



Manganese-promoted cobalt oxide as efficient and stable non-noble metal catalyst for preferential oxidation of CO in H₂ stream

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ABSTRACT

The modification by MnO_x significantly enhanced the activity and stability of Co₃O₄ for the preferential oxidation of CO in H₂-rich stream. The MnO_x-promoted Co₃O₄ catalyst with a Mn/Co molar ratio of 1/8 exhibited the best performance; CO conversion was 56% at 40 °C and increased to >90% as the temperature was raised to >75 °C. This catalyst could provide 100% CO conversion at 125–175 °C. CO conversions of 97% and 100% remained unchanged for 100 h at 100 and 125 °C, respectively, whereas the deactivation was observed over Co₃O₄ alone. Our characterizations using XRD, XPS and TEM indicated that the modification of Co₃O₄ with MnO_x caused the formation of smaller Mn_xCo_{3-x}O₄ solid-solution particles. The O₂-TPD, CO-TPD, and pulse reaction studies suggest that the incorporation of MnO_x into Co₃O₄ increased the amounts of reactive oxygen species and adsorbed CO species over catalyst surfaces and enhanced the regeneration ability of the reduced catalyst by O₂. All these enhancements are proposed to be responsible for the improved catalytic performance of the MnO_x-promoted Co₃O₄.

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1. Introduction

It is well known that CO (0.5–2 wt%) in H₂ produced mainly by reforming of hydrocarbons, followed by the water–gas shift (WGS) reaction, can poison the Pt-based anode in the polymer electrolyte membrane (PEM) fuel cell. The preferential oxidation (PROX) of CO in H₂-rich stream is regarded as one of the simplest and cost-effective routes for the removal of CO in H₂. Many catalysts, typically noble metal-based and transition metal oxide-based catalysts, have been reported for the PROX of CO [1–5]. Among the noble metal-based catalysts, supported Pt and Au catalysts show promising performances [6–9]. Conventional Pt catalysts typically work at higher temperatures (>150 °C) [6], and recent work has attempted to promote the low-temperature activity of the supported Pt catalysts by adding FeO_x [7,9], CoO_x [10] and other promoters or using peculiar supports such as FSM-16 [11]. On the other hand, supported Au catalysts such as Au/MnO_x, Au/Fe₂O₃, Au/TiO₂, and Au/CeO₂ could provide good CO conversions at lower temperatures but H₂ oxidation occurred seriously at temperatures >80 °C, resulting in lower O₂ selectivity for CO oxidation [12–20].

Because of the high cost and limited availability of noble metals, the catalysts based on transition metal oxides or composite oxides are promising alternatives for the PROX of CO [1,2,5]. Cu-

based supported or composite oxides, especially CuO–CeO₂, have been studied intensively for the PROX of CO [1,2,5,13,21–29]. Cobalt oxide (Co₃O₄) was known to exhibit good catalytic performance for the oxidation of CO by O₂ at lower temperatures [30–34]. There only exist a few studies on the PROX of CO in H₂-rich stream over Co₃O₄-based catalysts such as Co₃O₄/ZrO₂ and Co₃O₄–CeO₂ [35–42]. These Co₃O₄-based catalysts typically work effectively at 150–200 °C, providing similar or even better performances than the CuO–CeO₂ catalyst. The Co³⁺ site on catalyst surfaces appears to play a key role in the oxidation of CO both in the absence and the presence of H₂, and the lattice oxygen may participate in the transformation of CO [31,34,36,37]. However, the Co₃O₄-based catalysts usually deactivate with time on stream during the reaction [31,33,34,38,39]. For the PROX of CO in H₂ stream, several reasons, e.g., the partial reduction of Co³⁺ and the formation of carbonates, have been proposed to be responsible for the deactivation of Co₃O₄-based catalysts [37–39]. To date, none has succeeded in demonstrating a catalyst with satisfactory combination of activity, selectivity and stability for the PROX of CO in H₂ stream.

Recently, we found that the modification of Co₃O₄ with MnO_x could significantly increase its activity at lower temperatures and widen the operation temperature region. The stability of Co₃O₄ was also remarkably enhanced by the modification with MnO_x. Herein, we report the superior catalytic performances of the MnO_x-promoted Co₃O₄ catalysts in the PROX of CO in H₂. The effects of MnO_x modification will be discussed in detail on the basis of catalyst characterizations and pulse reaction studies.

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2. Experimental

2.1. Catalyst preparation

The MnO_x-promoted Co₃O₄ samples (denoted as Mn–Co–O hereafter) with different Mn/Co atomic ratios were prepared by a co-precipitation method. Typically, an aqueous solution of Na₂CO₃ were added dropwise into the mixed aqueous solution of Co(NO₃)₂ and Mn(NO₃)₂ with a fixed Mn/Co ratio under vigorous agitation, and then a suspension was obtained. The pH of the suspension was kept at 8.5–9.0. After further aging for 4 h, the solid was recovered by filtration, followed by washing with hot deionized water and drying at 80 °C for 24 h. The catalyst was finally calcined in air at 350 °C for 5 h. The Co₃O₄ and MnO₂ samples were prepared with the same procedure.

2.2. Catalyst characterization

N₂ physisorption was performed at –196 °C on a Micromeritics Tristar 3000 surface and porosimetry analyzer to obtain the surface areas of samples. Powder X-ray diffraction (XRD) patterns were collected on a Panalytical X'pert Pro diffractometer using Cu K_α radiation (40 kV, 30 mA). X-ray photoelectron spectroscopic (XPS) measurements were performed on a Quantum 2000 Scanning ESCA Microprobe (Physical Electronics) using Al K_α radiation (1846.6 eV) as X-ray source. The binding energy was calibrated using C 1s photoelectron peak at 284.6 eV as a reference. Transmission electron microscopy (TEM) was measured with a Tecnai F30 electron microscope (Phillips Analytical) operated at an acceleration voltage of 300 kV.

Oxygen temperature-programmed desorption (O₂-TPD) measurements were performed on a Micromeritics AutoChem 2920 II instrument. Typically, after pretreated by a 20 vol% O₂/He gas flow at 350 °C for 1.5 h, the sample was purged by high-purity He and was then cooled down to 50 °C in He flow. The adsorption of O₂ was performed in a 5 vol% O₂/He gas flow for 1 h at 50 °C. After purge by high-purity He, the sample was heated from 50 °C to 900 °C at a rate of 10 °C min⁻¹, and the desorbed O₂ was monitored using a mass spectrometer (Pfeiffer Vacuum ThermoStar GSD 301 T2). Carbon monoxide temperature-programmed desorption (CO-TPD) was measured with a similar procedure on the Micromeritics AutoChem 2920 II instrument. After pretreatment at 350 °C in a 20% O₂/He flow, followed by purge with He and cooling down to 50 °C, the sample was exposed to 5% CO/He at 50 °C for 1 h, and then the gas-phase CO was removed by He purge. The temperature was subsequently raised to 700 °C at a rate of 10 °C min⁻¹. The desorbed CO and CO₂ were monitored by the mass spectrometer.

2.3. Catalytic reactions

The PROX of CO was performed on a fixed-bed reactor operated at atmospheric pressure. The catalyst was pretreated in an O₂-containing He gas flow (O₂, 5 vol %) at 200 °C for 40 min before reaction. After the catalyst was cooled down to a certain reaction temperature, the reactant gas containing 1% CO, 1% O₂, and 50% H₂ in He was introduced into the reactor. Typically, 100 mg of catalyst was used, and the total gas flow rate was 50 mL min⁻¹, corresponding to a weight hourly space velocity (WHSV) of 30,000 mL g⁻¹ h⁻¹. The inlet and outlet gas compositions were analyzed by an on-line gas chromatograph equipped with TCD and FID. H₂, O₂, CO, and CO₂ were separated using a carbon molecular sieve (TDX-01) column. CO and CO₂ were further converted to methane by a methanation reactor and analyzed using a FID detector. The carbon balance in each run was 100 ± 3%. The conversion of CO and the O₂ selectivity

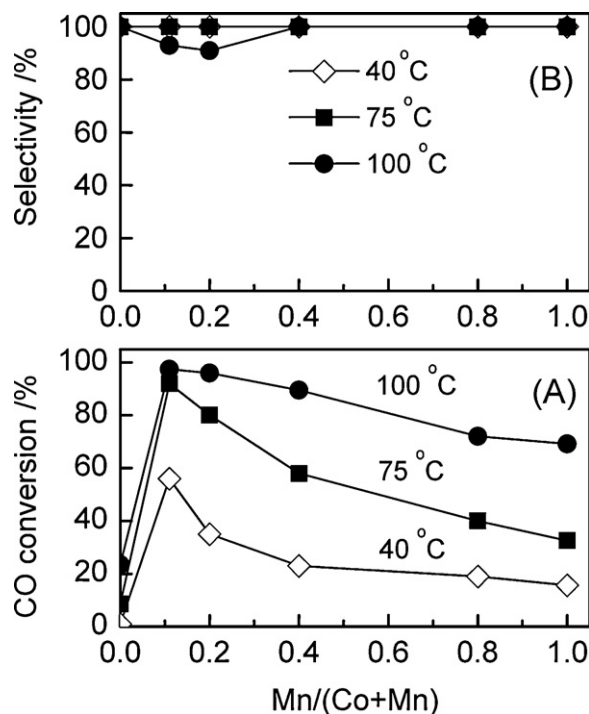


Fig. 1. Effect of the atomic ratio of Mn/(Co + Mn) on catalytic behaviors for the PROX of CO in H₂. (A) CO conversion; (B) O₂ selectivity for CO oxidation. Reaction conditions: catalyst, 0.10 g; reactant composition: 1% CO, 1% O₂, 50% H₂, 48% He; total flow rate, 50 mL min⁻¹.

for CO oxidation were calculated by the following equation:

$$\text{CO conversion (\%)} = \frac{1 - [\text{CO}]_{\text{out}}}{[\text{CO}]_{\text{in}}} \times 100\%$$

$$\begin{aligned} \text{Selectivity (\%)} &= \frac{1/2[\text{CO}_2]}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100\% \\ &= \frac{1/2([\text{CO}]_{\text{in}} - [\text{CO}]_{\text{out}})}{[\text{O}_2]_{\text{in}} - [\text{O}_2]_{\text{out}}} \times 100\% \end{aligned}$$

3. Results and discussion

3.1. Effect of the modification of Co₃O₄ by MnO_x on catalytic behaviors

Several research groups have demonstrated that Co₃O₄ is a promising catalyst for the PROX in H₂, but relatively high temperatures (150–200 °C) are required to attain a high activity [35–46]. Our results (Fig. 1) show that the single Co₃O₄ exhibits very low CO conversions (<10%) at temperatures ≤75 °C. The modification of Co₃O₄ by MnO_x significantly enhanced CO conversions at these temperatures (Fig. 1A). The Mn–Co–O catalyst with an atomic Mn/(Co + Mn) ratio of 0.11, i.e., Mn/Co ratio of 1/8, exhibited the highest CO conversions; CO conversions over this catalyst reached 56% and 92% at temperatures of 40 °C and 75 °C, respectively. These values are significantly higher than those obtained over the single Co₃O₄ and MnO₂ catalysts. The O₂ selectivities at ≤75 °C over these catalysts were 100% (Fig. 1B). An increase in temperature to 100 °C increased the CO conversion to 97% over the Mn–Co–O (Mn/Co = 1/8) catalyst, but the O₂ selectivity was slightly decreased to 93%.

Further comparisons in catalytic behaviors among the Mn–Co–O catalysts (with Mn/Co ratios of 1/8 and 2/8) and the single Co₃O₄ and MnO₂ are shown in Fig. 2. Over the Mn–Co–O catalyst with

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