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Gold nanoparticles supported on metal oxides as catalysts for the direct oxidative esterification of alcohols under mild conditions

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ABSTRACT

Gold nanoparticles supported on metal oxides were used to catalyze the direct oxidative esterification of alcohols; esters were obtained using molecular oxygen as an oxidant under ambient temperature and pressure. Higher activities for the reaction between the benzyl alcohol and methanol were obtained over Au/CeO_2 and Au/ZrO_2 than Au/TiO_2 (anatase), Au/HT (hydrotalcite) and Au/Al_2O_3. These catalysts were characterized using transmission electron microscopy (TEM), X-ray diffraction (XRD), atomic absorption spectroscopy (AAS) and X-ray photoelectron spectroscopy (XPS). The distribution of gold nanoparticles was uniform; no change of chemical states occurred for supports and gold nanoparticles after the catalysts were reused 10 times. The oxidative esterification of various alcohols over these catalysts could also occur under optimized reaction conditions. The substituted benzyl alcohols and cinnamyl alcohols were more active than heterocyclic alcohols and aliphatic alcohols because their α-H could be eliminated more easily during the induction of adsorbed dioxygen. Self-oxidative esterification was available for benzyl alcohol in inert solvents with low polarity indexes. A reaction mechanism was proposed for the synthesis of esters from alcohols with molecular oxygen.

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1. Introduction

Esterification is one of the most important reactions in fundamental organic synthesis. The broad application of esters in fragrances [1], pharmaceuticals [2] and adhesives [3], as well as the concept of green chemistry, require the improvement of ester synthesis methods. In traditional methods [4], carboxylic acids or carboxylic derivatives were first obtained using the corresponding alcohols before being mixed with alcohols to prepare esters under reflux. Those processes are usually operated at higher temperatures, inevitably generating by-products [5]. To simplify the operation and improve efficiency, the catalytic one-pot oxidative esterification of alcohols and aldehydes was proposed [6,7] using I_2 [8,9], $KHSO_5$ [10], MnO_2 [11,12] or H_2O_2 (33%) [13] as an oxidant. Later, the direct oxidative esterification of alcohols was achieved under O_2. Su et al. [14] reported that alcohols or aldehydes could form homologous methyl esters with methanol at 90 °C, 5 atm O_2 on Au/β-Ga_2O_3. The conversions and selectivities were high. Hao et al. [15] reported that benzyl alcohols and methanol could form methyl benzoate with Au/SBA-16 and K_2CO_3 at 25 °C under 6 atm of O_2. PI–CB/Au–Pd [16], Au–Ag

[17] and $[PdCl_2(CH_3CN_2)]$ [18] were applied as catalysts in many studies. These efficient protocols for aerobic oxidative esterification required higher temperatures or pressures; these conditions should be avoided for sustainable development in chemistry. Thus, the preparation of esters via direct oxidative esterification of alcohols using O_2 at ambient temperature and pressure is attractive.

In recent years, gold nanoparticles have been widely applied during the selective oxidation of alcohols [19–22], the reduction of nitroaromatic compounds [23] and Suzuki–Miyaura cross-coupling reactions [24]. Considering the interaction between the substrates and supports [25–27] as well as the oxygen molecular adsorption on 2–5 nm gold nanoparticle [17,28], we decided to use gold nanoparticles supported on metal oxides as catalysts.

In this investigation, we prepared gold nanoparticles supported on metal oxides (CeO_2, ZrO_2, TiO_2, HT and Al_2O_3) and tested their oxidative esterification activities of benzyl alcohol [29–31], using O_2 as an oxidant at ambient temperature and pressure. We found that Au/CeO_2 and Au/ZrO_2 showed excellent catalytic efficiencies with good recyclabilities; they were suitable for the catalytic oxidative esterification of various alcohols and the self-oxidative esterification of benzyl alcohol. More importantly, based on previous research achievements and the present experimental studies, a reaction mechanism was proposed.

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2. Experimental

2.1. Materials

Methanol, ethanol, hydrochloric acid, acetone, petroleum ether and DMSO were obtained from Fengchuan Chemical Reagent Technologies Co., Ltd., Tianjin, China, while CeO_2, ZrO_2, TiO_2 (anatase), $NaBH_4$, L-lysine and benzyl alcohol were purchased from Sigma–Aldrich. The hydrotalcite (Its shortening name is HT) was prepared by Jing Yu. Most alcohols, $HAuCl_4·3H_2O$, Cs_2CO_3, 1,4-dioxane, benzotrifluoride and mesitylene were purchased from J&K Scientific Ltd.

2.2. Preparation of catalysts with 3 wt% gold [32]

The gold nanoparticles were supported on a metal oxide powder (CeO_2, ZrO_2, TiO_2, HT and Al_2O_3). A quantity of metal oxide (2.5 g) was weighed and dispersed in deionized water (50 mL). To ensure a uniform dispersion, the suspension was stirred for 10 min and ultrasonically dispersed for 10 min. Then, $HAuCl_4$ (100 mL, 3.8×10^{-3} mol·L^{-1}), L-lysine (20 mL, 0.53 mol·L^{-1}) and $NaBH_4$ (10 mL, 0.35 mol·L^{-1}) were added sequentially to the above-mentioned suspension with a slow dripping speed and stirring. Afterward, dilute hydrochloric acid was added to adjust the pH value to approximately 9.5. The mixed solution was stirred for 1 h and left standing for 24 h to obtain a precipitate that could be used as a catalyst after being separated, washed and dried.

2.3. Characterization

Transmission electron microscopy (TEM) was performed on a FEI Tecnai F20 TEM at 200 kV. X-ray diffraction (XRD) patterns were recorded with an Empyrean diffractometer using Cu Kα radiation at 40 kV and 40 mA (λ = 1.5406 Å). The gold content of the supports was determined using a GBC AVANTA XY-05 atomic absorption spectroscopy (AAS) from the Inner Mongolia Minerals Experiment Research Institute. X-ray photoelectron spectroscopy (XPS) data were obtained on a Kratos XSAM800 with Al Kα radiation at the Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. The conversions and selectivities of the alcohol reactions were calculated according to the results determined by Gas Chromatograph -2014C (GC-2014C). The speciation of the products was measured with a Trace DSQII gas chromatograph–mass spectrometer (GC–MS) at Inner Mongolia University.

2.4. Activity test

Known amounts of catalyst, base and alcohol (RCH_2OH, 2 mmol) were mixed with methanol in a round bottomed flask. The reaction device was sealed after having been filled with O_2 at ambient pressure and then kept at a specified temperature with a magnetic stirrer. During the reaction, the O_2 was supplemented; a small amount of the mixture was extracted and filtered to remove the catalysts. The filtrate was analyzed using the GC-2014C.

3. Results and discussion

3.1. TEM

To reveal the size, shape and distribution of gold nanoparticles over catalysts, these samples were characterized by TEM. As shown in Fig. 1, the following features of the catalysts were identified. (1) The gold particles were spherical and uniformly distributed on the CeO_2 and ZrO_2 (Fig. 1a and c). (2) Most gold particles were within 3–6 nm for Au/CeO_2 and 4–7 nm for Au/ZrO_2. (3) However, for the recycled catalysts, the number of gold particles was slightly reduced on the support surfaces (Fig. 1b and d). (4) Moreover, part of the gold particle sizes became slightly larger as a result of aggregation due to reuse. (5) The electron-diffraction pattern (Fig. 1e) showed that the gold existed in mono-crystalline form and that its lattice spacing was close to 0.238 nm, corresponding to the Au(1 1 1) crystal plane.

3.2. XRD

The X-ray diffraction patterns of the supports and the catalysts are shown in Fig. 2. Clearly, the structures of the supports remained nearly unchanged after gold loading and reuse, revealing that they were stable enough for practical applications. No gold diffraction peaks were detected due to the smaller particle sizes and lower gold contents [33–35]. The gold contents of the supports were assessed by AAS: they were 2.8% for Au/CeO_2, 2.4% for recycled Au/CeO_2, 2.9% for Au/ZrO_2 and 2.1% for recycled Au/ZrO_2. Some of the gold was lost from the catalysts after they were reused 10 times, as observed by TEM and AAS.

3.3. XPS

The surface composition and chemical states of the catalysts were investigated by XPS. The full-range XPS spectra (Fig. 3a) clearly showed characteristic signals of O, Ce or Zr for the supports, as well as Au for the gold nanoparticles. The O signals could be attributed to CeO_2 or ZrO_2, as well as O_2 and H_2O adsorbed on the catalyst surfaces. For Au/CeO_2, the signals of Ce 3d (Fig. 3b) were fitted to two sets of triplets ($3d_{3/2}$ and $3d_{5/2}$): one set of binding energies (BEs) was 900.9, 907.1 and 916.5 eV, while the other was 882.5, 888.3 and 898.1 eV. The difference between the main signals was 18.4 eV (900.9−882.5 = 18.4 eV), similar to the standard values for CeO_2 (18.3 eV). The other signals, marked "S" in Fig. 3b, correspond to the satellite lines of CeO_2 $3d_{3/2}$ and $3d_{5/2}$. The two signals from Au/ZrO_2 (Fig. 3c) were 184.3 and 181.9 eV, respectively, corresponding to $3d_{3/2}$ and $3d_{5/2}$ of Zr^{4+}, respectively. The Au $4f_{5/2}$ and $4f_{7/2}$ BEs of Au/CeO_2 were 87.4 eV and 83.7 eV, respectively, equaling the values of metallic gold [24,32] (Fig. 3d). Therefore, the supported gold nanoparticles existed in the metallic state. As shown in Fig. 3e, the Au 4f BEs of Au/CeO_2 and the recycled Au/CeO_2 (87.4 and 83.7 eV) were similar to that of Au/ZrO_2 and recycled Au/ZrO_2 (87.2 and 83.5 eV). Although the signals of the recycled samples were significantly decreased and jagged due to their lower gold contents, the gold nanoparticles remained consistently in the metallic state. Therefore, CeO_2, ZrO_2 and Au state are stable because their XPS spectra remained unchanged after 10 reuses (not shown here).

3.4. Activity test

3.4.1. Activity test of benzyl alcohol and methanol

To assess the activity of the catalyst, a primary study on the oxidative esterification of benzyl alcohol (2 mmol) and methanol (10 mL) under the initial conditions (Au/CeO_2 (50 mg), Cs_2CO_3 (20 mol%, 0.2606 g), at 30 °C, and filled with O_2) was undertaken. The products were detected by GC; 98.3% conversion of benzyl alcohol and 99.7% selectivity of methyl benzoate were obtained after 3 h. Encouraged by this excellent result, we optimized the reaction conditions: 5 mL of methanol as a solvent, 10 mol% of Cs_2CO_3 as a base [36], 25 mg of catalyst and filled with O_2 under ambient temperature and pressure.

Benzyl alcohol and methanol were chosen as the model substrates, and the reactions were carried out under various conditions (Table 1). When the reaction was carried out without any