Research paper

Gold nanoparticle-decorated halloysite nanotubes – Selective catalysts for benzyl alcohol oxidation

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ABSTRACT

Preparation of gold nanoparticle-decorated halloysite nanotubes (Au-Hal) by a deposition method and evaluation of their catalytic activity in an oxidation of benzyl alcohol are reported. An electrostatic attraction between positively charged polyethylenimine (PEI)-capped gold nanoparticles and the negatively charged external surfaces of halloysite nanotubes (Hal nanotubes) was the key factor in fabrication of Au-Hal nanotubes. Au-Hal catalysts showed good conversions and surprisingly high benzaldehyde selectivities (above 90%) in the benzyl alcohol oxidation. Influence of the amount of PEI used as a capping agent, the gold content and calcination of Au-Hal catalysts on the conversion and selectivity was investigated. A notable increase in the benzaldehyde selectivity at higher PEI contents and a significant drop in the benzaldehyde selectivity on calcination clearly indicate the central role of PEI in the selective formation of benzaldehyde. The high benzaldehyde selectivity of uncalcined catalysts are probably due to PEI donor molecules coordinating to certain surface sites on Au nanoparticles and thus blocking the catalytic sites required for further oxidation of benzaldehyde to benzoic acid. The high combined selectivity of benzoic acid and benzyl benzoate obtained with the calcined catalysts indicates that naked gold nanoparticles have the catalytic sites available for the benzoic acid formation.

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1. Introduction

In the last few years, there has been a growing interest in developing new functional materials based on Hal nanotubes for the applications such as catalysis, polymerization, drug delivery, and fabrication of polymer nanocomposites (Levis and Deasy, 2002; Tierrablanca et al., 2010; Cai et al., 2011; Liu et al., 2013; Gómez et al., 2014; Yuan et al., 2015; Zou et al., 2015). These naturally available alumino-silicate nanotubes have been suggested to be a low cost replacement for multiwalled carbon nanotubes (Liu et al., 2014). The high surface area, porosity and opposite charges on the external and internal surfaces of Hal nanotube make them unique and suitable for various applications (Liu et al., 2014; Zou et al., 2015). Hal nanotubes are generally 0.2–2 μm in length, having an inner diameter size of 10–40 nm and an outer diameter size of 40–70 nm (Liu et al., 2014). On the basis of the water content, Hal nanotubes are classified into two types, Hal-(10 Å) [$Al_2Si_2O_5(OH)_4 \cdot 2H_2O$] and Hal-(7 Å) [$Al_2Si_2O_5(OH)_4$] (Liu et al., 2014).

The catalytic efficiency of gold nanoparticles has attracted attention of the research community after the pioneering work of Haruta et al. (1987). Catalytic activities of free and supported gold nanoparticles

(AuNP) have been extensively utilized in several chemical reactions, including CO oxidation, oxidation of benzyl alcohol, reduction of nitro compounds, Suzuki-Miyaura coupling reaction, hydrogenation reactions of 1,3–butadiene and crotonaldehyde, selective oxidation of cyclohexane, and epoxidation of propylene (Haruta et al., 1987; Hayashi et al., 1998; Okumura et al., 2002; Zhang et al., 2012; Rautiainen et al., 2014; Shah and Kaur, 2014). Gold nanoparticle-assisted oxidation of alcohols has a great industrial importance as the products of these reactions are important precursors in the synthesis of industrially important chemicals such as pharmaceuticals, cosmetics and perfumes (Zhang et al., 2012). Gold nanoparticles have been found to be very effective catalysts in alcohol oxidation in terms of the yield and selectivity (Zope et al., 2010; Rautiainen et al., 2014). Oxidation using molecular oxygen or air instead of stoichiometric oxidants makes this oxidation process environmentally and economically friendly (Dijksman et al., 2001).

There are several reports of gold nanoparticles deposited on various oxide supports such as Al_2O_3, SiO_2 and TiO_2 for catalytic applications (Hayashi et al., 1998; Okumura et al., 2002; Rautiainen et al., 2014). The main approach, which has been used for fabrication of Au-Hal, is based on functionalization of the Hal nanotubes with amino groups (Yuan et al., 2008; Gómez et al., 2014). Interaction between the nitrogen lone pairs of the amino groups and gold atoms enables anchoring of

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gold nanoparticles on functionalized Hal nanotubes (Gómez et al., 2014).

A new method for preparation of Hal nanotubes supported gold nanoparticles is described. In deposition of gold nanoparticles, an electrostatic interaction between positively charged gold nanoparticles and the negatively charged external surfaces of Hal nanotubes is utilized. In order to control the size and surface functionality as well as stability of gold nanoparticles, polyethylenimine (PEI) was employed in the gold nanoparticle synthesis as a capping agent and a stabilizer. As a cationic polyelectrolyte, PEI capping agent provides gold nanoparticles with a positive charge (Sun and Luo, 2005; Mohammed et al., 2013). PEI possesses a large number of amino groups, which at low pH are protonated. Thus no pre-functionalization of Hal nanotubes is required in this deposition method as the interactions between oppositely charged gold nanoparticles and Hal nanotubes enable a direct deposition of gold nanoparticles on nanotubes (Scheme 1). This deposition approach excludes influence of the support and enables to study the catalytic activity of mere gold nanoparticles.

Au-Hal nanotubes are examined as a catalyst in an oxidation reaction of benzyl alcohol. Previous studies on oxidation reactions catalyzed by Au-Hal nanotubes are rare (Cai et al., 2011; Fu et al., 2014). Influence of the gold content and the PEI capping agent on the conversion and selectivity of the benzyl alcohol oxidation will be elucidated with Au-Hal nanotubes having different gold and PEI contents and by calcination of Au-Hal nanotubes.

2. Experimental

2.1. Materials

$HAuCl_4 \cdot 3H_2O$ (Alfa Aesar, ≥99.99%), HCl (VWR Chemicals, 37%), NaOH (Merck), sodium borohydride ($NaBH_4$, Sigma Aldrich, ≥99%), benzyl alcohol (Sigma Aldrich, ≥99%), toluene (Sigma Aldrich, 99.8%), branched polyethylenimine (PEI, Sigma Aldrich, Mw = 25,000) and halloysite nanoclay ($Al_2Si_2O_5(OH)_4 \cdot 2H_2O$, CAS NUMBER: 1332-58-7, Sigma Aldrich) were used without further purifications. Deionized water was used in all experiments.

2.2. Characterization methods

Powder X-ray diffraction (PXRD) analyses of the Au-Hal samples were performed with a Bruker AXS D8 Advance instrument using Cu Kα radiation (λ = 1.5406 Å). For the analysis, the finely powdered samples were mounted on a silver mirror. The step size was 0.06° and the time per step was 10s. The data collected in the scanning range of 2θ = 5–85°.

The FTIR spectra of the catalyst samples were obtained using a Bruker Vertex 70 FTIR. A powdered sample was analyzed using a single reflection diamond ATR sampling module. The scanning range was between 4000 and 400 cm^{-1}. A Perkin Elmer Lambda 900 UV/Vis/NIR spectrometer was used to measure localized surface plasmon resonances of gold nanoparticles in aqueous solutions. The scanning transmission electron microscopy (STEM) analysis of Au-Hal and AuNP were performed using a Hitachi S-4800 FE-SEM scanning electron microscope at a voltage of 30 kV and a current of 25 mA. The samples for a STEM analysis were mounted on Lacey carbon films coated Cu grids.

An atomic absorption spectroscopy (AAS) using a Varian AAS 220 spectrometer with flame atomization was used for determination of the gold content of the catalyst samples. The samples were dissolved using 2 mL of aqua regia, and then diluted to 100 mL with deionized water. The calibration curve for the analysis was obtained with six standards with concentrations between 1 and 25 mg/L. The total measurement time of the analysis was 5.0 s with a pre-read delay of 3.0 s. The gold contents of Au-Hal nanotubes are given in Table 2.

2.3. Synthesis of positively charged gold nanoparticles

Branched polyethylenimine (PEI) was used as a capping agent and also to provide a positive charge to the gold nanoparticles (AuNP). Gold nanoparticle solutions used for preparation of Au-Hal catalysts were synthesized by a slightly modified version of a previously reported procedure (Erola et al., 2015). In a general procedure, 25 mM aqueous $HAuCl_4 \cdot 3H_2O$ was diluted to get a final concentration of 1.5 mM. To this gold salt solution, different volumes of 0.6 mM aqueous solution of PEI were added (Table 1). The obtained solutions were stirred for 2 min. Then 36 mL of 10 mM freshly prepared ice cold solution of $NaBH_4$ was added quickly to the above reaction mixture, followed by vigorous stirring for 30 min. The synthesis reactions were carried out at two different temperatures: ambient and 1 °C. The total reaction volume was either 80 mL or 300 mL.

2.4. Preparation of Au-Hal nanotubes

The Hal nanotubes having different gold contents were prepared by a deposition method. Hal nanotubes (1.0 g) were mixed with different volumes of freshly prepared gold nanoparticle solutions (Solutions 1–6 in Table 1) for 15 min (Table S1 in Supplementary material). The mixture was then centrifuged at a speed of 3500 rpm for 2 min. Au-Hal nanotubes were isolated by decanting the solution and the Au-Hal
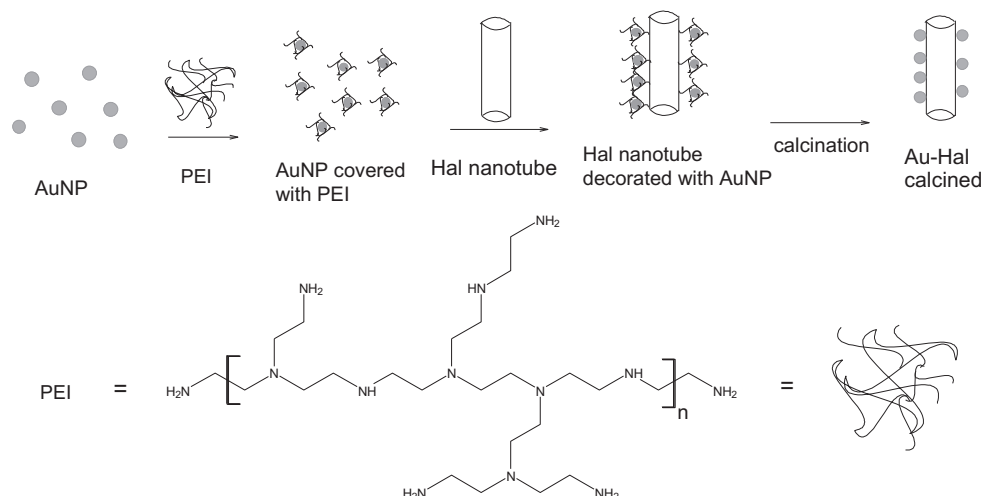
Scheme 1. Schematic representation of the preparation of Au-Hal catalysts.