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Multi-wall carbon nanotubes as support of copper–cerium composite for preferential oxidation of carbon monoxide

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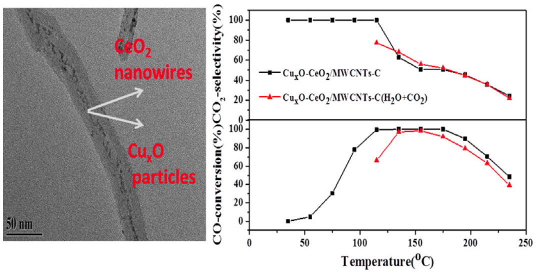
HIGHLIGHTS

- There are hydrophilic functional groups of hydroxyl and carboxyl in catalysts.
- Most of Cu_xO particles and CeO_2 nanowires are filled in tubes of MWCNTs.
- MWCNTs can help the dispersion of Cu_xO and CeO_2 to expose more active surface.
- MWCNTs with high BET surface area weaken poisoning effect of H_2O and CO_2.

GRAPHICAL ABSTRACT



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ABSTRACT

The Cu_xO/MWCNTs, CeO_2/MWCNTs and Cu_xO-CeO_2/MWCNTs catalysts were synthesized by a simple impregnation method, and characterized via X–ray diffraction, N_2 adsorption–desorption, Fourier transformed infrared spectroscopy, transmission electron microscopy, H_2 temperature–programmed reduction and X–ray photoelectron spectra. The catalytic performance for preferential CO oxidation was carried out in the hydrogen-rich gasses. It is found that the hydrophilic functional groups of hydroxyl and carboxyl in the samples are favorable for the incorporation of Cu_xO and CeO_2 into the tubes of the MWCNTs. Most of Cu_xO particles and CeO_2 nanowires are filled in the tubes of MWCNTs, and a small amount of nanoparticles are deposited on the surface of MWCNTs. The MWCNTs have high BET surface area, which is helpful for the dispersion of Cu_xO and CeO_2 to expose more active surface for CO-PROX reaction over the Cu_xO-CeO_2/MWCNTs catalysts. The Cu_xO-CeO_2/MWCNTs-C catalyst shows good catalytic activity and the temperature window of CO total conversion is from 135 °C to 175 °C. MWCNTs with high BET surface area weaken poisoning effect of H_2O and CO_2 after 135 °C.

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1. Introduction

Operational conditions in proton-exchange membrane fuel cells (PEMFC) require the presence of “pure” hydrogen fuels, i.e. hydrogen streams without any significant pollutant. Taking into account that CO in the hydrogen streams is a poison for the Pt-based anodes used in fuel cell technology [1], it is very essential to selectively remove CO to a trace-level from the reforming streams without the simultaneous oxidation of H_2 to H_2O. Preferential CO oxidation (CO-PROX) in hydrogen-rich streams is

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considered as the most promising and economic approach for purifying hydrogen among the different methods [2–8].

Noble metal supported catalysts are used for the CO-PROX reaction. Their application has been restricted in CO-PROX process due to the limited availability of precious metals as well as their poor selectivity at very low CO concentration. In particular, it has been found that the $CuO-CeO_2$ catalytic system is highly active and exceptionally selective for the preferential oxidation of CO [9–17]. The catalytic performance of copper oxide for CO oxidation is enhanced by the generation of oxygen vacancies in the ceria, which provokes higher oxygen mobility and diffusion from the lattice to the interface of copper oxide and ceria.

Carbon nanotubes (CNTs) have attracted enormous interest over the past decades due to their special physical and chemical properties since the discovery of them by Iijima [18–23]. CNTs have been proposed as nano-reactors due to the well-defined structure in terms of inner hollow cavities and a high aspect ratio [24]. Among the reported supports, CNTs are promising ones for improving the activity and selectivity of catalysts because of their favorable structure and unique properties [25]. Zhao et al. [26] reported that ceria nanoparticles can be homogeneously supported on multi-wall carbon nanotubes (MWCNTs) by a single-step supercritical hydrothermal synthesis method without additional treatment. In 2010 Zhang et al. [27] found that the CeO_2/CuO/CNT nanocomposites have an excellent catalytic performance for the CO oxidation with the lowest T_{50} at 113.5 °C, which is much lower than that of CeO_2/CNT or CuO/CNT nanowires.

Taking into account these advantages, Cu_xO-CeO_2/MWCNTs composite catalysts were prepared using a simple impregnation method in this work. Their catalytic performance was also carried out for preferential oxidation of carbon monoxide in hydrogen-rich gasses. The multi-technique characterizations were employed in order to further investigate the dispersion effect of MWCNTs and influence on the chemical state of CuO and CeO_2 on the surface of catalysts.

2. Experimental

2.1. Catalyst preparation

The MWCNTs with 10–20 nm diameter and 10–30 μm length (Chengdu Organic Chemicals) were suspended in the concentrated HNO_3 (68 wt.%) and treated under ultrasonic condition for 3 h. After filtration, the MWCNTs were washed thoroughly with deionized water until the PH value was adjusted to approximate 7.0, and then dried at 80 °C for 12 h.

The treated MWCNTs were added into an aqueous solution including $Cu(CH_3COO)_2$ and $Ce(NO_3)_3\cdot 6H_2O$ and subsequently treated under ultrasonic condition for 30 min. Then the solvent was evaporated slowly at 80 °C overnight in the drying oven. The resulting solid mixture was gradually heated to 140 °C and maintained for 3 h. Further, the temperature was increased to 350 °C at a rate of 2 °C/min and the solid mixture was calcined at 350 °C for 3 h in N_2 atmosphere. The obtained catalysts were denoted as Cu_xO/MWCNTs (10 wt.% CuO), CeO_2/MWCNTs (10 wt.% CeO_2), Cu_xO-CeO_2/MWCNTs-A (5 wt.% CuO, CuCe molar ratio = 1:1), Cu_xO-CeO_2/MWCNTs-B (10 wt.% CuO, CuCe molar ratio = 1:1) and Cu_xO-CeO_2/MWCNTs-C (20 wt.% CuO, CuCe molar ratio = 1:1).

2.2. Catalyst characterization

2.2.1. X-ray diffraction

Powder X-ray diffraction patterns of the samples were carried on a PANalytical X'pert PRO diffractometer. The diffraction patterns were recorded at room temperature with Cu *Kα* source (λ = 0.15406 nm) and a power setting of 40 kV and 100 mA in the range of 2θ between 20° and 80°.

2.2.2. N_2 adsorption–desorption isotherms

The textural properties of the samples were determined by nitrogen physisorption at liquid nitrogen temperature using a Micromeritics Apparatus (Model ASAP2020). The surface area and pore size distribution were determined by the Brunauer–Emmett–Teller (BET) and the Barrette-Joynere-Halenda (BJH) methods, respectively.

2.2.3. FT-IR measurements

Fourier transform infrared spectroscopy (FT-IR) was measured using a Nicolet 6700 FTIR spectrometer with attenuated total reflection (ATR) mode. Each FTIR spectrum was collected after 40 scans with a nominal resolution of 2 cm^{-1} in a scanning range from 500 to 4000 cm^{-1}.

2.2.4. Temperature–programmed reduction

H_2 temperature–programmed reduction was conducted on a Micromeritics Apparatus (AutoChemII2920). The experiments were operated in a quartz reactor, and the amount of H_2 consumption was analyzed by a thermal conductivity detector. The reduction gas was 10% H_2/Ar gas mixture and the flow rate of gas was 50 ml/min. Before reduction, the sample was pretreated at 200 °C for 1 h in an Ar stream in order to remove the contaminants, and then cooled to room temperature. The H_2/Ar mixture was switched on and the sample was heated with a heating rate of 10 °C/min. The experiments were performed from room temperature to 900 °C.

2.2.5. Transmission electron microscopy

Transmission electron microscopy images of the samples were performed via a FEI Tecnai G2 F20 S-Twin transmission electron microscope. The sample was dispersed into ethanol with ultrasonic treatment for 15 min, and a drop of the suspension was placed on a copper grid for TEM observation.

2.2.6. X-ray photoelectron spectroscopy

X-ray photoelectron spectra of the samples were collected using a Thermo ESCALAB 250Xi spectrometer that was carried out under the requirement of UHV conditions with tapered anode Al *Kα* radiation for the analysis of the core level signals of C 1*s*, O 1*s*, Ce 3*d* and Cu 2*p*. During data processing of the XPS spectra, the binding energy values were calculated with the reference to the C 1*s* peak of contaminant carbon at 284.8 eV.

2.3. Catalytic performance evaluation

The preferential oxidation of CO in the hydrogen-rich gasses was carried out in a quartz reactor with an inner diameter of 9 mm at atmospheric pressure. The reaction mixture consisted of 1% CO, 1% O_2 and 50% H_2 (volume fraction) with N_2 as a balance gas, and the space velocity was 40,000 $ml\cdot g_{cat}^{-1}\cdot h^{-1}$. The reaction was operated between 35 °C and 235 °C. The reaction temperature was measured by means of a K-type thermocouple positioned at the middle of catalyst bed and controlled by a temperature controller. The amount of catalyst was 100 mg. The thickness of catalyst bed was 10 mm. Product and reactant analyses were conducted by a GC-2014C gas chromatograph. 5A molecular sieve column was used to separate CO, O_2 and N_2. CO and CO_2 were determined by a TDX-01 column. Water was trapped before the gasses entering the GC and CO_2 was absorbed before entering 5A molecular sieve.

The conversion of CO (C_{CO}) and the selectivity towards CO_2 (S_{CO_2}) were calculated according to Equations (1) and (2) [10,28]:

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