



## Optimization of a highly active nano-sized Pt/CeO<sub>2</sub> catalyst via Ce(OH)CO<sub>3</sub> for the water-gas shift reaction

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### ABSTRACT

Crystalline cerium hydroxy carbonate (CHC: Ce(OH)CO<sub>3</sub>) was prepared by a novel precipitation/digestion method at room temperature in air. The nano-sized CeO<sub>2</sub> supports were obtained by the thermal decomposition of CHC and the Pt/CeO<sub>2</sub> catalysts were prepared by an incipient wetness impregnation method. The pre-calcination temperature and aging time were optimized to obtain a highly active Pt/CeO<sub>2</sub> catalyst for the water gas shift reaction (WGS). The Pt/CeO<sub>2</sub> catalyst exhibited the highest CO conversion (82%) and the lowest activation energy (55 kJ/mol) at a very high gas hourly space velocity (GHSV) of 45,515 h<sup>-1</sup> when the optimized synthesis parameter (pre-calcined temperature = 400 °C and aging time = 4 h) was used in the synthesis of CeO<sub>2</sub>. This is mainly due to the high BET surface area, nano-sized CeO<sub>2</sub>, and intimate interaction between Pt and CeO<sub>2</sub>.

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### 1. Introduction

The water-gas shift reaction (WGS) is an important reaction used in the chemical industry for the production of clean hydrogen [1–3]. Recently, a Pt/CeO<sub>2</sub> catalyst has been identified as a promising catalyst for the WGS due to the unique redox property and high oxygen storage capacity (OSC) of CeO<sub>2</sub> [4–6]. It is well known that nano-sized CeO<sub>2</sub> supports help to stabilize Ce–PtO<sub>x</sub> species which are known to be active species for the WGS [7–10]. It has also been reported that nano-sized Pt stabilizes CeO<sub>2</sub> supports against sintering or loss of surface area [7–10]. As a consequence, various wet chemical synthesis routes have been studied to obtain nano-sized CeO<sub>2</sub> supports with controlled physical and chemical properties for the WGS [9–11].

To obtain high quality nano-sized CeO<sub>2</sub> supports, one of the simplest approaches is the thermal decomposition of a molecular precursor like cerium hydroxy carbonate (CHC: Ce(OH)CO<sub>3</sub>) [9,12–16]. The morphology, crystallite size, and physicochemical nature of CeO<sub>2</sub> can be easily controlled by using CHC [13]. Several routes have been pursued to synthesize CHC by a chemical

precipitation reaction employing aqueous solutions containing cerium (III) nitrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O) with excess urea [13,14] or ammonium carbonate [15,16] as precipitants. However, it is necessary to employ an excess precipitant (urea or ammonium carbonate) and to increase the temperature up to 80 °C for the precipitation of CHC.

In a previous study, we developed a novel chemical precipitation/digestion method to synthesize CHC by employing mixed precipitants (KOH + K<sub>2</sub>CO<sub>3</sub>) at room temperature in air [9]. As a result, the Pt/CeO<sub>2</sub> catalyst prepared by a developed precipitation/digestion method shows significant WGS activity [9]. The catalytic performance of Pt/CeO<sub>2</sub> is reported to depend on the synthesis parameters. In particular, it is well known that the pre-calcination temperature and aging time have significant effects on the physicochemical properties of catalysts and the catalytic performance [17–20]. Rahemi et al. [17] demonstrated that the pre-calcination temperature plays a significant role in determining the crystallite size and the interaction between the metal and support. Koo et al. [18] also reported that a catalyst pre-calcined at low temperature exhibited a high activity and stability due to the small crystallite size and intimate interaction between the metal and support. Zhang et al. [19] reported that an extended precipitation aging time can improve the reducibility of catalysts. Although we reported [9] that a high BET surface area of pre-calcined CeO<sub>2</sub> results in a high

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activity for the WGS, the effect of the synthesis parameters on the crystallite size, interaction between metal and support, and reduction property has not been investigated with a Pt/CeO<sub>2</sub> catalyst via CHC.

The objective of this study is to study the effects of the synthesis parameters (pre-calcination temperature and aging time) on the physicochemical properties and catalytic performance of Pt/CeO<sub>2</sub> prepared via CHC in the WGS. The effects of the synthesis parameters on the physicochemical properties and catalytic performance were characterized by BET, XRD, and TPR and were related to the activity results in the WGS. We also attempted to determine the optimum synthesis parameter of the Pt/CeO<sub>2</sub> catalyst which resulted in maximized its activity in the WGS.

## 2. Experimental

### 2.1. Catalyst preparation

The CeO<sub>2</sub> supports were prepared by a novel chemical precipitation/digestion method used for the synthesis of the CHC precursor, as reported earlier [9]. The precipitates during the synthesis of CHC were aged at room temperature (RT) in air. The aging time was changed systemically from 0 to 8 h. The precipitates were washed with distilled water to remove K<sup>+</sup> ion impurities and air-dried at RT. The as-dried precursor, CHC, was pre-calcined at various temperatures for 4 h in air to obtain the CeO<sub>2</sub> supports. The pre-calcination temperature was varied from 400 to 700 °C. Unless otherwise stated, the aging time and pre-calcination temperature were fixed at 4 h and 400 °C. 1 wt% Pt was loaded on the pre-calcined CeO<sub>2</sub> supports by an incipient wetness impregnation method where Pt(NH<sub>3</sub>)<sub>4</sub>·(NO<sub>3</sub>)<sub>2</sub> (99%, Aldrich) was used as a precursor. The calcination of the catalysts was carried out at 400 °C for 4 h in air.

### 2.2. Characterization

The BET surface area was measured by nitrogen adsorption at −196 °C using an ASAP 2010 (Micromeritics) instrument. The XRD patterns were recorded using a Rigaku D/MAX-IIIIC diffractometer (Ni filtered Cu–K radiation, 40 kV, 50 mA). Temperature programmed reduction (TPR) experiments were carried out using an Autochem 2910 (Micromeritics). TPR was performed using 10% H<sub>2</sub> in Ar from 20 to 600 °C at a heating rate of 10 °C/min. The sensitivity of the detector was calibrated by reducing a known weight of NiO [21–23].

### 2.3. Catalytic reaction

Activity tests were carried out from 200 to 360 °C under atmospheric pressure in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. The detailed procedure for the WGS reaction has been explained in the literature [24–28]. The simulated reformed gas was composed of 6.5 vol% CO, 7.1 vol% CO<sub>2</sub>, 0.7 vol% CH<sub>4</sub>, 42.4 vol% H<sub>2</sub>, 28.7 vol% H<sub>2</sub>O, and 14.5 vol% N<sub>2</sub>. The feed H<sub>2</sub>O/(CH<sub>4</sub> + CO + CO<sub>2</sub>) ratio was fixed at 2.0 due to the fact that a H<sub>2</sub>O/CH<sub>4</sub> ratio is typically 3.0 in the steam reforming of methane (SRM: H<sub>2</sub>O + CH<sub>4</sub> = 3H<sub>2</sub> + CO) to avoid coke formation [29–32]. To screen catalysts for the WGS, we tested Pt/CeO<sub>2</sub> catalysts at a GHSV of 45,515 h<sup>−1</sup>, which is 15 times higher than that of the typical experimental conditions employed for the WGS. The effluent gases from the reactor were analyzed on-line using a micro gas chromatograph (Agilent 3000).

## 3. Results and discussion

### 3.1. Effect of the pre-calcination temperature

#### 3.1.1. Catalyst characterization

Fig. 1 shows the XRD patterns of the fresh and used Pt/CeO<sub>2</sub> catalysts pre-calcined at various temperatures. Characteristic Pt metal peaks are not detected on account of the low loading content of Pt (≤1 wt%). All characteristic peaks can be assigned to CeO<sub>2</sub> with a fluorite structure [9,10]. The intensity of the CeO<sub>2</sub> peak increases due to the increasing crystallite size with increasing pre-calcination temperature from 400 to 700 °C. To evaluate the effect of the pre-calcination temperature on the crystallite size of CeO<sub>2</sub>, the crystallite size was estimated by the Scherrer equation [27,28]. Table 1 summarizes the CeO<sub>2</sub> crystallite size and BET surface area of the fresh and used Pt/CeO<sub>2</sub> catalysts pre-calcined at various temperatures. The CeO<sub>2</sub> crystallite size of the Pt/CeO<sub>2</sub> catalyst pre-calcined at 400 °C is the smallest among the prepared catalysts, while that of the catalyst pre-calcined at 700 °C is the largest. Clearly, the BET surface area dramatically decreases with increasing pre-calcination temperature, as shown in Table 1. These results indicate that the Pt/

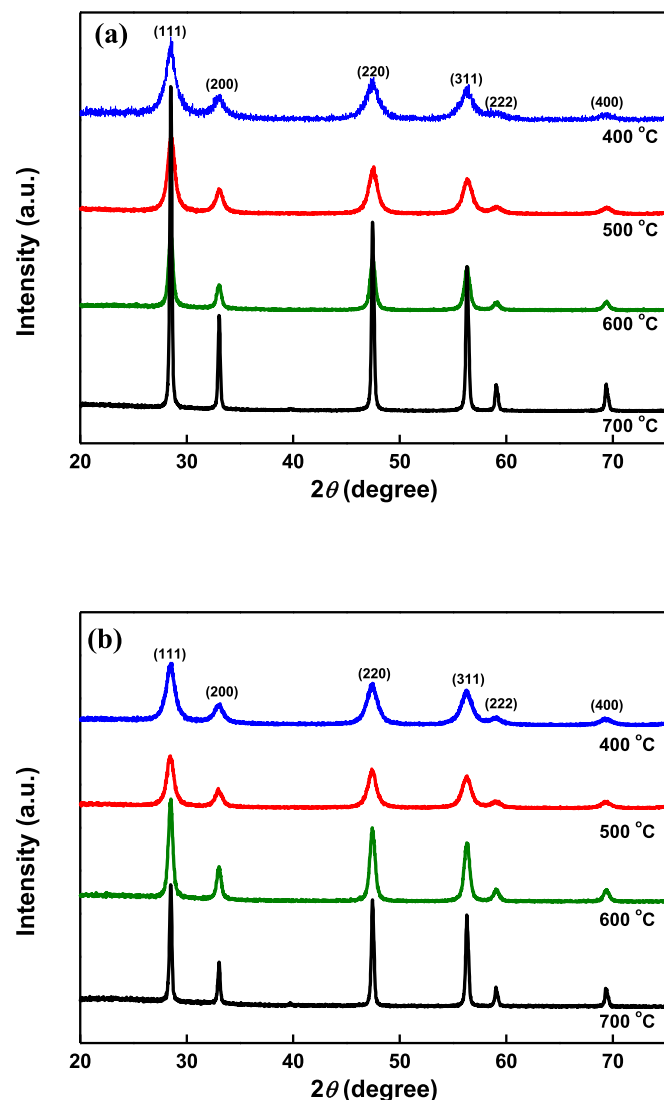


Fig. 1. XRD patterns of the (a) fresh and (b) used Pt/CeO<sub>2</sub> catalysts pre-calcined at various temperatures.

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