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Removal of CO in excess hydrogen over $CuO/Ce_{1-x}Mn_xO_2$ catalysts

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ABSTRACT

$Ce_{1-x}Mn_xO_2$ mixed oxides were used as supports for preparing $7\%CuO/Ce_{1-x}Mn_xO_2$ catalysts by impregnation for the preferential oxidation (PROX) of CO in excess hydrogen. Incorporating an appropriate amount of manganese into CeO_2 to form $Ce_{1-x}Mn_xO_2$ solution increased the mobility of lattice oxygen and improved performance of $CuO/Ce_{1-x}Mn_xO_2$ catalysts in the PROX of CO. CO oxidation proceeded at the interfacial perimeter through an interaction between CuO clusters and $Ce_{1-x}Mn_xO_2$, involving not only the redox behavior of CeO_2 but also that of MnO_x. The PROX reaction was not weakened as the fraction of manganese incorporated in the $7\%CuO/Ce_{1-x}Mn_xO_2$ catalysts increased up to 0.3. A small amount of doped Mn^{4+} and an appropriate amount of incorporated Al_2O_3 could obtain a good candidate such as $7\%CuO/Ce_{0.9}Mn_{0.1}O_2$-$20\%Al_2O_3$ for a PROX unit in a polymer electrolyte membrane fuel cell system for removing CO. Its activity was comparable with, and its selectivity was much larger than, that of the noble catalyst $5\%Pt/Al_2O_3$.

1. Introduction

Fuel cell-powered systems for transportation and residential applications have received much attention because of their high fuel efficiency, and low environmental impact. Of all of the fuel cells that have been developed, the polymer electrolyte membrane fuel cell (PEMFC) fueled with hydrogen is the most promising. Ideally, the only reaction product in PEMFC is H_2O. Hydrogen is generally generated from hydrocarbons or methanol by steam/autothermal reforming or partial oxidation, followed by a water–gas shift reaction [1–3]. Typical effluents from such a process contain 0.5–1% CO in an excess of H_2 (50–75%), 10–20% CO_2 and 5–10% H_2O [4]. Carbon monoxide must be removed to avoid poisoning of the anode electro-catalysts. The acceptable CO concentration is below 10 ppm at the Pt anode and below 100 ppm at CO-tolerant alloy anodes [1]. The CO concentration can be reduced to acceptable levels by pressure swing adsorption, catalytic methanation, Pd-based membrane separation and PROX of CO [1,5–7]. Of these methods, the PROX of CO with O_2 appears to be the simplest and most effective means of removing CO [8–10]. Developing efficient catalysts for the PROX of CO in the presence of excess hydrogen is a challenge in the field of the heterogeneous catalysis of the preparation of H_2 for use in PEMFCs [1]. The most important requirements of catalysts for the PROX of CO are a high oxidation rate of CO and a high selectivity with respect to the side oxidation reaction of H_2. Such catalysts should also tolerate the presence of CO_2 and H_2O [10].

The Pt-based catalysts are generally used for the PROX reaction due to their suitable range of reaction temperatures (100–150 °C) in a PEMFC system and high resistance to CO_2 and H_2O [1,11,12]. The selectivity in the PROX reaction is only about 45–55% for the Pt-based catalysts. The copper catalysts of CuO-CeO_2 have been reported to be active and comparable to the Pt-based catalysts in the oxidation of CO [1,13,14].

Mixed oxides of CuO-CeO_2 have recently been proposed as good candidates for selectively removing CO from reformate streams and have attracted much attention [15–19]. They can be used in the temperature range 100–150 °C with a selectivity of 95–80%. Cerium oxide is well known to have a high oxygen exchange (storage/release) capacity, which is related to the reversible exchange between Ce^{4+} and Ce^{3+} [20,21]. CeO_2 enhances CO oxidation for the CuO-CeO_2 catalysts through a synergistic effect. Based on DRIFTS and XANES analyses, Gamarra et al. [22] proposed that CO oxidation takes place at the interfacial perimeter of the dispersed copper oxide entities. The reduction of CeO_2 has been demonstrated to proceed via a surface reaction that involves CO [23]. Hence, the oxygen from the support of CeO_2 oxidizes CO adsorbed on the metal particle at the interface [24,25], and the oxygen vacancies are then replenished by O_2.

Doping zirconium into CeO_2 has been reported to improve the oxygen storage capacity, the redox property and the thermal resistance of the resulting mixed oxide $Ce_{1-x}Zr_xO_2$ [26–28]. The solid solutions of $Ce_{1-x}Zr_xO_2$ ($x = 0.4$–0.5) have oxygen capacities

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of three to five times that of pure CeO_2 [26], but the CO oxidation over $CuO/Ce_{0.5}Zr_{0.5}O_2$ is weakened [29]. Wang et al. [30] indicated that $CuO/Ce_{0.8}Zr_{0.2}O_2$ catalyst had better thermal resistance than CuO/CeO_2 and had inferior activity of CO oxidation than the CuO/CeO_2. Our previous study found that the incorporation of an appropriate amount of zirconium ($x = 0.1$) into CeO_2 for $CuO/Ce_{1-x}Zr_xO_2$ catalysts not only increased the mobility of lattice oxygen but also promoted the PROX reaction [31]. However, the PROX reaction is weakened as the doped fraction of zirconium exceeded 0.1. Incorporating tin into CeO_2 also improves the redox properties of $Ce_{1-x}Sn_xO_2$ [32] and the PROX reaction over $CuO/Ce_{1-x}Sn_xO_2$ catalysts [33]. Unlike zirconium, the PROX reaction is not weakened, as the doped fraction of tin increases up to 0.3 [33].

Manganese oxides, which reportedly have a high oxygen storage capacity, exhibit a high activity in catalytic reactions [34–36]. Hopcalite, an oxide mixture based on copper and manganese oxides, has been used for many years to remove air pollutants such as carbon monoxide and nitrous oxide from exhaust gas. In CO oxidation, its high activity is usually attributed to the resonance system $Cu^{2+}Mn^{3+}/Cu^{+}Mn^{4+}$ and the high adsorption of CO on Cu^{2+}/Mn^{4+} and of O_2 on Cu^{+}/Mn^{3+} [37,38]. Additionally, CeO_2-MnO_x mixed oxides applied for removal of CO and VOCs showed much higher activity than those of pure ceria and MnO_x [39–41]. The oxidation of benzene over CeO_2-MnO_x is effectively promoted by CuO [42]. Predictably, the association of CeO_2-MnO_x and CuO could yield effective catalysts for the PROX reaction of CO.

In this study, $Ce_{1-x}Mn_xO_2$ mixed oxides were prepared and used as supports for preparing $CuO/Ce_{1-x}Mn_xO_2$ catalysts. X-ray diffraction (XRD), Raman spectra, X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR) and pulse adsorption of CO were used to characterize supports and catalysts. The redox property of $Ce_{1-x}Mn_xO_2$ and the PROX of CO in excess hydrogen over $CuO/Ce_{1-x}Mn_xO_2$ catalysts were examined to elucidate the effect of the fixing of Mn^{4+} in CeO_2. Al_2O_3 was also incorporated with $Ce_{1-x}Mn_xO_2$ to increase the stability of the catalysts. The activities and selectivities of a series of $CuO/Ce_{1-x}Mn_xO_2(\text{-}Al_2O_3)$ catalysts in the PROX reaction were evaluated. The best catalyst was also tested in the feed in the presence of CO_2 and H_2O.

2. Experimental

2.1. Preparation of catalysts

$Ce_{1-x}Mn_xO_2$ mixed oxides ($x = 0.1$–0.5) were prepared by co-precipitation. Cerium nitrate (Merck) and manganese nitrate (Merck) were dissolved in deionized water, and then sufficient NH_4OH was added to the mixed aqueous solution. The $Ce_{1-x}Mn_xO_2$-$w\%Al_2O_3$ mixed oxides were prepared by the suspension/co-precipitation method. Cerium nitrate and manganese nitrate were dissolved in deionized water, and then sufficient NH_4OH was added to the mixed aqueous solution suspended by Al_2O_3 (Merck) in it. The precipitate was washed several times in deionized water, and then dried overnight at 120 °C. The resulting powders were calcined at 650 °C for 4 h in air. The $CuO/Ce_{1-x}Mn_xO_2$ (or $CuO/Ce_{1-x}Mn_xO_2$-$w\%Al_2O_3$) catalysts were prepared by the incipient impregnation of an aqueous solution of copper nitrate (Merck); they were dried at 120 °C overnight, and then calcined at 650 °C for 4 h in air.

2.2. Characterization of catalysts

XRD patterns were collected using a Siemens-500 diffractometer at 40 kV and 30 mA, using Cu K_α radiation. Microscopic Raman spectroscopy was performed using a RENISHAW in Via Raman Microscope at 25 mW, which was equipped with a 514.5 nm single-frequency argon laser and a CCD detector at ambient temperature under moisture-free conditions. The specific surface areas (S_{BET}) of samples were determined by nitrogen adsorption with a Micromeritics ASAP-2020 apparatus at −196 °C following degassing at 250 °C.

XPS measurements were made using a Thermo VG Scientific Sigma Prob spectrophotometer with Al K_α radiation (1486.6 eV). The nanoparticles were firstly pressed into a 10 mm-diameter disk; these disks were fixed onto the sample holder, and immediately transferred to the pretreatment chamber. In the chamber, each sample was degassed overnight at 1×10^{-6} Torr to remove the volatile contaminants and was then transferred to the analyzing chamber for XPS analysis. The spectra were obtained using an analyzer pass energy of 25.5 eV and an electron take-off angle of 45°. The vacuum in the test chamber was maintained at below 1.33×10^{-8} Torr during the collection. Binding energies were corrected for surface charging by referencing them to the energy of the C 1s peak of the contaminant carbon at 284.6 eV.

H_2-TPR measurements were made in a flow system that consisted of a quartz micro-reactor attached to a thermal conductivity detector. The catalyst (200 mg) was pretreated at 400 °C for 1 h under a stream of argon, and then cooled to room temperature. It was then reduced by increasing the temperature to 1000 °C at a rate of 10 °C min^{-1} in a stream of 10% H_2/Ar. The water thus produced was trapped using a 3A molecular sieve; hydrogen consumption was monitored using a thermal conductivity detector.

2.3. Selective oxidation of CO

A total of 180 mg of catalyst was loaded into a tubular stainless-steel reactor with an inner diameter of 12 mm and a length of 500 mm. The reactor was placed in a three-sectional temperature-controlled oven. Each catalyst was fixed with a quartz wool plug and pretreated in situ in air at 400 °C for 2 h. Following pretreatment, the temperature was reduced to room temperature in helium and then the feed $H_2/CO/O_2/He$ (50/1/1/48) mixture was diverted to the reactor at a flow rate of 30 ml min^{-1} ($F/W = 10{,}000\ ml\ h^{-1}\ g_{cat}{}^{-1}$). The reaction temperature was increased stepwise from room temperature to 140 °C. The products of reaction were passed through a cooling trap to condense H_2O and were then analyzed in a gas chromatograph that was equipped with a 1/8 in. × 15 ft 60/80 Carboxen-1000 column (SUPELCO) and a thermal conductivity detector. The effects of CO_2 and H_2O were examined by adding 15% CO_2 and 10% H_2O to the feed.

Amounts of CO, O_2 and CO_2 were measured by the absolute calibration method. The CO conversion was calculated based on the CO consumption and the selectivity of CO_2 was defined as the oxygen consumed by CO oxidation:

$$\text{CO conversion} = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100\,(\%)$$

$$CO_2\ \text{selectivity} = \frac{0.5 \times ([CO]_{in} - [CO]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100\,(\%)$$

where in and out refer to the inlet and outlet gaseous stream, respectively.

2.4. Pulsing adsorption of CO

A total of 200 mg of catalyst was loaded into a U-shaped quartz tube with an inner diameter of 3 mm. The catalyst was pretreated in situ using helium at 400 °C for 1 h and then cooled to room temperature in helium. CO (1 ml) was injected with a sampling valve