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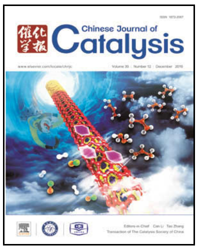

Article

Hierarchical Ni–Al hydrotalcite supported Pt catalyst for efficient catalytic oxidation of formaldehyde at room temperature

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ABSTRACT

Catalytic oxidation at room temperature is recognized as the most promising method for formaldehyde (HCHO) removal. Pt-based catalysts are the optimal catalyst for HCHO decomposition at room temperature. Herein, flower-like hierarchical Pt/NiAl-LDHs catalysts with different $[Ni^{2+}]/[Al^{3+}]$ molar ratios were synthesized via hydrothermal method followed by $NaBH_4$ reduction of Pt precursor at room temperature. The flower-like hierarchical Pt/NiAl-LDHs were composed of interlaced nanoplates and metallic Pt nanoparticles (NPs) approximately 3–4 nm in diameter were loaded on the surface of the Pt/NiAl-LDHs with high dispersion. The as-prepared Pt/NiAl21 nanocomposite was highly efficient in catalyzing oxidation of HCHO into CO_2 at room temperature. The high activity of the hierarchical Pt/NiAl21 nanocomposite was maintained after seven recycle tests, suggesting the high stability of the catalyst. Based on in situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) studies, a reaction mechanism was put forward about HCHO decomposition at room temperature. This work provides new insights into designing and fabricating high-performance catalysts for efficient indoor air purification.

1. Introduction

Formaldehyde (HCHO) is widely used in particle board, door panels and coatings for building, furnishing and interior decoration materials. Gaseous HCHO emitted from these industrial products leads to an inevitable air pollutant in indoor environment. HCHO can pose a terrible threat to human health including eyes and nose irritation, headache and respiratory diseases, and even cancer etc. [1–5].

Various methods including physical adsorption [6], chemical oxidation [7,8], photocatalytic degradation [9] and catalytic oxidation [10–13] have been studied to remove gaseous HCHO from indoor air. Among these methods, room-temperature catalytic oxidation of HCHO into CO_2 and water is appealing because of the avoidance of secondary pollution and no need for additional energy input (for heating or light illumination). Supported noble metals are the most effective catalysts for HCHO decomposition at room temperature. It is generally believed that the performances of the catalysts usually rely on the architectures, composition and surface property of the supports, which in turn would affect the particle size, dispersion and stability of the supported noble metal nanoparticles. Most

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of the reducible oxides such as TiO_2 [14–16], MnO_2 [17,18], CeO_2 [19,20], Fe_xO_y [21–23] and Co_3O_4 [24,25], are investigated as the support of the noble metals. It is considered that the redox property of the supports favors the formation of a strong interaction between the support and the metal induced by their close contact in nanoscale. This surface interaction resulted from the charge transfer between the noble metal and the support facilitates the generation of active oxygen species, which play an important role in the catalytic oxidation of HCHO at room temperature. Moreover, non-reducible metal oxides like SiO_2, Al_2O_3 [26] and AlOOH [27] were also found as wonderful supports of noble metal for HCHO decomposition into CO_2 and H_2O at room (or ambient) temperature. The abundance of active surface hydroxyls is responsible for the superior activity. In our previous investigation, ferrihydrite exhibited an excellent activity towards HCHO oxidation at room temperature, combining a reducible property and plenty of surface hydroxyls [23]. More recently, we reported that CeO_2 nanoparticles can enhance formaldehyde oxidation on AlOOH-supported Pt catalyst at room temperature [28], which could be attributed to the combination of the advantages of AlOOH nanoflakes and reducible ceria. However, the fabrication of efficient nanomaterials with the advantages of reducible supports and abundance of surface hydroxyls for gaseous HCHO removal at room temperature is still interesting and desirable.

By virtue of the versatility in morphology, composition and architecture [29], layered double hydroxides (LDHs) have been widely used as adsorbents, catalysts, electrochemical materials and catalyst promoters. As a typical two-dimensional brucite $Mg(OH)_2$-like layered inorganic materials, NiAl-LDHs consist of mixed nickel and aluminum hydroxide layers with charge-balancing anions located in the interlayer space. Due to the relatively high redox activity of Ni and the confinement effect of the hierarchical pores, hierarchical NiAl-LDHs based composites have received much attention in many fields including electrode material [30] and heterogeneous catalysts [31]. For example, Du et al. [31] found that flower-like NiAl-LDHs supported Au catalyst showed an excellent catalytic activity toward alcohol oxidation due to the cooperation of Ni and Au, and the confinement effect of the hierarchical pores. Taking consideration of the characteristics of the aforementioned supports for room-temperature oxidation of HCHO, hierarchical NiAl-LDHs is expected to be a perfect alternative to support noble metal because it simultaneously possesses the merits of reducible metal species (Ni), abundance of hydroxyls resulted from the hydroxide, and hierarchical nanostructure. The hierarchical pore structure not only favors high dispersion of accessible noble metal nanoparticles, but also promotes diffusion and transport of reactants and products, which are thought as important factors in HCHO catalytic oxidation. To the best of our knowledge, hierarchical NiAl-LDHs nanoflowers as supports of Pt catalysts have not yet been reported for HCHO decomposition at room temperature. Herein, NiAl-LDHs with hierarchical pore structure supported Pt was prepared and investigated for room-temperature catalytic oxidation of HCHO. The composition influence of the flower-like catalysts on the catalytic performance was studied. In addition, the synergistic effects between Ni, Pt and surface hydroxyls were also clarified by identifying the oxidation states and the redox process. Based on the catalyst characterization and DRIFTS analysis, the catalytic reaction mechanism of HCHO over NiAl-LDHs was proposed.

2. Experimental

2.1. Sample synthesis

Synthesis of support. The hierarchical NIAl-LDHs with different $[Ni^{2+}]/[Al^{3+}]$ molar ratios were synthesized by a urea decomposition method with the assistance of NH_4F as a morphology control agent [31]. In brief, $Ni(NO_3)_2·6H_2O$ (0.001 mol) or (0.002 mol) or (0.003 mol), $Al(NO_3)_3·9H_2O$ (0.001 mol), urea (0.02 mol) and NH_4F (0.008 mol) were dissolved in deionized water (50 mL) with vigorous stirring to give a transparent solution. The resulting solution was aged in a 100-mL sealed Teflon-lined with autoclave at 110 °C for 36 h. The precipitate was collected by centrifugation, washed with deionized water and ethanol three times and dried in an oven at ca. 80 °C overnight. The as-synthesized NiAl-LDHs prepared from 0.001, 0.002 or 0.003 mol of $Ni(NO_3)_2·6H_2O$ was denoted as NiAl11, NiAl21 and NiAl31, respectively. For the purpose of comparison, the preparation of sole Ni or Al-containing support was performed similarly, but only $Ni(NO_3)_2·6H_2O$ (0.004 mol) or $Al(NO_3)_3·9H_2O$ (0.004 mol) was used instead of both of $Ni(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$, and the obtained samples were abbreviated as Ni and Al, respectively.

Synthesis of Pt catalyst. 0.4 g of the as-prepared sample (NiAl11, NiAl21, NiAl31, Ni or Al) was dispersed into 30 mL of deionized water. Then a certain amount of an aqueous solution of $H_2PtCl_6·6H_2O$ was added into the above suspension under magnetic stirring (with a nominal Pt loading of 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 rapidly added to the suspension under vigorous stirring for 30 min. Finally, the suspension was collected by centrifugation, washed with deionized water and ethanol two times, and dried an oven at ca. 80 °C. The resulting samples were designated as Pt/NiAl11, Pt/NiAl21, Pt/NiAl31, Pt/Ni and Pt/Al, respectively. In addition, the Pt/NiAl21 treated at 150 °C for 4 h was denoted as Pt/NiAl21-c.

2.2. Characterization of the catalyst

The X-ray diffraction (XRD) patterns of the as-prepared catalysts were obtained by a Philips X'Pert powder X-ray diffractometer (Rigaku, Japan) using Cu K_α radiation (λ = 0.15419 nm) at a scan rate of 0.05 ° s^{-1}. The morphology and microstructure of the samples were observed on a JEOL JSM-7500 Field emission scanning electron microscopy (FESEM) with a 15 kV accelerating voltage and a JEOL JEM-2100F transmission electron microscope (TEM) with a 200 kV accelerating voltage. Energy-dispersive X-ray spectroscopy (EDS) and elemental mapping analysis of the Pt/NiAl21 sample was carried out on EDS in-