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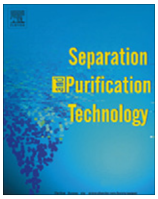

Use of multifunctional nanoporous $TiO(OH)_2$ for catalytic $NaHCO_3$ decomposition-eventually for $Na_2CO_3/NaHCO_3$ based CO_2 separation technology

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ABSTRACT

In general, CO_2 capture from flue gas is a costly procedure, usually due to the energy required for regeneration of the capture medium. One potential medium which could reduce such an energy consumption, however, is Na_2CO_3. It has been well studied as a sorbent, and it is understood that the theoretical energy penalty of use of Na_2CO_3 for CO_2 separation is low, due to the relatively low heat of reaction and low heat capacity of the material. While it offers some advantages over other methods, its primary downfall is the slow reaction with CO_2 during adsorption and the slow Na_2CO_3 regeneration process. In an effort to reduce the energy penalty of post-combustion CO_2 capture, the catalytic decomposition of $NaHCO_3$ is studied. Nanoporous $TiO(OH)_2$ is examined as a potential catalytic support for a cyclic $Na_2CO_3/NaHCO_3$ based CO_2 capture process. FT-IR, SEM, and XRD characterization of $NaHCO_3$ supported on nanoporous $TiO(OH)_2$ treated with different processes indicate that $TiO(OH)_2$ is stable within the temperature range necessary for such a process, up to about 200 °C. More importantly, the $TiO(OH)_2$ has a catalytic effect on the decomposition of $NaHCO_3$, reducing the activation energy from about 80 to 36 kJ/mol. This significant drop in activation energy could translate into a much lower operating cost for regenerating Na_2CO_3. The reaction rate of $NaHCO_3$ decomposition, or CO_2 desorption, is observed to increase by as much as a factor of ten due to this decrease in activation energy.

1. Introduction

Anthropogenic CO_2 is considered a major contributor to global warming. One of the primary sources of anthropogenic CO_2 is the flue gas from fossil fuel-fired power plants. As such, an ideal method of CO_2 abatement is to remove CO_2 from flue gas. Several techniques exist to accomplish this, including absorption using liquid solvents, membrane separation, cryogenic separation, and adsorption onto solid sorbents [1–9]. Each technique has its own advantages and disadvantages.

Currently, the most developed and commercially viable CO_2 separation technology is stripping CO_2 with aqueous amine solutions. Due to its many advantages, this technology has been commonly used to remove CO_2 and other acid gases as impurities from natural gas for over 60 years [1,5]. Study on its use for CO_2 separation from flue gas is fairly recent, however. The solvents have typically been designed for low temperature absorption, below the temperatures of typical flue gas, and as such, have poor thermal stability [1,5,10]. The amines cannot only be poisoned by common impurities in the flue gas, such as SO_x and NO_x gases, but also oxygen [1,5]. Some of the amine can be lost through evaporation to the gas stream during use, thus requiring replacement [10,11]. Moreover, amines are toxic and corrosive, and therefore are pollutants to the environment. Because of their corrosive properties, amines typically need to be diluted with water; with more water present, more energy is required for desorption of CO_2. This dilution also lowers the CO_2 capture capacities of amine solutions [1,5,10,11].

In an alternative liquid absorption process, CO_2 is captured by an aqueous alkali metal carbonate solution via the reaction

$$M_2CO_3 + CO_2 + H_2O \leftrightarrow 2MHCO_3 \tag{R1}$$

where M represents the alkali metal, primarily sodium and potassium. In this reversible reaction, carbonation occurs at temperatures typical of flue gas, 50–80 °C, and decarbonation is achieved by boiling the solution [12–19]. When M is sodium, R1 can be specifically written as

$$Na_2CO_3 + CO_2 + H_2O \leftrightarrow 2NaHCO_3 \tag{R2}$$

Using alkali carbonates has several advantages. The primary one is their capital costs; alkali carbonates are readily available and less expensive. Another one is that they are thermally stable; Na_2CO_3, for instance, decomposes at temperatures over 800 °C, while some

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Nomenclature

A	frequency factor (min^{-1})
α	fraction of decomposed $NaHCO_3$
B	dimensional conversion coefficient
C_e	specific heat capacity of equipment (kJ/kg K)
C_{p,CO_2}	specific heat capacity of CO_2 (kJ/kg K)
$C_{p,\ NHT}$	specific heat capacity of NHT (kJ/kg K)
E_A	activation Energy (kJ/mol)
$F(\alpha)$	mechanism of decomposition
ΔH	heat of reaction (kJ/mol)
k	rate constant (min^{-1})
L	CO_2 loading (kg CO_2/kg NT)
m	reaction order for A_m
m_{CO_2}	mass of CO_2 adsorbed (kg)
m_e	mass of equipment (kg)
M_{CO_2}	molecular weight of CO_2 (g/mol)
n	reaction order for R_n
R	molar gas constant (kJ/(mol K))
T	absolute temperature (K)
T_{CO_2-a}	adsorption temperature (K)
T_{CO_2-d}	desorption temperature (K)
t	time (min)
w	mass of $NaHCO_3$ at a given time (mg)
w_0	initial mass of $NaHCO_3$ (mg)

amines, on the other hand, decompose at temperatures as low as 120 °C [1]. Alkali carbonates, like most salts, have negligible vapor pressures, meaning that there will be little losses during CO_2 sorption or sorbent regeneration. Losses can occur through poisoning since SO_2 and NO_x gases react irreversibly with the carbonate anion [14,17]. Any losses that do occur, however, can be easily and inexpensively replaced, due to the ease of handling alkali carbonates and their low prices.

Using aqueous alkali carbonates has the potential to reduce energy consumption [18,19] due to their lower reaction heats, but the associated reactions proceed slowly. Piperazine [15,16] and boric acid [16] have been used to accelerate CO_2 sorption rates. However, the energies required to heat the aqueous solutions for CO_2 desorption or bicarbonates desorption are high, as with other liquid absorption processes.

Recently, people started to develop solid sorbents for CO_2 separation in flue gas due to their higher CO_2 loading and lower heat capacities [20]. The performances of some solid sorbents, zeolites in particular, are deteriorated by the presence of water in the flue gas because their porous structures are plugged with condensed water [20]. However, solid alkali carbonates need water for the capture of CO_2 according to R1. Pure carbonates and supported carbonates have been studied as solid chemical adsorbents, and it has been shown that some of them are stable and capable of removing 90% of CO_2 from a flue gas stream [17,21–32]. Impregnation of K_2CO_3/Na_2CO_3 onto a porous matrix improves the sorption capacity as well as the reaction rate, though to date most work in regards to kinetics has been qualitative [21,28,30].

As with aqueous solutions [12], K_2CO_3 has a higher sorption capacity for CO_2 and the reaction proceeds faster than with Na_2CO_3 [23,24,26]. One primary advantage of Na_2CO_3 over K_2CO_3, however, is its much lower price. In addition, Na_2CO_3 is more widely available, especially in Wyoming which has the world's largest deposit of trona and supplies about 90% of the soda ash in the US [33]. Therefore, Na_2CO_3 is still a promising CO_2 separation agent.

Sorption of CO_2 onto Na_2CO_3 is spontaneous under flue gas conditions. Because the sorption of CO_2 is spontaneous, as with most other technologies, the most energy intensive step in the use of Na_2CO_3 for CO_2 capture is sorbent regeneration or CO_2 desorption, which, essentially, is that the sorbent is heated in order to shift the equilibrium of R2 towards the left. The kinetics of the decomposition reaction of pure $NaHCO_3$ have been studied extensively [34–36], but little information is available on the effect of a supporting material on CO_2 desorption or decomposition of pure $NaHCO_3$ on the surface of a supporting material.

An ideal supporting material should not only maximize surface area of the $NaHCO_3$/Na_2CO_3 but also be a good catalyst to accelerate the desorption rate of CO_2 and consequently reduce the overall energy consumption of CO_2 separation. To the best knowledge of this research team, the second role of supporting materials during CO_2 desorption process has been neglected in the past. However, it is very imperative, since the reduction in energy consumption for CO_2 desorption by avoiding or reducing use of water alone is limited. Therefore, finding new multifunctional materials which can support Na_2CO_3/$NaHCO_3$ and catalyze the desorption of CO_2 or decomposition of $NaHCO_3$ resulting from sorption of CO_2 with Na_2CO_3 is crucial.

One potential supporting material is nanoporous titanium oxyhydrate, $TiO(OH)_2$. It can decompose into TiO_2 via the following reaction

$$TiO(OH)_2 \leftrightarrow TiO_2 + H_2O. \qquad \text{(R3)}$$

However, this reaction begins to proceed towards the right side only at temperatures above 300 °C [37–39], making it a stable supporting material of Na_2CO_3 for synthesis of solid sorbents for CO_2 capture from flue gas with Na_2CO_3. More importantly, people are interested in using it as a catalyst [40].

Accordingly, the aim of this research is to explore the possibility of using nanoporous $TiO(OH)_2$ as a multifunctional material for Na_2CO_3 based CO_2 separation process. The focus of the study is on the kinetic properties of catalytic desorption of CO_2 on the interface between $NaHCO_3$ and nanoporous $TiO(OH)_2$. It should be mentioned that optimizing the CO_2 sorption capacity of CO_2 is outside the scope of this research.

2. Experimental

2.1. Preparation of $NaHCO_3$/$Ti(OH)_2$

Pure $NaHCO_3$ was obtained from BDF Chemical. When Pure $NaHCO_3$ was used for decomposition tests, it was crushed and sieved such that only particles with diameters less 300 μm were used. $TiO(OH)_2$ is prepared in the lab with $Ti(OC_2H_5)_4$ from Acros containing 33–35 wt.% TiO_2. The first preparation step was to add the predetermined quantity of $Ti(OC_2H_5)_4$ to water with the H_2O:$Ti(OC_2H_5)_4$ molar ratio being 26.3:1, followed by stirring the resultant mixture for 1 h. Then, the precipitate, $TiO(OH)_2$, was filtered, washed with deionized water, and dried at 120 °C for about 1.5 h.

$NaHCO_3$ was loaded on $TiO(OH)_2$ by mixing predetermined amounts of $TiO(OH)_2$ and $NaHCO_3$; the mass of each is determined by the specific weight percent of $NaHCO_3$ on the final product, $NaHCO_3$/$TiO(OH)_2$ (hereafter called NHT). The 90, 50, and 20 wt.% NHT samples (containing 90, 50 and 20 wt.% $NaHCO_3$, respectively) were used for CO_2 desorption kinetic study. The specific NHT preparation steps include dissolving the needed $NaHCO_3$ with sufficient distilled water to dissolve the $NaHCO_3$, stirring the aqueous $NaHCO_3$ and solid $TiO(OH)_2$ mixture at ambient conditions for at least