Short Communication

The supported CeO_2/Co_3O_4–MnO_2/CeO_2 catalyst on activated carbon prepared by a successive-loading approach with superior catalytic activity and selectivity for CO preferential oxidation in H_2-rich stream

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ABSTRACT

The supported CeO_2/Co_3O_4–MnO_2/CeO_2 catalyst on activated carbon (AC) prepared by a successive loading approach to support ceria, cobalt-manganese oxide and ceria on activated carbon exhibits superior catalytic activity and selectivity to Co_3O_4–MnO_2–CeO_2/AC prepared by a one-step loading for CO preferential oxidation in H_2-rich stream, although the same loading of Co, Mn and Ce was used, which illustrates that the addition of ceria doesn't always enhance catalytic performance in CO PROX reaction, and appreciate supporting method is essential. The superior catalytic activity and selectivity of developed catalyst can be ascribed to high reducibility, well dispersion, unique porous structure, and strong interaction between Co_3O_4–MnO_2 and CeO_2.

1. Introduction

The CO preferential oxidation (PROX) has already been considered as a straightforward and effective strategy for eliminating trace CO to clean hydrogen feed for proton-exchange membrane fuel cells (PEMFCs) [1–4]. To develop highly active and selective catalysts for CO PROX is highly desirable. Among the reported catalysts, the nonprecious copper- [5–8] and cobalt- [9–16] based catalysts have been considered to be promising and interesting alternatives to precious metal catalysts in view of their high catalytic performance besides their good availability and low cost. The copper-based catalysts exhibit high activity but narrow temperature window for CO PROX. Many efforts are being made to further increase their catalytic performance [5–8,17–20]. The cobalt-based catalyst, as a promising candidate, has illustrated a wider temperature window for 100% CO conversion, but their catalytic activity at low temperature is definitely required to be improved [3,9–16]. In our Nano Catalysis and Energy Storage (NCES) research group, the continuing efforts are being made to improve its catalytic performance

especially catalytic activity at low temperature [21–24]. It has been shown that the supported Co–Mn catalyst can be a promising candidate CO PROX [9–16,21–24]. However, the further improvement in catalytic activity at low temperature besides H_2O/CO_2 tolerance is essential for practical applications in PEMFCs.

Due to high oxygen mobility and excellent oxygen storage-release properties, the promoting effect of ceria on cobalt and copper based catalysts has been illustrated [17–24]. From references, the high catalytic activity of heterogeneous catalysts comprising metal or metal oxide supported on oxide support mainly comes from the unique interfacial regions [25–27], and the promoting roles of ceria on copper catalysts for CO PROX have been efficiently reinforced by fabricating inverse CeO_2/CuO catalysts to enlarge the contact interface [17–19]. It's proposed that the catalytic performance of Co–Mn based catalysts for CO PROX can be further improved by enlarging contact interface between Co–Mn and ceria. In this paper, we present an efficient CeO_2/Co_3O_4–MnO_2/CeO_2/AC catalyst (denoted as Ce/Co–Mn/Ce/AC) prepared by a successive DP approach (Scheme 1A), which exhibits notedly superior catalytic activity to Co_3O_4–MnO_2–CeO_2/AC formula (denoted as Co–Mn–Ce/AC) prepared by a one-step DP method (Scheme 1B) with the close molar ratio of Co/Mn/Ce (8.23:1:0.97 and 8.18:1:0.96, respectively) measured by EDX. The excellent catalytic performance of developed catalyst may be ascribed to the integrated interfacial effect and ceria roles.

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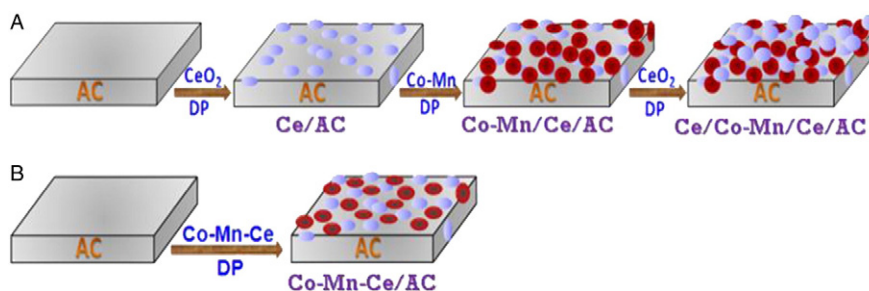
Scheme 1. Illustration of preparation process for the (A) Ce/Co–Mn/Ce/AC and (B) Co–Mn–Ce/AC catalysts by a successive DP approach and one-step DP method, respectively.

2. Experimental

2.1. Preparation of catalysts

A series of $Ce_y/Co–Mn/Ce_x/AC$ catalysts with 8:1 of Co/Mn atomic ratio and 27.5 wt.% of fixed Co_3O_4 loading were prepared by a successive DP approach to support inner ceria, cobalt-manganese oxide and outer ceria on the modified AC prepared based on previously report [24]. Firstly, the Ce/AC was prepared by DP method with aqueous solution containing a certain amount of $(NH_4)_2Ce(NO_3)_6$ as Ce precursor. Secondly, by using $Co(NO_3)_2 \cdot 6H_2O$ (Tianjin Bodi, AR) and $Mn(CH_3COO)_2 \cdot 4H_2O$ (Shenyang Reagent Corp., AR) as Co and Mn precursors, respectively, the desired loading of Co–Mn was deposited on the as-prepared Ce/AC to obtain Co–Mn/Ce/AC. Thirdly, the outer Ce was loaded on Co–Mn/Ce/AC sample by using DP method using the same Ce precursor. After each loading step, the sample was dried at 105 °C for 2 h to evaporate the solvent. The final sample was calcined in Ar atmosphere from room temperature to 160 °C with a ramp rate of 5 °C min^{-1}, and maintained for 0.5 h, and then to 180 °C at a 1 °C min^{-1} of lower ramp rate to prevent the intense decomposition of metal nitrates, and keeping at 180 °C for 0.5 h, and then further increased to 300 °C at a ramp rate of 10 °C min^{-1} and maintained for 2.5 h. The $Ce_y/Co–Mn/Ce_x/AC$ catalysts with the 27.5 wt.% of Co_3O_4 loading (8:1 of Co/Ce ratio) and the diverse x and y values (x = 0.1, 0.2 and 0.3; y = 0.6, 0.8, 1.0 and 1.2) were obtained. For comparison, the Co–Mn/AC and Co–Mn–Ce/AC were prepared by the one-step DP method with same drying and calcination process [23].

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. Specific surface areas were calculated by BET method and pore size distributions were calculated from desorption branch of the isotherm by BJH model. SEM/EDX experiments were performed on JEOL JSM-5600LV SEM/EDX instrument. Laser Raman spectra were collected on powdered samples under ambient conditions using a Thermo Scientific DXR Raman Microscope with 633 nm helium–neon laser as excitation source.

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 (introdcuing 10 vol.% CO_2 and 10 vol.% H_2O into feed for simulated syngas). 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 (no methanation or WGS was detected in our investigated temperature range, although cobalt is a good catalyst for those reactions):

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

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

$$H_2\ conversion\ \chi_{H_2}(\%) = 2 \times \frac{\chi_{O_2} \times [O_2]_{in} - 0.5 \times \chi_{CO} \times [CO]_{in}}{[H_2]_{in}} \times 100$$

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

CO or H_2 oxidation rate is calculated on the basis of the converted CO or H_2 molar amount per surface area of loaded catalysts in reactor.

3. Results and discussion

The CO PROX reaction results over the $Ce_{0.8}/Co–Mn/Ce_{0.2}/AC$ and Co–Mn–Ce/AC catalysts with the same Co, Mn and Ce loadings are depicted in Fig. 1 and S1 (see SI). From Fig. 1, the developed $Ce_{0.8}/Co–Mn/Ce_{0.2}/AC$ catalyst in this work exhibits notably superior catalytic activity to Co–Mn–Ce/AC, close to 100% CO conversion at 90 °C can be obtained on the former but at 140 °C on the latter, as well as its catalytic activity is higher than that of the supported Co–Mn catalyst on AC, suggesting the promoting effect of ceria [23]. From Fig. S1, the O_2 selectivity to CO_2 at the initial full removal temperature point over $Ce_{0.8}/Co–Mn/Ce_{0.2}/AC$ (86.1% selectivity) is obviously higher than that over Co–Mn–Ce/AC (70.8% selectivity). H_2 conversions are 0.3% and 0.8% over $Ce_{0.8}/Co–Mn/Ce_{0.2}/AC$ and Co–Mn–Ce/AC catalysts at the initial temperature point for full CO removal, respectively. The transformed CO and H_2 molar amount per hour and per surface area is an efficient parameter (turnover of frequency, TOF) to evaluate the catalytic efficiency of heterogeneous catalyst. Then we compare the reaction rates (or TOF, CO and H_2 oxidation rate, calculated on the basis of transformed amount per hour and