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Preferential oxidation of CO in H₂-rich feeds over mesoporous copper manganese oxides synthesized by a redox method

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ABSTRACT

Mesoporous copper manganese oxides with high surface areas (>268 m²/g) were prepared using the redox method and tested in the preferential oxidation of CO. These materials were highly active and selective under typical operating conditions of a proton-exchange membrane fuel cell. The synthesized catalysts preferentially oxidized CO with a stoichiometric amount of oxygen in the feed gas. The presence of CO₂ and H₂O in the feed gas retarded catalytic activity significantly at low (<90 °C) temperatures. The catalysts showed stable activity in long-term (12 h) experiments with realistic feeds. The high catalytic activity was attributed to a combination of factors, including high surface area, low crystallinity, low activation energy for CO oxidation, compositional homogeneity of the copper manganese oxides, and the presence of readily available lattice oxygen for CO oxidation. The high selectivity (100% with stoichiometric reactants) was ascribed to the lower activation energy for CO oxidation compared to the activation energy for H₂ oxidation.

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1. Introduction

Low temperature (80–100 °C) polymer electrolyte membrane (PEM) fuel cells have attracted considerable interest due to their potential use as an alternative energy source for both mobile and stationary applications. The efficiency, high energy and power densities obtainable in H₂-fueled PEM fuel cells coupled with benign tailpipe emissions make them very attractive power sources for electric vehicles, and small-scale energy devices [1–3]. The PEM fuel cell is designed to operate using hydrogen gas produced by reforming of methanol or hydrocarbon fuels, and the feed gas typically contains 45–75 vol.% H₂, 15–25 vol.% CO₂, 0.5–2 vol.% CO, and a few vol.% H₂O [4]. Although the PEM

cell is completely CO₂ tolerant, the anode is highly susceptible to CO poisoning with consequent voltage losses [5,6]. Thus, the total concentration of CO in the gas stream should be reduced to below 10 ppm in order to obtain optimum performance [7].

Several approaches have been investigated to remove CO from H₂-rich streams including selective diffusion, methanation, and preferential CO oxidation. Preferential oxidation of CO (PROX) is one of the most promising cost-effective methods of reducing the concentration of CO to acceptable levels especially for automotive applications [8,9]. There are two temperature levels that are ideal for the PROX reaction: the fuel cell operating temperature (80–100 °C) or the temperature level of the reformer unit (250–300 °C).

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Catalysts reported to be active for the PROX reaction are broadly divided into three groups namely; supported noble metals, metal oxides and mixed metal oxides. Supported Pt [10–15], Ru [16–18], and Rh [19–21] catalysts have good catalytic activity and moderate selectivity in the temperature range of 150–250 °C. Supported gold catalysts have been reported to be highly active and selective at low temperatures (<100 °C) but they are highly susceptible to CO₂ poisoning [22–28]. Moreover, the selectivity of supported gold catalysts rapidly decreases with reaction temperature.

Among the mixed metal oxides the CuO–CeO₂ system has been intensively studied and found to be quite active and selective for the PROX reaction [4,29–35]. The drawbacks of CuO–CeO₂ catalysts include their low activity and selectivity at high space velocities, and their poor resistance to deactivation by water. Cobalt oxide (CoO) has been reported to show the best performance among the metal oxides and completely oxidized CO at 100 °C with high selectivity (~ 90%) in the absence of CO₂ and H₂O [36].

There still exists a need to develop stable cost-effective catalysts for the PROX reaction with high activity, selectivity, and tolerance to CO₂ and H₂O. Mixed copper manganese oxide catalysts have been extensively used to remove CO from breathing air due to their low cost. However, they have not been widely studied for the PROX reaction presumably due to their low catalytic activity at near ambient temperatures and their rapid deactivation by moisture [37–40]. Recently, Hasegawa et al. [41] have synthesized copper manganese oxides using the sol-gel method and found them to be highly active and selective for PROX at temperatures below 100 °C. A nanosized copper manganite (CuMn₂O₄) catalyst synthesized via the silica aquagel confined co-precipitation method was active for preferential oxidation of CO but deactivated during the reaction [42]. Additionally, Hernández and co-workers [43] have synthesized copper modified cryptomelane-type manganese dioxide nanomaterials via the milling method and found them to be active for the preferential oxidation of CO at high (140–180 °C) temperatures. However, in the afore-mentioned studies the feed gas did not contain CO₂ and H₂O (two components of reformat gas that have deleterious effect on catalytic conversion).

In our previous study [44] we prepared copper manganese oxides using a novel redox method and found them to have excellent catalytic activity for CO oxidation at ambient temperatures. Moreover, they were significantly better at withstanding moisture than commercial copper manganese oxides. In our present work, amorphous manganese oxide and binary copper manganese oxides synthesized by the afore-mentioned method are examined for their activities and selectivities for the PROX reaction using a realistic feed gas. The influence of the presence of 25% CO₂ and 3% H₂O in the feed gas on the catalytic activity, selectivity, and stability is also investigated.

2. Experimental

2.1. Preparation of catalysts

Amorphous manganese oxide (AMO) and binary copper manganese oxides were synthesized using a redox method

described previously [44]. Briefly, AMO was prepared by the dropwise addition of 1.80 M solution of manganese (II) acetate tetrahydrate (Mn(CH₃COO)₂·4H₂O, Alfa Aesar; AR) to an equal volume of 1.20 M potassium permanganate (KMnO₄, Fisher Scientific; 99.3%) under vigorous stirring. The resultant precipitate was stirred continuously for 24 h, filtered, washed, vacuum dried, and ground into powder. The afore-mentioned procedure was modified slightly to prepare binary copper manganese oxide precursors with nominal copper/manganese molar ratios of 5/95, 10/90, and 15/85 by adding appropriate amounts of copper (II) nitrate hemihydrate (Cu(NO₃)₂·2.5H₂O, Mallinckrodt Baker; AR) to the manganese (II) acetate solution before reduction. The copper manganese oxide precursors were calcined in air for 2 h at 300 °C and the resultant samples designated CuMnO_{x-5}, CuMnO_{x-10}, and CuMnO_{x-15} based on the nominal copper content.

2.2. Characterization of catalysts

The morphology of the samples was studied by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM). The FE-SEM micrographs were taken using a JEOL JSM-6335F microscope at an accelerating voltage of 10.00 kV and a beam current of 12 μA. Samples were prepared for analysis by dispersing them in ethanol and coating a monolayer on a silicon wafer. The low-resolution TEM (LR-TEM) images, selected area electron diffraction (SAED) patterns, and elemental maps were obtained with a FEI Tecnai T12 TEM/STEM equipped with an energy dispersive (EDS) detector at an accelerating voltage of 120 kV. High-resolution TEM (HR-TEM) images were recorded with a JEOL 2010 FasTEM microscope operating at an accelerating voltage of 200 kV. Samples were ultrasonically dispersed in ethanol. A drop of the resulting suspension was then deposited onto Quantafilm holey carbon-coated grids and allowed to dry before analysis.

The textural properties of the samples were determined by performing nitrogen sorption measurements using a Micrometrics ASAP 2010 instrument. The surface areas and pore size distribution were determined by the Brunauer-Emmett-Teller (BET) and the Barrett-Joyner-Halenda (BJH) methods, respectively. The adsorption and desorption experiments were done at 77 K after initial pretreatment of the samples by degassing at 150 °C for 12 h. Elemental analysis was performed using a Perkin Elmer Model 3100 flame atomic absorption spectrometer (FAAS) by standard calibration method.

Thermal analysis was performed using a TA instruments SDT Q600 TGA/DSC Thermogravimetric Analyzer. Samples were loaded into alumina pans and heated from room temperature to 1000 °C in N₂ atmosphere (100 mL/min) at a ramp rate of 20 °C/min. Gases desorbing from the samples during thermal treatment were monitored using Diablo 5000A Real-Time Gas Analyzer (RTGA) equipped with an Agilent Technologies 5975 quadrupole Mass Selective Detector (MSD). The samples were heated from room temperature to 1000 °C in a flow (100 mL/min) of UHP helium at a ramp rate of 20 °C/min.

Temperature programmed desorption/reduction (TPD/R) experiments were carried out using a Diablo 5000A real-time gas analyzer (RTGA) equipped with an Agilent Technologies 5975 quadrupole MSD detector. The catalyst (100 mg) was

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