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Pt/MnO_x–CeO_2 catalysts for the complete oxidation of formaldehyde at ambient temperature

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Abstract

MnO_x–CeO_2 mixed oxides with a Mn/(Mn + Ce) molar ratios of 0–1 were prepared by a modified coprecipitation method and investigated for the complete oxidation of formaldehyde. The MnO_x–CeO_2 with Mn/(Mn + Ce) molar ratio of 0.5 exhibited the highest catalytic activity among the MnO_x–CeO_2 mixed oxides. Structure analysis by X-ray powder diffraction and temperature-programmed reduction of hydrogen revealed that the formation of MnO_x–CeO_2 solid solution greatly improved the low-temperature reducibility, resulting in a higher catalytic activity for the oxidation of formaldehyde. Promoting effect of Pt on the MnO_x–CeO_2 mixed oxide indicated that both the Pt precursors and the reduction temperature greatly affected the catalytic performance. Pt/MnO_x–CeO_2 catalyst prepared from chlorine-free precursor showed extremely high activity and stability after pretreatment with hydrogen at 473 K. 100% conversion of formaldehyde was achieved at ambient temperature and no deactivation was observed for 120 h time-on-stream. The promoting effect of Pt was ascribed to enhance the effective activation of oxygen molecule on the MnO_x–CeO_2 support.

Keywords: MnO_x–CeO_2 mixed oxides; Pt/MnO_x–CeO_2 catalyst; Complete oxidation; Formaldehyde; Platinum precursor

1. Introduction

Formaldehyde emitted from the widely used construction and decoration materials is becoming one of the major indoor pollutants in airtight buildings. Long-term exposure to the air even containing a few ppm of HCHO could cause adverse effects on the eyes and respiratory system [1]. Thus, great efforts have been made to reduce the indoor emission of HCHO for satisfying the stringent environmental regulations. Conventional physical absorption and/or chemical reactions with impregnated potassium permanganate and organic amines were proved to be efficient for HCHO elimination at field experiments, but these adsorbents were effective for only a short period due to their limited removal capacities [2,3].

Heterogeneous catalytic oxidation of HCHO is regarded as one of the most promising technologies for indoor air purification. However, the development of effective catalysts possessing high activity for the complete oxidation of HCHO with very low concentrations into harmless CO_2 and water at ambient temperature is still the main challenge. Supported noble metals were demonstrated to be promising for the complete oxidation of HCHO at low temperatures and even at ambient temperature. For example, complete oxidation of HCHO was obtained over a Ru/CeO_2 catalyst at 473 K [4]. Pd–Mn/Al_2O_3 catalysts were recently reported to possess high activity for the complete oxidation of HCHO at about 363 K in air stream [5]. Pt supported on ceramics also gave 100% conversion of HCHO at about 423 K [6]. Recent studies on the adsorption and oxidation of HCHO over supported noble metal (Pt, Rh, Pd or Au) catalysts made significant progress on lowering the reaction temperature [7–10], and particularly the Pt/TiO_2 catalyst was found to be active enough to oxidize HCHO into CO_2 and H_2O even at ambient temperature [9,10].

It was also demonstrated that transition metal oxides, like MnO_x and CeO_2, could show catalytic activities as high as or slightly higher than those of the supported noble metals for

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oxidation of formaldehyde [11]. MnO_x–CeO_2 mixed oxides, as environmental-friendly catalysts, have been extensively studied for the wet oxidation of ammonia [12], phenol [13] and acrylic acid [14]. It was revealed that the chemical composition of the MnO_x–CeO_2 mixed oxides greatly influenced the catalyst activity, and the optimum composition often depended on the nature of the reactants. MnO_x–CeO_2 with a Mn/(Mn + Ce) molar ratio of 0.5 was found to be more active for the oxidation reactions of phenol [13] and polyethylene glycol [15], due to the synergetic effect through the interaction between the mixed oxides. Promoting effect of noble metals on the MnO_x–CeO_2 mixed oxides also has been investigated to enhance the catalytic performance. Imamura et al. [16] reported that the addition of Ru to MnO_x–CeO_2 resulted in a significant increase in the catalytic activity for the wet-oxidation of a model domestic wastewater. Pt promotion of MnO_x–CeO_2 enhanced the CO_2 selectivity and reduced the amount of carbon deposits in the deep oxidation of phenol, which were ascribed to great improvement in the redox properties of MnO_x–CeO_2 by Pt [17,18].

We recently reported that MnO_x–CeO_2 mixed oxides could exhibit high catalytic activity for the complete oxidation of HCHO at 373 K [19]. In this work, we extended to study the effects of the chemical composition of the MnO_x–CeO_2 mixed oxides and the promoting effect of Pt on the catalytic activity for HCHO oxidation. Structure analysis of the catalysts were performed with N_2 adsorption, X-ray powder diffraction (XRD) and H_2 temperature-programmed reduction (H_2-TPR), and subsequently correlated with their catalytic performances.

2. Experimental

2.1. Catalyst preparation

MnO_x–CeO_2 mixed oxides with Mn/(Mn + Ce) molar ratios of 0 to 1 were prepared by a modified coprecipitation method, as described elsewhere [19]. Briefly, 2 M KOH aqueous solution was slowly added to an aqueous solution containing $Mn(NO_3)_2\cdot 6H_2O$, $KMnO_4$ and $(NH_4)_2Ce(NO_3)_6$ at 323 K until the pH value of the mixture reached 10.5 under vigorous stirring. The molar ratio of $Mn(NO_3)_2\cdot 6H_2O$ to $KMnO_4$ was kept at 3:2. The precipitate was further aged at 323 K for 2 h in the mother liquid. After filtrating and washing with distilled water, the obtained solid was dried at 383 K for 12 h and calcined at 773 K for 6 h in air.

Two Pt/MnO_x–CeO_2 catalysts were then prepared by the conventional impregnation process. The MnO_x–CeO_2 powder with a Mn/(Mn + Ce) molar ratio of 0.5 was added to an aqueous solution of H_2PtCl_6 or $Pt(NH_3)_2(NO_2)_2$ containing 3 wt.% of platinum with respect to the MnO_x–CeO_2. The mixture was evaporated with a rotary evaporator at 323 K to remove water, and the obtained solid was then dried at 383 K for 12 h and finally calcined at 673 K for 4 h in air. These Pt/MnO_x–CeO_2 catalysts were designated as Pt–Cl (prepared from H_2PtCl_6) and Pd–N (prepared from $Pt(NH_3)_2(NO_2)_2$), respectively.

2.2. Catalyst characterization

BET surface areas of the samples were measured by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2000 instrument. Prior to the measurement, the samples were degassed at 573 K for 2 h.

Elemental analysis was performed by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on a Plasam-Spec-I spectrometer.

X-ray powder diffraction patterns were recorded with a D/Max-2500/PC diffractometer (Rigaku, Japan) operated at 40 kV and 250 mA, using nickel-filtered Cu Kα (λ = 0.15418 nm) radiation. The lattice parameters were calculated according to the Cohen procedure [20].

Hydrogen temperature-programmed reduction (H_2-TPR) measurements were carried out on a CHEMBET 3000 adsorption instrument (Quantachrome, USA) equipped with a TCD detector. 30–50 mg samples were loaded and pretreated with He at 573 K for 1 h to remove the adsorbed carbonates and hydrates. After cooling to room temperature and introducing the reduction agent of a 5% H_2/Ar mixture with a flow rate of 50 mL/min, the temperature was then programmed to rise at a ramp of 10 K/min. A calibration curve of the TCD response signal expressed by the integral area of the peak as a function of the amount of the hydrogen consumption was established by reducing known amounts of pure CuO to Cu. For the determination of the oxidation state of manganese in the samples, MnO was assumed to be the final state after the reduction at temperatures below 1173 K [21].

2.3. Activity measurement

The oxidation of HCHO was performed in a continuous flow fixed-bed reactor under atmospheric pressure. 200 mg catalyst (40–60 mesh) was sandwiched by quartz wool layers in a quartz tube reactor. Typically, the MnO_x–CeO_2 mixed oxides were used as-prepared, and the Pt/MnO_x–CeO_2 catalysts were pretreated with hydrogen at 473 K for 1 h. Gaseous HCHO was generated by flowing He coming from a mass-flow controller through paraformaldehyde (96%, ACROS ORGANICS) in an incubator. The temperature of the incubator and/or the flow rate of He gas were adjusted to obtain desired concentration of HCHO (30–580 ppm). The HCHO-containing stream was then mixed with the main gas stream of 20 vol.% O_2/He, which was introduced through another mass-flow controller. The gas hourly space velocity (GHSV) was 30,000 mL/g_{cat} h. Effluents from the reactor were analyzed by on-line HP 6890 gas chromatograph equipped with TCD and FID. To determine the exact concentration of produced carbon dioxide, a nickel catalyst converter was placed before the FID and used for converting CO_2 quantitatively into methane in the presence of hydrogen. In typical runs, the reaction data were obtained after HCHO oxidation was performed for 3 h in order to achieve the steady state. No other carbon-containing compounds except CO_2 in the products were detected for all the tested catalysts.