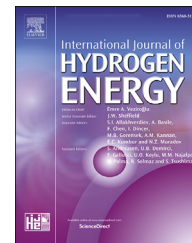




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# Preparation of highly dispersed Cu/SiO<sub>2</sub> doped with CeO<sub>2</sub> and its application for high temperature water gas shift reaction

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## ABSTRACT

Highly dispersed Cu/SiO<sub>2</sub> catalysts doped with CeO<sub>2</sub> have been successfully prepared via in-situ self-assembled core-shell precursor route. The prepared catalysts were characterized by XRD, SEM, TPR, chemisorption and XPS techniques. The results showed that our newly developed method could not only prepare highly dispersed supported metal catalysts but also highly dispersed supported CeO<sub>2</sub> on silica. The highly dispersed CeO<sub>2</sub> showed strong interaction with highly dispersed Cu. The synergy between the highly dispersed CeO<sub>2</sub> and the highly dispersed Cu exhibited high catalytic activity for high temperature water gas shift reaction compared to the catalysts prepared with the routine method of incipient impregnation.

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## Introduction

The water-gas shift reaction (WGS),  $\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$ , is used in many industrial processes such as ammonia synthesis, methanol synthesis and other processes in which hydrogen is involved. The WGS is moderately exothermic, and the reaction equilibrium will shift to left at high temperatures to lower the conversion of CO. Generally, the WGS is carried out in two stages based on two temperature regions as the reaction is kinetically favorable at high temperatures. The first step is typically operated at 310–450 °C, named as high

temperature shift (HTS), using Fe–Cr based catalysts. The second stage is approximately operated at the temperature between 180 and 250 °C, named as low temperature shift (LTS), with Cu–Zn based catalysts. Fe–Cr based catalysts have been used for HTS since the reaction has been discovered [1,2]. However, Fe<sub>2</sub>O<sub>3</sub>–Cr<sub>2</sub>O<sub>3</sub> must be pre-reduced critically in order to achieve the active phase of Fe<sub>3</sub>O<sub>4</sub> and a small amount of non-toxic Cr<sub>2</sub>O<sub>3</sub> can be oxidized to form toxic Cr<sup>6+</sup>, which is toxic as it is a strong carcinogen, doing harm to human health and the environment [3]. Therefore, it is highly desirable to replace Cr with other non-toxic elements. Nickel based catalysts for HTS exhibited high CO conversions, however, low

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yields to H<sub>2</sub> were achieved as the side-reaction of CO methanation to form methane were occurred as monometallic nickel based catalysts were used [4,5]. Great efforts have been made to suppress the formation of methane via methanation reaction by doping with alkaline metal oxide or transition metals into the nickel based catalysts [6–10]. Unfortunately, the side-product of methane could not be eliminated totally. Copper based catalysts have been widely adopted as LTS catalysts due to their high catalytic activities and high selectivities to H<sub>2</sub>, although they are sensitive to temperature excursions and strictly operated in a narrow temperature zone of 200–250 °C. Recently, copper based catalysts for HTS have been garnered attention for their high activities and inexpensiveness. Flytzani-Stephanopoulos reported that copper-ceria is a stable catalyst for HTS in CO<sub>2</sub>-rich gases [11]. Ozkan's group found that the activities of Fe-Al-Cu catalysts for HTS strongly depended on the catalyst preparation [12]. Catalyst prepared with the sol-gel method exhibited highest activity and surpassed the commercial catalyst over a wide reaction temperature range [13–15].

Previously, we reported highly dispersed M/SiO<sub>2</sub> (M: Cu, Ni) catalyst (M particle size < 4.0 nm) via *in-situ* self-assembled core-shell precursor route [16–18]. We found that highly dispersed supported metal catalysts could be easily obtained by addition of a small amount of oleic acid (OA) to an impregnation solution which could *in-situ* self-assemble to form core-shell structured precursors on silica support. We found that the highly dispersed Cu/SiO<sub>2</sub> catalyst displayed better catalytic performance for WGS than the catalyst prepared with a conventional impregnation method. However, the CO conversion was <50% at 300 °C on the highly dispersed Cu/SiO<sub>2</sub> catalyst. Therefore, the catalytic activity of Cu/SiO<sub>2</sub> should be further improved. In this paper, we use CeO<sub>2</sub> as a promoter to improve the activity of Cu/SiO<sub>2</sub>. The choice of CeO<sub>2</sub> promoter is further rationalized by the following consideration. Several groups have reported that the performances of Fe<sub>2</sub>O<sub>3</sub>-Cr<sub>2</sub>O<sub>3</sub> or Cr-free Fe<sub>2</sub>O<sub>3</sub> catalysts were enhanced by the addition of cerium oxide [19–21]. Additionally, CeO<sub>2</sub> plays a vital role to stabilize the active sites of Cu at temperatures as high as 450 °C under WGS conditions [11]. Moreover, our group also found that CeO<sub>2</sub> is a very good support for HTS as nickel-copper alloy or nickel doped with a small amount of sodium oxide was used as active metal [7,22]. Cu/SiO<sub>2</sub> doped with CeO<sub>2</sub> is far cheaper than the catalyst with bulk CeO<sub>2</sub>, which is an important factor for commercialization. Additionally, it is necessary to investigate whether the method we newly developed previously can be worked to prepare highly dispersed multi-components catalyst, although the method have been adopted to prepared supported catalysts successfully by independent research groups [23,24].

## Experimental

### 10%Cu/10%CeO<sub>2</sub>/SiO<sub>2</sub> catalyst preparation and WGS conditions

The chemicals using in the preparation of catalysts were listed as following. Oleic acid (OA), Ce(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O from

Sigma-Aldrich were analytical pure reagents using without further purifications. The spherical silica support, with 753 m<sup>2</sup>/g specific surface area and 7.5 nm mean pore size, was provided by Kanto Chemical Co.

10%Cu/10%CeO<sub>2</sub>/SiO<sub>2</sub> catalysts were prepared by sequential incipient wetness impregnation in the presence/absence of OA, with copper and CeO<sub>2</sub> loadings of 10 wt%. The procedures are briefly described as follow according to our previous report [16]. Firstly, 3.154 g (7.26 mmol) Ce(NO<sub>3</sub>)<sub>3</sub>·3H<sub>2</sub>O was dissolved in appropriate amount of D.I. water equaled to the pore volume of a support, and then 0.513 g (1.82 mmol, n<sub>OA</sub>/n<sub>Ce</sub> = 0.25) of OA was added into the solution. Finally, 10 g spherical silica was introduced into the above solution. Subsequently, the sample was stirred for a while and impregnated at room temperature (RT) for > 6 h and then dried overnight at 100 °C. The above dried samples were calcined at 450 °C for 4 h to achieve CeO<sub>2</sub>/SiO<sub>2</sub> support. The procedure to prepare the support of CeO<sub>2</sub>/SiO<sub>2</sub> in absence of OA was similar with the support of CeO<sub>2</sub>/SiO<sub>2</sub> prepared in presence of OA except that the OA was added or not. 10%Cu/10%CeO<sub>2</sub>/SiO<sub>2</sub> catalysts were prepared using copper nitrate as precursor in the presence/absence OA following the same procedure with the support of CeO<sub>2</sub>/SiO<sub>2</sub>. The 10%Cu/10%CeO<sub>2</sub>/SiO<sub>2</sub> catalysts were abbreviated with Cu-OA/Ce-OA/Si, Cu/Ce-OA/Si, Cu-OA/Ce/Si, Cu/Ce/Si, respectively. “-OA” meant OA was used during a catalyst was synthesized. For example, Cu/Ce-OA/Si meant that the support of 10%CeO<sub>2</sub>/SiO<sub>2</sub> was prepared in presence of OA but OA was absent during impregnation with copper nitrate.

In order to investigate the catalytic performances of the prepared catalysts, the WGS reaction was chosen as a probe reaction and carried out at 300 °C unless otherwise stated. The feed gas (5 mol.% CO, 25 mol.% H<sub>2</sub>O and He balance) was controlled by mass controller with a total flow rate of 50 ml/min. An online HP-GC equipped with a Haysep D column was used to quantify the composition of effluent gases. All catalysts were weighted 0.05 g and reduced at 300 °C in pure hydrogen atmospheres for 1 h before the onset of WGS.

### Catalyst characterization

The Powder X-Ray Diffraction (XRD), on Shimadzu XRD-6000 using a Cu target K $\alpha$ -ray (40 kV and 30 mA) as the X-ray source, was used to characterize the crystal phases of samples and the crystalline sizes of Cu (CuO). The XRD analysis was promptly conducted after the catalysts had undergone reduction at 300 °C for 1 h and the transfer of sample to the XRD chamber was carried out with minimal exposure to air. Thereafter, the crystalline sizes of CeO<sub>2</sub>, CuO and Cu were calculated by Scherrer equation using diffraction peaks of (111) planes located at 2 $\theta$  = 28.6, 35.5 and 43.4°, respectively.

The morphologies of catalysts were observed via a Scanning Electron Microscope (SEM, Jeol JSM-6700). Prior to analysis, the samples were degassed under vacuum and coated with around 10 nm thick layer of Pt at 20 mA for 120 s. Before SEM analysis, the 10%Cu/10%CeO<sub>2</sub>/SiO<sub>2</sub> catalysts were reduced ex-situ under H<sub>2</sub> flow at 300 °C for 60 min.

H<sub>2</sub>-Temperature Programmed Reduction (H<sub>2</sub>-TPR) characterizations were conducted on Quantachrome CHEMBET-3000 according to our previously reported procedures [9]. Before the onset of H<sub>2</sub>-TPR, the catalysts were pretreated in helium

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