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Enhanced room-temperature catalytic decomposition of formaldehyde on magnesium-aluminum hydrotalcite/boehmite supported platinum nanoparticles catalyst

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GRAPHICAL ABSTRACT
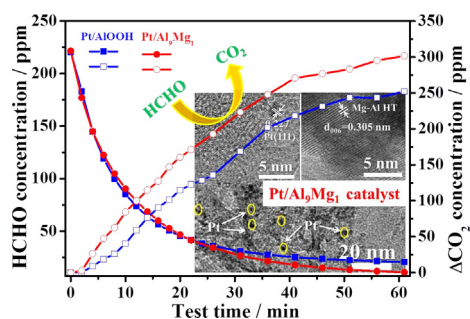
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ABSTRACT

Magnesium-aluminum hydrotalcite (Mg-Al HT)/boehmite (AlOOH) composite supported Pt catalysts were obtained via one-pot microemulsion synthesis of Mg-Al HT/AlOOH composite and $NaBH_4$-reduction of Pt precursor processes. The catalytic performances of the catalysts were evaluated for formaldehyde (HCHO) removal at room temperature. The performance tests showed that the catalyst obtained by immobilizing Pt nanoparticles (NPs) on Mg-Al HT/AlOOH support with Al/Mg molar ratio equivalent to 9:1 (Pt/Al_9Mg_1) displayed a superior catalytic activity and stability for HCHO removal. In order to find out the causes of its higher activity, X-ray diffraction, transmission electron microscopy, N_2 adsorption/desorption, X-ray photoelectron spectroscopy, temperature programmed desorption of CO_2 and reduction of H_2 were used to analyze the physicochemical properties of Pt/Al_9Mg_1 and Pt/AlOOH. The remarkable catalytic performance of Pt/Al_9Mg_1 is mainly attributed to the relatively larger amount of surface oxygen species, and more reactive oxygen species led by the interaction of Mg-Al HT and AlOOH/Pt, and relatively larger number of weak base sites caused by Mg-Al HT. The formate species are the main reaction intermediate over Pt/Al_9Mg_1 during HCHO oxidation at room temperature, which could be further oxidized into CO_2 and H_2O in the presence of O_2. This study might shed some light on further improving the catalytic performance of the catalyst for indoor air purification at room temperature.

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1. Introduction

Formaldehyde has been widely applied in the manufacturing of a variety of consumer products including furniture adhesive, room decoration, painting and pharmacy, etc. Long-time exposure to HCHO pollutant may cause some diseases to human beings such as skin irritation and nasal tumors [1–5]. As a notorious environmental pollutant, removal of HCHO has been extensively studied and continues to be of focus [6–18]. The complete decomposition of HCHO into CO_2 and H_2O at room (or ambient) temperature is considered as one of the most potential approaches due to the reusability of catalyst, energy conservation and environmental friendliness.

Supported noble metals (e.g. Pt, Pd and Au) are the most effective catalysts for HCHO oxidation at room temperature [19–26]. The used supports play an important role in the catalytic activity of the composites. For example, the support with a large surface area facilitates high dispersion of noble metal NPs, resulting in a large quantity of reactive sites. The close contact between the support and noble metal NPs may induce electronic perturbations at the interface of the composite, leading to an unexpected catalytic performance. So far, various materials including TiO_2 [27–29], SiO_2 [30], CeO_2 [31], Mg–Al layered double hydroxide [32], Al_2O_3 [33,34], iron oxide [35,36], Co_3O_4 [37,38] and MnO_2 [39], etc. have been investigated as the catalyst supports. However, choosing properly functional support is still of necessity for developing effective catalyst for HCHO removal at room temperature.

Magnesium-aluminum hydrotalcites with a unique layered structure have been studied as adsorbents, catalysts, catalyst precursor and catalyst promoters [32,40–42]. Hydrated hydrotalcites (HTs) have plenty of weak basic cites [43,44], and the weak basic sites might play a positive role in HCHO removal. In our previous investigation, AlOOH nanoflakes supported Pt catalyst (Pt/AlOOH) showed higher catalytic activity toward room-temperature catalytic oxidation of HCHO than commercial Al_2O_3 and P25 supported Pt at the same test conditions [45]. The excellent activity of the Pt/AlOOH catalyst was attributed to the abundance of surface hydroxyls, excellent adsorption performance of AlOOH, and unique textural structure. Recently, we found that cerium (CeO_2) with good oxygen storage ability could further enhance the catalytic activity of Pt/AlOOH toward HCHO decomposition at room temperature [46]. In spite of significant progresses in the development of the supports, functional composite supports are still of interest for fabricating high-performance catalysts for HCHO removal at room temperature. Herein, Mg-Al HT was firstly introduced into the AlOOH nanoflakes, aiming to achieve an enhanced surface chemical property of AlOOH support. It is expected that the introduction of HT into AlOOH may improve the catalytic performance of Pt/AlOOH due to the weak basic sites of HT, which would facilitate the catalytic oxidation of HCHO molecules at room temperature.

2. Experimental section

2.1. Sample synthesis

All the supports were obtained by one-pot synthesis in water-in-oil microemulsion. Briefly, a mixture containing 100 mL cyclohexane and 20.4 g polyethyleneglycol (PEG 400) was heated to 70 °C under magnetic stirring. Next, 20 mL of the mixture of Al$(NO_3)_3 \cdot 9H_2O$ (0.009 mol) and $Mg(NO_3)_2 \cdot 6H_2O$ (0.001 mol) followed by 3.50 g of NH_3 solution (27 wt%) were added to the above solution. After aged for 2 h, the mixed solution was separated by centrifugation and the resulting hydrogel was washed carefully using deionized water and ethanol. Finally, the hydrogel was dried

at 80 °C overnight and denoted as Al_9Mg_1 based on the molar ratio of Al/Mg used. The other support was synthesized via a similar process of the Al_9Mg_1 sample, but a different solution such as Al$(NO_3)_3 \cdot 9H_2O$ (0.007 mol) and $Mg(NO_3)_2 \cdot 6H_2O$ (0.003 mol) mixture or $Al(NO_3)_3 \cdot 9H_2O$ (0.005 mol) and $Mg(NO_3)_2 \cdot 6H_2O$ (0.005 mol) mixture or $Mg(NO_3)_2 \cdot 6H_2O$ (0.01 mol) solution or $Al(NO_3)_3 \cdot 9H_2O$ (0.01 mol) solution was used to obtain the following support of Al_7Mg_3, Al_5Mg_5, $Mg(OH)_2$ or AlOOH.

The Al_9Mg_1 supported Pt catalyst was prepared by adding 0.4 g of the as-prepared Al_9Mg_1 into 30 mL of deionized water under magnetic stirring. Then a specified amount of $H_2PtCl_6 \cdot 6H_2O$ solution was added to acquire a nominal weight of Pt equal to 0.8 wt %. After impregnation for 20 min, 5 mL of a mixed solution of $NaBH_4$ (0.1 mol/L) and NaOH (0.1 mol/L) was quickly added to the suspension. After vigorously stirred for 30 min, the suspension was collected by centrifugation, and washed using deionized water and ethanol two times, respectively. Finally the obtained sample was dried in an oven at ca. 80 °C and denoted as Pt/Al_9Mg_1. For the sake of comparison, the same calculated weight of Pt was loaded over Al_7Mg_3 (denoted as Pt/Al_7Mg_3), Al_5Mg_5 (Pt/Al_5Mg_5), AlOOH (Pt/AlOOH), $Mg(OH)_2$ ($Pt/Mg(OH)_2$), and over P25 (Pt/TiO_2).

2.2. Characterization

X-ray diffraction (XRD) patterns were determined on a Philips X'Pertpowder X-ray diffractometer (Rigaku, Japan) employing a monochromatized Cu Kα radiation (λ = 1.54056 Å) source. An inductively coupled plasma-mass spectrometer (ICP-MS, ICAPQC, Thermo) was used for determining the concentrations of metal elements. Temperature programmed desorption of CO_2 (CO_2-TPD) were conducted on a BELCAT-B (Japan) instrument. Typically, 0.05 g of the catalyst was pre-treated in a pure He flow (50 mL min^{-1}) at 120 °C for 1 h and then cooled to 50 °C. After being saturated with CO_2 at 50 °C for 0.5 h, the catalyst was flushed with pure helium flow (50 mL min^{-1}) for 1 h at 50 °C to remove the weakly physically-adsorbed CO_2. The desorption curves of CO_2-TPD were collected from 50 to 500 °C at 10 °C min^{-1}. Brunauer–Emmett–Teller (BET) specific surface areas (S_{BET}) were achieved from nitrogen (N_2) adsorption isotherms, which were obtained on a Micromeritics ASAP 2020 nitrogen adsorption apparatus (USA). The pore-size distribution (PSD) was analyzed using the adsorption branch of the N_2 sorption isotherm. The morphologies of the samples were characterized on a field-emission scanning electron microscopy (FESEM, S-4800, Hitachi, Japan) with energy dispersive X-ray spectrometer attached, and transmission electron microscope (TEM, JEOL JEM-2100F). The X-ray photoelectron spectra (XPS) were acquired from an ESCALAB250xi spectrometer (Thermon Scientific). Temperature-programmed reduction of H_2 (H_2-TPR) measurement was conducted on the BELCAT-B (Japan) instrument at room temperature. In situ diffuse reflectance infrared Fourier transform (in situ DRIFT) experiments were performed on Thermo Fisher Nicolet 6700 FTIR spectrometer. The spectrum was measured after the pretreated catalyst in a dried air flow at 150 °C for 1 h, was cooled to 298 K. All spectra were recorded at a resolution of 4 cm^{-1} for 100 scans.

2.3. HCHO removal tests

HCHO removal tests were carried out in an organic glass box with a layer of aluminum foil covering on its inner wall. The experimental setup is diagrammatically shown in Fig. 1. The tested sample (0.1000 g) was dispersed in a glass petri dish, and then put into the reactor and covered with a glass slide. Next, a specified amount of condensed HCHO solution (38%) was injected into the reactor. After HCHO solution was completely volatilized under the aid of a 5 W fan, the gaseous HCHO concentration in the reactor reached