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Short Communication

Hierarchically nanoporous Co–Mn–O/FeO_x as a high performance catalyst for CO preferential oxidation in H_2-rich stream

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ABSTRACT

A novel and highly-efficient hierarchically nanoporous Co–Mn–O/FeOx catalyst fabricated by a hard/soft dual-templating and subsequent deposition–precipitation (HSDT/DP) approach demonstrates unexpectedly high catalytic activity with 100% CO conversion at 75 °C and wide temperature window of 75–200 °C with complete CO removal for CO preferential oxidation (CO PROX), ascribed to the unique microstructure and strong interaction between finely dispersed cobalt–manganese and FeO_x. The excellent catalytic performance allows it to be a practical candidate for CO elimination from H_2-rich stream.

1. Introduction

Hydrogen as one of the cleanest and most efficient new energy source for fuel cell is generally obtained by catalytic reforming of hydrocarbons and followed by water gas shift (WGS) reaction [1]. However, because of the limited activity of current WGS catalysts for complete CO conversion, a thermodynamically favored reaction at a low temperature, approximately 0.5–1.0 vol.% of residual CO still remains in syngas and requires to be decreased to less than 100 ppm to avoid poisoning the anode of proton-exchange membrane fuel cell (PEMFC) [2,3], one of the most efficient candidates for full use of hydrogen energy [4]. The CO PROX reaction has been considered to be a straightforward and effective protocol for eliminating trace CO to purify hydrogen [5–7]. The CO PROX reaction unit can be attached to a PEMFC (typically working at 80–100 °C) or to a WGS reactor (typically working at 200–250 °C), and it can also be a medium unit between a Fuel Cell and a WGS reactor for immobile electricity-production station [8]. Therefore, to develop highly active and selective CO PROX catalysts with a wide temperature window is highly desirable.

Among a number of active catalysts reported for CO PROX, the precious metal-free copper [9–11] and cobalt [12–17] based catalysts have been considered to be promising and interesting alternatives in view of their high catalytic performance besides their good availability and low cost. Generally, copper-based catalysts exhibited high activity but narrow temperature window and also not satisfactory selectivity, and many efforts are being made to further improve activity and selectivity and also to widen temperature window for full CO removal [9–20]. The 100% CO conversion (40–60 °C) of the highest activity towards copper based catalyst has been reported recently [18], which is most efficient catalyst for single CO PROX unit, but the narrow temperature window limits its flexibility of industrial application [8]. Through fabricating inverse CeO_2/CuO configuration, the operation temperature window can be broadened to 60 °C (90–150 °C) [9], but the activity was depressed. As the other candidate for CO PROX, the cobalt-based catalysts have illustrated a wider temperature window for complete CO removal, but their catalytic activity at low temperature is definitely required to be improved [12–17]. In our “Nano Catalysis and Energy Storage” research group, continuing efforts are being made to improve catalytic performance especially catalytic activity at low temperature of cobalt based catalysts [21–26], and the Co–Mn based catalysts have been considered to be a promising candidate [12–17,21–26]. However, the further improvement in catalytic activity at low temperature is essential for practical applications in PEMFC.

The catalytic performance of supported-type catalysts is strongly dependent on their element content and microstructure of support [18–20,27–29]. Iron oxides or hydroxides, as novel and effective supports, have been used in CO low-temperature oxidation and CO PROX reactions [30–32]. The reported results illustrate that the hierarchically mesoporous macroporous catalysts, due to the unique microstructure and the metal-support interaction, exhibit excellent catalytic performance in various reactions [33,34]. The crystal plane of supported active

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phase dependent on the support nature may strongly affect the catalytic performance [35]. We envision that the hierarchically porous FeOx supported Co–Mn–O catalyst may be a promising candidate for CO PROX. However, to the best of knowledge, no report on supported Co–Mn based catalysts on iron oxides can be found. In this paper, we report a facilely prepared but high performance Co–Mn–O/FeO_x catalyst by HSDT/DP method (Scheme S1 in supporting information), exhibiting significantly superior catalytic performance.

2. Experimental

2.1. Preparation of catalysts

The hierarchically porous Co–Mn–O/FeO_x catalyst was prepared by a HSDT/DP route. The typical experimental procedure was as follows: firstly, monodispersed SiO_2 microsphere was synthesized by using classical Stöber method, and then 0.2 g SiO_2 was re-dispersed into 10 ml ethanol assisted by ultrasound. 0.819 g cetyltrimethylammonium bromide (CTAB) was dissolved into 22.5 ml ethanol. Secondly, the dispersed SiO_2 ethanol solution and CTAB ethanol solution were combined into one dual-template system. Thirdly, 4.83 g iron nitrate was dissolved into 20 ml deionized water, and gradually dropped into the above dual-template system under strong stirring, subsequently gelled by dropping ammonia. Then the resulted gel was transferred into autoclave, and suffering from a hydrothermal process at 180 °C for 6 h. After filtering, washing, drying, and removing CTAB by calcinations at 500 °C for 5 h via a step of 50 °C from 200 to 500 °C, 2.0 M NaOH solution was used to remove SiO_2 template. The obtained FeOx was denoted as FeO_x (Si + CTAB). By only using one kind of templates, FeO_x (Si) and FeO_x (CTAB) were prepared, respectively. The FeO_x was also prepared by traditional precipitation method, and denoted as FeO_x (traditional). The various iron oxides (FeO_x) were used as supports. The supported Co–Mn–O catalysts on diverse FeO_x with an optimized 50% loading (from SEM, Co–Mn–O layer deposited on nanoporous FeOx) were prepared by our previously reported deposition–precipitation (DP) method (300 °C for 2.5 h) [23], and denoted as Co–Mn–O/FeO_x (Si + CTAB), Co–Mn–O/FeO_x (Si), Co–Mn–O/FeO_x (CTAB) and Co–Mn–O/FeO_x (traditional), respectively.

2.2. Characterization of catalysts

X-ray diffraction (XRD) profiles were collected from 10° to 80° at a step width of 0.02° using Rigaku Automatic X-ray Diffractometer (D/Max 2400) equipped with a CuKa source ($\lambda = 1.5406$ Å). The average crystalline particle size estimation was performed according to the Scherrer equation over multiple characteristic diffraction peaks. H_2 temperature-programmed reduction (H_2-TPR) experiments were performed in an in-house constructed system equipped with a thermal conductivity detector (TCD) to measure H_2 consumption. A quartz tube was loaded with 50 mg of catalyst which was pretreated by calcination in Ar at 300 °C for 30 min and then was cooled to ambient temperature in Ar. After that, it was reduced with a 10 vol.% H_2/Ar mixture (30 ml min^{-1}) by heating up to 800 °C at a ramp rate of 10 °C min^{-1}. Nitrogen adsorption and desorption isotherms were determined on a Micromeritics apparatus of model ASAP-2050 system at −196 °C. The specific surface areas were calculated by the BET method and the pore size distributions were calculated from desorption branch of the isotherm by BJH model. Scanning electron microscope (SEM) experiments were performed on JEOL JSM-5600LV SEM/EDX instrument. High-resolution transmission electron microscopy (HRTEM) images were obtained by using Tecnai F30 HRTEM instrument (FEI Corp.).

2.3. Catalytic performance measurement

Catalytic reaction experiments were performed in a stainless steel, fixed bed flow reactor (6 mm O.D.) with 200 mg of catalyst held between quartz wool plugs. Typically, the reaction feed consisted of 1.0 vol.% CO, 1.0 vol.% O_2, 50 vol.% H_2 and Ar balance (with or without 10 vol.% CO_2 and 10 vol.% H_2O) and Ar balance). Samples were pretreated in Ar at 300 °C for 30 min. Temperatures were measured using K-type thermocouples and controlled by a PID controller. The analysis of the effluent gas was performed using a gas chromatograph on-line with a molecular sieve column and a Porapaq Q column. The CO and CO_2 signals were detected by the FID detector after the gas passing through a methanizer. CO conversion and CO_2 selectivity were calculated on the basis of the equations as follows:

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

$$O_2 \text{ conversion} \quad \chi_{O_2}(\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100$$

$$O_2 \text{ selectivity to } CO_2 \quad S_{CO_2}(\%) = \frac{\chi_{CO}}{2 \times \chi_{O_2}} \times 100.$$

3. Results and discussion

Fig. 1 illustrates the reaction results of the diverse Co–Mn–O/FeO_x catalysts for CO PROX reaction in H_2-rich gas. As illustrated in Fig. 1, in comparison of the other three, the developed Co–Mn–O/FeO_x (Si + CTAB) catalyst by a HSDT/DP approach in this work demonstrates the remarkably superior catalytic performance, and the CO can be complete eliminated in a wide temperature range of 75–200 °C. The catalytic performance of the supported Co–Mn catalyst on FeO_x is significantly affected by the microstructure of supports. The catalytic activity of the developed catalyst has been near to those of precious metal ones reported in literatures [6,36]. From previous literatures, the supported Ni–Co catalysts on activated carbon could provide 100% CO conversion only at narrow temperature range of 130–150 °C [16]. The CO conversion on MnO_x-promoted Co_3O_4 catalyst can reach 100% only at 125–175 °C [15,25,26]. The initial temperature of 100% CO conversion is obviously lower than those obtained over the previously reported Co-based catalysts in references [12–17,21–26]. The newly reported Cu-based catalyst exhibited very high activity [18], however, as a bottle-neck of Cu-based catalysts, the only 40–60 °C of too narrow temperature window for full CO removal limits its industrially applications. Although 100% CO conversion over the developed catalyst in this work

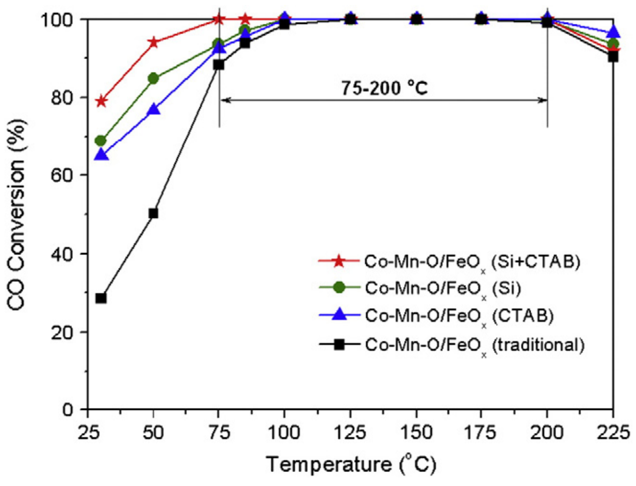

Fig. 1. Catalytic activity curves of the various supported Co–Mn–O catalysts for CO preferential oxidation in H_2-rich stream. Operation conditions: GHSV = 15,000 ml h^{-1} g^{-1}, 1.0% CO, 1.0% O_2, 50% H_2 and Ar balance.