Chemical Engineering Journal 291 (2016) 161–173

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Double sodium salt-promoted mesoporous MgO sorbent with high CO_2 sorption capacity at intermediate temperatures under dry and wet conditions

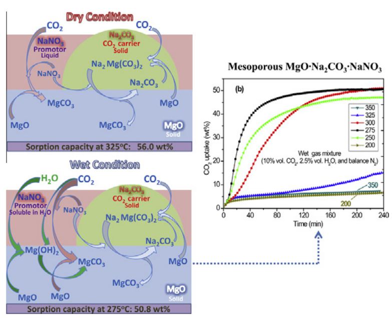
Anh-Tuan Vu [a,b], Keon Ho [a], Seongmin Jin [a], Chang-Ha Lee [a,*]

[a] Department of Chemical and Biomolecular Engineering, Yonsei University, Republic of Korea
[b] School of Chemical Engineering, Hanoi University of Science and Technology, Vietnam

HIGHLIGHTS

- The $MgO{\cdot}Na_2CO_3{\cdot}NaNO_3$ composites were prepared using an aerogel method.
- The composite showed a high CO_2 sorption capacity at intermediate temperatures.
- Na_2CO_3 worked as a CO_2 carrier while $NaNO_3$ functioned as a reaction promoter.
- $Mg(OH)_2$ in wet condition led to fast sorption rate and high sorption capacity.
- One phase condition of $NaNO_3$ in cyclic test resulted in high stability of sorbent.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 24 November 2015
Received in revised form 18 January 2016
Accepted 19 January 2016
Available online 1 February 2016

Keywords:
MgO composite
Aerogel method
Sorption
CO_2 capture
Intermediate temperature

ABSTRACT

Mesoporous $MgO{\cdot}Na_2CO_3{\cdot}NaNO_3$ composites were prepared using supercritical drying of methanol for CO_2 capture in power plants at an intermediate temperature range between 250 and 450 °C. The effects of the molar ratio of salt, temperature, and gas composition on the CO_2 sorption were investigated under dry and wet conditions in order to clarify the sorption mechanisms and roles of $NaNO_3$ and Na_2CO_3. The composites exhibited excellent sorption capacities of 56.0 wt.% at 325 °C in pure CO_2 and 50.8 wt.% at 275 °C in a wet gas mixtures (10% CO_2, 2.5% H_2O, and balanced N_2). The CO_2 sorption mechanism was dominated through the formation of $MgCO_3$ and $Na_2Mg(CO_3)_2$ with Na_2CO_3 working as a CO_2 carrier, while $NaNO_3$ functioned as a reaction promoter. Under wet conditions, the formation of $Mg(OH)_2$ resulted in fast sorption rates and high capacities even at low CO_2 concentrations in the gas feedstock. One phase (liquid) condition of $NaNO_3$ and water vapor during a sorption and regeneration cycle resulted in a high stability of the sorbent. The working capacity in a 14 cycle test under N_2 regeneration (10 min) at 450 °C was 31.8 wt.% at 325 °C in pure dry CO_2 and 29.4 wt.% at 275 °C with a wet CO_2 mixture.

1. Introduction

An excess of CO_2 in the atmosphere is widely accepted as one of the main contributors toward global warming [1]. Since fossil fuel-based power plants represent a massive CO_2 emission source, various efforts have been directed toward capturing CO_2 from the effluent gases to reduce the levels of CO_2 within the atmosphere.

CO_2 sorption based on solid materials has received considerable attention toward overcoming the problems inherent to current CO_2 capture technologies. Various porous solid materials such as activated carbons [2,3], zeolites [4,5], porous silica composite [6],

* Corresponding author. Tel.: +82 02 2123 2762; fax: +82 02 312 6401.
E-mail address: leech@yonsei.ac.kr (C.-H. Lee).

http://dx.doi.org/10.1016/j.cej.2016.01.080
1385-8947/

polymers [7,8] and metal organic frameworks [9–11] have been studied for the removal of CO_2 from emission gases. However, since the performances of these materials are not enough for practical application to CO_2 capture, the improved materials with higher CO_2 capacity are needed.

Recently, magnesium oxide (MgO) has received enormous interest as an alternative solid sorbent for the sorption of toxic chemicals and carbon dioxide due to its excellent physical properties, including: its large specific surface area, high pore volume, narrow pore size distribution, and high sorption capacity [12–15].

Many MgO-based sorbents have focused on post-combustion CO_2 capture and sorbent evaluations are usually carried out at relatively low temperatures (below 100 °C) [16–23]. Another important aspect related to carbon capture and sequestration (CCS) is pre-combustion CO_2 capture, which requires intermediate to high temperature conditions. If CO_2 can be efficiently captured from the effluent gas of a water–gas-shift reactor (WGSR), gasifier or combustor, at intermediate to high temperature conditions, more energy-efficient combustion processes with CO_2 capture can be designed due to relatively mild operating temperatures and accessible regeneration heat sources. For example, the temperature of flue gas in the Integrated Gasification Combined Cycle (IGCC) process is usually supplied to a gas turbine in the range of 150–450 °C [24]. Furthermore, low temperature WGSR can be applied to the synthesized gas to maximize H_2 production in the IGCC. Therefore, sorbents can be regenerated by using heat sources obtained from process heat network.

The incorporation of alkaline metal salts to MgO materials has been shown to enhance the CO_2 sorption capacity at intermediate temperatures. It was reported that the peculiar effects of alkali metal nitrates were attributed to the presence of a high concentration of oxide ions in the molten alkali metal nitrates [25]. Mixtures of MgO and K_2CO_3 prepared via a precipitation method exhibited a CO_2 sorption capacity of 8.69 wt.% at 375 °C and 1 bar under dry CO_2 condition [26]. The MgO·KNO_3 composite prepared from an aerogel method had a maximum sorption capacity of 13.9 wt.% at 325 °C and 1 bar under dry CO_2 condition. In particular, MgO promoted by double sodium salts synthesized via a wet mixing method had the highest CO_2 sorption capacity of 15.4 wt.% at 380 °C and 1 bar under dry CO_2 condition [27,28], but the roles of $NaNO_3$ and Na_2CO_3 in CO_2 sorption need to be clarified. The performance was still lower than those obtained for CaO at high temperatures and metal organic framework (MOF) and porous carbon at low temperatures [10,29,30].

To reduce the costs associated with CO_2 capture, the performance of the sorbent needs to be further improved with regard to the sorption capacity and rate. And developed sorbents must be evaluated under the emitted gas conditions which contain water vapor for practical application. Typically, effluent gases from power plants contain 10–15% CO_2 with water vapor and the composition of effluent gas from WGSR in syn-gasifier plants is 15–60% CO_2, 20–30% H_2O, and other components [31–33]. Furthermore, it is reported that the presence of steam in the feed gas accelerates the CO_2 capture in several adsorbents [34]. Furthermore, the working capacity of sorption and regeneration is more important than the absolute sorption capacity.

In this study, we report the mesoporous MgO·Na_2CO_3·$NaNO_3$ composite materials prepared via supercritical drying of methanol for CO_2 capture at intermediate temperatures. The CO_2 sorption capacity and rate of the as-prepared composites were evaluated at an intermediate temperature range between 200 and 400 °C under dry and wet gas conditions. The mechanisms of CO_2 sorption at dry and wet gas conditions were elucidated by controlling compositions of double sodium salts quantitatively. The sorption mechanism of CO_2 uptake on the composite was analyzed through X-ray diffraction patterns (XRD), transmission electron microcopy (TEM), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), N_2 adsorption/desorption isotherms, and CO_2 sorption isotherms. In addition, the stability and working capacity of the composites were evaluated via cyclic testing under both wet (10% CO_2, 2.5% H_2O, and balanced N_2) and dry (10% CO_2 and balanced N_2) conditions.

2. Experimental

2.1. Chemicals

The following materials were used in this study: Toluene (Daejung, Korea; 99.8%), magnesium methoxide in methanol (Aldrich, USA; 7.85%), Na_2CO_3 (Aldrich, 99.5%), and $NaNO_3$ (Duksan, Korea; 99.0%) were used without any further purification. N_2 (Deokyang, Korea; 99.999%) was used as a purge gas during activation and cyclic regeneration. CO_2 (Deokyang; 99.999%) was applied for sorption. De-ionized water was used to generate the wet gas mixture.

2.2. Sorbent preparation

Mesoporous MgO·Na_2CO_3·$NaNO_3$ composites were synthesized via an aerogel method with a supercritical drying. At room temperature, a mixture of toluene (100 mL) and magnesium methoxide (20 mL) was stirred in a glass reactor for 30 min. Na_2CO_3 and $NaNO_3$ (varying mass) were dissolved in distilled water (2.0 mL) and slowly added to the previously prepared solution via syringe. To minimize evaporation, the top of the reactor was covered with aluminum foil. The mixture was stirred vigorously overnight at room temperature to undergo full hydrolysis.

The hydrolyzed gel was transferred into a high pressure autoclave reactor. The reactor was subsequently flushed and pressurized up to 1 bar with N_2 gas. The autoclave reactor was gradually heated from room temperature to 265 °C at the rate of 1.0 °C/min, and maintained at 265 °C for 10 min. The reactor pressure was rapidly reduced by releasing solvent vapors. The isolated powder was dried in an oven at 120 °C for 12 h to remove residual organic solvents. As a final step, the dried powder was placed in a furnace. The following calcination procedure was applied under air: the temperature was ramped to 450 °C at a heating rate of 10 °C/min and soaked at 450 °C for 3 h. The sample was stored for CO_2 sorption measurement.

Since some experimental temperatures were higher than the melting temperature of $NaNO_3$ (308 °C), excessive addition of $NaNO_3$ to the composite may lead to filling the composite pores with liquid $NaNO_3$ during sorption and/or regeneration. Therefore, the CO_2 sorption capacity and the sorption rate of MgO·$NaNO_3$ composite at the molar ratio of 1:0.2 were higher and faster than those of other composites at different molar ratios (1:0.5; 1:0.1; 1:0.4; and 1:0.6) (Fig. S1). It was similar to the results observed from MgO·KNO_3 composites in the previous report [35]. Therefore, under the fixed molar ratio of MgO/$NaNO_3$ at 1:0.2, the effects of additional Na_2CO_3 content on the physical properties and CO_2 sorption behavior of the MgO·Na_2CO_3·$NaNO_3$ composites were investigated. The MgO·Na_2CO_3·$NaNO_3$ composites was investigated by fixing the molar ratio of $NaNO_3$. MgO·Na_2CO_3·$NaNO_3$ composites with a mole ratio of MgO/Na_2CO_3/$NaNO_3$ [1:X:0.2] (where 1, X, and 0.2 were the molar contents of MgO, Na_2CO_3, and $NaNO_3$, respectively) were denoted as MgONaNa-X, where X = 0.05, 0.1, 0.2, 0.4, and 0.6 for the Na_2CO_3 molar ratio. Additionally, pure MgO, MgO·Na_2CO_3, and MgO·$NaNO_3$ composites were prepared via the same procedure to be compared with the MgO·Na_2CO_3·$NaNO_3$ composites.