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Enhanced formaldehyde oxidation on Pt/MnO_2 catalysts modified with alkali metal salts

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ABSTRACT

Novel Pt/MnO_2 catalysts modified with alkali metal salts were prepared and exhibited excellent catalytic activity for formaldehyde oxidation. The effects of both cation and anion in the salts were investigated on the structure of catalysts and their catalytic activity. The Na^+ modification was demonstrated to be a facile and effective method to improve the catalysts performance for formaldehyde oxidation, but the anions remaining on the support might act as a mild poison by covering the surface active sites of manganese oxides. The enhancing effect of anions in the salts follows the order of $CO_3^{2-} > SO_4^{2-} > NO_3^-$. A 100% formaldehyde conversion can be obtained at 50 °C over the Na_2CO_3-modified catalyst. Further analyses indicate that strong metal-support interaction, well-dispersed Pt nanoparticles with small particle sizes and large surface area are important for high catalytic activity.

1. Introduction

Formaldehyde (HCHO) is regarded as a serious indoor air pollutant. Great efforts have been dedicated to control over the indoor concentration of HCHO due to its harmful effects on human health and atmospheric environment [1–4]. Among various methods for combating HCHO pollution, heterogeneous catalytic oxidation has proved to be one of the most promising methods, which yields CO_2 and H_2O as harmless final products.

Supported noble metals are typically used to investigate their catalytic performance for decomposing HCHO. Many remarkable researches have been reported on supported Pt [5,6], Pd [7], Au [8–10], and Ag [11,12], which possess high catalytic activity and stability. Among them, Pt catalysts, which have attracted considerable research interests, exhibit superior catalytic activity for HCHO decomposition at relatively low temperatures, even at ambient temperature in some cases. For instance, Huang and Leung [6] reported that complete decomposition of HCHO was reached at ambient temperature over reduced Pt/TiO_2 catalysts with 0.1% Pt loading. Complete oxidation of HCHO at low temperature could be achieved over Pt/Fe_2O_3 because of the well dispersed Pt nanoparticles and relatively strong interaction between Pt and iron oxide support [5]. Tang et al. [13,14] reported that $Ag/MnO_x–CeO_2$ and $Pt/MnO_x–CeO_2$ could completely oxidize HCHO at 100 °C and ambient temperature, respectively. These supports with high specific surface area can supply more active sites, prevent aggregation of nanoparticles and bring synergistic effects between Pt nanoparticles and support.

Manganese oxides (MnO_x) have been previously demonstrated to be the most effective metal oxides for HCHO degradation without releasing harmful byproducts [15]. As two important forms of MnO_x, cryptomelane and birnessite have been investigated in previous reports as catalysts for HCHO oxidation [16,17]. It was found that manganese oxides show excellent catalytic efficiency for HCHO decomposition at low temperature, which is highly desired for indoor air purification. Very recently, several studies have been carried out to improve the catalytic ability of birnessite and cryptomelane by loading noble metals, thereinto, Pt-modified manganese oxide catalysts exhibit high activity for HCHO oxidation at low temperature [18,19].

The synergistic effects between support and Pt nanoparticles could enhance catalytic performance, and the addition of alkali metal provides an even more efficient pathway to catalytic decomposition of HCHO [20–22]. Alkali metals were previously applied as promoter in heterogeneous catalysis to enhance catalytic activity and durability in many reactions, such as CO oxidation [23,24] and hydrogen production from ethanol [25]. For instance, Han

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et al. [23] investigated the effect of alkali modification on nanoporous gold catalysts toward CO oxidation and found that the roles of the alkaline were to provide OH^- anions to form $Au–OH^-$ sites, which can promote catalytic activity. Very recently, considerable efforts were made to improve the HCHO catalytic oxidation with alkali metals, and the results showed that modification with alkali metal (Na_2CO_3, NaOH) significantly enhanced the catalytic performance of HCHO oxidation. Pt-O$(OH)_x$-Na clusters were proposed as the active sites which alters the ambient-temperature HCHO oxidation pathway by promoting the reaction between surface OH and formate species at room temperature, and thus greatly enhancing the HCHO oxidation activity [20]. However, most of these researches have been focused on the support of TiO_2 [20,26].

Different positive effects of alkali metals are now well recognized. Up to now, however, few works have been attempted to investigate the effect of alkali metal salts with different anions on the catalytic activity in HCHO oxidation. Thus, herein Pt-loaded birnessite catalysts were modified with different alkali metal salts. The effects of Pt reduction method and alkali metal salt on the catalyst activity were investigated.

2. Experimental

2.1. Materials

$KMnO_4$, oleic acid, ethanol, $H_2PtCl_6{\cdot}6H_2O$, Na_2CO_3, Na_2SO_4 and $NaNO_3$ were purchased from Beijing Chemical Reagent Company. They were of analytical grade and used without further purification. Ultrapure water was used throughout the experiments and was obtained from a three-stage Millipore Mill-Q Plus 185 purification system (Academic).

2.2. Preparation of catalysts

Flaky birnessite-type manganese oxide was synthesized using a simple soft chemistry route described in detail in a previous publication [18]. The syntheses of Pt/MnO_2 catalysts are described below.

300 mg birnessite was uniformly dispersed in aqueous H_2PtCl_6 (20 mg/mL, 1%wt Pt loading). After impregnating for 1 h, 0.83 mL of aqueous KBH_4 (molar ratio KBH_4:Pt = 20:1) was quickly added into the suspension with vigorous stirring. After reduction for 1 h, the suspension was evaporated by a rotary evaporator at 60 °C. The obtained sample was dried at 60 °C for 12 h, and was denoted as Pt/MnO_2-R, where R represents preparation by reduction. In addition, keeping otherwise identical conditions, a catalyst was also prepared by adding 0.69 mL Na_2CO_3 (20 mg/mL, 2 wt% Na loading) immediately after the H_2PtCl_6 addition, and was referred to as Pt/MnO_2-R-C, where C represents sodium carbonate.

Meanwhile, a series of samples were synthesized as follows to investigate the influence of the alkali metal salt on the catalyst activity. Firstly, aqueous H_2PtCl_6 (20 mg/mL) was added in birnessite suspension under stirring. Subsequently, a given volume (0.69 mL, 0.93 mL and 1.11 mL) of aqueous Na_2CO_3, Na_2SO_4 or $NaNO_3$ (20 mg/mL, 2 wt% Na loading) was added dropwise, respectively. After stirring for 1 h, the solution was evaporated by a rotary evaporator at 60 °C. The samples were further dried at 110 °C for 12 h, followed by heating at 400 °C in air for 2 h. Finally, the samples were subjected to 5% H_2/Ar reduction at 300 °C for 30 min. The obtained products were designated as Pt/MnO_2-H-C, Pt/MnO_2-H-S and Pt/MnO_2-H-N, respectively for those synthesized with Na_2CO_3, Na_2SO_4 and $NaNO_3$, where H represents high-temperature heat treatment. The sample without alkali metal salt was also prepared and referred to as Pt/MnO_2-H.

2.3. Characterization

The X-ray diffraction (XRD) analyses of as-prepared products were carried out on a Bruker D8 Focus X-ray diffractometer using Cu Kα radiation. Thermo-gravimetric–differential thermal analysis (TG–DTA) was performed on a SDT Q600 thermal gravimetric analyzer. Transmission electron microscopic (TEM) images were obtained by a JEOL JEM-200CX transmission electron microscope operated at 200 kV. Energy-dispersive X-ray analysis (EDX) was used for chemical compositions analysis employing a 6853-H (Horiba Instruments) spectrometer and reported in atomic weight percentages. N_2 adsorption–desorption measurements were performed on a Quadrasorb SI automated surface area and pore size analyzer at 196 °C, using the volumetric method. Surface areas and pore size distributions were calculated according to the Braunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

2.4. Catalytic activity test

The catalytic activity of the samples for HCHO oxidation was assessed in a quartz tubular fixed-bed reactor with 100 mg catalyst (40–60 mesh). Gaseous HCHO was introduced with the aid of a controlled purified air flow passing through the HCHO solution in an incubator kept at 0 °C, leading to a feed gas with 200 ppm of

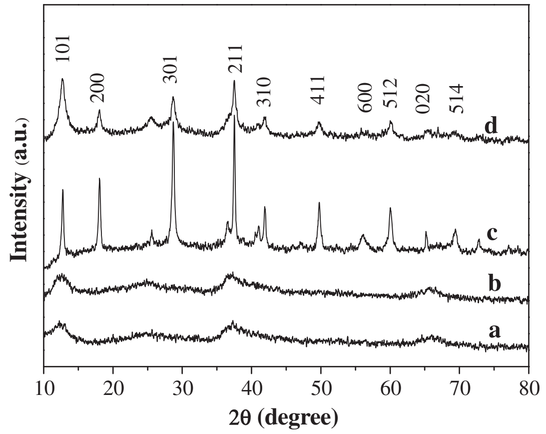

Fig. 1. XRD patterns of (a) as-prepared MnO_2, (b) Pt/MnO_2-R, (c) Pt/MnO_2-H, and (d) heat-treated MnO_2 (400 °C).

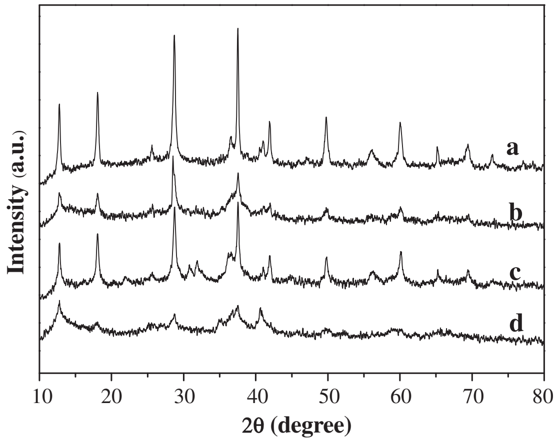

Fig. 2. XRD patterns of Pt/MnO_2 prepared with varied alkali metal salts: (a) Pt/MnO_2-H, (b) Pt/MnO_2-H-C, (c) Pt/MnO_2-H-S, and (d) Pt/MnO_2-H-N.