



Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Gold-mediated selective transformation of lignin models to aromatic esters in the presence of molecular oxygen

Xuli Zhuang^a, Xinli Tong^{a,*}, Yongtao Yan^a, Song Xue^a, Linhao Yu^a, Yongdan Li^b

^a Tianjin Key Laboratory of Organic Solar Cells and Photochemical Conversion, School of Chemistry & Chemical Engineering, Tianjin University of Technology, Tianjin 300384, PR China

^b School of Chemical Engineering, Tianjin University, Tianjin 300072, PR China

ARTICLE INFO

Keywords:

Vanillin
Methyl vanillate
Oxidation
Gold
Molecular oxygen

ABSTRACT

A highly efficient and selective transformation of lignin-derived vanillin and vanillyl alcohol to prepare methyl vanillate has been developed in the presence of molecular oxygen. A series of supported Au, Pd and Pt catalysts were prepared and employed for the selective oxidation of vanillin. It is found that, in the presence of Au-h/Al₂O₃ catalyst, a 98.1% conversion of vanillin and 99.9% selectivity of methyl vanillate was obtained in methanol under 0.3 MPa of O₂ at 140 °C for 4 h. Moreover, the oxidative esterifications of isovanillin, syringaldehyde, *p*-anisaldehyde and 3, 4, 5-trimethoxybenzaldehyde were successfully performed, and 70.2–98.0% yields of methyl aromatic esters are obtained. The recycling experiment showed that the Au-h/Al₂O₃ still keep a high catalytic activity after being reused five times. Next, the oxidation of vanillyl alcohol was studied, and 99.9% conversion and 99.6% selectivity of methyl vanillate was attained at 140 °C for 12 h with the Au-h/Al₂O₃ as catalyst. Finally, based on the reaction phenomena and experimental results, a possible reaction mechanism for the oxidation of vanillyl alcohol is proposed.

1. Introduction

The selective transformation of biomass or bio-based platform compound is beneficial to improve the sustainability of energy, produce new large-scale medical intermediates and develop the current chemical industry [1–3]. Lignin, as a main part of lignocellulosic biomass, is a promising renewable material, which is available at a relatively low cost for the production of a range of valuable chemicals [4,5]. The annual industrial production, mainly from the paper and pulp industry as non-cellulosic waste, approximates 50 million tons [6]. As known to all, lignin is an amorphous three dimensional polymer which consists of oxygen rich subunits derived from phenol, *p*-coumaryl, coniferyl, and sinapyl alcohols typically connected with ether linkages, making it a potential renewable carbon resource for the production of aromatic compounds [7,8]. Therefore, the valorization of lignin into the production of chemical feedstocks represents a real challenge in terms of both sustainability and environmental protection.

Up to now, the synthetic production process of aromatic aldehydes accounts for about 15% from lignin oxidation [9]. Thus, the selective oxidation has also been considered as a promising strategy for the conversion of lignin. Recently, the demand for renewable aromatic aldehydes and esters has rejuvenated the interest for the lignin route,

most especially the efficient production of vanillin (4-hydroxy-3-methoxybenzaldehyde), vanillic acid (4-hydroxy-3-methoxybenzoic acid), methyl vanillate (methyl 4-hydroxy-3-methoxybenzoate) and other vanillin-derived compounds [10]. In general, vanillin is commercially isolated through the oxidation of lignin under alkaline conditions [11]. Nowadays, the commercial process for the production of vanillin or vanillic acid is focused on using the hydrothermal pretreatment of lignosulfonates, by-products of the sulfite paper industry [12–14]. Besides, catalytic wet air oxidation of lignin to aromatic aldehyde is mostly preferred due to its mild conditions, good selectivity and environmental friendliness. Various catalysts, such as the homogeneous copper salts, have been used in catalytic oxidation reactions and wood delignification [15]. During the lignin oxidation, Cu (II) is reduced to Cu (I), which may be oxidized back to Cu (II) species in the presence of molecular oxygen [16]. On the other hand, Perovskite-type composite metal oxides, i.e., LaFe_{1-x}Cu_xO₃ (*x* = 0, 0.1 and 0.2), and Pd/Al₂O₃ catalysts were also reported to catalyze the oxidative transformation of alkaline lignin, producing vanillin and syringaldehyde [17,18].

In order to further enlarge the efficient utilization of lignin on the chemical synthesis and polymer production, the selective transformation of lignin models such as vanillin and vanillyl alcohol has paid scientists' extensive attentions [19]. For example, the vanillic acid or

* Corresponding author.

E-mail addresses: tongxinli@tju.edu.cn, tongxli@sohu.com (X. Tong).

<http://dx.doi.org/10.1016/j.cattod.2017.04.050>

Received 24 November 2016; Received in revised form 13 April 2017; Accepted 22 April 2017
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alkyl vanillate, which is generated from vanillin or vanillyl alcohol has been considered as a very promising and revealing bio-based aromatic monomer [20,21]. The incorporation of vanillates to the structure of polymers can improve the mechanical properties and the thermal stability owing to their inherent aromatic nature.

The production of vanillic acid or alkyl vanillate is often through the efficient oxidation of vanillin or vanillyl alcohol by the strong oxidants. Some works on oxidation of vanillin by hexacyanoferrate (III) [22], diperiodatoargantate (III) [23], cerium (IV) [24], bismuth (V) [25] and diperiodatonickelate (IV) [26] have been presented. Moreover, it was found that, during the aqueous alkaline oxidation of lignin, vanillin is also slowly converted to vanillic acid [27]. Due to the benign nature of molecular oxygen, its utilization as a potential oxidant [28] can help mitigate the use of hazardous reagents, which lead to the generation of greenhouse gases and wasteful byproducts [29]. Therefore, the oxidation of vanillin and vanillyl alcohol to produce methyl vanillate using molecular oxygen as oxidant is a green and sustainable process in chemical industry.

In this article, we propose an efficient method for the selective oxidation of vanillin and vanillyl alcohol in the presence of molecular oxygen. It is found that a 98.1% conversion of vanillin and 99.9% selectivity of methyl vanillate was obtained with the Au-h/ Al_2O_3 as catalyst under 0.3 MPa of O_2 at 140 °C for 4 h. Moreover, in the aerobic oxidation of vanillyl alcohol, a 99.9% conversion and 99.6% selectivity of methyl vanillate could be attained under the optimal conditions.

2. Experimental section

2.1. Chemicals

Vanillin, isovanillin, syringaldehyde, *p*-anisaldehyde, 3,4,5-trimethoxy benzaldehyde, vanillyl alcohol, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{NH}_3 \cdot \text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{HPO}_4$, FeSO_4 , $\text{Fe}_2(\text{SO}_4)_3$, NaOH , $\text{CO}(\text{NH}_2)_2$, NH_4CO_3 , Nb_2O_5 , $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$, PdCl_2 , and $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ are of analytical grade, and purchased from Aladdin reagent company (Shanghai, China). The methyl vanillate as the standard sample is obtained from Alfa Aesar, A Johnson Matthey Company. Oxygen supplied in a high-pressure cylinder is used through a reducing valve without further treatment. Methanol, ethanol, *n*-propanol, isopropanol, *n*-butanol and other solvents are purified by distillation before use. The electrical resistivity of deionized water is more than 18 M Ω cm.

2.2. The preparation of catalysts

2.2.1. The synthesis of Au/ Al_2O_3 catalysts by NaOH precipitation

The synthesis methods of different supports including CeO_2 , hydroxyapatite (H), Fe_xO_y -hydroxyapatite (FH), Fe_3O_4 and Al_2O_3 are given in the supporting information.

In a typical synthesis of the Au/ Al_2O_3 solid catalyst, 10.5 mL HAuCl_4 aqueous solution (0.01 g/mL) and about 40 mL deionized water are charged into a 100 mL flask. Under stirring, a certain amount of NaOH solution (0.1 mol/L) was added dropwise into the above mixture to adjust the pH value to 9 which is monitored by the acidity meter. Next, 1.0 g Al_2O_3 support above was placed into the mixed solution, and the pH value keeps at 9 through the adjustment with NaOH solution. The obtained mixture is heated to 65 °C and held for 1 h. The final precipitate is filtered, and washed using the deionized water repeatedly until the pH value is near to 7; then, the obtained solid is dried at 60 °C overnight, and further calcined at 400 °C for 3 h. The obtained material was designated as the Au/ Al_2O_3 catalyst.

Similarly, the catalysts such as Au/ CeO_2 , Au/H, Au/FH, Au/ Fe_3O_4 , Au/ Nb_2O_5 , Pd/ Al_2O_3 , and Pt/ Al_2O_3 are also prepared by NaOH precipitation, respectively.

2.2.2. The synthesis of Au-h/ Al_2O_3 catalyst by homogeneous precipitation

In a typical preparation, a 10.5 mL of HAuCl_4 aqueous solution

(0.01 g/mL) is diluted to 100 mL with deionized water, and then was added dropwise into the alumina slurry in 200 mL water at room temperature. Afterwards, the urea solution (0.42 mol/L) was added into the mixture. Next, the obtained solution was heated up to 80–90 °C, which allows the slow decomposition of urea and the pH value can reach the final 8–9. Then, the mixture was kept at 80–90 °C for another 4 h under stirring. The power sample was collected after the filtration and thorough washing using hot deionized water (about 70 °C). The solid sample was dried overnight under vacuum conditions, and further calcined at 400 °C for 3 h. The obtained material is designated as Au-h/ Al_2O_3 catalyst.

2.2.3. The synthesis of Au-R/ Al_2O_3 catalyst by NaBH_4 reduction

A typical procedure for the synthesis of Au-R/ Al_2O_3 catalyst is given as follows: 1.0 g Al_2O_3 support and 10.5 mL $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ solution (0.01 g/mL) are completely mixed in a three-neck flask, and then 5 mL deionized water is added into the mixture and stirred for 10 h under ultrasonic radiation. Next, the flask is transferred into bath oil and slowly heated. When the temperature arrives at 105 °C, about 5 mL of a newly prepared NaBH_4 solution (0.02 g/mL) was dropwise added into the above solution, and refluxed for 5 h to achieve the reduction of Au element. Next, the obtained sample is filtered, and washed with deionized water for several times. The solid is further dried for 10 h under the vacuum conditions. The obtained material is designated as the Au-R/ Al_2O_3 catalyst.

2.3. General procedure for the oxidation of vanillin and vanillyl alcohol

In a typical oxidation of vanillin and vanillyl alcohol, a mixture of 0.2 g vanillin (or vanillyl alcohol), 0.05 g catalyst and 15 mL methanol is charged into a 120 mL reactor, and the atmosphere inside is replaced with oxygen after the reactor is sealed. Then, pure oxygen is charged to 0.3 MPa at room temperature. In the following, the autoclave is heated to 140 °C under stirring, and then kept for 4 h. After reaction, the autoclave was cooled to room temperature and excess gas was purged. The obtained products are analyzed by GC with the internal technique (The analysis conditions of GC and GC/MS are provided in the supporting information).

3. Results and discussion

3.1. The XRD patterns of different catalysts

In Fig. 1, the XRD patterns of different catalysts are exhibited. The peak at 35.6° in the Au/H and Au/FH catalysts is contributed to the representative diffraction of Au_2O_3 crystalline; meanwhile, a large number of typical diffraction peaks of hydroxyapatite crystalline appear which indicates the supports have good crystal structures. Moreover, the peaks at $2\theta = 38.2^\circ$, 44.3° , 64.6° or 77.5° in the Au/ Fe_3O_4 , Au/ Al_2O_3 , Au-h/ Al_2O_3 , Au-R/ Al_2O_3 and Au/ CeO_2 catalysts are attributed to the representative diffraction of planes of (111), (200), (220) and (311) of the Au(0) crystalline, which indicates the formation of Au crystal particles on these supports. For the Au/ Nb_2O_5 catalyst, only the characteristic peaks of support is indicated, which is attributed to the low amount of Au nanoparticles on support or irregular crystal structures of Au particles. In addition, the peaks at $2\theta = 33.9^\circ$, 54.8° or 60.8° in the Pd/ Al_2O_3 catalyst are attributed to the representative diffraction of PdO crystalline. For the Pt/ Al_2O_3 catalyst, the peaks at $2\theta = 39.9^\circ$, 46.2° or 67.5° are attributed to the representative diffraction of Pt crystalline. These results show that the supported catalysts are successfully prepared and most of them keep the regular crystal structures.

The other characterization results of these catalysts such as BET measurement, TPD detection, SEM images and TEM images are provided in the supporting information.

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