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# The microstructure and stability of a Ni-nano-CaO/Al<sub>2</sub>O<sub>3</sub> reforming catalyst under carbonation–calcination cycling conditions

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## ABSTRACT

The paper investigated the effect of carbonation–calcination cycling conditions on the microstructure and CO<sub>2</sub> sorption property of a sorption complex catalyst. The carbonation operation condition consisted of temperature of 600 °C with 20% CO<sub>2</sub>–80% N<sub>2</sub> and 20% CO<sub>2</sub>–80% steam atmosphere to simulate the methane reforming reaction conditions; the calcination condition was 800 °C with 100% N<sub>2</sub>. The Brunauer–Emmer–Teller (BET) surface area and thermogravimetric analysis (TGA) were measured to investigate the microstructure and variation in sorption property of the catalyst after multiple cycles under each condition. Results showed that the microstructure and CO<sub>2</sub> sorption capacity of the sorption complex catalyst decayed significantly in the initial carbonation–calcination cycles, especially under a steam atmosphere. X-ray diffraction analysis revealed that a stable compound Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> formed gradually during the initial carbonation–calcination cycle seven at a temperature of 800 °C. A model is proposed to explain the observed effect of carbonation–calcination cycling on Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> formation. Furthermore, based on our findings, a new sorption complex catalyst was prepared by pretreating at a high temperature of 900 °C. Evaluation of the catalyst prepared by the ReSER hydrogen production process through 10 circulations revealed significant improvement instability.

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## Introduction

Hydrogen is an environmentally friendly energy source with a wide array of applications in the chemical and petroleum industries. Among various feedstock, natural gas is the major source for production of hydrogen via steam methane reforming (referred to as SMR) [1,2]. In recent years, an improved SMR-based method for hydrogen production called

sorption enhanced reaction process (referred to as SERP) has attracted strong attention. SERP involves the use of a CO<sub>2</sub> adsorbent to enhance the methane reforming process by in situ removal of CO<sub>2</sub>. It has advantages of low reaction temperature, high concentration hydrogen outlet and controllable emission of the greenhouse gas CO<sub>2</sub> [3–5].

In a traditional SERP process, the CO<sub>2</sub> adsorbent and nickel reforming catalyst are mixed together mechanically, and CaO wastypicallyselected as the CO<sub>2</sub> adsorbent because of its high

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CO<sub>2</sub> sorption capacity and natural abundance [6,7]. Recently, Wu et al. [8] proposed a concept of reactive sorption-enhanced methane reforming (referred to as ReSER) process based on the use of a sorption complex catalyst that is a composite of a nano-particulate CaO adsorbent and a Ni-based catalyst in a single micro-spherical particle. Compared with mechanically mixed adsorbent and catalyst, this sorption complex catalyst can reduce resistance to heat and CO<sub>2</sub> diffusion transfer during the reforming process and also offers other advantages such as increased efficiency for enhanced reforming and convenient handling in a fluidized bed reactor [9–11].

Despite the advantages of the sorption complex catalyst, previous studies showed that its catalytic activity decreased after several ReSER cycles [8]. Various methods have been proposed to improve its stability and activity. Wang and Feng [12,13] used ZrO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> as additives to improve the stability of the catalyst by increasing dispersion of nickel and inhibiting the formation of NiAl<sub>2</sub>O<sub>4</sub> spinel. Zhang and Tang [14] used polyethylene glycol (PEG-6000) as a template to expand the pore size and thereby enhance the dispersion of nickel to increase the activity. All of the aforementioned solutions mainly focused on improving the stability and activity of nickel catalyst, but ignored the influence of nano-particulate CaO on the sorption catalyst. Since the embedded CaO needs undergo multiple carbonation–calcination cycles to keep its sorption activity, this process may have a negative influence on the sorption complex catalyst.

The effect of carbonation–calcination cycles on the stability of the catalyst is not clear, and the deactivation mechanisms of the catalyst are not well understood. Numerous studies have found structural destruction and decline in sorption activity of CaO-based adsorbent after multiple carbonation–calcination cycles [15–18]. In addition, steam in the carbonation process has been reported to accelerate the CaO sintering rate, resulting in a rapid decline in its sorption property [19–21]. However, no study has been undertaken to understand structural destruction of CaO in the complex sorption catalyst and its influence on catalyst activity during carbonation–calcination cycles.

In this study, we prepared Ni-nano-CaO/Al<sub>2</sub>O<sub>3</sub> sorption complex catalyst and subjected it to three different carbonation–calcination cycling conditions to determine the mechanism of micro-structural changes and activity decline. Then, a Ni-nano-CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorption complex catalyst was prepared based on our findings in order to improve the stability of the complex catalyst.

## Experiment

### Preparation of catalyst

#### Preparation of Ni-nano-CaO/Al<sub>2</sub>O<sub>3</sub> sorption complex catalyst

The Ni-nano-CaO/Al<sub>2</sub>O<sub>3</sub> complex catalyst was prepared by impregnating Ni(NO<sub>3</sub>)<sub>2</sub> solution on the nano-CaO/Al<sub>2</sub>O<sub>3</sub> support as described in the literature [13]. The support was prepared by mixing nano-CaCO<sub>3</sub> (70 nm, >95% purity, Hu Zhou Linghua Co., Ltd., China) with alumina sol (10%, Zibo Longao Co. Ltd., China). The mixed slurry was dried and extruded into a cylinder with a diameter of approximately 2 mm. The final

Ca/Al molar ratio in the slurry was 1:1.4. The support was calcined at 550 °C for 2–4 h and ground to 1.3–1.5 mm. A 0.2 M Ni(NO<sub>3</sub>)<sub>2</sub> solution (98% purity, Shanghai HengXin Chemical Reagent Co., Ltd., China) was prepared and infused into the nano-CaCO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> support, and the catalyst was dried at 100–150 °C and calcined at 500–800 °C. The final Ni content was about 15%, and the catalyst was named “CA-cat1”.

#### Preparation of Ni-nano-CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub> sorption complex catalyst

Preparation of the sorption complex catalyst was similar to that of the catalyst described in section Preparation of Ni-nano-CaO/Al<sub>2</sub>O<sub>3</sub> sorption complex catalyst. The nano-CaCO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> support was obtained in the same way and calcined at 900 °C for 2 h to form nano-CaO/Ca<sub>12</sub>Al<sub>14</sub>O<sub>33</sub>. Then impregnated the same Ni(NO<sub>3</sub>)<sub>2</sub> solution as described above. The catalyst was named ‘CA-cat2’.

### Characterization of the sorption complex catalyst

Surface area and pore structures of the sorption complex catalyst were characterized by nitrogen physical sorption in liquid N<sub>2</sub> at 77 K using an apparatus (BELII-mini Japan). Surface area was calculated according to the Brunauer–Emmett–Teller (BET) formula, and pore size distribution was calculated using the Barrett–Joyner–Halenda (BJH) model. Micro-crystallinity of the samples was measured by X-ray diffraction (XRD) on a Rigaku D/MAX-RA X-ray diffractometer (Japan) equipped with a copper anode. The measurement conditions were: voltage 40 kV, current 40 mA, and diffraction angle 2θ with a range of 10° to 80°.

Thermogravimetric analysis (Pyris1, Perkin–Elmer, USA) was used to measure the sorption property of the samples. The sorption process was conducted at 600 °C under 0.02 MPa of CO<sub>2</sub> in N<sub>2</sub>. Regeneration was performed at 750 °C in pure N<sub>2</sub>.

The sorption capacity was calculated according to Equation (1):

$$\text{Sorption capacity} = \frac{\text{CO}_2 \text{ sorption mol amount}}{\text{Mass of catalyst}} \times 1000 (\text{mol/kg}) \quad (1)$$

### Evaluation of catalyst

#### Evaluation of ‘CA-cat1’ by carbonation–calcination cycling

A fixed-bed reactor was used for the carbonation–calcination cycling test. Further details of the fixed-bed are provided elsewhere [12,13]. Mass flow controllers and water pump were utilized to achieve the desired inlet gas concentrations. Two cyclic carbonation conditions were employed: 600 °C for 1 h with 20% CO<sub>2</sub>–80% N<sub>2</sub>, and 20% CO<sub>2</sub>–80% H<sub>2</sub>O respectively. All calcinations were carried out at 800 °C with 100% N<sub>2</sub> for 1 h. To determine the effect of temperature variation, a cyclic condition in which the temperature was varied between 600 °C and 800 °C with 100% N<sub>2</sub> for the same time was used. A total of 30 carbonation–calcination cycles were performed and 10 g of catalyst was used to obtain different samples that were tested after the 1st, 3rd, 7th, 15th, and 30th cycles. The samples were designated as ‘Sn-m’ where ‘n’ represents the carbonation condition and ‘m’ represents the number of cycle. The condition with pure N<sub>2</sub> without carbonation was defined as ‘S1-m’

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