

Nd- or Zr-modified CuO–CeO₂/Al₂O₃/FeCrAl monolithic catalysts for preferential oxidation of carbon monoxide in hydrogen-rich gases

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Abstract

This work presents a study on the role of the additives over CuO–CeO₂/Al₂O₃/FeCrAl monolithic catalysts for the preferential oxidation of CO. The monolithic catalysts were prepared by in situ combustion method and characterized using SEM, XRD and TPR techniques. The results show that the addition of neodymium or zirconium in the CuO–CeO₂/Al₂O₃/FeCrAl catalysts influences the dispersion state of copper oxide and ceria, lowers the activity of hydrogen oxidation and broadens the temperature window for total CO-conversion.

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1. Introduction

Proton exchange membrane fuel cell (PEMFC) fuelled with hydrogen is an attractive technology for power generation owing to its high-energy conversion efficiency and nearly zero emission [1–3]. The conventional method of hydrogen production combines steam reforming of hydrocarbons with water-gas-shift reaction (WGSR) and the resulting hydrogen-rich gases contain about 0.5–2% CO [4–7]. The Pt electrodes of PEMFC are readily poisoned by even minimum CO, therefore, it is necessary to reduce CO concentration to less than 10 ppm in the steams [5–8]. Preferential oxidation (PROX) of CO by introducing small amount of oxygen is regarded as the favorable method for the purification of carbon monoxide in hydrogen-rich gases due to its efficiency and simplicity [1–3]. So far, various particle catalysts have been studied for CO-PROX, from base metal oxides like Cu and Co, to noble metals such as Pt, Pd, Ru and Au [4–13]. The reports indicate that CuO–CeO₂ catalysts are promising candidate for CO-PROX [5,6].

In this system, it also involves hydrogen oxidation, reverse water-gas-shift reaction (r-WGSR) and methanation reaction besides CO oxidation [9,13]. Methanation reaction is neglectable under reaction temperature of 300 °C, while hydrogen oxidation competes for limited oxygen and influences CO-conversion, also r-WGSR produces CO and decreases net CO-conversion [13,14]. Thus improving the selectivity of oxygen for CO oxidation is a crucial issue. In addition, broad temperature window for complete CO oxidation is of great significance for the CO-PROX, which requires high CO oxidation selectivity. Therefore, it is necessary to restrain hydrogen oxidation and r-WGSR and broaden the temperature window of total CO-conversion over the catalysts for the PROX.

In order to produce hydrogen on-board or in small scale for feeding PEMFC, CO-PROX catalysts should be prepared as monolith or microchannel reactor [14,15]. Monolith or microchannel reactors are mainly made of metal, such as FeCrAl, or ceramic, typically cordierite. FeCrAl support presents some advantages over cordierite ceramic support such as higher thermal conductivity, lower heat capacity and greater thermal and mechanical shock resistance [16,17]. Good thermal conductivity of FeCrAl monolith can ensure temperature homogeneity and avoid hot spots, which is beneficial for restricting r-WGSR.

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A key challenge for loading oxide catalysts on the FeCrAl support is improving adhesion stability [18]. Biamino [19] used in situ solution combustion method to deposit perovskite type oxide catalyst on silicon carbide and cordierite honeycombs for diesel particulate removal. It was proposed that in situ solution combustion is an effective and convenient method for supporting oxide catalysts on metal substrate with good adhesion stability [19–23].

In this work, in situ solution combustion method was applied for loading CuO–CeO₂ on FeCrAl monolith, and it is found that Nd or Zr modification can restrain hydrogen oxidation and r-WGSR and broaden the temperature window for total CO-conversion.

2. Experimental

2.1. Material and catalyst preparation

FeCrAl honeycombs with cell densities of 400 cells/in.² were chosen as the metallic supports. The wall thickness, length and diameter of the honeycomb monolith are 0.04, 15 and 7 mm, respectively. The chemical composition of the FeCrAl alloy (in M) is 0.035 C, 0.5 Si, 0.5 Mn, 0.018 P, 0.015 S, 0.5 Ni, 0.2 Ce, 20.5 Cr, 5.0 Al and Fe balance. Before coating, the supports were washed with acetone in an ultrasonic bath for 30 min to remove the superficial impurities, and then rinsed with de-ionized water. The metallic supports were put into NaOH solution of 60 °C for 10 min and then rinsed with de-ionized water. The supports were pretreated in the oxidative solution for 2 min at room temperature, which consisted of 10% HNO₃, 1.5% oxalic acid, 1% CrO₃ and 87.5% de-ionized water, followed by rinsing with de-ionized water. Finally, the metallic supports were heated from room temperature to 950 °C with heating rate of 5 °C/min and oxidized at 950 °C for 5 h in a muffle, and then cooled to room temperature.

The CuO–CeO₂/Al₂O₃/FeCrAl honeycomb catalysts were prepared as follows: (i) Cu(NO₃)₂, Ce(NO₃)₃ and urea were dissolved in de-ionized water to obtain the solution with Cu/(Cu + Ce) molar ratio of 0.15, urea/(Cu + Ce) molar ratio of 4.17 and 200 g/l solution concentration of Cu(NO₃)₂ and Ce(NO₃)₃; (ii) the pretreated FeCrAl honeycombs were inserted into the above solution and held for 3 min, then the honeycombs were taken out and calcined at 550 °C for 1 h.

The procedure for loading CuO–Ce_{0.9}M_{0.1}O₂ (M = Nd and Zr) on FeCrAl was the same as for preparing CuO–CeO₂/Al₂O₃/FeCrAl honeycomb catalysts, except that part of cerium nitrate was replaced by neodymium or zirconium nitrate.

The solutions made in step (i) were calcined at 550 °C for 1 h to prepare CuO–CeO₂ and CuO–Ce_{0.9}M_{0.1}O₂ particle catalysts for comparison.

2.2. Adhesion tests

Adhesion properties of the oxide catalysts on the substrate surface were measured through ultrasonic adhesion tests and thermal shock tests. The catalysts were immersed in petroleum ether and treated with 40 kHz/100 W ultrasonic waves for

30 min to measure the weight loss caused by exposure to the ultrasonication. The thermal shock test was carried out by heating the monolithic catalysts to 800 °C and kept at this temperature for 20 min, and then quenched in water at 25 °C. This thermal shock process was repeated 10 times for each sample, after which the weight loss was measured.

2.3. Catalyst characterization

The textural structure of the monoliths was analyzed by a scanning electron microscope (PHILIPS XL 30 ESEM) equipped with energy dispersive X-ray detector (EDS). X-ray diffraction (XRD) patterns of the samples were recorded on a Philip X'Pert Pro diffractometer. Cobalt K α radiation ($\lambda = 0.178901$ nm) was used with a power setting of 40 kV and 40 mA. Temperature-programmed reduction (TPR) was carried out on a Thermo-Finnigan instrument with 30 ml/min flow rate and 10 K/min heating rate in the 5% H₂/Ar gas mixture.

2.4. Catalytic performance tests

Tests for CO catalytic oxidation in hydrogen-rich gases were performed on a quartz reactor inserted in a vertical furnace. In order to simulate composition of the reforming gas, the reaction mixture consisted of 0.5% CO, 0.5% O₂, 7.5% CO₂, 10% H₂O and 50% H₂ in volume ratio with N₂ as balance gas. H₂O was fed with a syringe pump, while heating the gas lines to avoid condensation of water. The space velocity was 7000 h⁻¹. SP-3420 gas chromatograph was used for product analysis with 5A molecular sieve column to separate CO, O₂ and N₂ and GDX-502 column for CO₂ analysis. Water was trapped before the gases entering the gas chromatograph. CO₂ was absorbed before entering the 5A molecular sieve.

The conversion of CO (C_{CO}) and the selectivity of oxygen for CO oxidation (S_{CO}) were calculated according to the following equations:

$$C_{CO} = \frac{\text{inlet CO concentration} - \text{outlet CO concentration}}{\text{inlet CO concentration}} \times 100\% \quad (1)$$

$$S_{CO} = \frac{\text{inlet CO concentration} - \text{outlet CO concentration}}{2(\text{inlet O}_2 \text{ concentration} - \text{outlet O}_2 \text{ concentration})} \times 100\% \quad (2)$$

3. Results

3.1. Adhesion stability

Table 1 lists weight increase after loading and weight loss via the ultrasonic and thermal shock tests on the monolithic catalysts. The ultrasonic and thermal shock test data show that the oxide catalysts adhere to FeCrAl monoliths with high stability, and the adhesion stability is superior to the CuO–

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