



Mesoporous Co-CeO₂ catalyst prepared by colloidal solution combustion method for reverse water-gas shift reaction

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ABSTRACT

A series of mesoporous Co-CeO₂ catalysts with different Co contents were prepared with a colloidal solution combustion method and used for the reverse water-gas shift reaction. Characterizations demonstrate that the Co-CeO₂ catalysts have uniform mesoporous structures, high specific surface areas and pore volumes. The spherical pore wall is formed by intimately connected small CeO₂ and Co₃O₄ nanoparticles, and such structure results in the strong interaction between Co₃O₄ and CeO₂. The catalytic results show that the mesoporous 5%Co-CeO₂ catalyst possesses high activity and selectivity in reverse water-gas shift reaction, and shows a good stability during 10h at 600 °C. The excellent performance of the mesoporous 5%Co-CeO₂ catalyst should be owing to the small Co particles intimately interacted with CeO₂ in the pore walls.

1. Introduction

The utilization of CO₂ has received much attention, and extensive efforts have been devoted to conversion of CO₂ to fuels and chemicals [1,2]. The reverse water gas shift reaction (RWGS), CO₂ + H₂ → CO + H₂O, can convert CO₂ to CO, which can be converted into hydrocarbons via the Fischer-Tropsch synthesis. The RWGS reaction has been recognized as a promising candidate for large-scale conversion of CO₂ and renewable H₂ [3,4].

Pt, Co, and Ni-based catalysts have been applied for the RWGS reaction [5–10]. However, the main problem of these catalysts is methanation [6,8,11], CO₂ + 4H₂ → CH₄ + 2H₂O and CO + 3H₂ → CH₄ + H₂O, which will decrease the selectivity of the RWGS reaction. The selectivity of the RWGS reaction was sensitive to metal particle size, and large metal particle was more favorable to methanation rather than RWGS reaction [12]. Highly dispersed metal with small particle size were essential for the RWGS catalyst with high activity and selectivity [9,13]. In our previous study [14], Co-CeO₂ catalyst with small Co particle was found to be selective for RWGS. However, Co/CeO₂ catalyst with Co particle large than 10 nm had been reported to be very active for methanation reaction [15]. Yang et al. found TOF for methane formation increased with particle size and remained constant at higher particle sizes in CO methanation [16].

In our previous study [14], co-precipitated 2%Co-CeO₂ catalyst, with small Co particle dispersed on CeO₂, are very selective for CO production in RWGS reaction. However, the highly dispersed Co-CeO₂

catalyst prepared by conventional method is not stable in high temperature RWGS reaction.

Mesoporous CeO₂ with a high surface area is an excellent support to produce highly dispersed catalysts [17–22]. Mesoporous CeO₂-based catalysts have been used for many reactions, such as selective oxidation of hydrocarbons [17], CO oxidation [18], CO₂ methanation [19]. Recently, mesoporous Ni-CeO₂ have been used for RWGS reaction [23,24], and shows enhanced CO selectivity and stability. Dai et al. [25] had reported the reverse water-gas shift reaction on mesoporous Co-CeO₂ catalysts, and found the mesoporous Co-CeO₂ catalysts was easy to produce the byproduct CH₄ comparing with Cu-CeO₂ catalysts.

Colloidal solution combustion method has been applied to synthesis a uniform mesoporous CeO₂ catalyst with a large surface area [26]. In the present study, mesoporous Co-CeO₂ catalysts with different Co contents was prepared by the colloidal solution combustion method and employed in the RWGS reaction. The effect of Co content on the catalytic performance and structural properties was investigated. In addition, Co-CeO₂ catalysts prepared by conventional co-precipitation and impregnation methods were compared with the mesoporous Co-CeO₂ catalysts.

2. Experimental

2.1. Catalyst preparation

Mesoporous Co-CeO₂ catalysts with Co loading of 1, 2, 5, 10 wt%

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were synthesized using a colloidal solution combustion method. The colloidal solution is colloidal SiO₂ (LUDOX TMA, 34 wt % of an ~20–22 nm SiO₂ suspension in water; $\rho = 1.23 \text{ g mL}^{-1}$), which was used as template to create pores. The solution combustion reaction, using glycine as fuel and nitrate as oxidizer, is an exothermic reaction. Under heated condition, glycine and nitrate metal can react to produce metal oxides and gases (CO₂, N₂, and H₂O) [27]. Firstly, 0.006 mol of precursors (Co(NO₃)₃·6H₂O and Ce(NO₃)₃·6H₂O) and 0.008 mol of glycine (NH₂NH₂COOH) were dissolved into 5 ml of deionized water. 1.26 ml of colloidal SiO₂ was added in the solution and ultrasonicated for 20 min. Then the solution was heated on an electric hot plate maintained at 200 °C. After several minutes under heated condition, the solution started to boil, and then glycine and nitrate metal reacted to combustion and produced metal oxides and lots of gases (CO₂, N₂, and H₂O). The resulting powder was heated in a muffle furnace at 600 °C for 4 h. In order to etch the silica, the powder was immersed in 2 M NaOH solution at 80 °C for 4 h under stirring. After washing the powder with deionized water and ethanol three times and drying at 80 °C for 12 h, the mesoporous Co–CeO₂ material was obtained. The mesoporous Co–CeO₂ material was denoted as X%Co–CeO₂-M, where X% represented the Co content by weight. Mesoporous CeO₂ was prepared by the same method except the absence of Co, and denoted as CeO₂-M.

For comparison, 5%Co–CeO₂ catalysts were prepared by conventional co-precipitation and impregnation methods. The co-precipitated catalyst was prepared by dropwise addition of 0.2 M Na₂CO₃ and a mixed solution of Co(NO₃)₃·6H₂O and Ce(NO₃)₃·6H₂O to vigorous stirring deionized water at room temperature, and maintain a constant pH of 10. After stirring for 4 h, the precipitant was aged overnight. Then the precipitant was filtered and washed with deionized water for three times to remove Na ions. The co-precipitated 5%Co–CeO₂ catalyst was obtained after drying the precipitant at 80 °C for 12 h and calcination at 600 °C for 4 h. The co-precipitated 5%Co–CeO₂ catalyst was denoted as 5%Co–CeO₂-CP.

The 5%Co–CeO₂-IM catalyst was prepared by the conventional impregnation method. An aqueous solution containing the required amount of cobalt nitrate was mixed with CeO₂ support, where the ceria support was prepared by the colloidal solution combustion method. After the same drying and calcining treatments as for the 5%Co–CeO₂-CP catalyst, the 5%Co–CeO₂-IM catalyst was obtained.

2.2. Catalyst characterization

N₂ isotherms were measured using an Autosorb-iQ analyzer (Quantachrome Instruments, USA) at –196 °C. The sample was degassed at 300 °C for 6 h prior to measure. The BET specific surface area was measured, and the pore size distribution was calculated by the density functional theory method using the adsorption branch. XRD measurements were carried out to investigate the structural features of fresh and reduced catalyst on a DX-2700 X-ray diffractometer (Haoyuan Instrument, China) using Cu K α radiation. The reduced catalysts used for XRD measurements were reduced in a fix bed reactor with 20% H₂/Ar at 50 ml/min at 600 °C for 40 min, then purged with Ar at 40 ml/min and cooled down to room temperature. TEM measurements were performed on a Tecnai G2 F20 (FEI company, USA) microscope. H₂-TPR measurements were performed on a Xianquan TP-5080 equipment under 5% H₂/Ar (30 mL/min) with a rate of 10 °C/min to 900 °C. Before H₂-TPR measurements, the samples were purged with Ar (20 mL/min) at 400 °C for 5 min. The out gas was monitored by a TCD detector. H₂-consumption during TPR was calibrated by the reduction of a known amount of CuO. Oxygen temperature-programmed desorption (O₂-TPD) tests were conducted on the same instrument with H₂-TPR. For each measurement, 50 mg of sample was loaded in a quartz reactor, and the sample was firstly pretreated by 5%O₂/He at 400 °C for 10 min, followed by cooling down to room temperature in the 5%O₂/He flow. Then, the sample was purged with He for 25 min. Finally, the sample was heated from room temperature to 900 °C at a rate of 10 °C/min. To

measure the coke content of the used catalyst, the thermogravimetry (TG) was performed on a HCT-1 TG thermal analyzer at a linear heating rate of 10 °C/min in air.

2.3. Catalytic test

The RWGS reaction was performed in a packed-bed quartz reactor (I.D. = 8 mm) operated under an atmospheric pressure at 600 °C. For the RWGS reaction, 10 mg of catalyst (100–200 mesh) was used by feeding a stream of H₂/CO₂ at 100 ml/min with a 1:1 feed ratio, and the WHSV is $6 \times 10^5 \text{ mL/g}_{\text{cat}}/\text{h}$. 100 mg of inert SiO₂ (100–200 mesh) was used to dilute the catalyst. The catalyst was reduced in situ at a rate of 10 °C/min up to 600 °C for 40 min in a flow of a 20% H₂/N₂ mixture (50 mL/min) prior to the reaction. The catalyst was tested for 10 h at each reaction. The 5%Co–CeO₂-M catalyst was also test at 400 and 500 °C for 1 h. The long-term stability test of 5%Co–CeO₂-M catalyst was performed at 600 °C, using 5 mg catalyst with a high WHSV of $1.2 \times 10^6 \text{ mL/g}_{\text{cat}}/\text{h}$. The feed and product gas streams were analyzed using an online gas chromatograph equipped with a packed column (TDX-01) and a thermal conductivity detector (TCD).

3. Results and discussion

The nitrogen adsorption/desorption isotherms of Co–CeO₂-M catalysts are shown in Fig. 1(A). These Co–CeO₂-M catalysts exhibit typical IV shape isotherms with hysteresis loops, corresponding to a diameter in the mesoporous range [28]. From Fig. 1(B), it can be seen that these Co–CeO₂-M catalysts possess pore size distributions around 21 nm.

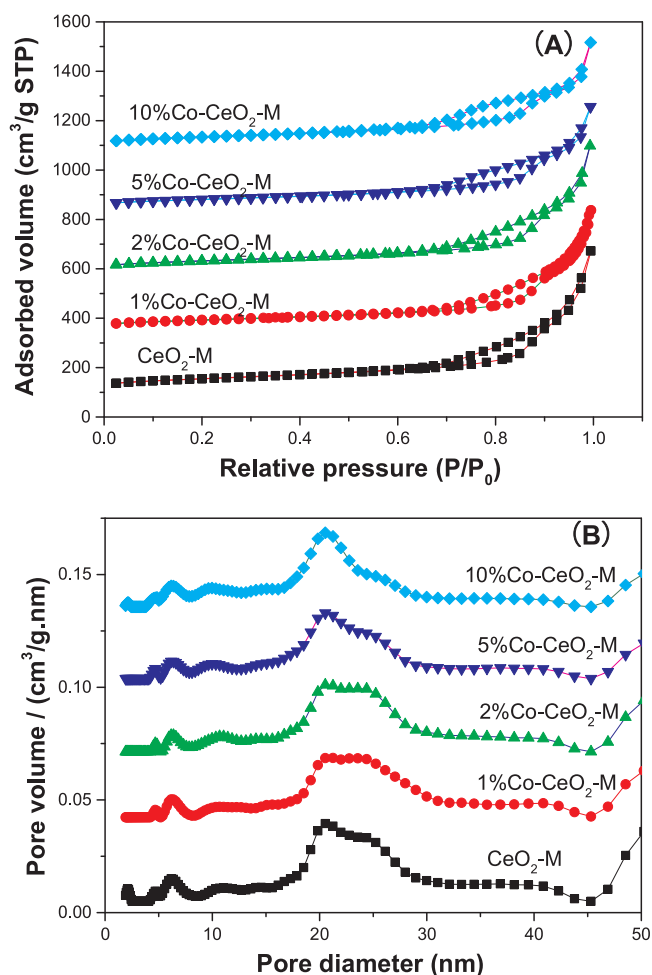


Fig. 1. (A) N₂ isotherm and (B) pore size distribution of Co–CeO₂-M catalysts.

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