Applied Catalysis B: Environmental 163 (2015) 306–312

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Efficient catalytic removal of formaldehyde at room temperature using AlOOH nanoflakes with deposited Pt

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ARTICLE INFO

Article history:
Received 5 May 2014
Received in revised form 7 July 2014
Accepted 8 August 2014
Available online 17 August 2014

Keywords:
Aluminum oxyhydroxide
Pt/AlOOH
Adsorption
Formaldehyde removal
Catalytic decomposition

ABSTRACT

Mesoporous AlOOH with deposited Pt (Pt/AlOOH) catalyst was prepared by combining the microemulsion-assisted synthesis of AlOOH nanoflakes with $NaBH_4$-reduction of Pt precursor, and exhibited a remarkable catalytic activity as well as stability for elimination of formaldehyde (HCHO) vapor at room temperature. As compared to Pt deposited on calcined AlOOH (Pt/AlOOH-c), Pt on a commercial Al_2O_3 (Pt/c-Al_2O_3) and Pt on P25 (Pt/TiO_2), the Pt/AlOOH nanoflakes showed the highest catalytic activity toward decomposition of HCHO at room temperature. The excellent performance of Pt/AlOOH nanoflakes could be attributed to the abundance of surface hydroxyls, high dispersion of Pt nanoparticles, excellent adsorption performance of AlOOH, and its high specific surface area and large pore volume. The mechanism of HCHO decomposition was investigated with respect to the behavior of adsorbed intermediates on Pt/AlOOH surface at room temperature using in situ DRIFTS. The result suggests that surface formate is the main reaction intermediate during the HCHO oxidation and it could be directly oxidized to CO_2 in the presence of O_2. By taking advantage of high adsorption affinity of AlOOH nanoflakes and excellent catalytic activity of Pt nanoparticles toward HCHO it was possible to design a superior nanostructured catalyst for room temperature decomposition of HCHO. This strategy can be also used to fabricate novel nanostructured catalysts for advanced applications such as environmental remediation.

1. Introduction

Formaldehyde (HCHO) is considered as a major indoor air pollutant, which can cause serious health problems [1–3]. Considerable efforts have been made to eliminate HCHO from air in order to meet the strict environmental regulations [3–10]. Room-temperature HCHO oxidation over supported noble metals (like Pt, Pd and Au) is an effective and promising technology for reducing the HCHO concentration in atmosphere due to its simple operation, low energy demand and complete conversion of toxic HCHO into CO_2 and water [11–13]. Various metal oxides including TiO_2 [11,12], MnO_2 [14], Fe_2O_3 [15], Al_2O_3 [16,17], ZrO_2, MgO [18], In_2O_3 [19], CeO_2 and Co_3O_4 [20,21] and the composites like MnO_x–CeO_2 [22] and Co_3O_4–CeO_2 [13], as well as non-metal oxides like SiO_2 [23] have been investigated as solid supports for noble metal catalysts used for complete decomposition of formaldehyde at room (or ambient) temperature. The aforementioned supports can greatly promote the activity of the deposited noble metal catalysts due to their high dispersion and electronic structure alteration, redox properties of the supports and/or synergistic interaction with the noble metal catalyst and support. Currently, the development of efficient and feasible materials for HCHO removal from air is still an interesting and incompletely solved problem.

Recently, mesoporous nanostructures with designed surface functionality and unique morphology have attracted a widespread attention because of their potential applications in catalysis, adsorption, separations, controlled drug delivery and biosensing [24–32]. Among mesoporous materials, the nanostructured AlOOH, due to its low cost, environmental friendliness and easy processing has gained a lot of attention because of its high surface affinity and tunable morphological and structural features such as shape, specific surface area and pore/particle size. As a result, AlOOH materials with novel morphological and structural features have been extensively explored to enhance its performance in a wide range of potential applications [32–38]. For example, hierarchical boehmite was shown to be a very effective sorbent for removal of Congo red, phenol and Cr(VI) from model wastewater [39,40]. However, to the

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http://dx.doi.org/10.1016/j.apcatb.2014.08.017

best of our knowledge, AlOOH with high surface area and strong affinity has not yet been investigated as a support for Pt nanoparticles for complete oxidation of gaseous HCHO at room temperature.

It is generally accepted that a good support should influence the nature of the active component and subsequently, its catalytic activity by affecting the formation, distribution and dispersion of the active component on the support surface [41]. In our previous work [42], we showed that the microemulsion-assisted synthesis afforded AlOOH with abundance of hydroxyl groups, which was shown to be a very effective adsorbent for HCHO. Herein, we report the synthesis of AlOOH nanoflakes with deposited Pt, which exhibit respectively both high adsorption affinity (AlOOH nanoflakes) and high catalytic activity (highly dispersed Pt nanoparticles) toward adsorption and catalytic degradation of HCHO at room temperature. As compared to the reported Al_2O_3 support [16,17], the as-made AlOOH nanoflakes are expected to promote the performance of the aforementioned nanostructured catalyst toward degradation of HCHO due to the following aspects: (1) AlOOH with nanoflake-type morphology possesses a plenty of hydroxyl groups, unique porosity and high surface area that enhance HCHO adsorption; (2) high specific surface area of AlOOH assures high dispersion of noble metal, resulting in large concentration of catalytically active sites; and (3) enhanced adsorption of HCHO on AlOOH nanoflakes increases concentration of HCHO molecules in the proximity of Pt nanoparticles, facilitating catalytic decomposition of HCHO into CO_2 and H_2O.

2. Experimental

2.1. Preparation of AlOOH and Pt/AlOOH catalyst

AlOOH was synthesized as follows: a mixture containing 100 mL of cyclohexane and 20.46 g of polyethyleneglycol (PEG 400) was magnetically stirred and heated to 50 °C. After stirring for 10 min at 50 °C, 20 mL of $Al(NO_3)_3$ solution (0.32 M) and 3.50 g of NH_3 solution (27 wt%) were added stepwise to the above mixture, and then aged for 8 h to allow precipitation of aluminum oxyhydroxide. At the end of the synthesis, about 30 mL of isopropanol was added to the mixture to destabilize the microemulsion structure. The resulting mixture was separated by centrifugation and the powder was collected after washing with deionized water (four times) and ethanol (two times) and drying at ca. 65 °C overnight under vacuum and at 80 °C for ca. 30 min. For the purpose of comparison, the as-prepared AlOOH powder was calcined at 450 °C for 2 h at a heating rate of 2 °C min^{-1}, and the resulting powder was denoted as AlOOH-c.

AlOOH-supported Pt catalyst (Pt/AlOOH) was obtained by adding 0.4 g of the as-prepared AlOOH into an H_2PtCl_6 solution under magnetic stirring (the nominal weight of Pt was 0.8 wt%). After impregnation for 20 min, 5 mL of the mixed solution of $NaBH_4$ (0.1 mol/L) and NaOH (0.1 mol/L) was quickly added into the suspension under vigorous stirring for 30 min, and then the suspension was evaporated at 80 °C under stirring. Finally, the resulting powder was continuously dried overnight at 80 °C. For the purpose of comparison, the same nominal weight of Pt was introduced into commercial Al_2O_3 (denoted as Pt/c-Al_2O_3), AlOOH-c (denoted as Pt/AlOOH-c) and over P25 (denoted as Pt/TiO_2).

2.2. Characterization

X-ray diffraction (XRD) measurements were performed using a Philips X'Pert powder X-ray diffractometer with Cu Kα radiation ($\lambda = 0.15419$ nm). Transmission electron microscopy (TEM) images were obtained with a JEM-2100F electron microscope (JEOL, Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM800 XPS system with Al Kα source and a charge neutralizer, and all the binding energies were referenced to the C 1s peak at 284.8 eV of the surface adventitious carbon. Nitrogen adsorption–desorption isotherms were obtained on an ASAP 2020 (Micromeritics Instrument, USA). All samples were degassed in vacuum at 100 °C prior to adsorption measurements. The Brunauer–Emmett–Teller (BET) surface area (S_{BET}) was determined by a multipoint BET method using adsorption data in the relative pressure P/P_0 range of 0.05–0.2. The single-point pore volume (V_p) was estimated from the amount adsorbed at a relative pressure of 0.98. The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption–desorption isotherms by the improved KJS method [37,43]. Fourier transform infrared spectra (FTIR) were collected using a Shimadzu IRAffinity-1 FTIR spectrometer in the frequency range of 4000–400 cm^{-1}. In situ diffuse reflectance infrared Fourier transform spectra (DRIFTS) were recorded in Thermo Fisher 6700. The catalysts were pretreated in a dried air gas flow at 150 °C for 1 h in an in situ cell reactor, and then the reactant gas mixture (78 ppm HCHO + O_2) was introduced into the DRIFT cell at room temperature via separate mass flow meters at flow rates of 30 mL min^{-1}. All spectra were measured with a resolution of 4 cm^{-1}. A background spectrum was subtracted from each spectrum. Hydrogen temperature programmed reduction (H_2-TPR) and metal dispersion were performed on the BELCAT-B (Japan) instrument. In each experiment, 60 mg of the sample was loaded into the U-type quartz tube. Prior H_2-TPR experiment, the sample was pretreated in He (50 mL min^{-1}) at 200 °C for 1 h and then the temperature was ramped from room temperature to 550 °C at 10 °C min^{-1} with introducing the reducing gas (10% H_2/Ar) at a flow rate of 30 mL min^{-1}. Measurement of the metal dispersion by CO pulse chemisorption was carried out at room temperature by a pulse injection method. The samples were first reduced under pure hydrogen (50 mL min^{-1}) at 200 °C for 1 h and further outgassed under He (50 mL min^{-1}) for 0.5 h at the same temperature. Subsequently, CO pluses were injected into the carrier gas intermittently after the sample was cooled to room temperature, and the whole process was detected by a TCD.

2.3. Adsorption and catalytic activity tests

The room temperature adsorption and catalytic oxidation of HCHO were performed in an organic glass reactor with a volume of 6 L covered by a layer of aluminum foil on its inner wall. 0.1 g of the as-prepared sample was dispersed in 5 mL of water under stirring. Then, the suspension was coated on the bottom of glass petri dish having diameter of 14 cm and dried in an oven at 80 °C for 1 h. After placing the sample-coated dish in the bottom of reactor with a glass slide cover, a certain amount of condensed HCHO (38%) was injected into the reactor having a 5 W fan at the bottom of the reactor. After 1–2 h, the HCHO solution was volatilized completely and the concentration of HCHO was stabilized. The analysis of HCHO, CO_2, CO and water vapor was conducted online with a Photoacoustic IR Multigas Monitor (INNOVA air Tech Instruments Model 1412). The HCHO vapor was allowed to reach adsorption equilibrium within the reactor prior to the experiment. The relative humidity was 25% and the adsorption time or catalytic oxidation time was 51 min. The initial concentration of HCHO after adsorption equilibrium was controlled at ca. 127 for adsorption test and ca. 139 ppm for catalytic oxidation test. All the adsorption and catalytic oxidation tests were carried out at room temperature and the relative humidity was near 25% RH, as well as the test time was 51 min. During the catalytic oxidation reaction, carbon dioxide concentration increased and HCHO concentration decreased steadily with time. The HCHO concentration decrease and CO_2 concentration increase (ppm, ΔCO_2, which is the difference between CO_2 concentrations at t reaction time