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The effect of titration time on the catalytic performance of Cu/CeO_2 catalysts for water-gas shift reaction

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ABSTRACT

We herein report the preparation of ceria (CeO_2) via a simple precipitation method for use as a catalyst support in the water-gas shift (WGS) reaction. More specifically, we optimized the titration time required to obtain highly active CeO_2-supported catalysts for the WGS reaction. As such, Cu was employed as the active metal coupled with the CeO_2 support. Notably, the CeO_2–0 supported Cu catalyst (where the precipitant was immediately injected into a cerium nitrate solution) exhibited the highest CO conversion at a gas hourly space velocity of 36,050 h^{-1}. This high catalytic activity of the Cu/CeO_2–0 catalyst was mainly due to its high Brunauer-Emmett-Teller (BET) surface area, enhanced Cu dispersion, high number of oxygen vacancies, and enhanced reducibility.

1. Introduction

The water-gas shift reaction (WGS, $H_2O + CO \leftrightarrow H_2 + CO_2$) is a crucial step in the production/purification of H_2 for use in fuel cell applications, ammonia synthesis, and other applications [1–4]. Due to the thermodynamic limitations, the WGS reaction is conducted on a commercial scale in two stages, namely the high-temperature water-gas shift reaction (HT-WGS) and the low-temperature water-gas shift reaction (LT-WGS), using Fe/Cr and Cu/Zn/Al catalysts, respectively. However, these commercial catalysts exhibit several shortcomings, including pyrophoricity and lengthy in-situ pre-reduction steps [5–7]. Recently, CeO_2-supported catalysts have demonstrated great potential as alternatives for LT-WGS catalysts because of their high catalytic performance resulting from a high oxygen storage capacity (OSC) [5,8].

To date, several preparation methods have been reported for the synthesis of CeO_2-supported catalysts, including sol-gel, precipitation, impregnation, and hydrothermal approaches [9–12]. Among the various synthetic methods available, the precipitation route is perhaps the most common method, as it is a relatively simple and cost-effective way to achieve large-scale catalyst preparation.

As previously reported [13–15], the preparation method employed for the synthesis of CeO_2 has a large influence on the final properties (i.e., surface area, morphology, OSC, and thermal stability) of the supported CeO_2 catalysts. In addition, several parameters of the precipitation method significantly affect the physicochemical properties of the final CeO_2 material [16]. Although a number of studies have focused on the effects of pH, precipitant, and concentration of the precursor solution [16–18], the effect of titration time on the water-gas shift activity of CeO_2-supported catalysts has not yet been examined.

Thus, we herein report our investigation into the effect of titration time in the precipitation process on the physicochemical properties of CeO_2-supported Cu catalysts for the WGS reaction.

2. Experimental

2.1. Catalyst preparation

The CeO_2 supports were prepared via a previously reported precipitation method [7]. Following the dissolution of $Ce(NO_3)_3{\cdot}6H_2O$ (99%, Aldrich) in distilled water. A 15 wt.% KOH solution was added with constant stirring at 80 °C until a pH of 10.5 was achieved. The injection time of the 15 wt.% KOH solution was varied between 0 and 30 min, and the prepared CeO_2 supports were calcined at 400 °C for 6 h and denoted as $CeO_2 - x$, where $x = 0, 5, 10$, or 30. CeO_2-supported Cu catalysts (Cu loading = 5 wt.%) were prepared by an incipient wetness impregnation method using $Cu(NO_3)_3{\cdot}xH_2O$ (99% Aldrich). The prepared 5 wt.% Cu/CeO_2 catalysts (denoted as $Cu/CeO_2 - x$ ($x = 0, 5, 10$, or 30)) were also calcined at 400 °C for 6 h.

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2.2. Characterization

The Brunauer-Emmett-Teller (BET) surface area was determined using an ASAP 2010 (Micromeritics) system and the N_2 isotherms were measured at −196 °C. Prior to measurement, all samples were outgassed for 12 h at 110 °C in a vacuum less than 0.5 mmHg. X-ray diffraction (XRD) analysis was performed on a Rigaku D/MAX–IIIC diffractometer (Ni-filtered Cu − Kα radiation, 40 kV, 100 mA) with a scan step of 0.02° and the crystallite size was estimated using the Debye–Scherrer equation. The microstrain of each catalyst was then obtained using the Williamson-Hall plot method. Hydrogen-temperature programmed reduction (H_2–TPR) experiments were carried out in an Autochem 2920 (Micromeritics) system using a previously reported [19]. N_2O-chemisorption was performed on using an Autochem 2920 (Micromeritics) system as previously described [20]. X-ray photoelectron spectroscopy (XPS) was carried out using a PHI 5000 VersaProbe (ULVAC PHI) spectrometer employing a Al Kα monochromator (1486.6 eV), and the binding energies were calibrated using the C 1s transition, which appeared at 284.6 eV. Raman spectra were recorded using a Renishaw (InVia) instrument with a 532 nm laser and a 2 μm focal beam. The concentration of oxygen vacancies (N) was calculated using the spatial correlation model from the relationship between the correlation length (L) and the grain size (d_g), as previously described [21].

2.3. Catalytic reaction

The catalytic activity tests were carried out at 1 atm between 200 and 400 °C in a fixed-bed micro-tubular quartz reactor with an inner diameter of 4 mm. A catalyst charge of 48 mg was employed. Prior to each catalytic experiment, the catalyst was reduced in a 5 vol% H_2/N_2 atmosphere upon heating from 25 °C to 400 °C at a rate of 3.1 °C/min, prior to maintaining the peak temperature for 1 h. After this time, the temperature was decreased to 200 °C. The gas feed for the catalytic reaction was composed of 9.0 vol% CO, 10.0 vol% CO_2, 1.0 vol% CH_4, 60.1 vol% H_2, and 19.9 vol% N_2, and the flow rate was controlled using Brooks 5850E mass flow controllers. The feed $H_2O/(CH_4 + CO + CO_2)$ ratio was intentionally fixed at 2:1, and a gas hourly space velocity (GHSV) of 36,050 h^{-1} was applied to screen the catalysts. Water was injected using a syringe pump and was vaporized at 180 °C upstream of the reactor. The reactor effluent was chilled, passed through a cold trap to condense the residual water, and then analyzed using a micro-gas chromatograph (Agilent 3000).

3. Results and discussion

3.1. Catalyst characterization

Following catalyst preparation using a range of titration times (i.e., 0–30 min), a number of analytical techniques were employed to analyze the CeO_2 supports and the Cu/CeO_2 catalysts. As shown in Table 1, a decrease in the BET surface areas of the CeO_2 supports was observed upon increasing the titration time, with CeO_2–0 exhibiting the highest BET surface area (136.7 m^2/g). On the contrary, the BET surface area of CeO_2–30 was greatly decreased to 33.6 m^2/g. After loading 5% Cu onto the CeO_2 support, the BET surface area decreased, and these values continued to decrease further with increasing titration time. This result clearly indicates that titration time has a significant effect on the BET surface area. In addition, high BET surface areas are known to increase catalytic activity due to greater numbers of active sites being available for catalytic activity and exposure to the reactants [22].

Table 1
Variation in the characteristics of the Cu/CeO_2 catalysts with titration time.

Titration time	BET S.A.[a] (m^2/g)		Crystallite size[b] (nm)		Cu dispersion[c] (%)
	CeO_2	Cu/CeO_2	CeO_2	Cu/CeO_2	Cu/CeO_2
0 min	136.7	119.4	6.6	6.4	4.9
5 min	113.4	91.4	8.2	8.6	3.5
10 min	107.1	89.1	8.6	8.7	3.2
30 min	33.6	22.3	13.1	11.8	2.0

[a] Estimated from N_2 adsorption at −196 °C.

[b] Calculated from XRD results.

[c] Estimated from N_2O-chemisorption results.

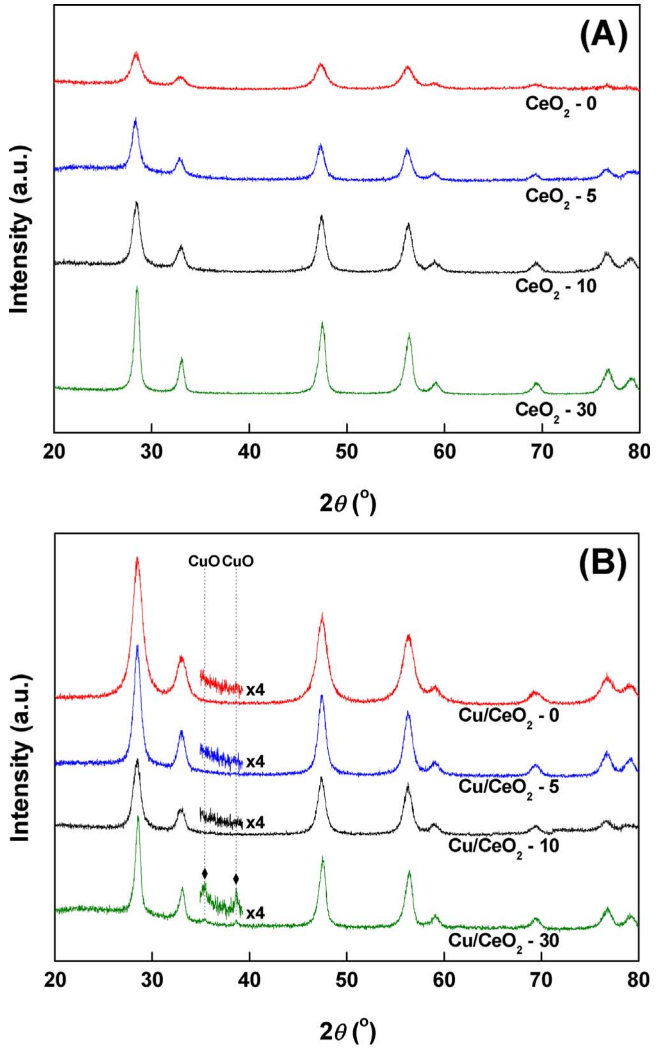

Fig. 1. XRD patterns of (a) the CeO_2 supports and (b) Cu/CeO_2 catalysts prepared at different titration times.

The XRD patterns of the CeO_2 supports prepared over a range of titration times are provided in Fig. 1(A), where the observed diffraction peaks could be attributed to the typical fluorite CeO_2 structure [23]. Interestingly, an increase in the intensity of the diffraction peaks with increasing titration time indicated that CeO_2–0 is composed of CeO_2 nanoparticles exhibiting low crystallinity [24]. As indicated by the crystallite sizes of the CeO_2 supports estimated from the Scherrer equation using the peak width at half maxima of the diffraction peaks (see Table 1), the crystallite sizes of CeO_2 supports decreased in the order: CeO_2–30 > CeO_2–10 > CeO_2–5 > CeO_2–0. In addition, Fig. 1(B) shows the XRD patterns of the obtained Cu/CeO_2 catalysts, where the trend relating to the CeO_2 crystallite size in the Cu/CeO_2 catalysts was similar to that of the CeO_2 supports. However, following doping with 5% Cu, the peak intensities increased for Cu/CeO_2–0 and Cu/CeO_2–5. Furthermore, two weak signals at 35.4° and 38.6°

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