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# Carbon dioxide removal using calcium aluminate carbonates on titanic oxide under warm-gas conditions<sup>☆</sup>

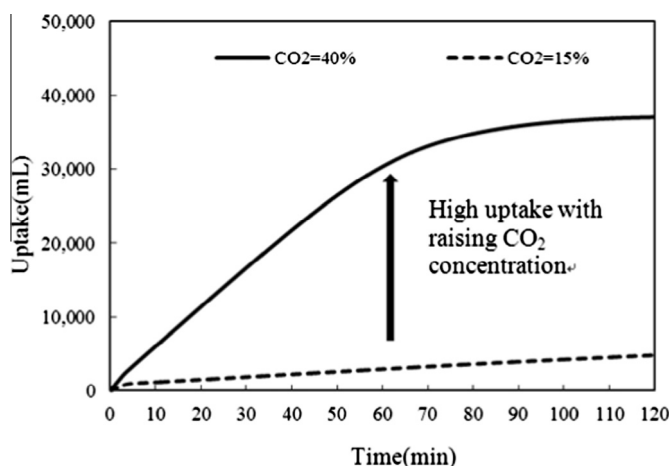
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## HIGHLIGHTS

- CO<sub>2</sub> sorbents of Ca/Al/Ti<sub>x</sub> was prepared by precipitation-and-deposition method.
- Sorption CO<sub>2</sub> was tested at 750 °C by TG analysis and fixed-bed reactor.
- CO<sub>2</sub> capture stability was 96–98% after ten cycles at 750 °C by TG analysis.
- Scale-up production of Ca/Al/Ti<sub>x</sub> granule and their CO<sub>2</sub> capture in reactor was tested.

## GRAPHICAL ABSTRACT



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## ABSTRACT

This study presents a scale-up production method for Ti including Ca/Al sorbents and their CO<sub>2</sub> sorption test under warm gas conditions by thermogravimetric (TG) analysis and fixed-bed reactor experiments. The Ca/Al/Ti<sub>x</sub> sorbents are made by the precipitation-and-deposition method where Ca<sup>2+</sup> and Al<sup>3+</sup> ions are deposited via an alkaline solution of OH<sup>-</sup>/CO<sub>3</sub><sup>2-</sup> on TiO<sub>2</sub> powder. The titanium dioxide binder facilitates CO<sub>2</sub> capture and enhances the CO<sub>2</sub> capacity and multicycle stability by adjusting the Ti/Ca ratio. The results showed that these sorbents exhibited excellent CO<sub>2</sub> capture stability of 96–98% after ten cycles at 750 °C by TG analysis. Characterization by XRD indicated that the reduction in the deterioration of the sorbent during the cycle test could possibly result from the formation of an anti-sintering compound such as CaTiO<sub>3</sub> along with calcium aluminate hydroxides related to katoite. Using a reactor as test rig, the amount of sorbent and total capture weight was significantly increased. This TiO<sub>2</sub>-coated sample of Ca/Al/O–TiO<sub>2</sub> provides a feasible route for the manufacture of cheap CO<sub>2</sub> sorbents.

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## 1. Introduction

Emerging energy technologies have emphasized environmental risk management for solid waste, air quality, water repopulation, and most importantly carbon control. The removal of CO<sub>2</sub> from given emission points such as coal-fired plants, energy

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consumption industries, and incinerators using solid sorbents is of great significance in the development of greenhouse gas reduction technology. The optimal capture method chiefly depends on environmental factors, such as concentration, temperature, and pressure. At fixed pressure conditions, the sorption of concentrated CO<sub>2</sub> has the advantages of high capacity and low equipment requirements; therefore, separation of CO<sub>2</sub> from numerous gas streams is favorable at elevated temperature. The capture of CO<sub>2</sub> by solid sorbents can be easily carried out under warm gas conditions, which significantly enhances the capacity by more than 4 mmol/g compared with capture capacity of monoethanolamine (MEA) [1]. Alkaline materials such as CaO have high sorption capacities and rapid kinetics, making them suitable candidates for CO<sub>2</sub> capture [2–4]. High temperature CO<sub>2</sub> capture by CaO has been studied in related works [5–7]; they demonstrate that warm CO<sub>2</sub> capture with calcium oxides is feasible for use in related industrial applications.

Carbon dioxide mitigation by calcium looping involves repeated CO<sub>2</sub> sorption/desorption steps from CaO. After the sorption of CO<sub>2</sub> by CaO, the product CaCO<sub>3</sub> covers neighboring CaO kernels, deactivating the sorbent. The modification of CaO-based sorbents significantly improves the long-term stability and extends the CO<sub>2</sub> sorption capability. Several strategies for enhancing the capacity of Ca-compound-containing synthetic sorbents and mineral-based materials have been investigated [8]. The improvement of CaO activation by steam hydration treatment focuses on morphological changes caused by the decomposition of calcium hydroxides within micropores and the formation of more channels for sorption sites [9]. Alternatively, preparing sinter-resistant Ca-rich sorbents is another strategy. Inorganic oxides, such as Mg, Al, Si, Zr, or Ti with high Tammann temperatures, are incorporated as separator compounds that can seclude local CaCO<sub>3</sub> lumps. The sorbent stability can be significantly enhanced by incorporating suitable inert particles into CaO, yielding well-distributed oxides within the calcium oxides. Impregnating CaO with an inert particle helps to avoid the deterioration of the spent sorbent, for example, of CaO/SiO<sub>2</sub> [10], Ca/Al-oxide [11], Zr/Ca complex [12], limestone/kaolin [13], CaO/aluminate cement [14], and extruded particles of Ca(OH)<sub>2</sub>/cement [15].

Sintering and mechanical strength are crucial considerations for the use of CO<sub>2</sub> sorbent in a fixed-bed reactor. The sintering of sorbent is due to the poor heat transfer developed within the nascent CaO structure [16]. The heat expansion may create an asymmetric stress difference in grains, leading to crushed particles, which was improved by addition of binder as support [17]. Florin reported a sorption capacity of a synthetic Ca/Al sorbent (CaO–Ca<sub>2</sub>Al<sub>14</sub>O<sub>33</sub> of 85:15 wt.%) of 29 wt.% after 15 thermogravimetric (TG) cycles; the capacity was reduced to a mere 13 wt.% after 15 cycles in a fluidized bed reactor [18]. A fast chemical reaction occurs between the gas and the fresh sorbent surface in the initial stage, yielding high conversion and a fast reaction rate. However, CaCO<sub>3</sub> is formed and increases with time through chemical bonding, which significantly decreases the reaction rate in the following phase, because the unreacted CO<sub>2</sub> must eventually penetrate the interior pore through the compact CaCO<sub>3</sub> surface layer. Therefore, in a reactor with considerable gas stream, the CaO capture capacity during multiple cycle tests can be improved by incorporating anti-sintering binders. The CaO boundary should be isolated by bonding with a suitable inorganic binder as a supported material. Titanium oxide is a commercially available material that has been applied as a binder during the fabrication of adsorbents for TG analysis; these include TiO<sub>2</sub>/nano-CaO [19], CaTi-x/limestone [20], and TiO<sub>2</sub>/Ca-LDHs [21].

The critical reviews [22,23] indicated that CO<sub>2</sub> capture technology by solid sorbents of CaO has continually developed. For instance, demonstrations of the CaL process with capacities of

1 MW<sub>th</sub> and 1.7 MW<sub>th</sub> by Technische Universität Darmstadt (EST-TUD, Germany) and the EU CaOling Project. ZEG power integrated CO<sub>2</sub> capture (>600 °C) in “Sorption Enhanced Steam Methane Reforming” process. Integrated coal Gasification Fuel Cell combined cycle (IGFC) in EAGLE (Coal Energy Application for Gas, Liquids and Electricity) project has been developed with CaO at 650 °C at HyPr-Ring process by Japan. High temperature CO<sub>2</sub> capture has been tested in cement plant with 1.9 MW<sub>th</sub> pilot-scale using calcium looping process (CaL) by Industrial Technology Research Institute (ITRI, Taiwan). It demonstrates that capturing CO<sub>2</sub> with CaO at high temperature is possible to be used in related industrial applications. The life cycle analysis (LCA) demonstrated that the emission intensity of a 500 MW<sub>e</sub> coal-fired power plant with CaO looping process is comparable with one using MEA-solvent [24]. Kumar et al. reviewed potential adsorbents and technologies for high-temperature CO<sub>2</sub> capture, concluding enhancement of adsorption capacity as well as cycling stability was needed further investigations for Ca-base material [25]. The factors affecting the carbonation process and method to improve adsorption capacity and conversion of calcium-based sorbent in fixed-bed reactor were advanced investigated [26]. Furthermore, the upgrade production of sorbent and their stability improvement are crucial routes, including of using low-cost material such as alkaline mineral or industrial wastes. This study provides a potential way to fabricate kg-grade solid sorbent and the stability test via Ca–Al–CO<sub>3</sub> material with suitable binder in 10 kW reactor, which has the novelty in comparison to the previous studies.

The scaled-up production of Ca/Ti sorbents is still needed for the further development of the kW reactor test. Under alkaline conditions, the hydrophilic interaction between Ca<sup>2+</sup> and Ti(OH)<sub>4</sub><sup>−</sup> makes TiO<sub>2</sub> a good additive. The hydrophilic character of layered double hydroxides (LDHs) enhances the hydration of the synthetic sorbent composed of microcrystals of CaO and Ca(OH)<sub>2</sub>. Thus, the co-leading Ca<sup>2+</sup> and Al<sup>3+</sup> ions can leach into the lamella compound and subsequently deposit on the TiO<sub>2</sub> surface. This study reports the synthesis of Ca/Al/Ti<sub>x</sub> materials by the precipitation-and-deposition method and conducts CO<sub>2</sub> sorption testing using TG analysis and fixed-bed reactor.

## 2. Experimental

### 2.1. Synthesis of sorbents

The sorbents were prepared from Ca(OAc)<sub>2</sub>·H<sub>2</sub>O (94.0%, Merck Inc., Germany), Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (98.9%, J. T. Baker Co., USA), NaOH (99.0%, Merck Inc., Germany), and Na<sub>2</sub>CO<sub>3</sub> (99.9%, Merck Inc., Germany). The chemicals comprised TiO<sub>2</sub> powder (98%, Degussa P25, Germany), CaTiO<sub>3</sub> (99%, Alfa Aesar Co., United Kingdom), and CaO (96%, AJAX Chemicals, Australia).

The synthesis procedure involves the precipitation and deposition of inorganic ions (Ca<sup>2+</sup>, Al<sup>3+</sup>, and CO<sub>3</sub><sup>2−</sup> ions) on TiO<sub>2</sub> powder under alkaline conditions. A cationic solution of Ca<sup>2+</sup>/Al<sup>3+</sup> with a molar ratio of 7:1 or 30:1 was prepared by dissolving both chemicals in Di-H<sub>2</sub>O. For example, the 30:1 solution (Ca<sub>30</sub>Al<sub>1</sub>Ti<sub>4.43</sub>) was prepared by dissolving 22.3 g Ca(OAc)<sub>2</sub>·H<sub>2</sub>O and 1.6 g Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O in 150 mL H<sub>2</sub>O and stirring to obtain a clear Ca/Al solution. Subsequently, the 4.43 mol (1.5 g) of TiO<sub>2</sub> powder was added into the Ca/Al solution. The addition of 0.16 mol (12.8 g) NaOH with 0.01 mol (2.12 g) Na<sub>2</sub>CO<sub>3</sub> in the stirred Ca<sup>2+</sup>/Al<sup>3+</sup> solution followed by filtering yielded the Ca/Al/Ti<sub>x</sub> (x = Ti/Ca = 14.8%) compound. These samples were further calcined at 750 °C to produce related powders to be used as CO<sub>2</sub> sorbents. The granule was used for the CO<sub>2</sub> sorption test by fixed-bed reactor, which was manufactured from synthetic Ca/Al/Ti powder using engineered facilities including dehydration, conveying, and

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