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Single- and double-stage catalytic preferential CO oxidation in H_2-rich stream over an α-Fe_2O_3-promoted CuO–CeO_2 catalyst

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Abstract

Single- and double-stage catalytic preferential CO oxidation (CO-PrOx) over-Fe_2O_3-promoted CuO–CeO_2 in a H_2-rich stream has been investigated in this work. The catalyst was prepared by the urea-nitrate combustion method and was characterized by X-ray diffractometer (XRD), X-ray fluorescence (XRF), Brunauer–Emmet–Teller (BET), transmission electron microscope (TEM), and scanning electron microscope (SEM). The catalytic activity tests were carried out in the temperature range of 50–225 °C under atmospheric pressure. The results of the single-stage reaction indicated that complete CO oxidation was obtained when operating at a O_2/CO ratio of 1.5, W/F ratio of 0.36 g s/cm^3, and at a reaction temperature of 175 °C. At these conditions, H_2 consumption in the oxidation was estimated at 58.4%. Applying the same conditions to the double-stage reaction, complete CO oxidation was found and H_2 consumption in the oxidation was reduced about 4.9%. When decreasing the double-stage reaction temperature to 150 °C, the results elucidated that CO could be converted to CO_2 completely while H_2 consumption in the oxidation was further reduced to 33.5%. A temperature blocking 2^2 factorial design has been used to describe the importance of the factors influencing the catalytic activity. The factorial design was according to the experimental results. When adding CO_2 and H_2O in feed, reduction of CO conversion for single- and double-stage reaction is obtained due to a blocking of CO_2 and H_2O at a catalytic active site. Comparing CO conversion obtained when operating with/without CO_2 and H_2O in feed for single- and double-stage reaction, less reduction is achieved when operating in double-stage reaction.

Keywords: Catalytic preferential CO oxidation; Cu–Ce–Fe–O composite-oxide catalyst; Single- and double-stage reaction

1. Introduction

H_2-fueled polymer electrolyte, or proton exchange membrane fuel cells (PEMFCs), have been widely investigated because of their higher energy conversion efficiency compared to conventional fossil fuel power sources. Under normal circumstances, pure hydrogen is the ideal fuel for a PEMFC, though hydrocarbon fuels are used as the hydrogen source. However, a fuel processor is necessary to produce a hydrogen-rich stream from natural gas, methanol, gasoline, diesel, etc. A reforming process in a fuel processor consists of steam reforming (SR), partial oxidation (POx), or a combination of the endothermic SR and exothermic POx reaction, called autothermal reforming (ATR) (Ersoz *et al.*, 2003) or oxidative reforming (Sopeña *et al.*, 2007). The reformate gas obtained from the processor always contains about 10% carbon monoxide (CO). Even with the use of the water–gas shift reaction, 1% CO still remains in the stream. CO has an affinity for the anodic platinum-electrocatalyst of a PEMFC. It strongly adsorbs on the Pt active site and then blocks the hydrogen from adsorbing on the site. Consequently, the fuel cell performance deteriorates dramatically. Literature suggests that a CO concentration as low as 10–100 ppm has a negative effect on the performance of a PEM fuel cell (Springer *et al.*, 2001). Thus, CO removal from the stream is necessary. Among the trace CO removing methods, catalytic preferential CO oxidation (CO-PrOx) seems to be an effective method to remove CO from the stream and to minimize the loss of hydrogen. The performance of the CO-PrOx depends on the nature of the catalyst, O_2/CO ratio, contact time, and stage design (Srinivas and Gulari, 2006). The desired exothermic and irreversible reaction in CO-PrOx is CO oxidation. However, in this reaction water is formed via hydrogen oxidation, reverse water gas shift, and CO-methanization reactions.

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Recently, the catalysts for CO-PrOx have been studied extensively, especially supported noble metal catalysts, including Pt (Avgouropoulos *et al.*, 2002; Rosso *et al.*, 2004), Rh (Ito *et al.*, 2004; Oh *et al.*, 1993), Ru (Snytnikov *et al.*, 2003; Wakita *et al.*, 2007), Pd (Rosso *et al.*, 2004; Snytnikov *et al.*, 2003), Co (Omata *et al.*, 2007), and Au (Avgouropoulos *et al.*, 2002; Monyanon *et al.*, 2007) are very active and stable for CO removal. These noble metal catalysts have a higher cost and are more sensitive to sulfur poisoning. Therefore, attention has been given to metal-oxide catalysts. For the supports, mostly metal oxides, ceria–zirconia is used as a three-way catalyst because of its redox property, stabilization of the metal dispersion, and high oxygen storage capacity. For instance, Cu–Ce–Fe–O (Sirichaiprasert *et al.*, 2007), CuO/(Ce,M)O_x (M = Zr, Tb) (Martínez-Arias *et al.*, 2005), CuO–CeO_2–ZrO_2 (Wang *et al.*, 2007), CuO–$Ce_xSn_{1-x}O_2$ (Chen *et al.*, 2006), and CuO/SiO_2–Al_2O_3 (Marino *et al.*, 2005) have been reported to have similar activity as noble metal catalysts and are more selective than Pt-supported catalysts when reacting at low temperature.

To develop the PEMFC application, it is necessary to remove CO from the reformate H_2-rich stream with minimal consumption of H_2. In this work, we have studied CO-PrOx in a single- and double-stage reaction to encourage CO oxidation. When all the oxygen is introduced to the reactor at the inlet, the excess oxygen might react with H_2. To minimize consumption of H_2, oxygen in the stream needs to be limited. Therefore, we have investigated comparatively the catalytic activity of α-Fe_2O_3-promoted CuO–CeO_2 catalyst prepared by the urea-nitrate combustion method for the single-stage preferential CO oxidation reaction with the double-stage preferential CO oxidation reaction. Here we studied the effect of ratio of O_2 to CO (O_2/CO ratio) and the ratio of the weight of the catalyst to the gaseous influent flow rate (W/F ratio) on the catalytic activity in the single-stage reaction. For the double-stage reaction, the effect of ratio of the inlet O_2 of the first reactor to the inlet O_2 of the second reactor (called the O_2 split ratio) and the ratio of the catalyst weight in the first reactor to the catalyst weight in the second reactor (called the catalyst weight (WC) split ratio) on the activity were investigated. During the catalytic activity in the double-stage reaction, the entire O_2/CO ratio and W/F ratio were held constant at the optimum value obtained from the single-stage reaction experiment. This work also used a temperature blocking 2^2 factorial design to determine the importance of the factors influencing the catalytic activity.

2. Experimental

2.1. Catalyst preparation

The α-Fe_2O_3-promoted CuO–CeO_2 catalyst, namely $Cu_{0.15}CeFe_{0.5}$, was synthesized by the urea-nitrate combustion method. Urea ($CO(NH_2)_2$, Asia Pacific Specialty Chemicals Limited), copper (II) nitrate trihydrate ($Cu(NO_3)_2{\cdot}3H_2O$, Merck), cerium (III) nitrate hexahydrate ($Ce(NO_3)_3{\cdot}6H_2O$, Merck), and iron (III) nitrate nonahydrate ($Fe(NO_3)_3{\cdot}9H_2O$, Merck) with a Cu/(Cu + Ce + Fe) molar ratio of 0.15, a Ce:Fe weight ratio of 1:0.5, and a urea/nitrate (U/N) ratio of 2.4 was mixed in a minimum amount of distilled water. A blue–brown transparent solution was obtained. The solution was then heated at 80 °C for 1 h. The solution became a viscous gel. The gel was preheated at 450 °C and further heated at 550 °C for 1 h in an open muffle furnace. After that, the material was powdered by gentle disaggregation in a glass mortar.

2.2. Catalyst characterization

The crystalline structure of the catalysts was analyzed by means of an X-ray diffractometer (XRD) system equipped with a RINT-2200 wide-angle goniometer employing Cu Kα radiation ($\lambda = 1.5406$ Å) and an X-ray power of 40 kV/30 mA. The average catalyst diameter was calculated from the X-ray line broadening using Scherrer's equation. X-ray fluorescence (XRF) (PW-2400) data were used to determine the Cu content on the supports and to determine the Ce:Fe weight ratio of the supports. The Brunauer–Emmet–Teller (BET) method (Quantachrome Corporation) was used to determined the specific surface area (S_{BET}), the pore volume (V_p), and the median pore width (W_p) of the catalyst by the adsorption and desorption isotherms of nitrogen at −196 °C. Transmission electron microscope (TEM) measurements and scanning electron microscope (SEM) images were used to obtain information about the crystalline structure and morphology of the catalyst, respectively.

2.3. Catalytic activity

The catalytic activity was operated at atmospheric pressure and performed in a double-stage packed bed reactor. The reactor system consisted of two U-shaped quartz tubes arranged in series. Each reactor was individually equipped with a temperature controller. A thermocouple was placed inside each reactor to monitor reaction temperature. The catalyst was placed between quartz wool layers inside a quartz tube with an inner diameter of 6 mm. Prior to the catalytic reaction tests, the catalyst underwent pretreatment under flowing 99.7% pure O_2 at 110 °C for 30 min, and then cooled down to 50 °C using flowing 99.9% pure He. The gaseous influent contained 1% CO, 1–2% O_2, 40% H_2, 0–10% H_2O, and 0–20% CO_2 balance in helium and the total flow rate of the gaseous mixture was 50 cm^3/min. The reaction temperature was in the range of 50–225 °C. To study the catalytic performance in a single-stage reactor, only the first reactor was used. The effluent from the first reactor was passed through an ice-cooled water condenser to trap water vapor before entering the GC. The effect of the ratio of O_2/CO and the ratio of the weight of catalytic sample to total flow rate of the gaseous mixture influent (W/F ratio) on the catalytic performance were chosen for study in a single-stage reaction. O_2/CO ratio and W/F ratio were varied from 1.0 to 2.0 and from 0.12 to 0.36 g s/cm^3, respectively. To study the catalytic activity in a double-stage CO-PrOx reaction, the effluent from the first reactor was passed directly to the second reactor, thereby providing a double-stage reactor. The