbents, in an ongoing project since 2010, RITE has studied the amine solid sorbents for CO_2 capture from its large emission sources such as coal-fired power plants. The project objectives are to develop an energy-saving CO_2 capture system with a target capture energy of 1.5 GJ/ton CO_2 and to establish evaluation standards of CO_2 capture systems [6].

In this study, we focus on the amine solid sorbents prepared by the wet impregnation method [7] and describe the methodology for structural design of high-performance amine impregnants. For this purpose, we apply quantum chemical calculations [8,9,10], organic synthetic methods [11], and blending of impregnants.

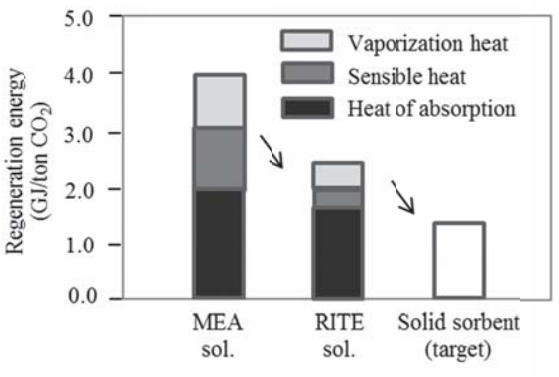

Fig. 1. Reduction of the energy cost of CO_2 capture.

2. Material design

Figure 2 schematically shows examples of our approach for obtaining novel CO_2 adsorbents with high performance. We screened substituents for energy-efficient regeneration of adsorbent by predicting Gibbs free energies of reluctant reactions, using the density functional theory (DFT) with solvation models such as a conductor-like screening model for real solvents and SMD [8,9,10].

For the reduction of regeneration energy, heat of CO_2 adsorption is considered to be the most important determining factor. This factor is governed by exothermic chemical reactions between CO_2 and amine. To predict the heat of reaction, we performed quantum mechanical/Monte Carlo (QM/MC) simulations with a droplet model [12].

Besides the regeneration performance, rate and amount of CO_2 adsorption are also important for the reduction of energy cost. We tested various amines to impregnate into pores of solid supports and found a synergistic effect between blended amines on the CO_2 adsorption amount. This synergistic effect was used for the development of new adsorbents.

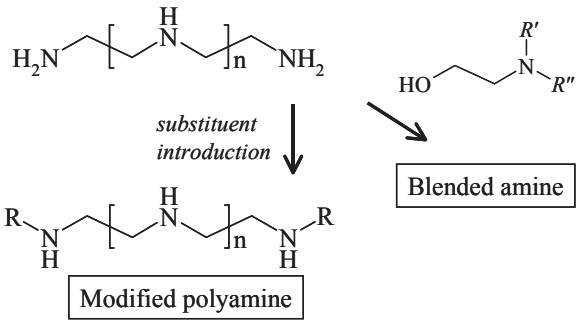

Fig. 2. Design of amine-impregnants.

3. Experimental

Tetraethylenpentamine (TEPA, Sigma-Aldrich, 98%), diethanolamine (DEA, Wako, 99%), methanol (Wako, 99.8%), mesostructured cellular form silica (MSU-F, Sigma-Aldrich), and other chemicals were purchased and used without further purification. Amine-functionalized mesoporous silica materials were prepared by wet impregnation method [7]. The silica material was added to the methanol solvent and agitated. Then, amines were added to the mixture. After agitating the mixture, solvent was removed in a rotary evaporator. The prepared samples were denoted as Ax-By/MSU-F, where x and y present the mass fraction of components A and B, respectively. For example, TEPA50-DEA10/MSU-F represents the sample prepared using 40 wt % MSU-F as a support loaded with 50 wt % TEPA and 10 wt % DEA.

Pure CO_2 adsorption isotherms were measured using a surface area and porosimetry measurement system (ASAP 2020, Micromeritics). The degassing was performed at 313 K for 6 h under vacuum prior to the measurement for removing any moisture and gas preadsorbed. Amine efficiency, defined as molar ratio of adsorbed CO_2 to amino group (mol CO_2/mol N), was determined based on the elemental analysis (Perkin Elmer, 2400II CHNS/O).

4. Results and discussion

We developed the droplet model of amine solvent as shown in Fig. 3 as well as that of water solvent for QM/MC simulations. The QM/MC//B3PW91/6-311++G(d,p) level of theory gave a high correlation coefficient between the calculated reaction enthalpy and experimental heat of absorption (> 0.9). The model to predict the heat of adsorption allowed us to design novel amine solid sorbents with low regeneration energy.

It was found that the efficiency of CO_2 desorption is governed by the amine carbamate stability constant, which corresponds to the free energy for the following reaction

$$RR'NCOO^- + H_2O \rightarrow HCO_3^- + RR'NH \quad (1)$$

where R and R' represent the substituent groups and by changing these groups, highly efficient CO_2 desorption was achieved. We predicted the reaction free energy by DFT calculations with the solvation models and designed novel amine structures. When we evaluated the efficient of desorption by vacuum regeneration, our adsorbents increased the efficiency to more than 95% form less than 40% by the modification as shown in Fig. 2.

Figure 4 shows CO_2 adsorption amounts of MSU-F impregnated with TEPA and DEA mixtures. The total concentrations of TEPA and DEA were kept at a constant of 60 wt%. The CO_2 adsorption amount at 313 K and at 15 kPa significantly increased as follows: TEPA60/MSU-F (3.2 mmol/g) < TEPA50-DEA10/MSU-F (3.6 mmol/g) < TEPA40-DEA20 (4.1 mmol/g). However, this parameter decreased as follows when the DEA loading was higher than 30 wt%: TEPA30-DEA30/MSU-F (3.9 mmol/g) > TEPA20-DEA40/MSU-F (3.4 mmol/g) > TEPA10-DEA50/MSU-F (2.9 mmol/g) > DEA60/MSU-F (1.6 mmol/g). These results confirm the existence of a synergistic

effect between TEPA and DEA with regard to adsorption amount. We also tested a variety of blended amines. The systematic structural modification of the impregnants revealed that the hydroxyl group acts synergistically with the amino group to enhance the CO_2 adsorption via the molecular interactions [7,13]. An optimal ratio between amino and hydroxyl groups in the impregnants offers the high adsorption performance for CO_2 capture.

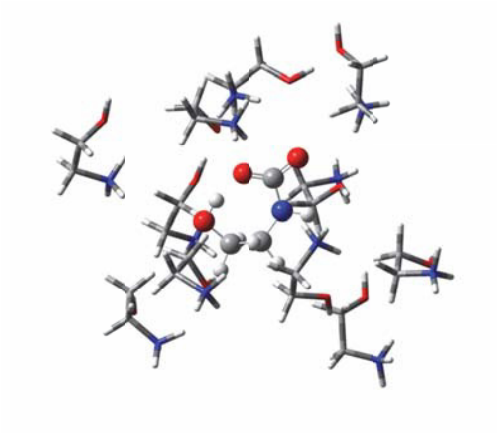

Fig. 3. Droplet model of amine solvent for QM/MC simulations.

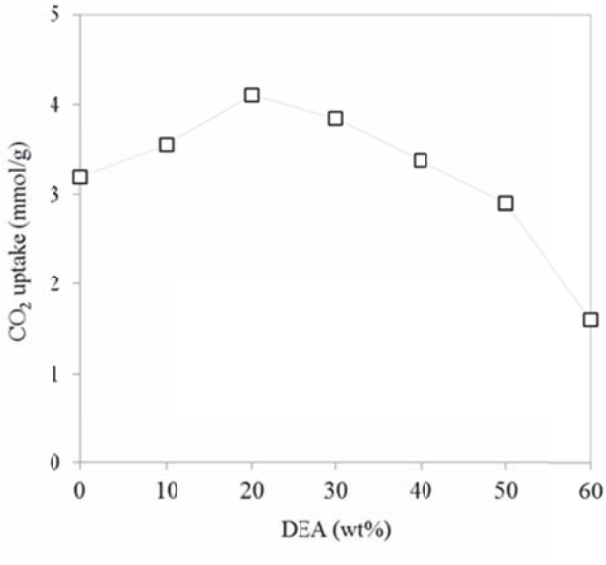

Fig. 4. Effect of DEA loading (y) on the CO_2 uptake of TEPAx-DEAy/MSU-F (x + y = 60) at 313 K and 15 kPa CO_2.

5. Concluding remarks

The relationship between amine structures and their CO_2 adsorption/desorption performances was established by computational chemistry for the development of amine solid sorbents with low energy cost. The findings led to the fabrication of a more efficient solid sorbent in terms of desorption performance and the sorption capacity. Currently, we are evaluating the solid sorbent process using a lab-scale test apparatus, and also carrying out simulation studies on the resulting efficiency penalty of power generation.

Acknowledgements

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