CHINESE JOURNAL OF CATALYSIS
Volume 33, Issue 3, 2012
Online English edition of the Chinese language journal

Cite this article as: Chin. J. Catal., 2012, 33: 425–431.

ARTICLE

Effect of La_2O_3 on Microstructure and Catalytic Performance of CuO/CeO_2 Catalyst in Water-Gas Shift Reaction

FANG Xing, CHEN Chongqi, LIN Xingyi*, SHE Yusheng, ZHAN Yingying, ZHENG Qi
National Engineering Research Center of Chemical Fertilizer Catalyst, Fuzhou University, Fuzhou 350002, Fujian, China

Abstract: The water-gas shift reaction was used to evaluate a series of La_2O_3 modified CuO/CeO_2 catalysts that were prepared by a parallel co-precipitation method. The catalytic activity and thermal stability improved significantly upon the introduction of La_2O_3, and CuO/CeO_2-La_2O_3 (2 wt%) gave the highest activity and had the best thermal stability. The microstructure of the as-prepared CuO/CeO_2-La_2O_3 catalysts and/or the CeO_2-La_2O_3 supports was characterized by X-ray diffraction, N_2 physisorption, Raman spectroscopy, and temperature-programmed reduction. The results indicate that larger specific surface areas and smaller crystal sizes of CuO and CeO_2 result in improved catalytic performance for the as-prepared catalysts. Moreover, the incorporation of La^{3+} into the ceria lattice promotes the generation of oxygen vacancies leading to a higher number of moderate copper oxides that interact with surface oxygen vacancies on the surface of the ceria. This enhances the activity and thermal stability of the CuO/CeO_2 catalyst.

Key words: copper oxide; ceria; lanthanum oxide; water-gas shift reaction; oxygen vacancy; Raman spectroscopy

Faced with massive and ever-growing energy demands, fuel cells are considered to be one of the most effective and environmental friendly technologies for the production of electric energy. Hydrogen is the most promising fuel for fuel cells and it can be produced by water-splitting, biomass, and the reformation of hydrocarbons [1,2]. However, most of the H_2 produced by reforming hydrocarbons contains a certain amount of CO, which has side effects in fuel cells such as the degradation of the Pt electrode performance [2–4]. Therefore, it is necessary to purify the syngas before it becomes a feasible fuel source for low-temperature fuel cells and other relevant areas. The water-gas shift (WGS) reaction ($CO + H_2O \rightarrow CO_2 + H_2$) is a vital process in eliminating CO and producing H_2 in low-temperature fuel cell system. The design of active, stable, and poison-resistant catalysts for the WGS reaction has been of great interest recently.

Ceria is a good support for metal and metal oxide catalysts because of its high oxygen storage ability, which plays an important role in redox reaction [3–11]. Ceria supported catalysts are considered as promising candidates for the WGS reaction, emissions-control, hydrocarbon-reforming, and hydrocarbon oxidation catalysis [5,7–10]. For all these applications, CeO_2 has been used as a support for both noble and cheap metals or metal oxides such as Au/CeO_2, Pt/CeO_2, and CuO/CeO_2 as it has the ability to cycle between Ce^{3+} and Ce^{4+} [8–13]. Compared with the precious metals based on ceria, the WGS catalysts loaded with transition metal (e.g. Co, Ni or Cu) oxides are of growing interest because of their significantly lower cost.

Metal oxides with valences lower than (4+) are commonly introduced to modify the catalytic performance of CuO/CeO_2 catalysts, such as La_2O_3 [9,14,15], Y_2O_3 [15,16], Al_2O_3 [17], Fe_2O_3 [18], and ZnO [19] etc. Li et al. [14] reported that Cu and Ni supported on La-doped-ceria retained high catalytic activity in a lower-temperature WGS reaction. Zhi et al. [9] investigated the influence of the preparation method on the performance of a CuO/CeO_2-La_2O_3 catalyst. She et al. [15] carried out a comparative study of the WGS reaction using a series of CuO/CeO_2 catalysts doped with trivalent rare earth oxides (RE_2O_3, RE = Y, La, Nd, and Sm). It was found that introduc-

---

Received 21 September 2011. Accepted 4 November 2011.

*Corresponding author. Tel: +86-591-83731234-8112; Fax: +86-591-83738808; E-mail: linxingyi@ fzu.edu.cn

This work was supported by the National Natural Science Foundation of China (20771025) and the Education Department of Fujian Province (JA08021).

DOI: 10.1016/S1872-2067(11)60337-9

tion of La_2O_3 promotes the generation of oxygen vacancies in ceria because the ionic radius and electronegativity of La^{3+} are close to that of Ce^{4+} [8,9,14,15]. To date no work has been carried out to determine the microstructure and catalytic performance of CuO/CeO_2 catalysts modified with different amounts of La_2O_3 for the WGS reaction.

In this work, CuO/CeO_2 catalysts modified with La_2O_3 were synthesized by co-precipitation and were calcined at 650 °C. The as-prepared CuO/CeO_2-La_2O_3 catalysts had dissimilar structures and redox properties and exhibited different catalytic performance for the WGS reaction when different amounts of lanthanum were introduced. The CuO/CeO_2 catalyst modified with (2 wt%) La_2O_3 showed the highest WGS reaction catalytic performance. The catalyst microstructures and catalytic performance were fully investigated by X-ray diffraction (XRD), N_2-physisorption, Raman spectroscopy, and temperature-programmed reduction (TPR) characterization, and the results are discussed in detail.

1 Experimental

1.1 Catalyst preparation

A series of CuO/CeO_2-La_2O_3 catalysts with 25 wt. % CuO and a specific La_2O_3 content (e.g., 0, 1, 2, 3, and 5 wt. %, calculated as La_2O_3) were prepared by the parallel co-precipitation method. The as-prepared samples were denoted as CCL0, CCL1, CCL2, CCL3, and CCL5, respectively. Typically, stoichiometric amounts of $Cu(NO_3)_2 \cdot 3H_2O$, $Ce(NO_3)_3 \cdot 6H_2O$, and $La(NO_3)_3 \cdot 6H_2O$ were initially dissolved in deionized water and, subsequently, the mixed aqueous solution was co-precipitated with an aqueous solution of KOH under vigorous stirring at 80 °C and at a pH of 10. A black suspension was acquired and aged with continuous stirring at 80 °C for another 6 h. The resulting precipitate was centrifuged and washed with deionized water several times and then dried at 110 °C for 12 h and finally calcined at 650 °C for 4 h (heating rate was 5 °C/min) in air.

1.2 Evaluation of catalytic performance

The catalytic activities and thermal stabilities of the catalysts for the WGS reaction were evaluated in a fixed bed reactor at atmospheric pressure. The catalyst (30–40 mesh) was placed between two layers of quartz granules within a stainless steel tube (i.d. = 12 mm) and evaluated from 200 to 400 °C at an interval of 50 °C for the first cycle. The ratio of vapor to feed gas (10% CO, 60% H_2, 12% CO_2, and balance N_2) was maintained at 1:1, and the space velocity was kept at 4500 h^{-1}. Residual water from the outlet was removed by a condenser before entry into a gas chromatograph equipped with a thermal conductivity detector (TCD) to monitor the outlet gas concentration of CO. After the first cycle the catalyst was kept at 400 °C for 12 h and then the temperature was decreased to 200 °C. The catalyst was then evaluated from 200 to 400 °C again for another cycle. Catalyst stability was also evaluated at a given temperature (ramp to 300 °C from room temperature and kept at 300 °C for 24 h). The activity is expressed by the conversion of CO and is defined as $X_{CO} = (1 - V'_{CO}/V_{CO}) \times 100\%/(1 + V'_{CO})$, where V_{CO} and V'_{CO} are the inlet and outlet CO contents, respectively.

1.3 Characterization

Powder XRD patterns of the as-synthesized samples were collected on a PANalytical X' pert Pro diffractometer equipped with Co (λ = 0.17902 nm) radiation operating at 40 kV and 40 mA for 2θ angles ranging from 25° to 75°. Crystal sizes of the ceria and the copper oxide were determined from peak broadening with the Scherrer equation. The specific surface areas (S_{BET}) were measured on an ASAP 2020 physical adsorption analyzer at –196 °C using nitrogen as the adsorption gas. Before each analysis the sample was degassed at 200 °C for 3 h. Raman spectra were obtained on a Renishaw Invia Plus system at ambient temperature. The emission line at 514.5 nm from an Ar^+ ion laser (Spectra Physics) was focused on the sample under the microscope. H_2-TPR measurements were carried out on an AutoChem 2910 instrument. The samples were pretreated under pure helium gas at 300 °C for 30 min and then the system was cooled to ambient temperature. Subsequently, H_2-TPR was performed by passing 10% H_2-90% Ar (flowing rate = 30 ml/min) over 50 mg catalyst at a heating rate of 10 °C/min from room temperature to 400 °C. The hydrogen consumption was monitored using a thermal conductivity detector (TCD).

2 Results and discussion

2.1 Catalytic performance

Figure 1 shows the results of the catalytic activity tests for the as-synthesized catalysts where the catalytic activity is expressed as CO conversion versus temperature. As shown in Fig. 1, the catalytic activity of the CuO/CeO_2 catalyst is apparently enhanced by the introduction of La_2O_3. The CCL2 sample gave the highest CO conversion during the whole testing temperature region, and this was as high as 93.1% at 250 °C for the first cycle, which is 9.6% higher than that of CCL0 (83.5%). However, the catalytic activities decrease rapidly as the amount of La_2O_3 increased further. A comparison between the first and the second cycle in Fig. 1 reveals that the thermal stability of the CuO/CeO_2 catalyst can also be improved by the introduction of La_2O_3, especially for the CCL2 sample.

Moreover, the thermal stabilities of the La_2O_3 modified CuO/CeO_2 catalysts were also investigated by keeping the