



Spectroscopic study on multicyclic and long-time stability of CO₂ adsorbent in flue gas conditions

Jhulimar M. Celedonio, Rose Mardie Pacia, Young Soo Ko*

Department of Chemical Engineering, Kongju National University, Cheonan, 31080, Republic of Korea

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ABSTRACT

Since the development of amine-functionalized adsorbent is critical for its large-scale implementation, an investigation on the stability in realistic process condition is significantly important. The amine-functionalized CO₂ adsorbents were prepared via impregnation of primary amine (1NS-P/SiO₂), secondary amine (1NS-S/SiO₂) and diamines (2NS/SiO₂) into a silica support. The degradation products that could have caused the deactivation of the adsorbents are determined and quantified by in-situ FT-IR measurement and deconvoluted FT-IR spectra. The adsorbents were evaluated for their stability in multiple temperature swing adsorption (TSA) cycles and long-time CO₂ or air exposure at elevated temperature. It revealed that the degradation of adsorbents and its rate depended on the amine structure and gas conditions and that two main degradation species were urea and amide. Primary amine was more prone to CO₂-induced degradation than secondary amine. Secondary amine was less stable than primary amine for O₂-induced degradation. Diamine showed both CO₂- and O₂-induced degradations. To assess which has a more detrimental effect on the stability of the adsorbents between CO₂ and O₂ gases, the effect of long-time exposure of the adsorbents in pure CO₂ or air was determined at 150 °C using both TG and in-situ FT-IR measurement. The long-time exposure of 1NS-P/SiO₂ to CO₂ caused about 50% loss in CO₂ uptake with the faster accumulation of linear urea. The long-time exposure to air caused just about 13% loss in CO₂ uptake with the slower accumulation of amide. 1NS-S/SiO₂ showed better stability for CO₂ than 1NS-P/SiO₂ without any decrease in capacity and without any changes in its spectra. 2NS/SiO₂ showed that urea formed faster than amide. It was degraded more in air than in CO₂ with about 92% and 51% loss of CO₂ uptake, respectively. It can be inferred from the results that O₂-induced degradation is more detrimental than CO₂-induced degradation.

1. Introduction

Global warming has been directly correlated to the build-up of greenhouse gases, especially CO₂, in the atmosphere. According to Watson and Albritton [1], and Houghton et al. [2], the concentration of anthropogenic CO₂ increased to over 380 ppm at present. This rising amount of atmospheric CO₂ was a result of the burning of fossil fuels, which accounts for 40% of the total CO₂ emissions [3,4]. Consequently, techniques in post-combustion capture (PCC) were being employed and developed, such as cryogenic distillation, membrane separation, absorption, and adsorption [5].

Absorption via aqueous amine liquid solvent is considered the conventional and mature process for PCC. However, this process demonstrates several drawbacks like high corrosion rate of equipment, low contact area between the gas and liquid, large equipment size and high energy consumption during adsorbent regeneration [6]. An alternative approach to overcome these issues is the usage of solid

counterparts of the solvents used in absorption as dry adsorbents. One of the recent efforts involving solid adsorbents is the development of amine-functionalized silica adsorbent. In principle, this type of adsorbent involves the introduction of an organic amine site to inorganic silica supports with a porous structure that could expose the basic amine groups as adsorption sites of weakly acidic CO₂.

In order for this technology to be considered viable in an industrial process and advantageous over the conventional technique, it must operate effectively in realistic conditions. One of the issues significantly being attended to is the improvement of stability since the actual application will require repeated use of the adsorbent. Also, a typical flue gas not only contains CO₂ but also O₂, H₂O, SO_x, and NO_x; so it is interesting to examine the stability of the adsorbents in the presence of these impurities.

One of the most common potential degradation pathways for amine-functionalized silica adsorbents is caused by the presence of CO₂ at relatively high temperature [7]. It was found out that among the mono

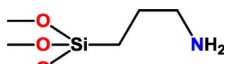
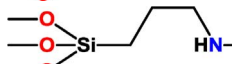
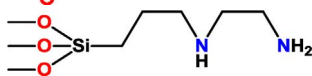
* Corresponding author.

E-mail address: yoko@kongju.ac.kr (Y.S. Ko).

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Table 1
Structure of the amine compounds used in the preparation of the adsorbents.

Amine Compound	Structure
(3-aminopropyl)trimethoxysilane (1NS-P)	
[3-(methylamino)propyl]trimethoxysilane (1NS-S)	
N-[3-(trimethoxysilyl)propyl]ethylenediamine (2NS)	

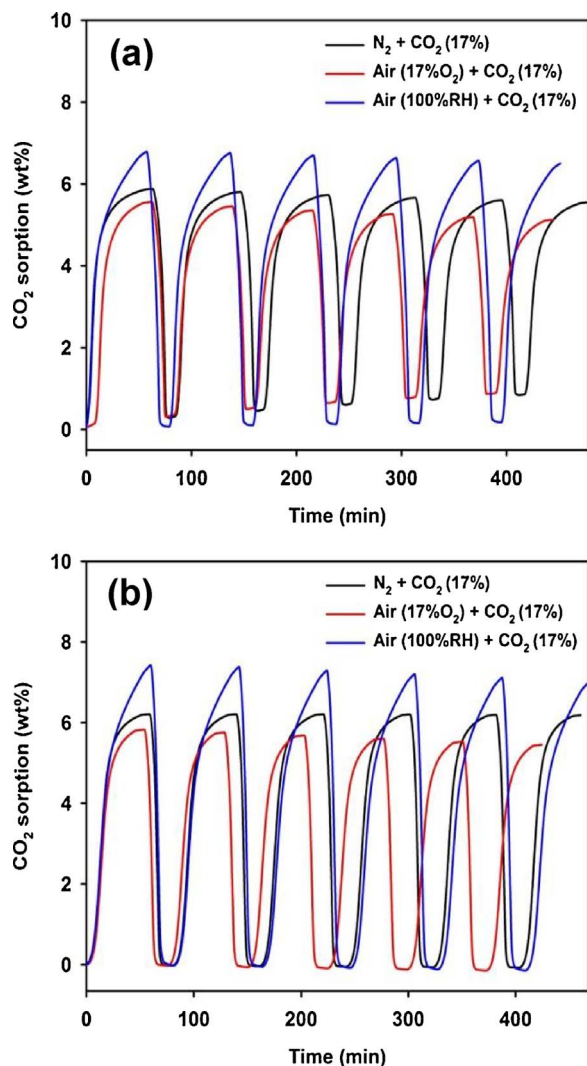


Fig. 1. Typical TGA curves of the cyclic adsorption/desorption of (a) 1NS-P/SiO₂, (b) 1NS-S/SiO₂ in different gas conditions.

Table 2
CO₂ uptake loss of the adsorbents after 6 TSA cycles in N₂ + CO₂ (17%), air (17% O₂) + CO₂ (17%), and air (100%RH) + CO₂ (17%).

Gas Condition	loss in CO ₂ uptake		
	1NS-P/SiO ₂	1NS-S/SiO ₂	2NS/SiO ₂
N ₂ + CO ₂ (17%)	18%	0%	12%
Air (17% O ₂) + CO ₂ (17%)	23%	4%	33%
Air (100%RH) + CO ₂ (17%)	7%	7%	16%

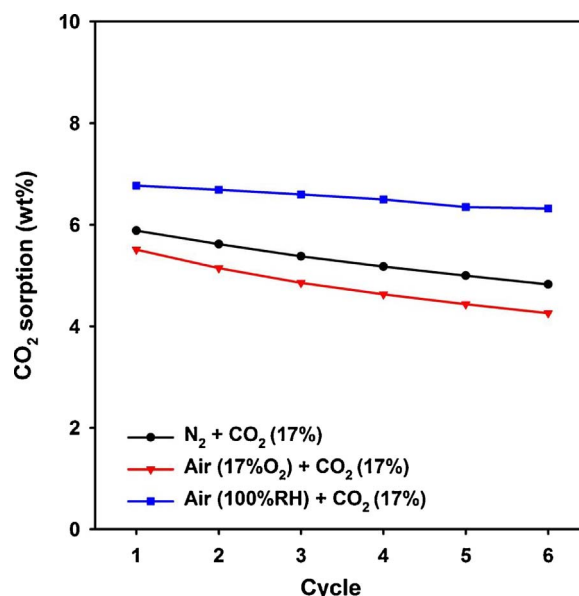


Fig. 2. CO₂ adsorption capacity for TSA cycles over 1NS-P/SiO₂ in N₂ + CO₂ (17%), air (17% O₂) + CO₂ (17%), and air (100%RH) + CO₂ (17%).

amines (primary, secondary and tertiary amines), only primary amine showed deactivation from CO₂ through the formation of linear urea. Conversely, diamine, which contains both primary and secondary amine, also showed remarkable degradation with CO₂ at high temperature via the formation of cyclic urea [8]. Nevertheless, use of humidified gas was observed to reduce such deactivation for urea formation can be completely reversed via hydrolysis of such groups [9]. Oxygen, which is one of the most abundant impurities of flue gases, also causes deactivation of amine at elevated temperature via amide and/or imide formation [10]. However, the spectroscopic studies on the rates of change in molecular structure of aminosilane during CO₂ adsorption-desorption cycles and long exposure to CO₂ and other gases have not been studied in detail.

In our previous studies, in-situ polymerization and functionalization technology of aminosilane inside the pore of silica was employed, resulting in that the adsorbent showed higher amine content and enhanced CO₂ adsorption capacity than the adsorbent prepared by conventional grafting method.

In this study, the stability of amine-functionalized CO₂ adsorbents prepared via chemical incorporation of mono- (primary and secondary) and di-amino organosilanes through in-situ polymerization and functionalization technique was investigated. The adsorbents were subjected to multiple temperature swing adsorption (TSA) cycle in the presence of CO₂, O₂, and H₂O. After which, the effect of the stability of different amine structure in varying gas conditions, and the detrimental effect CO₂- and O₂-induced degradation were evaluated. The degradation products were identified and quantified through in-situ infrared spectroscopy analysis including deconvolution of spectra. The changes of the degraded species with time were investigated when the adsorbent was exposed to CO₂ and O₂ at high temperature for 10 h in the in-situ IR cell.

2. Experimental

2.1. Materials

Aqueous silica sol (YGS-30, YOUNG IL CHEMICAL CO., Ltd.) and fumed silica (konasil300, OCI) were used for the synthesis of the silica support. The amino organosilanes used for the synthesis of the adsorbents were (3-aminopropyl)trimethoxysilane (1NS-P, Aldrich), [3-(methylamino)propyl] trimethoxysilane (1NS-S, Aldrich), N-[3-

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