



Magnesia-supported gold nanoparticles as efficient catalysts for oxidative esterification of aldehydes or alcohols with methanol to methyl esters



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ARTICLE INFO

Article history:

Received 9 October 2013
Received in revised form
23 November 2013
Accepted 2 December 2013
Available online 27 December 2013

Keywords:

Oxidative esterification
Gold nanoparticles
Magnesia
Bifunctional catalyst
Methacrolein
Methyl methacrylate

ABSTRACT

Magnesia-supported gold nanoparticles were found to be highly efficient catalysts for the oxidative esterification of methacrolein (MAL) with methanol in the presence of molecular oxygen into methyl methacrylate (MMA) under liquid base-free conditions. MAL conversion of 98% and MMA selectivity of 99% were obtained over the Au/MgO catalyst at 343 K after a 2 h reaction. Besides the Au nanoparticles, the support also played pivotal roles in the oxidative esterification of MAL. The support with higher density of basic sites, particularly stronger basic sites, showed better performances for the formation of MMA. The enhancement of the intermediate formation by the basic sites is proposed to be the key reason for the superior activity of the Au/MgO catalyst. Our studies on the size effect of Au nanoparticles reveal that smaller Au nanoparticles favor the transformation of MAL, and the turnover frequency increases with decreasing mean size of Au nanoparticles. This suggests that the Au-catalyzed oxidative esterification of MAL is a structure-sensitive reaction. We have demonstrated that the Au/MgO catalyst is also applicable to the oxidative esterification of different aldehydes and alcohols.

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1. Introduction

Methyl methacrylate (MMA) is an important chemical, which is widely used for producing acrylic plastics (polymethyl methacrylate) or polymer dispersions for paints and coatings [1,2]. Currently, MMA is mainly produced by the acetone cyan hydrine (ACH) method [1,2]. However, this process suffers from the problems of using highly toxic hydrogen cyanide as the raw material and handling the resulting ammonium sulfide waste [2]. Therefore, many efforts have been devoted to developing environmentally benign alternatives for the production of MMA. The oxidative esterification of methacrolein (MAL) with methanol in the presence of O₂ is one the most attractive routes for the production of MMA (Scheme 1).

Supported Pd catalysts have been reported to be efficient for the direct oxidative esterification of MAL and other aldehydes or alcohols with methanol to the corresponding esters [2–6]. However, the selectivity of MMA is typically low over supported Pd catalysts. The modification of Pd catalysts by Pb forming Pd₃Pb phase could

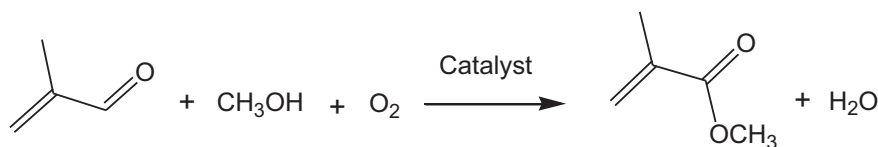
improve the selectivity of MMA [2], but Pb is quite toxic. Furthermore, the use of liquid base additives is required for the Pd-based catalysts.

On the other hand, Au catalysts have attracted considerable interest because of their unique catalytic behaviors, especially unique selectivity in many reactions [7–11]. Generally, the catalytic behavior of supported Au catalysts depends on the size and chemical state of Au particles, the property of the support, and the Au-support interaction. Au-based catalysts have been successfully used for the direct oxidative esterification of primary alcohols with methanol to methyl esters [12–24]. A wide range of materials such as Al₂O₃ [12], TiO₂ [13–15], CeO₂ [16–18], Ga₂O₃ [19], SiO₂ [20–22], polymers [23], and hydrotalcite [24] have been exploited as supports of Au catalysts for these reactions. However, in most cases, a liquid base additive, e.g., alkali carbonate (K₂CO₃, Na₂CO₃), alkali hydroxide (NaOH, KOH), or NaOCH₃ is required to achieve high yields of the target ester [16,18,19,24]. This makes the process less green and less cost-effective.

Recently, we have aimed at developing efficient Au catalysts capable of working for the oxidative esterification of MAL with methanol to MMA in the absence of any liquid bases. Here, we report our finding that Au nanoparticles loaded on a solid base, i.e., MgO, are highly efficient catalysts for liquid base-free oxidative esterification reactions. The effects of the support and the Au

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Scheme 1. Oxidative esterification of methacrolein with methanol to methyl methacrylate.

particle size will be discussed in detail. The substrate scope of the Au/MgO catalyst will also be investigated.

2. Experimental

2.1. Catalyst preparation

The supported Au catalysts were prepared by a deposition–precipitation (DP) method using urea as a homogeneous precipitant. In brief, urea was first added into an aqueous solution of HAuCl₄ (typically 0.48 mmol L⁻¹) with a molar ratio of urea/Au of 100:1. Then, the support was added into the mixed aqueous solution, and the suspension was vigorously stirred at 353 K. After aging for a certain time (typically 4 h), the solid product was recovered by centrifugation followed by thorough washing with deionized water to remove the remaining chloride anion. The resulting powdery solid was dried in air at 353 K for 1 h, and finally reduced in H₂ at 523 K for 2 h. The concentration of HAuCl₄ and the aging time were regulated to control the size of Au nanoparticles as reported previously [25]. The target Au loading in each catalyst used in this work was 0.5 wt%.

2.2. Catalyst characterization

Transmission electronic microscopy measurements were carried out on a JEM-2100 electron microscope operated at an acceleration voltage of 200 kV. The mean size of Au nanoparticles in the sample was estimated from the TEM micrographs by counting around 150–200 particles. By assuming a spherical model of Au nanoparticles, the Au dispersion (*D*) could be estimated by using the following relationship, $D = 1.17/d(\text{nm}) \times 100\%$, where *d* is particle diameter [26]. Inductively coupled plasma mass spectrometry (ICP-MS) measurements were performed with an Agilent ICP-MS 4500 instrument to measure the content of Au in each sample. Specific surface areas of the catalysts were measured by N₂ adsorption with Micromeritics Tristar II 3020.

CO₂ adsorption measurements were performed on a Micromeritics ASAP 2020 instrument. Typically, the sample loaded in a quartz tube was first pretreated with high-purity He at 423 K for 2 h. After the sample was cooled down to 323 K, the reactor was evacuated for 1 h. Then, CO₂ adsorption was performed by dosing certain amount of CO₂. After adsorption for 30 min, the gas phase and the weakly adsorbed CO₂ were evacuated. Then, CO₂ adsorption amount was evaluated by the difference between the CO₂ amounts injected and evacuated.

The strength of basicity for different supports was estimated by Hammett titration. The methyl red, bromothymol blue, phenolphthalein, 2,4-dinitroaniline, and 4-nitroaniline were used as the Hammett indicators with the pK_a values of +4.8, +7.2, +9.3, +15.0, and +18.4, respectively. The indicators were dissolved in petroleum ether of reagent grade and its concentration was ~0.1 wt%. After drying in vacuum, 100 mg of grinded sample was rapidly transferred into a tube and 1 mL of petroleum ether was injected to cover the sample. Subsequently, several drops of indicator solution were added followed by vigorous shaking. The strength of the basicity of supports was determined by the color change.

2.3. Catalytic reaction

The oxidative esterification of MAL and other aldehydes or alcohols to methyl esters was performed in a batch-type Teflon-lined stainless-steel autoclave. Typically, MAL purchased from Alfa Aesar (12 mmol) and the catalyst (typically, 0.50 g) were added into the reactor pre-charged with methanol (20 mL). After the introduction of O₂ with a certain pressure (typically 0.2 MPa), the mixture was heated up to a reaction temperature (typically 343 K) in an oil bath, and then the catalytic reaction was started by vigorously stirring. After a fixed time (typically 2 h, recorded as reaction time), the reaction was stopped by cooling down the reactor to room temperature in cold water. The products were analyzed by a gas chromatograph equipped with a FID detector and a capillary column (DB-FFAP, 60 m × 0.32 mm × 0.25 μm) using ethanol as an external standard for quantification.

3. Results and discussion

3.1. Catalytic behaviors of Au nanoparticles loaded on different supports

Table 1 shows the catalytic performances of Au catalysts loaded on different supports for the direct oxidative esterification of MAL with methanol in the presence of O₂ to MMA. Au catalysts loaded on some metal oxides without basicity such as SiO₂, TiO₂, and SBA-15 showed poorer activity for the conversion of MAL. The selectivities of MMA over these catalysts were also quite lower. Many side reactions occurred over these catalysts, and the main by-products included isobutyric acid, isobutyl aldehyde, dimers of the methacrolein, and CO₂. The employment of Al₂O₃, ZnO, ZrO₂, and hydroxyapatite as the supports of Au catalysts provided moderate MMA selectivities (68–83%) although the conversions of MAL over these catalysts were not high. Among all of the catalysts examined in the present work, the Au/MgO and Au/hydroxalcalite (HT) exhibited the best performance for the conversion of MAL to MMA; the yields of MMA were 97% and 90% over the Au/MgO and Au/HT,

Table 1
Catalytic performances of Au catalysts loaded on different supports for the oxidative esterification of MAL with CH₃OH in the presence of O₂.^a

Catalyst	MAL conv. (%)	Selectivity ^b (%)			
		MMA	MIB	MAA	Others
Au/SiO ₂	16	16	0.5	1.1	82
Au/SBA-15	13	8.8	0.3	0.8	90
Au/Al ₂ O ₃	42	80	1.6	3.0	16
Au/TiO ₂	25	39	1.5	0.8	59
Au/ZrO ₂	33	67	0.2	0.2	33
Au/ZnO	28	78	2.7	0.1	19
Au/CeO ₂	58	99	0.3	0.3	0.4
Au/MgO	98	99	0.4	0.1	0.4
Au/HT	99	91	0.4	0.1	8.4
Au/HAP	31	83	0.6	0.2	16

^a Reaction conditions: catalyst (Au loading, ~0.45 wt%), 0.50 g; CH₃OH/MAL = 40:1 (molar ratio); CH₃OH, 20 mL; P(O₂) = 0.2 MPa; T = 343 K; t = 2 h.

^b MMA, methyl methacrylate; MIB, methyl isobutyrate; MAA, methacrylic acid; others include isobutyric acid, isobutyl aldehyde, dimers of the methacrolein, CO₂, and some unknown products.

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