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Complete elimination of indoor formaldehyde over supported Pt catalysts with extremely low Pt content at ambient temperature

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ABSTRACT

A series of highly active supported Pt catalysts, developed by sodium borohydride reduction under mild preparation conditions, were used to eliminate indoor formaldehyde (HCHO) at ambient temperature. The influences of oxidation state, support and size of Pt particles, and the operating parameters were investigated. The reduced Pt nanoparticles with different supports are highly active for catalytic oxidation of HCHO. For example, nearly 100% HCHO conversion was obtained on the reduced Pt/TiO_2 catalysts (denoted as Pt–TiO_2) even with 0.1% Pt loading while it was less than 25% on the oxidized ones. Negatively charged metallic Pt nanoparticles, which probably facilitate the electron transfer and formation of active oxygen, provide the active sites for HCHO oxidation. The turnover frequencies (TOFs) of HCHO oxidation on Pt nanoparticles with different supports are not sensitive to the reducibility of support but somewhat affected by the Pt particle sizes. A maximum TOF of 2.87 s^{-1} was obtained on the 1% Pt–MgO with Pt particle size of about 3 nm. The 0.1% Pt–TiO_2 catalyst remained highly active and stable in humid air with a wide gas hourly space velocity range between 40,000 and 240,000 h^{-1} and initial HCHO concentration range between 5 and 30 ppm.

1. Introduction

Formaldehyde (HCHO), commonly emitted from construction and decorative materials for buildings, is one of the major indoor air pollutants [1–5]. Long-term exposure to indoor air containing HCHO, even a few ppm, may cause adverse effects on human health [6,7]. Great efforts have been made to reduce the indoor HCHO concentration to satisfy the stringent environmental regulations. Conventional physical adsorption and/or chemical reaction with impregnated potassium permanganate and organic amine were efficient for HCHO elimination, but these adsorbents were effective for a short period only due to their limited removal capacities [8–10]. Catalytic oxidation is recognized as the most promising HCHO removal technology [10–13], which, however, can only occur at high temperature [6,14,15] or illumination by light sources [16–18] over most of the reported catalysts. For example, 100% HCHO conversion was achieved at 453 K over a MnO_x–SnO_2 catalyst [15] and a maximum HCHO conversion (64.0%) was obtained over a N,S-codoped TiO_2 photocatalyst with visible light irradiation [18]. In these cases, an extra heating or illumination apparatus is needed, causing higher operating cost and more severe reaction conditions. Therefore, it is not suitable for the control of indoor air pollution [6]. Catalytic oxidation of HCHO at room temperature is highly desirable due to its environmental-friendly reaction conditions and energy-saving consideration [10,11,19]. For indoor air cleaning, low energy demand and low concentration of HCHO strongly require a catalyst to exhibit high activity for complete oxidation of HCHO. However, the development of effective catalysts for the complete oxidation of low-concentration HCHO at ambient temperature is still a challenging subject for scientists [8,10].

Recently, several studies have been carried out on removing HCHO at low temperature and even at ambient temperature using supported noble metal catalysts [2,10,11,14,20,21]. For example, 0.73% gold/iron-oxide catalysts (mass concentration, hereinafter inclusive) showed no activity in HCHO oxidation at room temperature; however, complete HCHO oxidation was obtained at 80 °C when the gold content was increased to 7.1% [14]. Álvarez-Galván et al. [22] reported that 100% HCHO conversion was achieved over a Pd/Al_2O_3 catalyst at 363 K. Particularly, Pt/TiO_2 is found most active for HCHO oxidation among the supported noble catalysts [11,20]. Zhang and He [20] reported that HCHO could be completely oxidized into CO_2 and H_2O over 1 wt% Pt/TiO_2 at room temperature. Peng and Wang [9] found that HCHO conversion was only 14.3% at 20 °C and increased to 97% at 120 °C on the 1% Pt/TiO_2 catalyst. Although supported Pt catalysts have been proved to be effective for HCHO oxidation at low temperature, even at room temperature in some cases, however, high loading of Pt is generally

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needed for effective oxidation of HCHO, which greatly limits its widespread application due to the expensive cost of Pt [6]. One alternative is to use cheap transition metal oxides, such as Co_3O_4, MnOx, and CeO_2, to substitute noble metal [6,7,23]. However, low efficiencies of these catalysts at room temperature limited their application [20]. Another alternative is to improve the catalytic activity and lower the Pt loading in Pt/TiO_2. In addition, the Pt catalysts for HCHO oxidation are generally pretreated in air at high temperature [8,10,11,20], which results in much energy consumption and the formation of PtOx. As known, Pt oxidation state is one of the most important factors controlling the catalytic activity [24]. The effect of metallic Pt on catalytic activity and the mechanism leading to high activity for HCHO oxidation at room temperature has not well demonstrated yet.

Herein, a series of highly efficient supported Pt catalysts were developed by sodium borohydride ($NaBH_4$) reduction under mild preparation conditions. Hydrogen is readily generated by $NaBH_4$ hydrolysis in H_2PtCl_6 solution, and Pt^{4+} can be easily reduced into metallic state by hydrogen at ambient temperature. The supported Pt catalysts were used to catalytically oxidize indoor HCHO at room temperature. The support and size of Pt particles and the operating parameters were investigated. The influence of Pt oxidation state and particle sizes, supports (i.e., TiO_2, Al_2O_3, CeO_2, ZrO_2, and MgO), and operating parameters (i.e., relative humidity, initial toluene concentration, and gas hourly space velocity (GHSV)) on catalytic activity was studied. Structural analysis of the catalysts were performed and subsequently correlated with their catalytic performances to investigate the mechanism leading to the high activity. The reduced catalysts, even with 0.1 wt% Pt loading, possess very high catalytic activity and excellent stability for HCHO oxidation at room temperature without any energy consumption. These catalysts have the advantage in low cost of preparation and use, which makes them possible to be widely applied in indoor HCHO purification.

2. Experimental

2.1. Catalyst preparation

Both oxidized and reduced Pt/TiO_2 catalysts were prepared using TiO_2 powder (P25, Degussa) as the support and H_2PtCl_6 as the Pt precursor compound. The oxidized Pt/TiO_2 catalysts (denoted as PtO–TiO_2) with 0.1% and 1% Pt loading were prepared via impregnation. Briefly, TiO_2 support was added into the H_2PtCl_6 solution under stirring. After impregnation for 1 h, the suspension was dried at 80 °C under stirring. The dried samples were heated at 120 °C for 4 h, followed by the calcinations at 400 °C in air for 4 h. The reduced Pt/TiO_2 catalysts (denoted as Pt–TiO_2) with 0.1% and 1% Pt loading were prepared by $NaBH_4$ reduction. Briefly, TiO_2 support was uniformly dispersed into the H_2PtCl_6 solution. After impregnation for 1 h, $NaBH_4$ solution was quickly added into the suspension under vigorous stirring. After reduction, the suspension was dried at 80 °C under stirring. Finally, the samples were dried at 120 °C in air for 4 h without further calcination at high temperature. Al_2O_3, CeO_2, ZrO_2, and MgO (all from Wan Jing Co. Ltd.) supported 1% reduced Pt catalysts were also prepared by $NaBH_4$ reduction with the same procedures as the 1% Pt–TiO_2, referring to Pt–Al_2O_3, Pt–CeO_2, Pt–ZrO_2, and Pt–MgO, respectively.

2.2. Catalyst characterization

Transmission electron microscopy (TEM) images were recorded on a Tecnai G2 20 microscope operated at 200 kV. X-ray powder diffraction (XRD) patterns were collected with a Bruker D8 Advance X-ray powder diffractometer operated at 40 kV and 100 mA, using Cu Kα (λ = 1.5418 Å) radiation. The intensity data were collected in a 2θ range from 20° to 90°. BET surface areas of the samples were measured by N_2 adsorption–desorption isotherms at 77 K using a Micromeritics ASAP 2020 instrument. Prior to the measurement, the samples were degassed at 523 K for 2 h. X-ray photoelectron spectroscopy (XPS) measurements of the catalysts were performed with a Physical Electronics 5600 multi-technique system using a monochromatic Al Kα source for the surface composition. The binding energy (BE) was determined by utilizing C1s line as a reference with energy of 285.0 eV. The Pt dispersion was determined by pulse CO chemisorption on a Micrometrics AutoChem II 2920 instrument at room temperature, using a thermal conductivity detector (TCD) to monitor CO consumption. A CO/Pt average stoichiometry of 1 has been assumed for the calculation of dispersion [25,26]. Prior to chemisorption, the catalyst was reduced in a stream of 10% H_2 diluted with helium at 200 °C for 60 min to remove its surface oxygen and then followed by cooling down to room temperature in a helium stream.

2.3. Measurement of catalytic activity

The catalytic oxidation of HCHO was performed in a quartz tubular (i.d. = 6 mm) fixed-bed reactor under atmospheric pressure at ambient temperature (25 ± 1 °C). Then, 0.5 g of the catalyst in 40–60 mesh was loaded in the reactor. An air mixture, containing 10 ppm HCHO and water vapor (50% relative humidity), was introduced as the reactants. Gaseous HCHO was generated by passing a stream of zero air through an HCHO solution in an incubator. The total flow rate was 1 L/min, corresponding to a GHSV of 80,000 h^{-1}. The HCHO and CO_2 in the airstream were analyzed by an HCHO monitor (Formaldemeter 400, PPM Technology) and a CO_2 monitor (HAL-HCO201, Chinaway Environment Instrument). Noted that it is difficult to make a direct comparison of the kinetic behavior of different Pt catalysts since they have different particle sizes and Pt loading and different numbers of Pt surface atoms. Apart from HCHO removal efficiency, the turnover frequency (TOF) (i.e., number of molecules reacted per Pt surface atom) is also used to evaluate the catalytic activities since it allows a better comparison of the rates for different Pt loadings, particle sizes, and supports.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. TEM

Representative TEM micrographs of the supported Pt catalysts are presented in Fig. 1, and their Pt particle sizes estimated from TEM are listed in Tables 1 and 2. It can be found that small and homogeneous Pt nanoparticles (Fig. 1b and d) are uniformly present on the Pt–TiO_2 catalysts, whereas no distinguishable Pt particles are observed over the PtO–TiO_2 catalyst (Fig. 1a and c), which is consistent with the observation in the previous study [11]. Different preparation methods lead to different size and morphology of Pt particles. Reduction treatment probably promotes the formation of Pt clusters. It also can be observed that density of Pt nanoparticles over the 1% Pt–TiO_2 catalyst is larger than that over the 0.1% Pt–TiO_2 catalyst, which is consistent with their Pt loading. However, the mean size of Pt nanoparticles over the 0.1% Pt–TiO_2 catalyst is only about 1.8 nm, which is greatly decreased compared with that of about 2.5 nm over the 1% Pt–TiO_2 catalyst. High Pt concentration leads to the aggregation and growth of Pt clusters during the preparation. In addition, the reduced Pt particles with different metal oxide supports also show varied size and morphology. The Pt particle sizes estimated from TEM images range from 2.4 nm to 5.2 nm