Modified secondary amine-functionalized adsorbents for CO_2 capturing process

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Abstract: Amine-functionalized silica adsorbents were synthesized via incipient wetness incorporation of secondary amines into the pores of silica. Two secondary amines used in this work were synthesized by reacting epoxides with di-aminosilane. Working capacity was examined at 30°C (15% and 3% CO_2, balance air) and 150°C (100% CO_2). Furthermore, stability during ads/des cycle under different gas conditions was extensively evaluated to assess the adsorbents' potential for large scale application.

Keywords: CCS, amine-functionalized silica adsorbents, incipient wetness.

1. Introduction

Global warming has been directly correlated to the build-up of greenhouse gases, especially CO_2, in the atmosphere. According to studies,[1,2] the concentration of anthropogenic CO_2 rose to over 380 ppm. In response, efforts have been dedicated in mitigating CO_2. One of these is the post-combustion capture (PCC) via adsorption in organic-inorganic hybrid adsorbents. Amine-functionalized silica adsorbents have emerged as promising materials for this technique due to their high CO_2 capacity and selectivity[3]. Synthesis of these adsorbents usually involves the incorporation of mono-(primary and secondary) and di-aminosilanes in the pores of silica.[4,5] Primary amine adsorbents, requires a relatively high temperature (> 120°C) to desorb CO_2 under a dry CO_2 condition, where a significant deactivation of amine via urea formation takes place.[5,6] From our previous study, it was found out that secondary amine adsorbent was not deactivated because urea compounds were not observed.[6]

In this work, secondary aminosilanes were evaluated for their CO_2 capture potential. Di-aminosilane was first modified with epoxides to convert its terminal primary amine into secondary amine. Subsequently, secondary aminosilane, pristine diaminosilane, and its modified species were incorporated in the pores of the silica via incipient wetness technique to synthesize the hybrid adsorbents. The potential of the adsorbents for industrial application was assessed by employing different gas conditions in the evaluation of CO_2 adsorption capacity, and stability during cyclic operations.

2. Experimental

Amorphous silica konasil80 was used as inorganic support. [3-(methylamino)propyl]trimethoxysilane (1NS-S) and N-[3-(trimethoxysilyl)propyl]ethylenediamine (2NS) were the aminosilanes used. 1,2-epoxypropane (EP) and 1,2-epoxybutane (EB) were used as the modification agents. 2NS was first reacted with EP or EB, in methanol and in equal molar ratios, at 40°C for 24 hours. The reaction mixture was then heated to 65°C to remove unreacted epoxide and methanol. The resulting amine compound was labelled as EP- or EB-2NS. The aminosilanes were added dropwise into the silica support. The resulting adsorbents were labelled as aminosilane/SiO_2.

The structures of EP- and EB-2NS were confirmed by ^{1}H-NMR, ^{13}C-NMR, and FT-IR. The amine-functionalized adsorbents were characterized via FT-IR spectroscopy and N_2 adsorption/desorption isotherms measurement. The CO_2 sorption capacities were determined using thermogravimetric analyzer (TGA). The difference in the CO_2 sorption capacities at 30°C for 15% CO_2 (and 3% CO_2) and at 150°C (100% CO_2) are the working capacities. The CO_2 ads/des cyclic performance study was conducted in TGA and in-situ FT-IR Spectrometer. Adsorption was conducted in 17% CO_2/Air at 30°C for 10 min. Desorption was employed in 100% CO_2 at 150°C for 10 min. The procedure was repeated for 10 cycles, where cooling was conducted using 100% N_2.

3. Results and discussion

Modification of 2NS with epoxide resulted to the transformation of the terminal primary amines into secondary amines. The structures were confirmed via NMR and FT-IR spectroscopy. Since the adsorbents are intended to be used in process operated at 30°C and 150°C for the ads./des., respectively, the working capacity of the adsorbents was evaluated between the sorption data in 15% CO_2/85% air and 3% CO_2/97% air at 30°C and in pure CO_2 at 150°C. Ideally, for the adsorbents to be considered regenerable, it should have high sorption capacity at the sorption step with no or little sorption at the desorption step. Therefore, the higher the working capacity is, the higher the efficiency of CO_2 capture is in the real process. Among the adsorbents, the 1NS-S/SiO_2 showed the highest working capacity.

In the cyclic process at different gas conditions, both adsorbents resulted to decreased capacity, between the two, EP-2NS exhibited better stability after 10 ads./des. cycles (Figure 1). The decrease in capacity is due to formation of deactivation species which were confirmed in Figure 2. Comparing the two, EP-2NS showed lesser deactivation species proving that it is more resistant to urea formation.

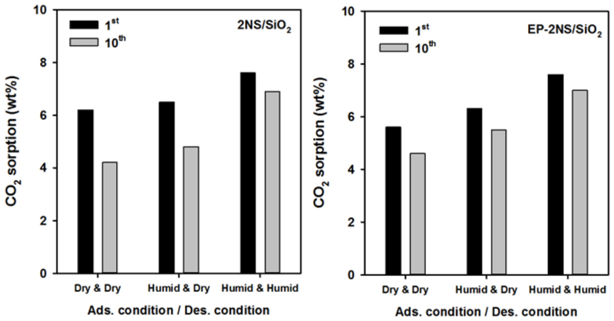

Figure 1. CO_2 sorption capacity after 10 cycles in different gas conditions.

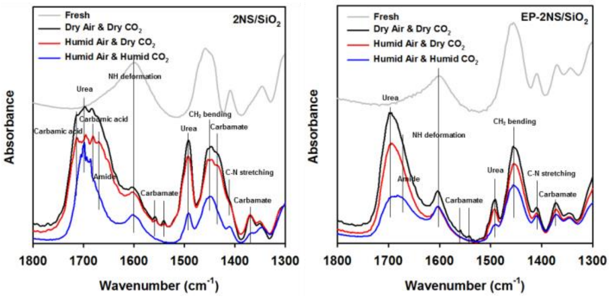

Figure 2. In-situ IR spectra of adsorbents after 10 cycles in different gas conditions.

4. Conclusions

It was confirmed that new amine structure could be formed with the addition of epoxy materials in 2NS. Most importantly, secondary amine-based adsorbent was concluded to be an excellent material for PCC .

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