Journal of CO_2 Utilization 24 (2018) 200–209

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

A novel application of α- and β-sodium ferrite as a CO_2-capturing solid in air with water vapor

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A R T I C L E I N F O

Keywords:
CO_2
Sodium ferrite
Water vapor
pH

A B S T R A C T

The CO_2 adsorption properties of synthesized sodium ferrites (α-$NaFeO_2$ and β-$NaFeO_2$) under air and CO_2 flows with various relative humidity (RH) were investigated. Thermogravimetry (TG) analysis showed the CO_2 adsorption reactions of α- and β-$NaFeO_2$ were promoted even at room temperature (RT) by increasing RH even in air with a low CO_2 concentration and the CO_2 reaction ratio of β-$NaFeO_2$ was larger than that of α-$NaFeO_2$. X-ray photo spectroscopy (XPS), X-ray diffractometry (XRD), and Fourier transform infrared spectroscopy (FTIR) clarified that $Na_2CO_3{\cdot}H_2O$ and $NaHCO_3$ were produced under air and CO_2 flows, respectively, and $Na_{1\text{-}x}FeO_2$ and α-Fe_2O_3 were produced for α- and β-$NaFeO_2$ after the CO_2 adsorption, respectively. The Na^+ concentration and pH were rapidly increased by dispersing $NaFeO_2$ into distilled water. It was therefore found that a basic solution was formed on the surface of $NaFeO_2$ by the adsorption of water molecules on the surface, giving rise to the promotion of CO_2 adsorption of $NaFeO_2$ at as low as RT in atmospheres with low CO_2 concentrations.

1. Introduction

Various inorganic metal oxides, including alkaline ions such as lithium silicate (Li_4SiO_4) [1–5], lithium zirconium (Li_2ZrO_3) [6], lithium ferrite ($LiFeO_2$) [7–11], lithium titanate (Li_2TiO_3) [12], and sodium silicate (Na_2SiO_3) [13] have been studied as CO_2 adsorption materials. These materials are useful for CO_2 capture under moderate and high temperatures by the production of lithium carbonates under a CO_2 atmosphere. However, the CO_2 adsorption rates of these materials at lower temperatures are very small, indicating that these inorganic metal oxides are not suitable for CO_2 capture at low temperatures ranging from room temperature to 100 °C. On the other hand, inorganic compounds such as O3-$LiFeO_2$, which has a layered structure with the space group *R*-3*m* and is composed of FeO_6 octahedra in which sodium ions are aligned [14–16], are unstable and produce carbonates under water vapor [11]. This is because the lithium ions are removed from the layered structure when the surface of the compound contacts water [17]. As for lithium compounds, it was also reported that lithium metasilicates (Li_2SiO_3) composed of a SiO_4 framework structure including Li^+ ions reacted with CO_2 at as low as 150 °C under water vapor [18].

Sodium ferrites (α-$NaFeO_2$) have a layered structure with the space group *R*-3m, similar to O3-$LiFeO_2$, [13–15] 14–16 and have been studied as cathode materials in rechargeable sodium-ion secondary batteries [19,20]. The structural features of α-$NaFeO_2$ suggest that sodium ions in the layered structure composed of FeO_6 octahedra are also easily removed from the structure, similar to the case for O3-$LiFeO_2$ [11]. In fact, α-$NaFeO_2$ can be easily dissolved into water, and the solution formed by the dissolution is capable of capturing CO_2 in air [21] because the dissolution of sodium ferrites into water leads to a large pH value. Therefore, $NaFeO_2$ are expected to be a CO_2-capture material under a low CO_2 concentration atmosphere due to the formation of a basic solution on the surface of $NaFeO_2$. The CO_2 adsorption mechanism of $NaFeO_2$ is different from that of traditional CO_2-capture materials such as M_2CO_3 (M = Li, Na, K) and zeolites [22], suggesting a novel application of $NaFeO_2$ for CO_2-adsorption materials.

Water vapor in air easily adsorbs on the surface of substances, suggesting that the adsorption of water vapor gives rise to the formation of a basic water droplet and/or a water film [23] on the surface of sodium ferrites and the chemical reaction of the basic water with CO_2 [24,25]. The crystal structure of β-$NaFeO_2$ consisting of FeO_4 tetrahedra [26] is different from α-$NaFeO_2$ consisting of FeO_6 octahedra, suggesting CO_2 adsorption properties of α-$NaFeO_2$ and β-$NaFeO_2$ are different from each other. In this study, β-$NaFeO_2$ was synthesized in addition to α-$NaFeO_2$ and the CO_2 adsorption properties of the synthesized α- and β-$NaFeO_2$ in atmospheres including CO_2 and H_2O were examined.

2. Experimental

Commercially available γ-Fe_2O_3 (> 99% purity, Wako, Japan) and

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https://doi.org/10.1016/j.jcou.2017.11.016
Received 29 July 2017; Received in revised form 28 November 2017; Accepted 29 November 2017

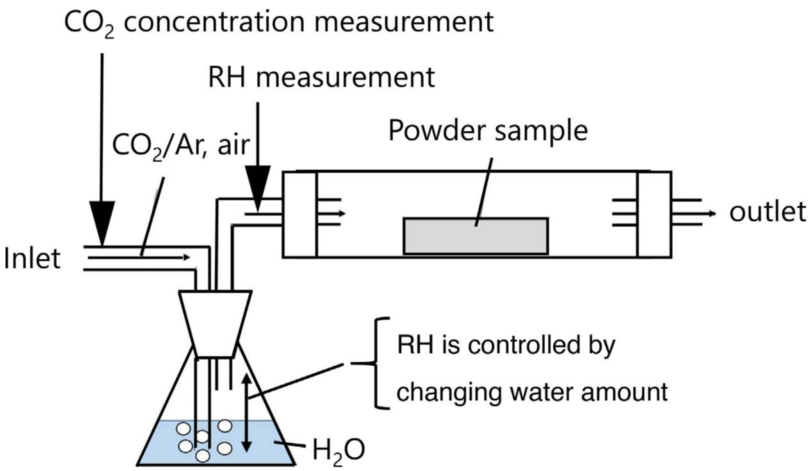

Fig. 1. Experimental apparatus for CO_2 adsorption under various gases (CO_2, Ar, air) with controlled relative humidity (RH). Here, the CO_2 concentration was 0.05%.

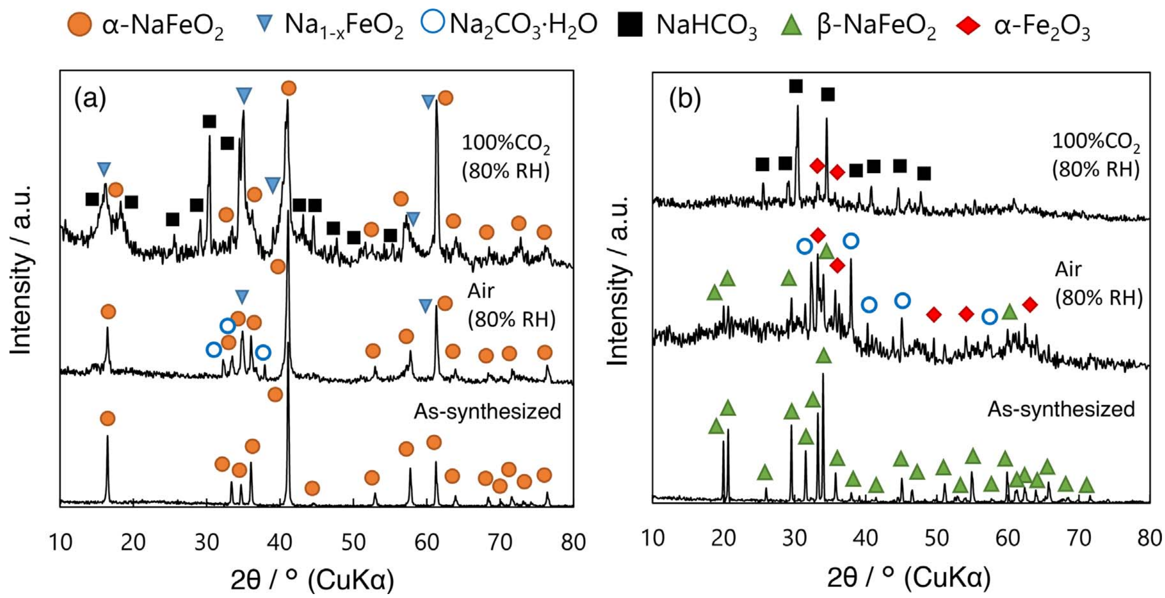

Fig. 2. XRD patterns of (a) α-$NaFeO_2$ and (b) β-$NaFeO_2$ absorbed CO_2 at room temperature (RT) under air (0.05% CO_2) or 100% CO_2 with 80% RH.

$NaNO_3$ (> 99% purity, Wako, Japan) powders were measured to have a molar ratio of Na/Fe = 1; then, the above two powders were mixed in ion-exchanged water for 1 h with ultrasonic treatment. After removing water with an evaporator, the mixed powder was dried and then heated at temperatures of 550 and 650 °C for 15 h in air to synthesize α-$NaFeO_2$ single-phase powders. Similarly, the mixed powder was dried and then heated at 800 °C for 4 h in air to synthesize β-$NaFeO_2$ single-phase powders.

The CO_2 adsorption reaction using α-$NaFeO_2$ was carried out in a mullite tube at various temperatures for 5 h under air or CO_2 gas with a pressure of 0.1 MPa and a flow rate of 200 ml/min (Fig. 1). The relative humidity (RH) in various gases with different CO_2 concentrations was controlled by bubbling the gases into water at room temperature (RT), as shown in Fig. 1. The CO_2 reaction ratio at RT of the synthesized powders were also investigated under CO_2 gas with a flow rate of 100 ml/min by thermogravimetry and differential thermal analysis (TG-DTA; Thermoplus TG8120, Rigaku). The CO_2 concentration and the relative humidity (RH) in various gases were controlled by mixing Ar gas and bubbling the gas into water, respectively, similar to Fig. 1. The CO_2 concentration in air was approximately 0.05% (500 ppm), measured before bubbling air. The produced phases in the CO_2-adsorbed powders were investigated by X-ray diffractometry (XRD) and Fourier transform infrared spectroscopy (FTIR) with an attenuated total reflection (ATR) attachment. The powder morphologies of the α-$NaFeO_2$ powders before and after CO_2 adsorption were examined using a field-emission scanning electron microscope (FESEM, S4100, Hitachi).

N_2 adsorption and desorption isotherms at −196 °C were used to determine the Brunauer-Emmett-Teller (BET) specific surface area, and CO_2 adsorption isotherms at 25 °C were measured using a BELSOPP-mini II (MicrotracBEL, Japan). Water vapor adsorption and desorption isotherms at 25 °C were measured using a BELSOPP-max II (MicrotracBEL, Japan). The concentrations of Na ions dissolved in water were measured by a sodium ion meter (Horiba, LAQUA B-722). Binding energies for Na 1 s of and Fe 2p in samples were determined using X-ray photospectroscopy (XPS; Kratos, Shimadzu) with MgKα radiation. The binding energies were calibrated using C 1s (284.6 eV) of contaminated carbon.

The theoretical mass increasing ratio for $NaFeO_2$ was estimated using reactions (1)–(3);

$$2NaFeO_2 + CO_2 \rightarrow Na_2CO_3 + Fe_2O_3, \quad (1)$$

$$2NaFeO_2 + CO_2 + H_2O \rightarrow Na_2CO_3{\cdot}H_2O + Fe_2O_3, \quad (2)$$

$$2NaFeO_2 + 2CO_2 + H_2O \rightarrow 2NaHCO_3 + Fe_2O_3. \quad (3)$$

Here, the theoretical reaction ratios of the above reactions were 19.9%, 28.0%, and 47.8%, respectively.