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Effect of crosslinking on the CO_2 adsorption of polyethyleneimine-impregnated sorbents

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HIGHLIGHTS

- Crosslinked PEI-impregnated sorbents were fabricated by wet-impregnation method.
- BDDE with diepoxide was selected as an optimal crosslinker.
- Leaching and evaporation of PEI were prevented by the crosslinking of PEI.
- The formation of urea was also prohibited with BDDE crosslinking.
- BDDE crosslinking of impregnated PEI improved physical and chemical stabilities.

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ABSTRACT

Amine-based silica sorbents for CO_2 capture prepared by an impregnation method generally show high adsorption capacity, but physical and chemical degradation for long-term operation are critical problems such as leaching and evaporation of amines, and urea formation, respectively. A strategy to form crosslinks between the impregnated amines was introduced to prevent these problems. Crosslinkers with two amine-reactive groups such as epoxy and halide were used to prepare crosslinked polyethyleneimine (PEI)-impregnated sorbents. A viscosity increase was observed in all crosslinked PEIs. The structure and the amine ratio of the crosslinked PEIs were investigated by ^{13}C NMR analysis. The highest reaction selectivity to primary amines and the formation of hydroxyl groups were observed for 1,3-butadienediepoxide (BDDE). In addition, BDDE-crosslinked PEI-impregnated sorbents exhibited the most stable long-term stability with the highest CO_2 adsorption capacity and the smallest weight gain after regeneration by simulated temperature swing adsorption (TSA) operations; the hydroxyl groups produced from BDDE-crosslinked PEI enhanced the CO_2 utilization by acting as proton acceptors. The effect of the BDDE content was investigated. The advanced physical stability was observed by an increase in the viscosity at high temperatures or gelation with increasing amounts of BDDE. The BDDE-crosslinked PEI-impregnated sorbents with the appropriate amount of BDDE showed an outstanding stability for the cyclic adsorption capacity (determined by simulated TSA operations) and resistance to urea formation (indicated by in situ infrared analysis).

1. Introduction

Extensive research has been performed for CO_2 capture from large stationary sources such as power plants and industrial sectors in an effort to reduce CO_2 emissions [1–5]. The chemical absorption process is currently the only commercial technology available to capture CO_2 from flue gas [6]. Aqueous amines such as monoethanolamine (MEA), diethanolamine (DEA), and 2-amino-2-methyl-1-propanol (AMP) are used for chemical absorption [7,8]. The amine scrubbing process is a mature technology that was originally used to remove CO_2 from natural gas; however, the CO_2 composition and temperature of the flue gas and natural gas are substantially different. Thus, a number of problems have been reported while applying this technology to flue gas, such as high regeneration energy, degradation and loss of amines, corrosive fumes, and negative environmental effects [9]. In contrast, the adsorption process using amine-based solid sorbents generally needs lower sensible heat and shows a higher CO_2 capture capacity and good resistance to contaminants [10]. Therefore, the adsorption process using amine-functionalized adsorbents is drawing attention as an alternative to the aqueous amine-based absorption process, though the adsorption process is a less-developed technology compared to the absorption process.

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