Preferential oxidation of CO in excess H_2 over the CeO_2/CuO catalyst: Effect of initial support

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Abstract

Three series of CeO_2/CuO samples were prepared by impregnation method and characterized by XRD, N_2 adsorption-desorption, temperature-programmed reduction (TPR), XPS and TEM techniques. In comparison with the samples prepared with CuO as initial support, the samples with $Cu(OH)_2$ as initial support have higher reducibilities and smaller relative TPR peak areas, and also larger specific surface areas at calcination temperatures of 400 °C–600 °C. As a result, $Cu(OH)_2$ is better than CuO as initial support for preferential oxidation of CO in excess H_2 (CO-PROX). The best catalytic performance was achieved on the sample calcined at 600 °C and with an atomic ratio of Ce/Cu at 40%. XPS analyses indicate that more interface linkages Ce-O-Cu could be formed when it was calcined at 600 °C. And the atomic ratio of Ce/Cu at 40% led to a proper reducibility for the sample as illustrated by the TPR measurements.

1. Introduction

Proton exchange membrane fuel cell (PEMFC) works with a H_2-rich gas in which the CO content must be less than 10 ppm generally to have a long-term electric power generation. The H_2-rich gas mixture obtained by steam reforming of hydrocarbons and the following water-gas shift reaction (WGS) contains 0.5%–2% CO besides 18% CO_2 (volume percent). For the small scale PEMFC stacks used in home and vehicle, the unit to remove CO from the reforming-WGS gas mixture must be small as can as possible in volume. Selective methanation of CO is a way to remove CO from the gas mixture with the prerequisite that methanation of CO_2 can be avoided or efficiently suppressed [1]. Preferential oxidation of CO in excess H_2 (CO-PROX) is another way to remove CO from the gas mixture [1−5]. CuO/CeO_2 composite as an efficient catalyst is extensively studied for the CO-PROX reaction [1]. Preparation methods influence its catalytic activity greatly [6−10]. Calcination temperature also has a noticeable effect [11−13]. In many cases calcination at 500 °C–700 °C is appropriate. On the reaction mechanism, it is proposed that the Cu-O-Ce structure on the interface of CuO and CeO_2 phases is catalytically active sites for CO oxidation, as shown in Equation (1) [14−17]. The oxygen vacancy □ is

then replenished by gaseous oxygen.

$$Cu^{2+}\text{-}O^{2-}\text{-}Ce^{4+} + CO = Cu^{+}\text{-}\square\text{-}Ce^{3+} + CO_2 \quad (1)$$
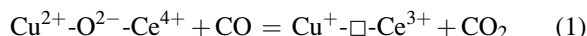
The Cu-O-Ce structure can be reduced even at room temperature by CO molecules [18]. And the following CO molecule binds to Cu^+ to form a Cu^+-CO complex. CO molecules can also bind to Cu^0 and Cu^{2+} to form complexes. But these complexes are weaker than the complex Cu^+-CO as illustrated by IR analyses [19,20]. Temperature-programmed reduction (TPR) measurement suggested several possible states of CuO entities on the CeO_2 support, i.e., highly dispersed CuO with strong interaction with the support, well dispersed CuO clusters, and CuO crystallites [12,13,20,21]. Due to the interaction of CuO phase with CeO_2 phase, a portion of CeO_2 in the CuO/CeO_2 composite may be reduced concurrently with the reduction of CuO, even though pure CeO_2 itself is reduced only at a much higher temperature [20,21]. It seems that a proper reducibility of CuO/CeO_2 composite is necessary to obtain a high CO-PROX activity [22]. This is because the catalyst in the CO-PROX reaction gas atmosphere may be in a reduced state and the sample which is easier reduced may contain more metallic Cu^0. Metallic Cu^0 has a role to promote oxidation of H_2 and thus lower

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CO-PROX activity. X-ray analytical technique has detected formation of Cu^0 and Cu^+ in the CO-PROX reaction [23]. On the other hand, if a sample is hard to be reduced, it implies that the sample has a low activity to release catalytically active oxygen.

The inverse configuration of CeO_2 and CuO, i.e., CeO_2/CuO, was reported as an alternative to the classical one (i.e., CuO/CeO_2) for CO-PROX reaction [24]. The use of CuO as support could change reducibility of the catalytically active sites and therefore obtain a wider temperature window with high CO conversion and high selectivity to CO_2 of O_2 for CO-PROX. In the previous work, effect of calcination temperature on the CeO_2/CuO catalyst was investigated [25]. In the present work, $Cu(OH)_2$ and CuO are used as initial support, respectively, and effect of the initial supports is assessed.

2. Experimental

2.1. Preparation of samples

2.1.1. CuO as initial support and calcined at 400–800 °C

A commercial $Cu(OH)_2$ powder (Guoyao Chemicals, Shanghai, China) was thermally decomposed in a muffle furnace at 350 °C for 2 h. The so-obtained CuO powder was used as support and impregnated with a water-ethanol solution of cerium nitrate ($Ce(NO_3)_3 \cdot 6H_2O$, Guoyao Chemicals, Shanghai, China), where atomic ratio of Ce/Cu was set at 40%. After dried in a supersonic agitator at 60 °C for 20 min, the solid was further dried in an oven at 120 °C for 4 h. At last, the solid was calcined in muffle furnace at a set temperature for 2 h. The set calcination temperature was 400 °C, 500 °C, 600 °C, 700 °C and 800 °C, respectively.

2.1.2. Cu(OH)₂ as initial support and calcined at 400–800 °C

The commercial $Cu(OH)_2$ powder was used as initial support and impregnated with a water-ethanol solution of cerium nitrate. Atomic ratio of Ce/Cu was still fixed at 40%. And similarly to the above, drying was carried out at 60 °C in a supersonic agitator for 20 min, and then continued in an oven at 120 °C for 4 h. At last, the solid was calcined in muffle furnace for 2 h. Calcination temperature was set at 400 °C, 500 °C, 600 °C, 700 °C and 800 °C, respectively.

2.1.3. Cu(OH)₂ as initial support at varying atomic ratio of Ce/Cu

The commercial $Cu(OH)_2$ powder was used as initial support and impregnated with a water-ethanol solution of cerium nitrate. Atomic ratio of Ce/Cu was set at 10%, 20%, 30%, 40%, 50% and 60%, respectively. After drying as above, the solid was calcined in muffle furnace at a fixed temperature of 600 °C for 2 h.

2.2. Characterizations

Phase identification of the CeO_2/CuO samples prepared above was carried out on an X-ray diffractometer (Shimadzu XRD-6000, Japan) with Cu K_α radiation. Specific surface areas (SSA) were measured by the BET method at liquid nitrogen temperature (JW-DA, Beijing Jingweigaobo Sci. & Tech. Co., China). Particle images were observed on a transmission electron microscope (Tecnai G^2 F20 U-TWIN, FEI).

Temperature-programmed reduction (TPR) measurements were performed on a TPR instrument (PX200, Tianjin Pengxiang Sci. & Tech. Co., China) with a thermal conductivity detector (TCD), where a reducing gas (10% H_2/N_2) was set at 40 mL/min and temperature was ramped from room temperature to 850 °C at 10 °C/min. Sample mass was fixed at 50.0 mg at each run.

X-ray photoelectron spectra (XPS) were recorded on an X-ray photoelectron spectrometer (PHI Quantera) using Al K_α radiation. The base pressure of the instrument was 2×10^{-9} Torr, and curve-fitting for the XPS peaks calibrated at binding energy of C 1s being 284.8 eV was performed with a Gaussian-Lorentzian profile.

2.3. Evaluation of catalytic activity for CO-PROX

Catalytic activity for CO-PROX of the CeO_2/CuO samples was evaluated in a fixed-bed flow reactor at atmospheric pressure. 200 mg of the sample granules (60−80 mesh) was loaded into a U type quartz tube reactor (8 mm i.d.) at each run. The CO-containing gas is composed of 2% CO, 75% H_2 and 23% N_2, set at 100 mL/min on a mass flow controller (MFC). Air was co-fed by another MFC, set at 15 mL/min. The reactions were carried out in temperature-rising way, and reaction products were analyzed after 1 h of reaction at a given temperature with a gas chromatograph (GC) equipped with a thermal conductivity detector. And then reaction temperature was raised to the next higher value. Helium gas is used as carrier gas of the GC, and a packed column (Shincarbon ST 50/80, Shimadzu Column Packing, Japan) is connected in the oven to separate H_2, O_2, N_2, CO and CO_2 gases.

3. Results and discussion

3.1. Effects of initial support and calcination temperature

Two series of CeO_2/CuO samples were prepared using CuO and $Cu(OH)_2$ as initial support, respectively, to investigate effect of the initial supports. Atomic ratio of Ce/Cu was fixed at 40%, and calcination temperature was varied from 400 °C to 800 °C.

Figure 1 compares XRD patterns of the two series of CeO_2/CuO samples. It is seen that the diffraction intensity of CeO_2 phase increases greatly as calcination temperature elevates. This indicates that both crystallite size and crystallinity of CeO_2 phase increased with calcination temperature increasing, since atomic ratio of Ce/Cu was constant at 40%. Figure 2 gives specific surface areas (SSA) of the samples. As