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Effect of amine structure on CO_2 adsorption over tetraethylenepentamine impregnated poly methyl methacrylate supports

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Tetraethylenepentamine (TEPA) was modified by Michael addition reactions to study the effect of primary, secondary, and tertiary amine structure on its ability to absorb or desorb carbon dioxide. TEPA and modified TEPA were impregnated in a poly(methyl methacrylate) support to obtain solid amines. The specific characteristics such as pH, viscosity, and thermal stability were measured to study the properties of liquid amine. Structural properties, adsorption capacity, rate of adsorption, desorption energy, and sorbent durability during CO_2 adsorption/desorption processes were measured to study the properties of solid amines.

The pH of modified liquid TEPA (T1AN, T2AN, and T3AN) was slightly reduced; however, both viscosity and thermal stability were increased. The increased viscosity of the modified amines was indicative of an increase in attraction between the amine molecules; accordingly, amine leaching decreased noticeably and thermal stability of amines increased. Modified amine-impregnated sorbent (ST1AN and ST2AN) showed slight decrease in CO_2 adsorption capacity but noticeable increase in rates of adsorption, durability during cyclic tests, and desorption characteristics compared to TEPA-impregnated sorbent (STEPA).

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1. Introduction

Global warming is caused by the increase in atmospheric CO_2 concentrations due to the indiscriminate use of fossil fuels [1,2]. An efficient and economic method to capture CO_2 from post-combustion gases is urgently required. For the past few years, extensive studies have been reported on technologies concerning CO_2 separation from post-combustion gases [3–6], such as physical/chemical absorption, physical/chemical adsorption, membrane processing, and oxygen recovery from O_2/CO_2 recycling combustion. CO_2 absorption technologies using liquid amine is recognized as most effective option for capture CO_2 from post-combustion gases. However, it has some inherent disadvantages such as corrosion, high regeneration energy during water evaporation process, and fouling of the process equipment. Adsorption is currently recognized as an alternatives to a liquid phase sorption because it consumes less wastewater, is less corrosive on equipment, and requires low regeneration energy during the desorption process. In adsorption studies, many researchers have investigated the use of various solid amine sorbents such as silica [7–9], activated carbons [10–12], zeolites [13–16], metal organic frameworks (MOFs) [17–21], and polymers as a medium that provides an interface between the gas phase and amine material. Mesoporous poly (methyl methacrylate) (PMMA) beads are less expensive than other supports and show high surface areas (~500 m^2/g, by manufacturer), pore volumes, and pore sizes. The moving (or fluidized) bed, which is generally used for adsorption processes, requires a sorbent having adequate particle size (at least micron scales) and high durability. PMMA supports exhibit appropriate bead sizes (300–710 μm, by manufacturer) and sufficient robustness, whereas most mesoporous supports for CO_2 capture are in powder form and require further forming processes, which raises the cost of sorbents and depletes their durability. Amine-impregnated solid sorbents using PMMA supports have already been used for CO_2 capture in life support systems of space shuttle [22]. However, a few attempts have been made to develop amine-impregnated PMMA-supported sorbents for CO_2 capture since these initial reports [22–24]. In the course of our study toward the use of polymers as a support, we decided to explore the properties of liquid amines immobilized within a porous support to improve the chemical adsorption capacity of the sorbent.

Studies on solid amine sorbents have been previously conducted to enhance only their CO_2 adsorption capacities. Although

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high CO_2 adsorption capacities were obtained, most studies showed relatively low amine efficiency (the stoichiometric ratio of CO_2 to amine: CO_2/mol amine(N)) or did not consider amine efficiency at all [25]. The maximum amine efficiency of both primary and secondary amines under dry conditions was only 0.5 mol CO_2 per mol amine(N); amine efficiency is defined as the ability to use the maximum amount of amine in capturing CO_2.

Besides CO_2 adsorption capacities, both adsorption/desorption kinetics and desorption characteristics are also important sorbent properties for industrial use. CO_2 adsorption/desorption characteristics of a chemical sorbent will vary depending on the type of the amine used [26]. In general, primary amines have a higher affinity than secondary amines, and the secondary amines exert a higher attractive force than tertiary amines. However, because of their affinity, the primary amines must have higher energy toward CO_2 desorption. Therefore, the secondary amines are known to be the most valuable in adsorption/desorption cyclic tests. Currently, research has been primarily conducted on amines that have many secondary amine sites such as tetraethylenepentamine (TEPA) [27,28]. Further research has focused on attempts to modify TEPA molecules to synthesize the secondary amines [29,30]; however, only few studies were conducted on the properties of modified amines, such as thermal stability, viscosity, and desorption characteristics.

Both viscosity and thermal stability of the amines are important because amine leaching during a adsorption/desorption cycle can be significant [31,32]. A decrease in CO_2 capacity will be observed after a few runs if leaching of the physisorbed amines from the support occurs [27]. The stability of CO_2 adsorption/desorption process and thereby the sorbent durability is shown to be enhanced with an improved thermal stability of the liquid amine via reaction between TEPA and acrylonitrile (AN) [28–30].

In this study, Michael addition reactions were conducted to prepare modified TEPA sorbents to identify the effect of amine type on CO_2 adsorption/desorption characteristics. TEPA was modified with various amounts of AN in order to find optimal ratio of which can be convert primary amines into secondary amines. The first aim of this investigation was to examine the physical and chemical characteristics of the modified TEPA sorbent; the second aim was to compare the CO_2 adsorption/desorption characteristics of solid amines with different amine structures.

2. Experimental

Acrylonitrile (AN; Sigma–Aldrich, Inc., purity > 99 + %), tetraethylenepentamine (TEPA; Sigma–Aldrich, Inc., purity > 99 + %), and MeOH (Sigma–Aldrich, Inc., purity > 99 + %) were used without further purification. The polymeric support poly(methyl methacrylate) (PMMA, HP2MG; manufacturer: Mitsubishi Chemical) was purchased from Sigma–Aldrich, Inc. with the following manufacturer specifications: effective particle size, 0.5 mm; pore volume, 1.2 mL/g; specific surface area, 500 m^2/g; average pore radius, 17 nm; density, 10.9 g/mL.

2.1. Synthesis of modified amines with different structures

TEPA was modified via a Michael addition reaction between TEPA and AN to synthesize secondary amines [30]. AN reacts predominantly with primary amines to produce secondary amine functionality. A general procedure for Michael adduct formation from TEPA and AN follows: a three-necked 100 mL round-bottom glass flask with a magnetic stirrer was initially charged with TEPA, to which AN was injected drop-wise at different ratios of TEPA:AN (Table 1). The rate of AN addition was limited to prevent the solution temperature from exceeding 45 °C. After completing AN addition, the solution was heated to 50 °C and stirred for 1 h to ensure complete reaction of the reactants. Fig. 1(a) shows the primary amines (—NH_2) of TEPA replaced with a secondary amines (—NH) through the Michael addition reaction of TEPA and AN. 2 molecules of AN can convert all of its primary amine sites. Fig. 1 also shows possible side reaction between secondary amines (—NH) and excessively injected AN. The products were referred to as TxAN, where x denotes the molar ratio of the reactants.

Table 1
Molar ratios for TEPA modification and expected amine type ratio (Primary:Secondary:Tertiary amine).

Product	Amine type (P:S:T)	TEPA (mol)	AN (mol)
TEPA	2:3:0	1	
T1AN	1:4:0	1	1
T2AN	0:5:0	1	2
T3AN	0:4:1	1	3

2.2. Synthesis of amine-impregnated sorbents

A wet impregnation process was used to produce the TxAN-impregnated sorbent. An amine:support ratio (mass of amine:mass of support) of 0.7:1.0 was previously determined; this showed optimal CO_2 sorbent adsorption performance [30].

A general procedure follows: PMMA support beads were initially washed with methanol and heated up to 100 °C to eliminate impurities. 0.7 g of amine was dissolved in methanol (7.0 g) in a vial with sonication for 20 min, following which PMMA (1.0 g) was added to the vial. Next, the vial was heated to 60 °C in a convection oven to remove methanol. TxAN-impregnated solid amines were obtained, and were referred to as STxAN.

2.3. Characterization of liquid amines

The pH values of the liquid amines were measured in a 25 wt% aqueous solution. The pH of the final solution was measured with an Orion 4-star pH benchtop meter (Thermo Scientific). All of the measurements were made at ambient temperatures. Each pH reading was measured after 60 s to allow the electrode to reach a steady-state value.

Creep tests were conducted to measure zero shear viscosity of liquid amines using an AR2000 stress rheometer (TA Instruments). Steady rate-sweep tests were performed at a shear rate between 0.01 and 100 s^{-1}.

Liquid amine thermal stabilities were measured by thermogravimetric analysis (TGA, Q50, TA Instruments). About 60 mg of liquid amine was loaded into an alumina sample pan. The liquid amine was heated to 400 °C at a heating rate of 10 °C/min under N_2 atmosphere.

2.4. Characterization of amine-impregnated sorbents

N_2 adsorption/desorption isotherms of sorbents were obtained on a Micromeritics ASAP-2020 sorptometer at a liquid N_2 temperature. The sorbents were out-gassed at 100 °C for more than 6 h on a high-vacuum line prior to adsorption. The specific surface areas of the samples were calculated by the Brunauer–Emmett–Teller (BET) method and pore sizes/distributions were obtained by the Barrett–Joyner–Halenda (BJH) method using the isotherm desorption branches.

CO_2 adsorption characteristics of the sorbents were measured by TGA. About 10–30 mg of sorbent was loaded into an alumina sample pan and subjected to CO_2 adsorption studies. The sorbent was pretreated by heating to 100 °C in a N_2 atmosphere and maintained at this temperature for 180 min. The temperature of the

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