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Gold-Catalyzed Selectivity-Switchable Oxidation of Benzyl Alcohol in

the Presence of Molecular Oxygen

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Abstract: A selectivity-switchable oxidation of benzyl alcohol by molecular oxygen is achieved with the iron doped graphene (Fe-Gr) supported gold catalysts. The oxidative esterification process is dominant with Au/Fe-Gr and K₂CO₃ as the catalyst in methanol where a 96.2% conversion of benzyl alcohol and 99.9% selectivity of methyl benzoate were obtained. While, the oxidation of benzyl alcohol is orientated to produce benzaldehyde in n-butanol using Au-Pd/Fe-Gr as the catalyst, in which an 89.1% conversion and 87.5% selectivity of benzaldehyde was attained. Moreover, the effects of the additive, reaction medium and reaction time were investigated. Also, the oxidation of different benzylic alcohols was successfully performed under the optimal conditions. Furthermore, the used catalysts were characterized by XRD, NH₃-TPD, SEM, Roman, TG-DTA and BET techniques. Based on the experimental results and phenomena, a possible reaction mechanism is proposed for the selective oxidation of benzyl alcohol with molecular oxygen in which alkyl benzoate is produce through the hemiacetal intermediate of benzaldehyde with short chain alcohol, and the generation rate of hemiacetal decides the selectivity of product.

Keywords: Selectivity-Switchable; Oxidation; Benzyl Alcohol; Graphene; Molecular Oxygen

1. Introduction

Recently there have been considerable research activities in the area of the oxidation of benzylic alcohols [1-2]. This interest was mainly motivated by the potential application of their oxidation products such as the aldehydes, alkyl benzoates, etc.. In view of increasing of environmental concerns, O₂ or air was often used to replace traditional stoichiometric oxidants during oxidation of benzylic alcohols [3-7]. In order to improve the conversion and selectivity of the reaction, tremendous efforts have been made to develop new catalysts, including supported-monometallic catalysts such as Au, Pt, Pd, Ag, etc. [8-9] and supported-bimetallic catalysts such as Au-Pd, Au-Cu, and Au-Ir catalysts [10-12]. Among them, Au-based catalysts usually show enhanced activity and selectivity in catalyzing oxidation of alcohols [12-14]. The catalytic performance of supported Au-based catalysts largely depends on the size and the shape of Au particles and the nature of the supports [15, 16]. The metal oxides (TiO₂, CeO₂, Fe₃O₄ and Al₂O₃) [17-19], metal-organic frameworks (MOFs) [20], mesoporous silica [21], cellulose nanofibers [22], and carbon materials [23] have been widely used as the support for the selective oxidation of alcohols. Among carbon materials, graphene-supported Au-based catalysts show impressive catalytic performance in the oxidation of alcohol because of the strong metal-graphene interaction [24, 25]. Thus, preparing high performance of the graphene support or functionalized graphene support may contribute to the enhanced performance of the graphene-supported Au-based catalysts [26, 27]. Moreover, the separation of solid catalyst will be more simple and convenient if the magnetic iron oxide can be incorporated into the support.

On the other hand, three significant factors in improving the catalytic activities and selectivity of the aerobic oxidation of alcohol cannot be ignored. (i) Effect of additives. Masai et al. [28] found that the alkali additives could efficiently promote oxidation of benzyl alcohol with Cu-Na-ZSM-5 as the catalyst. (ii) Effect of solvents. Repo et al. [29] mentioned that the use of toluene and water as solvent can affect the selectivity of product in the aerobic oxidation of benzyl alcohol. (iii) Effect of additional metal components. Some researchers have revealed that the bimetallic catalyst exhibited

higher catalytic activity than single metal catalyst for aerobic oxidation of benzyl alcohol [30]. However, there was no report about controlling the product selectivity for the aerobic oxidation of benzylic alcohols using similar catalyst system in simple and cheap alcoholic media.

Intrigued by a novel and efficient method for fabricating high-quality graphene in a large scale [31], we prepared iron doped graphene (Fe-Gr) and employed it as the support for synthesizing the heterogeneous Au-based catalysts. In this work, a gold-catalyzed and product selectivity-switchable process for the oxidation of benzyl alcohol in simple C_1 - C_4 alcohol solvent has been developed. As a result, a 96.2% conversion of benzyl alcohol and 99.9% selectivity of methyl benzoate were obtained in methanol with Au/Fe-Gr and K₂CO₃ as catalyst. Moreover, 89.1% conversion and 87.5% selectivity of benzaldehyde was attained in n-butanol using Au-Pd/Fe-Gr as the catalyst.

2. Experimental

2.1 Reagents and Instruments

Methyl benzoate, benzaldehyde and butyl benzoate as the standard samples were purchased from Aladdin. Other chemicals were of reagent grade and used without further purification.

X-ray powder diffraction (XRD) intensities were measured on a Rigaku D/max-IIIA diffractometer (Cu-Ka, $\lambda = 1.54056$ Å). The powder samples were scanned from 10° to 80° with a step of 0.2°/s. Raman spectroscopy was obtained using a SPEX-1403 laser Raman spectrometer with excitation by a 514.5 nm argon laser line in the back-scattering geometry. The morphology of catalytic materials was obtained by scanning electron microscope (SEM: JSM-6301F, JEOL) and TG experiments were performed in flowing N₂ on a NETASCH TG 209F3 instrument with a heating rate of 10 °C/min in the temperature range of 40-1000 °C. BET surface areas, pore volumes, and average pore diameters of the prepared samples were obtained from N₂ (77 K) adsorption measurements by using a Micromeritics ASAP2020M system, in which the samples were pretreated under vacuum at 150 °C for 4 h. The average pore diameters were calculated according to Barrett-Joyner-Halenda (BJH) model in adsorption and desorption period.

The quantitative analyses of the products were determined on a GC apparatus with FID detector or on the Agilent 6890/5973 Gas Chromatograph-Mass Spectrometer (GC-MS) instrument. The corresponding detection method and the obtained GC-MS spectra for the products of oxidation were given in the supporting information (see Figure S6-S10).

2.2 Preparation of Iron Doped Graphene (Fe-Gr)

Glucose (6.0 g, 0.033 mol) and FeCl₃·6H₂O (6.0 g, 0.022 mol) were added in a vessel and dissolved in 10 mL deionized water. The yellow solution was vaporized at 80 °C in air in an oven for 24 h, and the black solid was obtained. The black solid was calcined in a quart tube furnace at 700 °C for 6 h under N₂ atmosphere. Then, the furnace was cooled down to room temperature under a nitrogen flow. The produced solid was washed with deionized water to remove the water-soluble iron ions. Then the solid sample was dried at 60 °C in a vacuum oven. The as-obtained material was designated as Fe-Gr.

2.3 Preparation of the catalysts

Metal catalyst was deposited onto the supports via a deposition-precipitation method. Typically, $HAuCl_4$ aqueous solution (40 mL, 5wt.%) was taken into a beaker, whose pH was adjusted to 9 by addition of aqueous solution of 0.1 M NaOH under vigorous stirring dropwise. The Fe-Gr support (1.0 g) was added to the solution under stirring. The pH value of the resulted suspension was readjusted to 9 by adding 0.1 M NaOH aqueous solution. Then the suspension was heated to 65 °C and stirred for 1 h. The precipitate was filtered, washed with deionized water for several times and then dried at 60 °C in a vacuum oven overnight. The sample was further calcined in a quart tube furnace at 400 °C for 3 h (denoted as Au/Fe-Gr).

The preparation methods of Au-Pd/Fe-Gr, Au-Pt/Fe-Gr, Pd/Fe-Gr, and Pt/Fe-Gr catalysts were similar to the Au/Fe-Gr catalyst, except that HAuCl₄ aqueous solution was replaced by the mixed aqueous solution of HAuCl₄ and PdCl₂, the mixed aqueous solution of HAuCl₄ and H₂PtCl₆, PdCl₂ aqueous solution and H₂PtCl₆ aqueous solution, respectively.

2.4 General procedure for the selective oxidation of benzylic alcohol

All oxidation experiments of benzylic alcohol were performed in a 120 mL stainless steel autoclave equipped with the magnetic stirring and a temperature controller. Typical procedure for oxidation of benzyl alcohol is as follows: benzyl alcohol (0.162 g, 1.5 mmol), alcoholic solvent (15 mL), catalyst (0.05 g) and additive (0.05 g) were added into the autoclave. After the reactor was sealed, the pure oxygen was pumped to replace the atmosphere for several times. Then under pressure of 0.3 MPa, the mixture was preheated to 110 °C with magnetic stirring and kept for a certain time. After the autoclave was cooled and the excess gas was released, the as-obtained mixture was analyzed by GC and GC-MS.

3. Results and Discussion

3.1 Characterization of Catalysts

The XRD patterns of different metal nanoparticles/Fe-Gr samples are shown in the Figure S1 (included in the supporting information). All of the catalysts and the pristine Fe-Gr support exhibited the broad characteristic peak of graphene at 24° [32]. The characteristic diffraction peaks corresponding to the (220), (311), (400), (422), (511) and (440) plane of ferroferric oxide were observed for most of the metal/Fe-Gr catalyst systems except for Pd/Fe-Gr catalyst. While for Pd/Fe-Gr catalyst, the characteristic peaks of iron oxide at 24.1°, 33.2°, 35.6°, 40.9°, 49.5°, 54.1°, 62.5° and 64.0° appeared. Thus the mainly existing form of the iron element is ferroferric oxide in these metal nanoparticles/Fe-Gr catalyst systems with the one exception of Pd/Fe-Gr system. At the same time, the diffraction peaks of metal nanoparticles can also be observed from the XRD patterns of the correspondent metal nanoparticles/Fe-Gr catalyst systems. Only in Pt/Fe-Gr catalyst, Pt nanoparticles show very weak diffraction peaks, which demonstrates that the deposition-precipitation strategy may not apply to prepare the supported-Pt catalysts [33].

To reveal the size, shape and dispersion of metal nanoparticle over support, the catalyst Au/Fe-Gr, Au-Pd/Fe-Gr and Fe-Gr were respectively detected by SEM technique. As shown in

Figure S2 of supporting information, the gold nanoparticles in the Au/Fe-Gr sample were spherical, and the particle size was from 15 nm to 30 nm. Moreover, the metal particle seems to become smaller when a small quantity of palladium is introduced, where the particle size of the Au-Pd/Fe-Gr sample is less than 20 nm and distributed more uniformly on the surface of catalyst.

In order to further reveal the structure information of these catalysts, the prepared samples were further characterized by Raman spectrum. As indicated in the Figure S3 of supporting information, the peaks at 1342cm⁻¹ and 1592cm⁻¹ were respectively attributed to D-bands and G-bands of the graphene. The broad peak at 2500-3200 cm⁻¹ should be contributed as the combined peaks of 2D (at 2664 cm⁻¹, second order or overtone of D-band) and D + G (at 2926 cm⁻¹) bands in which the ratio of I_D/I_G and I_{2D}/I_G is 0.84 and 0.30, respectively. Compared to the structure of the graphene reported by Han's group, it can be deduced that the introduction metal nanoparticles aroused the topological defect and the disorder of obtained graphene sheets was increased [31]. At the same time, the appeared D+G bands also demonstrate the disordered arrangement and *in situ* modification of graphene sheets [34].

To evaluate the thermal stability of the catalysts, thermal weight experiment was performed under a nitrogen atmosphere with a heating rate of 10 °C/min, over the temperature range of 40-1000 °C. It was found that all of these catalysts have the similar thermal behaviour (presented in the Figure S4 of supporting information). There are one endothermic peak at 87 °C and one endothermic peak at 800 °C on the TG-DTG curves, corresponding to the loss of adsorbed water and the decomposition of graphene, respectively. From the TG-DTG curves, the temperatures of obvious weight loss are in the range of 40-100 °C and 770-800 °C, respectively.

In addition, the textural properties of the catalysts were detected by the nitrogen physisorption and the obtained results are shown in Table S1 of supporting information. It can be seen that the surface area and pore volume of the Au-Pd/Fe-Gr catalyst is larger than those of the other catalysts. Moreover, the surface area and pore volume of Au/Fe-Gr catalyst is slightly smaller than that of

Au-Pd/Fe-Gr catalyst. In addition, the average pore diameters of these catalysts are similar and distributed between 2.8 to 4.3 nm.

3.2 Catalytic test

Firstly, benzyl alcohol (1) was chosen as the model substrate, and the oxidation was carried out in methanol in which the main products include benzaldehyde (2), methyl benzoate (3) and (dimethoxymethyl)benzene (4) (shown in Scheme 1). The promotion of different catalysts was investigated and the obtained results are summarized in Table 1. It is found that the combination of Au/Fe-Gr and K₂CO₃ showed a good catalytic activity in which the conversion of **1** and selectivity of 3 was 91.0% and 95.5%, respectively (entry 3). The contrast experiment showed less 8.3% conversion was attained in the absence of the Au or Pd element (entries 1, 4 and 5). Moreover, in the presence of only Au/Fe-Gr catalyst, a 15.5% conversion of 1 and 88.3% selectivity of 3 were obtained (entry 2). Obviously, the synergistic interaction among the additive, metal nanoparticles and supports should be responsible for high conversion and excellent selectivity. Furthermore, it was found that the combination of Pt/Fe-Gr and K₂CO₃ shows little catalytic activity for the selective oxidation of 1 where only 3.2% conversion was obtained (entry 6). Otherwise, a 19.9% conversion of 1 and 90.5% selectivity of 2 was attained with Pd/Fe-Gr and K₂CO₃ as the catalyst. In the following, the bimetallic catalysts Pt-Au/Fe-Gr and Pd-Au/Fe-Gr were also synthesized and employed in the oxidation processes. As a result, a 25.1% conversion in 73.7% selectivity of 2 was obtained with Pt-Au/Fe-Gr and K₂CO₃ as the catalyst (entry 8), while a 95.1% conversion of 1 and 46.1% selectivity of 2 (containing a little 4) was attained in the presence of Au-Pd/Fe-Gr+K₂CO₃ (entry 9). Particularly, when the single Pd-Au/Fe-Gr catalyst was used, the conversion of 1 and the selectivity of 2 including 4 can reach 96.2% and 89.9%, respectively (entry 10). Thus, it can be concluded that the introduction of Pd nanoparticles can efficiently improve the activity of gold-based catalyst and selectivity of 2 in the methanol solvent.

((Scheme 1 is inserted here:))

((Table 1 is inserted here:))

In order to further confirm the role of K_2CO_3 as the additive, the effects of several additives were investigated on the oxidation of **1** and the data are presented in the entries 11-15 of Table 1. The results showed that the bases as additives can enhance the efficiency of Au-based catalyst. Moreover, the promotion of K_2CO_3 is more efficient than that of KOH for the oxidation reaction, in which only 71.5% conversion and 65.6% selectivity of **3** was obtained with KOH as additive in the presence of the Au/Fe-Gr catalyst. However, the addition of acidic additive can prevent the oxidation of **1** with Au/Fe-Gr as catalyst in which a 4.9% conversion and 31.3% selectivity of **2** was obtained.

Furthermore, different solvents were employed for the selective oxidation of **1** with heterogeneous gold catalysts and the results are shown in Table 2. It was found that the conversion of **1** using ethanol, n-propanol or isopropanol as the solvent is lower than that obtained using methanol as the solvent (entries 2, 3 and 4). Also, the Au/Fe-Gr-K₂CO₃ catalyst system showed good catalytic performance with n-butanol or n-hexanol as solvent, and the main product was **2** (entries 5 and 6). In view of economic and practical point, n-butanol is the most suitable solvent for producing **2**. In addition, as shown from the entry 9 of Table 1, it is seen that the Au-Pd/Fe-Gr catalyst is also benficial to the generation of aldehyde. Thus, the oxidation of **1** is further investigated using Au-Pd/Fe-Gr as the catalyst and n-butanol as the solvent. To our surprise, 82.6% conversion of **1** and 89.2% selectivity of **2** was obtained (entry 7 of Table 2). Otherwise, a 52.3% conversion and 94.1% selectivity of **2** was attained in the presence of Au-Pd/Fe-Gr catalyst and K₂CO₃ in n-butanol. Based on the obtained experimental results, it can be concluded that methanol is the most promising solvent for Au/Fe-Gr-K₂CO₃ to catalyze the oxidation of **1** to form **3**, while n-butanol is in favor of the high conversion of **1** and high selectivity of **2** in the presence of Au-Pd/Fe-Gr catalyst.

((Table 2 is inserted here:))

In the following, the effect of reaction time on the oxidation of 1 was further studied, and the results were shown in Figure 1. For the selective oxidation of 1 with Au/Fe-Gr-K₂CO₃ catalyst in methanol (Figure 1a), along with the reaction time increasing at first, the conversion and the selectivity of 3 increased rapidly, while the selectivity of 2 decreased. After 4 h, the amount of all substance almost kept unchanged, in which the conversion of 1 and the selectivity of 3 was 96.2% and 99.9% after 8 hours. For the oxidation of 1 to produce 2 catalyzed by the Au-Pd/Fe-Gr catalyst (Figure 1b), along with the increase of reaction time, the conversion was gradually increased and selectivity of 2 was slowly decreased. So the conversion and selectivity of 2 was comprehensively considered, the optimum reaction time was confirmed to be 6 hours, where the conversion of 1 and the selectivity of 2 were up to 89.1% and 87.5%, respectively.

((Figure 1 is inserted here:))

Considering the good catalytic performance of the Au/Fe-Gr-K₂CO₃ catalyst system in methanol for oxidative esterification of **1** to **3** (designated as **A** system) and the Au-Pd/Fe-Gr catalyst in n-butanol for oxidation of **1** to **2** (designated as **B** system), the selective oxidation of different benzylic alcohols were further investigated (Table 3). In both catalyst systems, electron-donating substituents in para-position of benzene ring are in favor of the proceeding of oxidation. As for the oxidation of 4-methoxy benzyl alcohol, the conversion and the selectivity of methyl 4-methyoxy benzoate were up to 99.1% and 91.7% in **A** system. Meanwhile, the conversion and the selectivity of 4-methoxy benzaldehyde were up to 99.5% and 97.2% in **B** system, respectively. In case of the oxidation of 4-nitrobenzyl alcohol, although the strong withdrawing groups such as -NO₂ group on

the para-position of benzene ring, the conversion and the selectivity of methyl 4-nitrobenzoate are 54.2% and 49.7% in **A** system, respectively (entry 2). In addition, the oxidation of cinnamic alcohol was also successfully performed. In **A** system, a 95.6% conversion and a 77.4% selectivity of methyl cinnamate was obtained; in **B** system, a 79.7% conversion and a 95.5% selectivity of cinnamaldehyde was attained (entry 3). On the other hand, the aerobic oxidation of α -phenylethanol and β -phenethyl alcohol were also carried out, in which a 66.9% conversion of α -phenylethanol and 100% selectivity of acetophenone was obtained in **A** system (entry 4). While, the oxidation of β -phenethyl alcohol hardly occurs in either **A** system (3% conversion) or **B** system (0% conversion) which demonstrates that the saturated aliphatic alcohols are suitable for being used as the solvents.

((Table 3 is inserted here:))

Finally, several control experiments are performed to determine the reaction mechanism for aerobic oxidation of **1** and the results are presented in Table S3. The conversion of **2** is much higher than that of benzoic acid, which indicates that the oxidation reaction happens through the formation of **2** as the intermediate, and benzoic acid is not formed during the catalytic process (entries 2 and 5 of Table S3). Moreover, the addition of K_2CO_3 efficiently accelerates the oxidation of **1** to **2** in the presence of Au/Fe-Gr catalyst. Then, the compound **2** reacts immediately with short chain alcohol to generate hemiacetal. In the following, the hemiacetal was further oxidized to produce the compound **3** (Scheme 2a). Besides, it need to be mentioned that Au-Pd/Fe-Gr catalyst is helpful to the formation of **4** during the oxidation reaction (Scheme 2b). When K_2CO_3 was employed, the conversion of **2** to **4** will become difficult, so that the conversion of **2** decreases and the hemiacetal can occur and further lead to generation of alkyl benzoate. In addition, along with the longer chain of the alcoholic solvent, the conversion from **2** to hemiacetal or **4** will become more difficult. Thus, the high conversion and excellent selectivity of aldehyde may be obtained with Au-Pd/Fe-Gr catalyst in n-butanol solvent.

((Scheme 2 is inserted here:))

4. Conclusions

A novel iron-doped graphene supported Au-based catalyst was prepared by the deposition precipitation method. With the assistance of the catalyst, a product selectivity-switchable oxidation of benzylic alcohols to produce aldehydes or alkyl benzoates is developed with dioxygen as oxidant. Therein, the Au/Fe-Gr-K₂CO₃ catalyst system showed a very high catalytic performance for the selective oxidation benzyl alcohol to methyl benzoate, in which a 96.2% conversion of **1** and 99.9% selectivity of **3** was obtained in methanol. The oxidation of benzyl alcohol to produce benzaldehyde can be successfully performed using the Au-Pd/Fe-Gr as catalyst and n-butanol as solvent, in which the conversion of **1** and the selectivity of **2** are as high as 89.1% and 87.5%, respectively. It provides a new approach to achieve product selectivity-switchable oxidation of benzylic alcohol with a green and cost-effective system.

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Supporting Information

The characterization of catalysts (such as XRD, SEM, Roman spectra, TG-DTA sata, BET and NH₃-TPD detection), GC and GC-MS spectra of products, and the results for investigating the reaction mechanism on the oxidation of benzyl alcohol are provided in the supporting information.

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Tables, Schemes and Figures Captions:

Table 1. The selective oxidation of 1 with different catalyst systems in methanol

Table 2. Effect of solvents on the selective oxidation of 1 with heterogeneous gold catalysts

 Table 3. Selective oxidation of different benzylic alcohols with the Au-based/Fe-Gr catalysts

Scheme 1. The equation for oxidation of benzyl alcohol by molecular oxygen

Scheme 2. Possible reaction mechanism for oxidation of 1 by heterogeneous gold catalysts

Figure 1. Influences of reaction time on the oxidation of 1 with Au/Fe-Gr- K_2CO_3 catalyst in methanol (a) or Au-Pd/Fe-Gr catalyst in n-butanol (b)

A CERMIN







Figure 1



Entry	Catalyst system	Conversion (0() ^b	Product distribution(%) ^b	
		Conversion (%) –	3	2(4) ^c
1	No	6.9	0	100
2	Au/Fe-Gr	15.5	88.3	11.7
3	Au/Fe-Gr+K ₂ CO ₃	91.0	95.5	4.5
4	K ₂ CO ₃	1.1	55.2	44.8
5	Fe-Gr+ K ₂ CO ₃	8.3	61.9	38.1
6	Pt/Fe-Gr+K ₂ CO ₃	3.2	13.2	86.8
7	$Pd/Fe-Gr+K_2CO_3$	19.9	9.5	90.5(4.3)
8	Au-Pt/Fe-Gr+K ₂ CO ₃	25.1	26.3	73.7
9	Au-Pd/Fe-Gr+K ₂ CO ₃	95.1	53.9	46.1(1.0)
10	Au-Pd/Fe-Gr	96.2	11.1	89.9(60.0)
11	Au/Fe-Gr+Na ₂ CO ₃	63.9	28.4	71.6
12	Au/Fe-Gr+Cs ₂ CO ₃	45.2	53.1	46.9
13	Au/Fe-Gr+Li ₂ CO ₃	22.9	46.2	53.8
14	Au/Fe-Gr+KHCO ₃	63.9	26.1	73.9
15	Au/Fe-Gr+KOH	71.5	34.4	65.6

Table 1. The selective oxidation of 1 with different catalyst systems in methanol^{*a*}

^{*a*} Reaction conditions: **1** (1.5 mmol), 0.05 g metal nanoparticles/Fe-Gr catalyst and 0.05 g additives in 15 mL methanol, under 0.3 MPa of O_2 , at 110 °C, for 4 h with magnetic stirring. ^{*b*} The data were obtained by GC with the internal standard method. ^{*c*} The selectivity of **2** including **4**, and the selectivity data of **4** were listed in brackets.

	Solvents		Product distribution(%) ^b	
Entry		Conversion (%)	2	ester
1	methanol	91.0	4.5	95.5
2	ethanol	26.5	91.1	8.9
3	n-propanol	33.2	95.4	4.6
4	isopropanol	53.6	98.8	1.2
5	n-butanol	85.2	71.8	28.2
6	n-hexanol	87.2	90.6	9.4
7 ^c	n-butanol	82.6	89.2	10.8
8 ^d	n-butanol	52.3	94.1	5.9

Table 2. Effect of solvents on the selective oxidation of 1 with heterogeneous gold catalysts^{*a*}.

^{*a*} Reaction conditions: **1** (1.5 mmol), 0.05 g Au/Fe-Gr catalyst and 0.05 g K_2CO_3 additive in 15 mL solvent, under 0.3 MPa of O_2 , at 110°C, for 4 h with magnetic stirring. ^{*b*} The data were obtained by GC with the internal standard method. ^{*c*} Reaction conditions: **1** (1.5 mmol), 0.05 g Au-Pd/Fe-Gr catalyst in 15 mL solvent, under 0.3 MPa of O_2 , at 110 °C, for 4 h. ^{*d*} Reaction conditions: **1** (1.5 mmol), 0.05 g Au-Pd/Fe-Gr catalyst and 0.05 g K_2CO_3 additive in 15 mL solvent, under 0.3 MPa of O_2 , at 110 °C, for 4 h.

lys.

Entry	Reactant	Conversion $(\%)^{b}$	Product distribution(%) ^b	
Entry			Aldehydes	Esters
1	н ₃ со Он	99.1	8.3	91.7
2 ^{<i>c</i>}	н ₃ со Он	99.5	97.2	2.8
3	O ₂ N OH	54.2	50.3	49.7
4 ^c	O ₂ N OH	3.6	100	0
5	ОН	95.6	22.6	77.4
6 ^c	ОН	79.7	95.5	4.5
7 ^d	OH	66.9	100	0
8	OH	3.7	0	100

Table 3. Selective oxidation of different aromatic alcohols with the Au-based/Fe-Gr catalysts ^a.

^{*a*} Reaction conditions: aromatic alcohol (1.5 mmol), 0.05 g Au/Fe-Gr catalyst and 0.05 g additive in 15 mL methanol, under 0.3 MPa of O_2 , at 110 °C, for 8 h with magnetic stirring. ^{*b*} The data were obtained by GC with the internal standard method. ^c Reaction conditions: aromatic alcohol (1.5 mmol), 0.05 g Au-Pd/Fe-Gr in 15 mL n-butanol, under 0.3 MPa of O_2 , at 110 °C, for 6 h with magnetic stirring. ^d The oxidized product in this reaction is acetophenone.

Graphical abstract



Gold-Catalyzed Selectivity-Switchable Oxidation of Benzyl Alcohol in

the Presence of Molecular Oxygen

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Research Highlights

- A product selectivity-switchable oxidation of benzyl alcohol has been developed.
- 96.2% conversion and 99.9% selectivity of methyl benzoate is obtained in methanol.
- 89.1% conversion and 87.5% selectivity of benzaldehyde is attained in n-butanol.
- A possible reaction mechanism for the oxidation of benzyl alcohol is proposed.