Contents lists available at ScienceDirect

Journal of Molecular Catalysis A: Chemical

Hydrotalcite-supported gold catalysts for a selective aerobic oxidation of benzyl alcohol driven by visible light

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ARTICLE INFO

ABSTRACT

Hydrotalcite-supported gold nanoparticles are studied as photocatalysts for the aerobic oxidation of benzyl alcohol and its derivatives without additional base under irradiation by visible light. The effects of the solvent, the hydrotalcite constitution and the gold content on the catalytic reaction are studied. The reactions utilizing benzotrifluoride as the solvent yield the best results. When varying the gold content and support, 2 wt% Au/HT-3 exhibits good catalytic activity. Furthermore, the rate of conversion under visible light is far superior to that in the dark. The catalytic activity can be tuned by manipulating the intensity or wavelength of the light. A reaction mechanism is proposed to rationalize these results: the primary reason for the lower activity observed on recycled catalysts is that the basic sites of hydrotalcite are decreased during the reaction in light.

1. Introduction

Using catalysts can enable access to mild and environmentally friendly conditions. Currently, researchers are focused on metal nanoparticles, particularly the catalytic activity of supported gold nanoparticles. Supported gold nanoparticles have been found to catalyze many reactions, such as C—C couplings [1], the reduction of nitrobenzene [2], the oxidation of organic contaminants [3], phenol hydrogenation to form cyclohexanone [4], the isomerization of epoxides to form allylic alcohols [5] and the esterification of alcohols [6]. Gold nanoparticles have a localized surface plasmon resonance effect (LSPR) [7] under visible light irradiation. The LSPR effect is the collective oscillation of conduction electrons of gold nanoparticles, which resonate with the electromagnetic field of the incident light, so forming high-energy electrons on the gold surface. These high-energy electrons can offer energy to the reaction system, so gold nanoparticles can absorb light energy, and make it into their internal energy [8], which can make the reactant across the reaction barrier. Consequently, sunlight can be utilized.

Hydrotalcite (HT : $[M^{2+}_{1-x}M^{3+}_x(OH)]^{x+}[A^{n-}]_{x/n}\cdot yH_2O$) is an interesting inorganic layered building block material that contains metallic hydroxide layers with interlayered anions to balance

the positive charges [9]. The metallic cations are in brucite-like sheets, while the anions in the interlayer are flexible and diverse [10]. Acidic and basic sites exist on hydrotalcite, and these sites can play crucial roles during reactions [11]. Moreover, the structure of the most common hydrotalcite is $Mg_6Al_2(OH)_{16}CO_3\cdot nH_2O$.

The dehydrogenation of benzyl alcohol is a representative photocatalytic reaction [12], and the various factors that affect the activity of the catalysts have been studied. Different carriers, such as TiO_2 [13], Al_2O_3 [14], zeolite [15], MOFs [16], MCFs [17] and different metals (such as Au [18], Pd [19], Ag [20], Au–Pd [21], Au–Pt [22], Au–Ag [23], Cu [24]) have been examined. Different catalytic conditions [25] and mechanisms [26] have also been assessed. However, despite the great effort has been expended, numerous aspects remain unclear.

In this study, gold nanoparticles were loaded onto various supports and used as photocatalysts for the selective aerobic oxidation of benzyl alcohol under mild conditions. Adding base is not necessary in this reaction. Usually, base is required in reactions over supported gold catalysts because the bases activate the hydroxyl group on the alcohols [27]. In our study, benzyl alcohol was converted into benzaldehyde with a high selectivity after 24 h under irradiation by visible light. Meanwhile, almost no reaction occurred in the dark under the same conditions. To confirm that the reaction is light-promoted, the light intensity and wavelength were varied. A possible reaction mechanism based on the experimental results was proposed.

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2. Experimental

2.1. Preparation of HT

The hydrotalcite supports (HT-x, x: Mg/Al mole rations, and x = 1, 2, 3 and 4) were prepared using a co-precipitation method. (1) A certain ratio of $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ was dissolved in redistilled water (1 L) under stirring. (2) NaOH and $Na_2CO_3 \cdot 10H_2O$ were dissolved in redistilled water (4 L). (3) The solution formed in (1) was added drop-wise into the solution formed in (2) with vigorous stirring over approximately 30 min. (4) The mixed suspension was centrifuged and a white solid was obtained. Subsequently the solid was washed six times with Na_2CO_3 (0.1 mol L^{-1}). (5) The wet cake was dried at 80 °C for 20 h in an oven [28].

2.2. Preparation of Au/HT-x catalyst

The 2 wt% Au/HT-3 catalysts were prepared using a sequential deposition/reduction approach. HT-3 (2.5 g) was dispersed in redistilled water (50 mL) and sonicated for 10 min. The pH of the solution was adjusted to 10 using NaOH (0.5 mol L^{-1}) with stirring. Afterward, the $HAuCl_4$ solution was added dropwise under sonication. Subsequently, lysine (20 mL) was added to the mixture. After stirring for 30 min, a fresh $NaBH_4$ solution was added. This slurry was filtered before being washed with deionized water and ethanol, respectively. The resulting mixture was dried at 60 °C for 12 h. The other catalysts, including 2 wt% Au/HT-x (x = 1, 2 and 4), y wt% Au/HT-3 (y: 0.5, 1, 2 and 3, respectively), 2 wt% Au/γ-Al_2O_3 and 2 wt% Au/Mg(OH)$_2$ were prepared using the same method [28].

2.3. Recycling use of catalyst

Method 1: Firstly, catalyst and reactant were separated via centrifugation. Afterward, the catalyst was washed with deionized water and ethanol. Finally, the catalyst was dried at 60 °C for 12 h. The recycled catalyst was reused in the next run under the same conditions [29].

Method 2: Firstly, catalyst and reactant were separated via centrifugation. Afterward, the catalyst was washed with Na_2CO_3 (0.1 mol L^{-1}) and ethanol. Finally, the catalyst was dried at 60 °C for 12 h. The recycled catalyst was reused in the next run under the same conditions.

2.4. Catalyst characterization

The X-ray diffraction patterns (XRD) of the samples were recorded on a RIGAKU D/MAX-2500 X-ray diffractometer using CuKα radiation (λ = 1.5405 Å) at 40 kV and 100 mA. The diffraction data were collected from 5° to 80°. The gold contents of the samples were quantitated using atomic absorption spectroscopy (AAS) on a GBC AVANTA YX-05 instrument. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos XSAM800 using AlKα radiation. The binding energy was calibrated using the C1s photoelectron peak at 284.8 eV as a reference. The particle sizes and morphologies of the samples were determined using transmission electron micrographs (TEM) taken on a FEI Tecnai G2 F20 S-Twin apparatus with a 200 kV acceleration voltage. UV–visible diffuse reflectance spectra (UV–vis DRS) were detected on U-3900 made by Hitachi. Temperature-programmed desorption of CO_2 (CO_2-TPD) was performed on a Micromeritics AutoChem 2920 II instrument. The product was quantitatively analyzed with a GC-2014C gas chromatograph (GC). The identity of the product was confirmed via gas chromatography–mass spectrometry (GC–MS) on a Finnigan LCQ Advantage MAX instrument.

Table 1
Crystal spacing of HT-x.

Entry	Catalysts	d value (nm)
1	HT-1	0.772
2	HT-2	0.783
3	HT-3	0.787
4	HT-4	0.796

2.5. Catalytic test: aerobic oxidation of benzyl alcohol

The reaction was carried out in a batch-type reaction with stirring. Typically, the catalyst powder (50 mg), benzyl alcohol (2 mmol) and solvent (10 mL) were placed in a 50 mL round-bottom flask; a LED lamp (200 W, 400–800 nm) was used as a light source. The system was filled with pure oxygen and sealed. A small amount of reactant was separated at regular intervals and quantitatively analyzed by GC. Afterward, the products were identified with a GC–MS spectrometer. For comparison, the reaction was performed simultaneously in the dark under the same conditions [30].

2.6. Hydrogen peroxide test

This kind of examination method is put forward by H. Bader et al. in 1988 [31]. The particular way is shown as follows: the sample (9 mL) after 24 h was placed in a 50 mL round-bottom flask. The buffer solution (pH = 6, 1 mL) was added to achieve pH 6 in the final solution with stirring. Then DPD reagent (N,N-diethyl-1,4-phenylenediammonium sulphate, 17 µL) and POD reagent (peroxidase product from horseradish, 17 µL) were added in the solution [31].

3. Results and discussion

3.1. Catalysts characterization

The structures of various supports and catalysts are confirmed by XRD analysis. Fig. 1A shows the XRD patterns of the supports, including γ-Al_2O_3, MgO and hydrotalcite with various Mg/Al ratios (HT-x, x stands for Mg/Al mole rations, x = 1, 2, 3 and 4), and revealing a series of characteristic patterns of inorganic structures. Fig. 1A (c–f) shows a series of characteristic patterns for the hydrotalcite structure. The diffraction peaks could be indexed to a pure hexagonal phase of hydrotalcites, especially the characteristic reflections (0 0 3) that exhibit a high intensity and a narrow line width [28]. The lattice parameters of HT-3 are a = 3.058 ± 0.004 Å, c = 23.969 ± 0.062 Å, α = 90°, β = 90°, γ = 120°, and V = 190.47 Å^3. Fig. 1B is the local amplification of Fig. 1A from 5° to 30°, and blue shifts of these peaks appear when increasing the Mg/Al ratio. The inter-planar crystal spacing is measured using the (0 0 3) diffraction peak with the Bragg formula ($2d \sin \theta = n\lambda$). The d value increases with the molar proportions of magnesium (Table 1). This phenomenon shows that a lattice expansion makes the XRD peaks move toward a smaller angle. Fig. 1C shows the characteristic peaks of supported samples (Au/γ-Al_2O_3, Au/Mg(OH)$_2$ and Au/HT-x) with the same gold content (2 wt%). An XRD pattern almost identical to HT-x was obtained for Au/HT-x, indicating that the crystal structure of the nano-crystalline support is conserved. Moreover, the characteristic diffraction peaks of the Au nanoparticles can be observed within the patterns. The MgO turned into brucite after the catalyst was prepared; possibly similar to a "memory effect" of hydrotalcite. (Calcined hydrotalcites can be reconstructed back to a layered structure when it is in contact with water and appropriate anions. This property is called retro-topotactical transformation. And it is also known as the "memory effect" [32].). Fig. 1D shows the XRD patterns of Au/HT-3 with different gold contents. The Au diffraction