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Grafted propyldiethanolamine for selective removal of SO_2 in the presence of CO_2

Ritesh Tailor, Abdelhamid Sayari *

Department of Chemistry, Centre for Catalysis Research and Innovation (CCRI), University of Ottawa, Ottawa, Ontario K1N 6N5, Canada

HIGHLIGHTS

- Grafted-diethanolamine adsorbs selectively, quantitatively and reversibly ppm SO_2 in CO_2.
- Material with 1.75 mmol/g amine adsorbs 2.84 at 23 °C in the presence of 1% SO_2/N_2.
- The SO_2 adsorption capacity is unchanged in the presence of oxygen under dry condition.
- The SO_2 uptake increased significantly in the presence of water vapor.

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ABSTRACT

Propyldiethanolamine-grafted pore-expanded mesoporous silica was developed for selective adsorption of SO_2 in the presence of CO_2. With 1.75 mmol/g amine loading, the adsorption capacity in the presence of 1% SO_2/N_2 under dry condition was found to be 2.84 and 2.14 mmol/g at 23 and 50 °C, corresponding to SO_2/N ratios of 1.63 and 1.30, respectively. Not only the material did not capture any CO_2 under typical adsorption conditions, but the presence of CO_2 did not affect SO_2 uptake under dry or humid condition. Moreover, the SO_2 adsorption capacity remained unchanged in the presence of 10% O_2/N_2 under dry condition. The presence of water vapor improved the SO_2 adsorption capacity of the material at room temperature by ca. 50% at 83% relative humidity. The SO_2-saturated adsorbent under dry condition was regenerated completely by flowing N_2 at 130 °C, and the SO_2 working capacity remained unchanged in consecutive adsorption/regeneration cycles. Based on earlier FTIR and ^{15}N NMR data using similar grafted tertiary amine, it is suggested that the adsorption takes place by charge transfer complexation between SO_2 and the tertiary amine nitrogen. Nonetheless, consistent with literature data, it is speculated that SO_2 adsorption also occurs through zwitterion formation involving interaction between OH groups and SO_2.

1. Introduction

Sulfur dioxide is a direct by-product of burning sulfur-containing fossil fuels and a chief component of acid rain and smog [1]. It has a detrimental effect on human health [2] as well as on plants and aquatic animals. As a result, it has been the subject of increasingly stringent regulations since the mid-1980s. SO_2 can be largely captured at the source by the use of sophisticated scrubbers on smokestacks or by catalytic converters in cars. Commonly, for industrial gases such as power plants flue gas, SO_2 capture may be achieved using dry, wet or semidry flue gas desulfurization processes [3–6]. Another popular approach is to use scrubbing solutions [7], such as amine or ionic liquid solutions [8–14] or physical solvents [14–17]. Although, they have good efficiency, amine absorption processes suffer a number of shortcomings such as high energy consumption for regeneration, large production of wastewater, corrosion issues and excessive amine loss by evaporation [13,18,19]. Amine solutions are also prone to chemical deactivation in the presence of different gaseous contaminants such as O_2 and SO_2 by forming heat stable chemicals [10,20–22].

Alternatively, removal of SO_2 by solid adsorbents is becoming increasingly more popular because it offers multiple advantages over the above mentioned technologies. This includes simplicity of operation, low energy requirements for regeneration, low or no use of water, no volatility or corrosion issue, no by-products or waste generated, and the availability of a wide range of adsorbents. This includes activated carbons [5,23–26], carbon fibers [27], zeolites [28–31], supported polymers [32] metal oxides and metal supported materials [33–35] and metal–organic frameworks (MOFs) [36,37].

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* Corresponding author.
E-mail address: abdel.sayari@uottawa.ca (A. Sayari).

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Carbon dioxide is another acid gas produced in exceedingly large amounts by fossil fuel combustion, mostly for electric power, heating and transportation. Carbon dioxide, which is accumulating in the atmosphere at an alarming rate, is a greenhouse gas believed to be the main culprit for global warming. The removal and sequestration of carbon dioxide is recognized to be the only strategy to significantly slow down, or hopefully decrease the CO_2 buildup in the atmosphere. Amine scrubbing is a mature technology for the removal of CO_2, whereas the use of solid-supported amines is a more recent development for CO_2 capture via adsorption. In both cases, because SO_2 is a stronger acid than CO_2, occurrence of SO_2 even in minute amounts in the gas feed, was found to be detrimental to the removal of CO_2. Indeed, SO_2 interacts irreversibly with primary and secondary amines, which are the most effective amines for CO_2 capture by amine solutions or amine-containing adsorbents [20,21,34,38–40], leading to irreversible loss of efficiency. Uyanga et al. [21] and Supap et al. [41] for example, demonstrated that monoethanolamine deactivates readily during CO_2 capture in the presence of SO_2 due to the irreversible generation of heat-stable sulfate salts. Khatri et al. [42] and Belmabkhout and Sayari [40] found that grafted propylamine and triamine deactivate in the presence of SO_2. Jones and coworkers [38,43–45] investigated the deactivation of primary and secondary amines supported on solid materials upon exposure to SO_2 demonstrating the irreversible nature of SO_2 adsorption on such amines. There are several other reports indicating the irreversible SO_2 interaction with amines, specifically with primary and secondary amines to form stable sulfate salts [46,47].

Power plants flue gas usually undergoes bulk desulfurization before CO_2 removal. However, regardless of the bulk desulfurization process, there remain always small concentrations of SO_2 in the flue gas. Since primary and secondary amines are sensitive to ppm levels of SO_2 even in the presence of much larger concentrations of CO_2, it is necessary to develop materials that are capable of adsorbing low levels of SO_2 selectively, quantitatively and preferably reversibly in the presence of high CO_2 concentrations. Such materials would be used as a filter to remove traces of SO_2 before exposing the amine-containing CO_2 adsorbent to the feed gas. We demonstrated in previous reports that contrary to primary and secondary amines, tertiary amines have low or no affinity for CO_2 under dry conditions, and even in humid condition, the interaction is very weak. Yet tertiary amines react readily and reversibly with SO_2 [48,49]. Few other reports dealt with the reversible adsorption of SO_2 in the presence of tertiary amines [46,50,51]. Using a 4.62 mmol/g triethanolamine-impregnated SBA-15 in the presence of 1340 ppm SO_2/N_2 at 25 °C, Zhou et al. [51] obtained a SO_2 uptake of 2.76 mmol/g ($SO_2/N = 0.6$). In addition, they found that humid condition promoted the SO_2 uptake to 3.23 mmol/g. Nonetheless, we found that triethanolamine-loaded SBA-15 exhibits significant loss of adsorption capacity due to amine evaporation [48]. In search for thermally stable materials, we demonstrated for the first time that *N,N*-dimethylpropylamine-grafted pore-expanded MCM-41 silica (PE-MCM-41) is a stable, reversible and highly selective adsorbent toward SO_2 vs. CO_2 [48]. Moreover, humid condition led to a threefold enhancement in SO_2 uptake. Further effort led to the development of novel supported poly-tertiary amine dendrimers and polymers with higher SO_2 uptake [49]. SO_2 uptakes well above 4 mmol/g were obtained at room temperature in the presence of 0.1% SO_2/N_2 gas mixture. Furthermore, we conclusively demonstrated the formation of charge transfer complexes between SO_2 and tertiary amine groups using FTIR and ^{15}N NMR spectroscopy [48,49]. The developed materials were found to be highly selective towards SO_2 in the presence of CO_2, O_2 and H_2O without any deactivation. However, in the presence of O_2 in humid condition, they exhibited small loss in adsorption after regeneration. Nonetheless, the strategy of using supported tertiary amines for the purpose of flue gas desulfurization before CO_2 capture needs to be further explored.

Ethanolamines are among the most popular amines for CO_2 scrubbing. Moreover, impregnated triethanolamine proved to be an effective SO_2 adsorbent [51], despite the gradual loss of amine by evaporation [48]. Hence, the hydroxyethylene group brings about improved adsorptive properties for the amine group. Based on such observations, the idea of immobilizing a tertiary amine bearing hydroxyethylene groups for the purpose of developing a stable, selective and reversible adsorbent for complete removal of SO_2 in the presence of CO_2 was borne. To meet this objective, we developed a new, selective adsorbent for SO_2, namely propyldiethanolamine-grafted PE-MCM-41. The effectiveness of hydroxyl-functionalized tertiary amine was evaluated in comparison to our earlier work, which may hopefully lead to a potential adsorbent for quantitative removal of SO_2 in CO_2-rich gas streams. The SO_2 selectivity and adsorption behavior associated with the effect of water vapor and O_2 were also investigated.

2. Experimental section

2.1. Materials and synthesis of the adsorbent

3-[Bis(2-hydroxyethyl) amino]propyl-triethoxysilane (62% in ethanol) was obtained from Gelest. All other chemicals for the synthesis of the adsorbent were obtained from Sigma–Aldrich and used as received. Ultra-high pure nitrogen (99.999%), CO_2 (20%, balance N_2), Air (0.1 grade) and SO_2 (0.01%, 0.1% and 1%, balance N_2) were supplied by Linde, Canada.

The grafting procedure of amine over pore-expanded MCM-41 (denoted here as PMC) was carried out using a procedure described in our earlier reports [52,53]. In brief, after vacuum drying (120 °C, 2 h), the PMC (1 g) was dispersed in 150 mL of toluene in a multi-neck glass flask and stirred for 15 min to achieve a homogeneous mixture. Then, 0.4 mL distilled deionized water was added and stirred for 30 min. The flask equipped with a condenser was then submerged in a silicon oil bath set at 85 °C using a temperature-controlled stirring hot-plate. Subsequently, 2 mL of 3-[bis(2-hydro xyethyl)amino]propyl-triethoxysilane (BHAP) was added after removal of ethanol using a rotary evaporator. The mixture was then left under stirring for 16 h. The resultant product was filtered and washed twice with toluene and pentane. The recovered solid material was dried overnight at room temperature. The material obtained will be referred to as BHAP-PMC.

2.2. SO_2 adsorption measurements

SO_2 adsorption was conducted in a packed-bed column as schematically presented in Fig. 1. A stainless steel column of

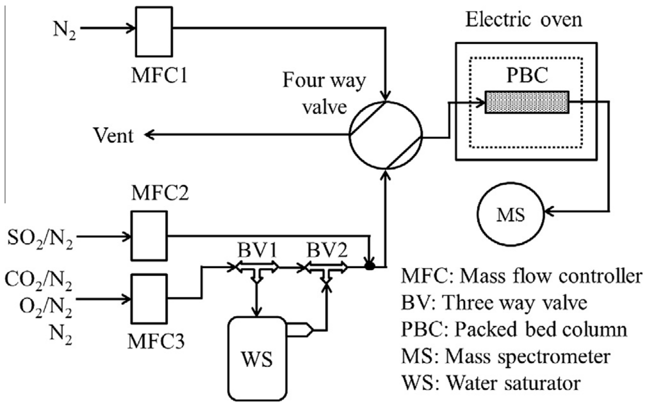

Fig. 1. Experimental setup for SO_2 adsorption in a packed-bed column.