Accepted Manuscript

Accepted Date:

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| PII: | \$0020-1693(14)00720-8 |
|----------------|---|
| DOI: | http://dx.doi.org/10.1016/j.ica.2014.11.024 |
| Reference: | ICA 16308 |
| To appear in: | Inorganica Chimica Acta |
| Received Date: | 10 August 2014 |
| Revised Date: | 20 November 2014 |

28 November 2014



Please cite this article as: H. Wei, J. Li, J. Yu, J. Zheng, H. Su, X. Wang, Gold Nanoparticles Supported on Metal Oxides as Catalysts for the Direct Oxidative Esterification of Alcohols under Mild Conditions, *Inorganica Chimica Acta* (2014), doi: http://dx.doi.org/10.1016/j.ica.2014.11.024

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Gold Nanoparticles Supported on Metal Oxides as Catalysts for the Direct Oxidative Esterification of Alcohols under Mild Conditions

Huili Wei, Jingyi Li^{*}, Jing Yu, Jianwei Zheng, Haiquan Su, Xiaojing Wang

College of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot, Inner Mongolia, 010021, P. R. China

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/CeO₂ and Au/ZrO₂ than Au/TiO₂ (anatase), Au/HT (hydrotalcite) and Au/Al₂O₃. 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

^{*} Corresponding author. Fax: +86-471-4992981, Telephone: +86-13848129221, E-mail: lijingyicn@163.com.

inert solvents with low polarity indexes. A reaction mechanism was proposed for the synthesis of esters from alcohols with molecular oxygen.

KEYWORDS: gold nanomaterial, catalysis, ester synthesis, dioxygen, polarity index

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 I₂ [8, 9], KHSO₅ [10], MnO₂ [11, 12] or H₂O₂ (33%) [13] as an oxidant. Later, the direct oxidative esterification of alcohols was achieved under O₂. Fangzheng Su et al. [14] reported that alcohols or aldehydes could form homologous methyl esters with methanol at 90°C, 5 atm O₂ on Au/ β -Ga₂O₃. The conversions and selectivities were high. Yajuan 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 O₂. PI-CB/Au-Pd [16], Au-Ag [17] and [PdCl₂(CH₃CN₂)] [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 O2 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 O₂ as an oxidant at ambient temperature and pressure. We found that Au/CeO₂ and Au/ZrO₂ 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.

2. Experimental Section

2.1. Materials. Methanol, ethanol, hydrochloric acid, acetone, petroleum ether and DMSO were obtained from Fengchuan Chemical Reagent Technologies Co., Ltd., Tianjin, China, while CeO₂, ZrO₂, TiO₂ (anatase), NaBH₄, L-Lysine and benzyl alcohol were purchased from Sigma-Aldrich. The hydrotalcite (Its shortening name is HT) was prepared by Jing Yu. Most alcohols, HAuCl₄·3H₂O, Cs₂CO₃, 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 (CeO₂, ZrO₂, TiO₂, HT and Al₂O₃). 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, HAuCl₄ (100 mL, 3.8×10^{-3} mol·L⁻¹), L-Lysine (20 mL, 0.53 mol·L⁻¹) and NaBH₄ (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 hour and left standing for 24 hours 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 CuK α 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 AlK α 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 (RCH₂OH, 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 Figure 1, the following features of the catalysts were identified. (1) The gold particles were spherical and uniformly distributed on the CeO₂ and ZrO₂ (Figure 1a and 1c). (2) Most gold particles were within 3-6 nm for Au/CeO₂ and 4-7 nm for Au/ZrO₂. (3) However, for the recycled catalysts, the number of gold particles was slightly reduced on the

support surfaces (Figure 1b and 1d). (4) Moreover, part of the gold particle sizes became slightly larger as a result of aggregation due to reuse. (5) The electron-diffraction pattern (Figure 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(111) crystal plane.

(Figure 1 here)

3.2. XRD

The X-ray diffraction patterns of the supports and the catalysts are shown in Figure 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/CeO₂, 2.4% for recycled Au/CeO₂, 2.9% for Au/ZrO₂ and 2.1% for recycled Au/ZrO₂. Some of the gold was lost from the catalysts after they were reused 10 times, as observed by TEM and AAS.

(Figure 2 here)

3.3. XPS

The surface composition and chemical states of the catalysts were investigated by XPS. The full-range XPS spectra (Figure 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 CeO₂ or ZrO₂, as well as O₂ and H₂O adsorbed on the catalyst surfaces. For Au/CeO₂, the signals of Ce 3d (Figure 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 CeO₂ (18.3 eV). The other signals, marked "S" in Figure 3b, correspond to the satellite lines of CeO₂ $3d_{3/2}$ and $3d_{5/2}$. The two signals from Au/ZrO₂ (Figure 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/CeO₂ were 87.4 eV and 83.7 eV, respectively, equaling the values of metallic gold [24, 32] (Figure 3d). Therefore, the supported gold nanoparticles existed in the metallic state. As shown in Figure 3e, the Au 4f BEs of Au/CeO₂ and the recycled Au/CeO₂ (87.4 and 83.7 eV) were similar to that of Au/ZrO₂ and recycled Au/ZrO₂ (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, CeO₂, ZrO₂ and Au state are stable because their XPS spectra remained unchanged after 10 reuses (not shown here).

(Figure 3 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/CeO₂ (50 mg), Cs₂CO₃ (20 mol%, 0.2606 g), at 30°C, and filled with O₂) 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 hours. Encouraged by this excellent result, we optimized the reaction conditions: 5 mL of methanol as a solvent, 10 mol% of Cs₂CO₃ as a base [36], 25 mg of catalyst and filled with O₂ 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 catalyst, gold, base or dioxygen, almost no methyl benzoate formed (Table 1, entries 1, 2, 9 and 10). Therefore, these components were essential for the oxidative esterification reaction. The reaction on micron-size gold particles gave a lower conversion of benzyl alcohols and a moderate selectivity for methyl

benzoate (Table 1, entry 3). Additionally, when comparing a set of catalysts, ideal catalytic activities were exhibited on Au/CeO₂ and Au/ZrO₂. Slightly lower catalytic activities were obtained on Au/TiO₂ and Au/HT. However, even lower catalytic activities were detected on Au/Al₂O₃ (Table 1, entries 4-8). The gold nanoparticle sizes ranged from 3-6 nm, 4-7 nm, 5-7 nm, 10-13 nm and 5-7 nm for Au/CeO₂, Au/ZrO₂, Au/TiO₂, Au/HT and Au/Al₂O₃, respectively (Figure 1 and Figure S1). Therefore, the catalytic performance was determined not only by the size of the gold nanoparticles but also by the interaction of substrate and the support [17, 28]. Generally, the smaller the size of gold nanoparticles is, the higher the reactivity of the catalyst is. Au/Al₂O₃ exhibited poor catalytic activity, because Al₂O₃ is easily damaged under alkaline conditions as an amphoteric oxide. The production of methyl benzoate declined in air due to the deficiency of dioxygen compared to that in pure oxygen (Table 1, entry 11).

(Table 1 here)

3.4.2. The recyclability of catalysts

Based on the excellent activities over Au/CeO₂ and Au/ZrO₂, further experiments were performed to test their recyclabilities. The test results are displayed in Figure 4. The conversion of benzyl alcohol and the selectivity of methyl benzoate reached 100% on Au/CeO₂ after 4 cycles and on Au/ZrO₂ after 5 cycles. After each cycle, the catalysts were washed with ethanol, centrifuged and dried at 60°C for the next cycle. When the catalysts were reused 10 times, their conversions were 94.0% and 92.0% on Au/CeO₂ and Au/ZrO₂, respectively. The selectivities were 100.0% and 88.4% on Au/CeO₂ and Au/ZrO₂, respectively. This slight decline was attributed to the shedding of some gold nanoparticles, as observed in the TEM images (Figure 1b and 1d) and AAS data. In summary, their high conversions and selectivities reflect the recyclability of Au/CeO₂ and Au/ZrO₂.

(Figure 4 here)

3.4.3. Activity test of primary alcohols (or benzyl aldehyde) and methanol (or ethanol)

To study the scope of this procedure, various primary alcohols and benzyl aldehyde were examined under optimized conditions. The experimental results are presented in Table 2. The results were as follows: (1) when comparing benzyl aldehyde with benzyl alcohol, benzyl aldehyde reacted more easily than benzyl alcohol (Table 2, entries 1, 2). (2) Catalytic activities on Au/CeO₂ and Au/ZrO₂ were similar in methanol. The same trend was observed in ethanol. (3) For most alcohols (R¹CH₂OH), their reactions with methanol (at 25°C) were easier than that with ethanol (at 30°C) due to the stronger nucleophilicity of the methoxy group relative to the ethoxy group. (4) Substituted benzyl alcohols (Table 2, entries 2-5) exhibited excellent activities, especially when reacting with methanol (conversions>99.0%). Based on the results with ethanol, their substituent effects can be estimated to have the following conversion order: $p-OCH_3 > p-CH_3 > p-H > p-Cl$. This sequence shows that when the electron-donating ability of the substituent group is stronger, the reactivity is higher. Conversely, p-nitrobenzyl alcohol (Table 2, entry 6) exhibits a stronger electron-withdrawing ability than p-chlorobenzyl alcohol and exhibits a higher reactivity in ethanol. (5) Cinnamyl alcohol was also successfully applied to the oxidative esterification system (entry 7). The selectivities of methyl cinnamate on Au/CeO₂ and Au/ZrO₂ reached 94.9% and 97.1% in methanol but only 53.3% and 51.5% in ethanol, with high conversions. The major by-product in ethanol was cinnamyl aldehyde, which was also the intermediate used to form methyl cinnamate; this species was stable due to its conjugated structure. (6) Heterocyclic alcohols and aliphatic alcohols exhibited low reactivities (entries 9-11) due to the difficulty encountered during α -H elimination [37, 38]. (7) Under these conditions, the oxidative esterification of 2-phenylethanol was difficult (entry 12). When the temperature was increased to 50°C, conversion reached only 7.9%, while the selectivity dropped to 78.1%. In addition, other methods were attempted to improve the conversion of 2-phenylethanol, such as the use of solvents with different polarities

(petroleum ether, toluene, 1, 4-dioxane, mesitylene, benzotrifluoride, acetone, DMSO and DMF), the application of a stronger oxidant (H_2O_2) or the introduction of visible light [39, 40]. However, those methods remained ineffective. Therefore, a better solution is required. Acetic acid esters were also detected in the ethanol system, but no formic acid esters were detected in the methanol system.

(Table 2 here)

3.4.4. Each species produced during the reaction of benzyl alcohol and methanol

To detect the contents of each species during the oxidative esterification of benzyl alcohol with methanol, an experiment with a slower reaction rate was designed in air. As observed in Figure 5, benzyl alcohol was completely converted into methyl benzoate after 8 hours. Benzaldehyde originally existed in the substrates and finally transformed into methyl benzoate. Moreover, a small amount of benylate appeared in the intermediate process. However, this species finally disappeared due to its transesterification with methanol.

(Figure 5 here)

3.4.5. The self-oxidative esterification of benzyl alcohol

To study the self-oxidative esterification of benzyl alcohol, some inert solvents were employed to replace methanol or ethanol, preventing cross-reactions with the two types of alcohols. The conversion of benzyl alcohol in different solvents increased when the reaction time was prolonged (Table 3). Analysis of the products revealed that the conversion of benzyl alcohol in petroleum ether reached 47.4%, 56.7% and 66.7% after 4, 8 and 12 hours, respectively, and the selectivities of benzaldehyde and benzylate were 25.7% and 74.3%, respectively (Table 3, entry 1). Obviously, the conversion of benzyl alcohol decreased as the solvent polarity index increased due to the solvation effect (Excluding CCl₄ and toluene; we will study the unusual phenomenon observed in CCl₄ and toluene in the future). However, the selectivity of benzaldehyde increased as the solvent polarity index increased due to an induction

effect caused by the solvent. The higher the solvent polarity index, the stronger interaction of the solvent with alcohol or aldehyde, and the reaction occurs more difficult. In conclusion, the polarity index of the solvent strongly affected the self-oxidative esterification of benzyl alcohol. A lower solvent polarity index corresponded to a higher ester yield. Thomas P. Wells et al. [41] reported that a polar solvent would slow the rate of esterification. Therefore, solvents with lower polarity indexes favor the self-reaction of benzyl alcohol.

(Table 3 here)

3.5. Reaction mechanism

As shown in Table 1 (entries 2, 3, 9 and 10), the gold, supports, base and O_2 were all needed during the aerobic oxidative esterification of alcohols. Moreover, the gold nanoparticle surfaces can adsorb O_2 to reduce the O=O bond energy or help dissociate O_2 to form active oxygen species [17, 28]. Therefore, a tentative mechanism was proposed for the oxidative esterification of alcohols and the transfer process for O_2 (Scheme 1) [17, 26, 28, 42].

(Scheme 1 here)

First, the alcohol molecules (R¹CH₂OH) were adsorbed on the support surface due to the difference in electronegativity between the two species. The interaction between the oxygen atoms of the alcohols and the metal cations of the supports, as well as the interaction between the hydrogen atoms of alcohol hydroxyl groups and oxygen anions of the supports, weakened the O—H bonds of the alcohols. Under basic conditions provided by Cs₂CO₃, the H⁺ from the alcohols' —OH was captured by CO₃²⁻, forming structure III with a negative charge on the oxygen atom. The α -H was attracted by the O₂ adsorbed on the gold nanoparticles surface, biasing the electron cloud of the oxygen atom toward the carbon atom. Then, the α -H was removed as H⁻ from structure III, forming an oxygen-carbon double bond. Concurrently, the O₂ double bond was broken, and an O—H bond was formed to

produce O_{ad} -O-H. (O_{ad} represents the oxygen ion adsorbed on the gold nanoparticles surface, and \leftarrow represents the coordination bond between O_{ad} and O.) Another un-adsorbed alcohol (R²OH) and structure IV rapidly undertook a nucleophilic addition reaction to form hemiacetal VI (structure V was quickly converted into structure VI). Similar to the interaction of R¹CH₂OH with the supports, an interaction between the hemiacetals and the supports weakened the bond of the hemiacetal hydroxyl group. Consequently, the H⁺ from the —OH of the hemiacetal was captured by CO_3^{2-} , forming structure VII. The α -H of structure VII was also attracted by the oxygen atom of $O_{ad} \leftarrow O-H$ (or adsorbed O_2) on the gold nanoparticles. Simultaneously, the two bonding electrons over $O_{ad} \leftarrow O$ in $O_{ad} \leftarrow O - H$ moved from the oxygen atom (O) to the adsorbed oxygen anion (O_{ad}). Concurrently, the H^+ in the O_{ad} - $\leftarrow O$ —H was strongly attracted by the electron-rich oxygen anion (O_{ad}). Finally, the H⁺ was transferred to O_{ad} , and the bond in $O_{ad} \leftarrow O$ was broken; 20H and an ester were formed, leaving the gold nanoparticles. The gold nanoparticle surfaces could then re-adsorb oxygen from the reaction environment, beginning a new reaction process.

As observed from scheme 1, negatively charged structure III was generated during the reaction. An electric field existed between structure III and the polar solvent, surrounding structure III with solvent molecules. Therefore, structure III became relatively stable, and its reactivity decreased, lowering the conversion of the alcohol. The interaction between the charged structure and the solvent molecules is the solvation effect mentioned above. An induction effect existed between structure IV and the polar solvents, reducing the electropositivity of the C on the C=O of structure IV and reducing the opportunities for nucleophilic addition reaction between aldehyde and alcohol when increasing the solvent polarity. Finally, ester formation was prevented, making the product more likely to remain an aldehyde. Therefore, in polar solvents, the alcohol conversion decreased, and the selectivity of the ester also decreased for the self-oxidative esterification of the alcohol. The interactions between

the solvent and reactant molecules always existed, but they were strongest in the appearance of structure III and structure IV mentioned above.

4. Conclusion

In summary, excellent catalytic performance was demonstrated during the direct oxidative esterification of alcohols to form esters over Au/CeO₂ and Au/ZrO₂ with the use of dioxygen as an oxidant under ambient temperature and pressure. Practical application is possible due to the simple process, mild conditions, excellent yields and environmental friendliness. A possible mechanism was provided, and the reaction pathways from the alcohols to the esters were described in detail.

Acknowledgements

This work was financially supported by NSFC (Nos. 20567002 and Nos. 21067007), as well as by the Scientific Research Startup Fund of Inner Mongolia University (203044), the Education Department of Inner Mongolia Autonomous Region (NJ04093), Chunhui Plan of the Education Ministry (Z2004-2-15030 and Z2009-1-01005), the Natural Science Fund of Inner Mongolia (2010MS0203 and 2014MS0201) and "513 talents" Plan of Inner Mongolia University and 2013 Annual Grassland Talents Project of Inner Mongolia Autonomous Region and 2013 Annual Inner Mongolia talent development fund.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version

at http:// xxxx.xx.xx.

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Figure captions

Figure 1. TEM images and gold particle size distributions (insets) of (a) Au/CeO₂, (b) recycled Au/CeO₂ after 10 reuses, (c) Au/ZrO₂, (d) recycled Au/ZrO₂ after 10 reuses, and (e) HRTEM image and electron-diffraction of gold particle of recycled Au/ZrO₂ after 10 reuses.

Figure 2. XRD patterns of (a) CeO₂, Au/CeO₂ and recycled Au/CeO₂ after 10 reuses, (b) ZrO₂, Au/ZrO₂ and recycled Au/ZrO₂ after 10 reuses.

Figure 3. XPS spectra of (a) the full-range XPS spectra of Au/CeO₂, recycled Au/CeO₂ after 10 reuses, Au/ZrO₂ and recycled Au/ZrO₂ after 10 reuses, (b) Ce 3d XPS spectrum of Au/CeO₂, (c) Zr 3d XPS spectrum of Au/ZrO₂, (d) Au 4f XPS spectrum of Au/CeO₂, and (e) Au 4f XPS spectra of Au/CeO₂, recycled Au/CeO₂ after 10 reuses, Au/ZrO₂ and recycled Au/ZrO₂ after 10 reuses.

Figure 4. The recyclability test of Au/CeO₂ and Au/ZrO₂ for oxidative esterification of benzyl alcohol with methanol. The reactions were conducted at 25°C in 1 atm O₂ using CH₃OH (5 mL) with benzyl alcohol (2.0 mmol), catalyst (100 mg), and Cs₂CO₃ (10 mol%) in 3 hours. The conversion and selectivity were determined by GC.

Figure 5. The oxidative esterification of benzyl alcohol with methanol in air. The reaction was conducted at 25°C in air using CH₃OH (5 mL) with benzyl alcohol (2.0 mmol), Au/CeO₂ (25 mg), andCs₂CO₃ (10 mol%). The concentration was determined by GC.

Table captions

Table 1. The oxidative esterification of benzyl alcohol with methanol in different conditions. ^[a]

Table 2. Oxidative esterification of alcohols (or aldehydes) on Au/CeO₂ and Au/ZrO₂.^[a]

Table 3. The self-oxidative esterification of benzyl alcohol in different solvents.^[a]

Scheme captions

Justin Ju Scheme 1. A proposed mechanism for aerobic oxidative esterification of alcohols by























Table 1

| ОН | + CH₂OH <u>25</u> | mg Cataly | st,10 mol% (| | OCH ₃ |
|-------|------------------------------------|---------------------------------|-----------------------|-------------------------|---------------------------|
| | 53011 | O ₂ , | 25,6h | | |
| entry | catalyst | base | atmosphere | Conv.(%) ^[b] | Select.(%) ^[c] |
| 1 | None | Cs ₂ CO ₃ | O ₂ | 0 | 0 |
| 2 | CeO ₂ | Cs ₂ CO ₃ | O ₂ | 1.3 | 0 |
| 3 | Au ^[d] | Cs ₂ CO ₃ | O ₂ | 12.9 | 58.2 |
| 4 | Au/CeO ₂ | Cs ₂ CO ₃ | O ₂ | 99.7 | 99.4 |
| 5 | Au/ZrO ₂ | Cs ₂ CO ₃ | O ₂ | 100.0 | 99.0 |
| 6 | Au/TiO ₂ ^[e] | Cs ₂ CO ₃ | O ₂ | 88.9 | 85.8 |
| 7 | Au/HT | Cs ₂ CO ₃ | O ₂ | 82.2 | 84.1 |
| 8 | Au/ Al ₂ O ₃ | Cs ₂ CO ₃ | O ₂ | 39.3 | 79.3 |
| 9 | Au/CeO ₂ | None | O ₂ | 0.5 | 25.7 |
| 10 | Au/CeO ₂ | Cs ₂ CO ₃ | Ar | 1.6 | 33.7 |
| 11 | Au/CeO ₂ | Cs ₂ CO ₃ | Air | 39.0 | 78.8 |

[a] Reaction conditions: benzyl alcohol (2.0 mmol); CH₃OH (5 mL); atmosphere, 1 atm. [b] Conversion of benzyl alcohol was determined by GC. [c] Selectivity of methyl benzoate was determined by GC. [d] Au is the micron-sized solid particles. [e] TiO₂ entirely exists in the form of anatase.

| Table | 2 |
|-------|---|
|-------|---|

 $\begin{array}{r} R^{1}CH_{2}OH \ (or \ R^{1}CHO) \ + \ R^{2}OH \ \hline \begin{array}{c} 25 \ mg \ Catalyst \ , \ 10 \ mol\% \ Cs_{2}CO_{3} \\ \hline O_{2} \end{array} } R^{1}COOR^{2} \end{array}$

| entry | RCH ₂ OH (or RCHO) | R′OH | Au/CeO ₂ | | Au/ZrO | 2 |
|---------------------------|----------------------------------|---|---------------------------|-------------------------|----------------|-------------------------|
| | | | Conv. (%) ^b | Select.(%) ^c | Conv. $(\%)^b$ | Select.(%) ^c |
| 1 | ⊳ 0 © | CH_3OH^d | 100.0 | 99.6 | 100.0 | 99.8 |
| 1 | | C ₂ H ₅ OH ^e | 99.6 | 99.2 | 99.5 | 99.1 |
| 2 | ∕OH | CH_3OH^d | 99.7 | 99.4 | 100.0 | 99.0 |
| | | C ₂ H ₅ OH ^e | 70.4 | 93.6 | 71.8 | 92.3 |
| 3 | гон | CH_3OH^d | 100.0 | 99.3 | 100.0 | 96.7 |
| осн | осн₃ | C ₂ H ₅ OH ^e | 100.0 | 72.6 | 100.0 | 73.8 |
| 4 | _∩ он © | CH ₃ OH ^d | 100.0 | 99.0 | 99.9 | 99.3 |
| 4 - CH ₃ | с́н ₃ | C ₂ H ₅ OH ^e | 82.7 | 87.2 | 86.3 | 89.8 |
| 5 | <mark>_ сон</mark> | CH_3OH^d | 100.0 | 98.9 | 100.0 | 97.4 |
| 5 | čı | C ₂ H ₅ OH ^e | 60.2 | 79.8 | 67.2 | 85.3 |
| 6 Ю NO ₂ | он | CH_3OH^d | 76.1 | 93.4 | 70.2 | 95.5 |
| | NO ₂ | C ₂ H ₅ OH ^e | 77.3 | 98.3 | 71.0 | 96.7 |
| 7 | ſŶ ^{ŶŶ} OH | CH ₃ OH ^f | 99.9 | 94.9 | 98.4 | 97.1 |
| 1 | | C ₂ H ₅ OH ^g | 91.9 | 53.3 | 90.1 | 51.5 |
| 8 | (<u>)</u> он | CH_3OH^f | 51.2 | 82.3 | 50.9 | 83.4 |



^{*a*} Reaction conditions: RCH₂OH (or R₁CHO), 2.0 mmol; R'OH, 5 mL; O₂, 1 atm. ^{*b*} Conversion of RCH₂OH was determined by GC. ^{*c*} Selectivity of RCOOR' was determined by GC. ^{*d*} Reaction time, 6 h; temperature, 25°C. ^{*e*} Reaction time, 24 h; temperature, 30°C. ^{*f*} Reaction time, 24 h; temperature, 25°C. The values in parentheses are conducted at 50°C. ^{*g*} Reaction time, 48 h; temperature, 30°C.

| $\bigcirc \bigcirc $ | | | | | | | |
|---|-------------------------|----------------------------------|------|------|------|---------------------------|----------|
| entry | solvent | Polarity Conv.(%) ^[b] | | | | Select.(%) ^[c] | |
| | | index | 4 h | 8 h | 12 h | benzaldehyde | benylate |
| 1 | petroleum ether | 0.01 | 47.4 | 56.7 | 66.7 | 25.7 | 74.3 |
| 2 | cyclohexane | 0.2 | 34.9 | 40.9 | 46.9 | 36.1 | 63.9 |
| 3 | carbon tetrachloride | 1.6 | 4.2 | 4.3 | 5.8 | 83.4 | 3.8 |
| 4 | toluene | 2.4 | 38.2 | 42.5 | 44.2 | 81.1 | 10.3 |
| 5 | dichloromethane | 3.1 | 22.1 | 30.9 | 37.3 | 85.0 | 14.5 |
| 6 | trichloromethane | 4.1 | 16.6 | 27.4 | 33.2 | 91.2 | 8.3 |
| 7 | 1, 4 - dioxane | 4.8 | 6.5 | 10.6 | 13.8 | 97.8 | 0 |
| 8 | pyridine | 5.3 | 0.1 | 0.3 | 0.4 | 100.0 | 0 |

[a] Reaction conditions: benzyl alcohol (2.0 mmol); solvents (5 mL); O₂,1 atm. [b] Conversion of benzyl alcohol was determined by GC. [c] Selectivities corresponded to the results in 12 h.

Table 3

0

Scheme 1



Appendix A. Supplementary data

Supplementary TEM image:



Figure S1. TEM images and gold particle size distributions (insets) of (a) Au/TiO₂, (b) Au/HT, (c) Au/Al₂O₃.

Calculation formula:

The conversion of benzyl alcohol, the selectivity of methyl benzoate and the yield of methyl benzoate were calculated using the following formula:

Conv. =
$$\frac{A_0 - A_t}{A_0} \times 100\%$$
 (1)
Select. = $\frac{A_t'}{A_0 - A_t} \times 100\%$ (2)
Yield = Conv. × Select. = $\frac{A_t'}{A_0} \times 100\%$ (3)

Conv.: the conversion of benzyl alcohol, A_0 : the peak areas of benzyl alcohol determined by GC before reaction, A_t : the peak areas of benzyl alcohol determined by

GC after the reaction for t hours.

Select .: the selectivity of methyl benzoate, At': the peak areas of methyl benzoate

determined by GC after the reaction for t hours.

Yield: the yield of methyl benzoate.

GC spectra:

The GC spectra after the first cycle on Au/CeO_2 as described in the text (Figure 4) were diaplayed in Figure S2.



Figure S2. The GC spectra of benzyl alcohol and methanol before reaction and after the reaction for 3 hours.

Peaks of the different retention times (t_r) represented different substances, which were shown in Table S1.

| t _r (min) | 3.8 | 8.0 | 8.7 | _ |
|----------------------|----------|----------------|-----------------|---|
| substance | methanol | benzyl alcohol | methyl benzoate | |

Table S1. The substances of different retention times.

As can be seen from Figure S2 and Table S1, all the benzyl alcohol was converted into methyl benzoate after the reaction for 3 hours.

Graphical abstract-pictogram



netal cation

Graphic abstract-synopsis

The interaction between oxygen atoms of alcohols and metal cations of supports and between hydrogen atoms of alcohol hydroxyl and oxygen anions of supports weakened the O—H bonds.