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Selective Hydrogenolysis of Carbon-Oxygen Bond with Formic Acid over a Au-Pt Alloy Catalyst

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We reported selective hydrogenolysis of carbon-oxygen species over a CeO₂-supported Au-Pt alloy catalyst (Au-Pt/CeO₂) using biomass-derived formic acid as the hydrogen source. This success is reasonably attributed to the high efficiency of Au-Pt/CeO₂ in the tandem steps of formic acid dehydrogenation and carbon-oxygen species hydrodeoxygenation.

Biomass has attracted much attention in the production of fuels and fine chemicals due to the shortage of fossil resources.1-4 One efficient route for biomass utilization is the fast pyrolysis of lignocellulosic feedstocks into phenolic bio-oil, which has been deemed a promising alternative to fossil fuels.⁴ However, it is impossible to directly use these crude bio-oils, because their high oxygen content causes low energy density, high viscosity, and poor stability. Therefore, upgrading the crude bio-oil by the selective cleavage of C-O/C=O bonds to decrease oxygen content is important to obtain high-quality alternative fuels.^{4,5} Because of the highly stable C-O/C=O linkages, the conventional hydrodeoxygenation (HDO) routes for the cleavage of C-O/C=O bonds require high temperature (>200°C) and gaseous hydrogen pressure, which lead to side reactions of over-hydrogenation, cracking, and coke formation. These features make the conventional HDO routes unsatisfactory in some cases due to lack of the product selectivity.

One solution to this issue is conducting the reaction under mild conditions, such as relatively low temperature and gaseous hydrogen pressure. However, the activities are very low and unsatisfactory for the cleavage of C-O/C=O bonds under the mild conditions. For example, vanillin (4-hydroxy-3methoxybenzaldehyde), a common component of pyrolysis oil, is excepted to be hydrodeoxygenated to 2-methoxy-4-

^aKey Laboratory of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, China methylphenol (MMP), which is one of potential biofuels in the future,⁶ but by-product of 4-hydroxymethyl-2-methoxyphenol (HMP) usually formed by uncompleted hydrogenation of vanillin. One possible strategy to achieve both high activity and selectivity is employing hydrogen sources with higher activity than gaseous hydrogen, which might be favourable in the hydrogenolysis reactions.

Recently, various organic molecules have been used as the hydrogen source in hydrogenation reactions *via* tandem dehydrogenation and hydrogenation, and better performance than with gaseous hydrogen was obtained in some cases.⁷ Formic acid (FA), which has high hydrogen density and is easily obtained from the hydrogenolysis of cellulose, has been considered one of the most promising hydrogen sources for wide application *via* a dehydrogenation at a low temperature of <100 \degree (HCOOH \rightarrow CO₂ + H₂).⁸⁻¹⁰ However, when the temperature is higher than 150 \degree (which is necessary for HDO), FA is usually transformed *via* dehydration (HCOOH \rightarrow CO + H₂O), hindering the formation of H₂ from FA dehydrogenation. The design of an efficient tandem process combining FA dehydrogenation and selective HDO is greatly challenging.

In this work, we report Au-Pt alloy nanoparticles supported on CeO₂ (Au-Pt/CeO₂) that exhibit not only good selectivity for FA dehydrogenation but also excellent selectivity for the hydrogenolysis of carbon-oxygen species in the HDO processes at 150 °C. For the tandem reactions of vanillin HDO with FA, the Au-Pt/CeO₂ is highly active, selective, and recyclable for the hydrogenolysis carbon-oxygen species in the reactants.



Scheme 1. Synthetic procedure for Au-Pt/CeO₂.

Scheme 1 shows the synthetic procedure for the Au-Pt/CeO_2 catalyst. The bimetallic Au-Pt colloid was synthesized with HAuCl_4 and H_2PtCl_6 as precursors and NaBH_4 as a

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reductant under the protection by polyvinyl pyrrolidone (PVP), followed by dialysis to remove undesirable Na⁺ and Cl⁻ ions. Then, the Au-Pt colloid was loaded on CeO₂ support, and then calcined for removing the PVP species to obtain Au-Pt/CeO₂ (See the XRD patterns in Figure S1). Based on ICP analysis, the Au and Pt loadings were 0.77 and 0.92 wt%, respectively.



Figure 1. (A-C) TEM images and metal nanoparticle size distribution of the Au-Pt/CeO₂. (D) Au4f and (E) Pt4f XP spectra of the (a) Au/CeO₂, (b) Au-Pt/CeO₂ and (c) Pt/CeO₂ samples.

Figure 1A shows a TEM image of Au-Pt/CeO₂, in which the metal nanoparticles are highly dispersed on the CeO₂ support. The high-resolution image of Au-Pt/CeO2 shows a lattice spacing of 2.31-2.32 Å for the {111} plane (Figure 1B). Based on measurements of more than 150 nanoparticles, the Au-Pt bimetallic particle sizes are distributed in a narrow range (1.6-3.0 nm, average of 2.3 nm, Figure 1C). In contrast, Au/CeO₂ and Pt/CeO₂ exhibit wider metal size distributions (2.0-6.0 and 2.0-7.0 nm, Figure S2). The high-resolution images of the Au/CeO₂ and Pt/CeO₂ (Figures S2B and E) show that the lattice spacing of {111} Au (2.36 Å) and {111} Pt (2.25 Å) are different from that for the Au-Pt alloys (2.31-2.32 Å), suggesting the successful formation of Au-Pt alloys on Au-Pt/CeO₂ rather than separate phases of Au or Pt. These results are consistent with those reported previously that the formation of bimetallic Au-Pt alloys might change the electronic structure of the Au and Pt species, leading to variation in lattice spacing.^{11a} Figure S3 shows the energy dispersive X-ray (EDX) analysis of randomly selected regions in Au-Pt/CeO₂, showing almost unchanged Au/Pt ratios and confirming the successful formation of Au-Pt alloys in the Au-Pt/CeO₂.

Figures 1D and E show the Au4f and Pt4f XP spectra of various samples. The Pt/CeO2 samples exhibits Pt4f7/2 electronbinding energy at 72.2 eV, assigning to Pt2+ species. In contrast, Au-Pt/CeO₂ gives $Pt4f_{7/2}$ binding energies of 70.8 eV, which is assigned to metallic Pt. These results demonstrate that the Pt should interact with Au on Au-Pt/CeO₂ catalyst to hinder the formation of Pt2+ species, forming Au-Pt alloys-all in good agreement with the results of electron microscopy. Additionally, it is worth noting that the $Au4f_{7/2}$ and $Pt4f_{7/2}$ electron-binding energies of AuPt/CeO₂ catalyst are decreased

from the standard metallic Au⁰ and Pt⁰ (Figures 1D and E). This phenomenon should be attributed to the attribute Au-Pd alloy nanoparticles and Ce³⁺ sites of CeO₂ support, which is well known as strong metal-support interaction and usually observed in the redox CeO2-supported catalysts.11b



Figure 2. (A) Scheme for the conversion of vanillin to HMP and MMP; (B) HDO of vanillin with FA over various catalysts; (C) Dependence of (a) FA, (b) vanillin conversion, (c) MMP and (d) HMP selectivity on the reaction time over the Au-Pt/CeO2 catalyst. Reaction conditions: 0.8 mmol of vanillin, 40 mg of catalyst, 8 mmol of FA, 10 mL of water, 15 bar N₂, 150 °C, and 4.5 h. The carbon balances are over 99% for all the tests.

The catalytic study start from the HDO of vanillin with FA in water solvent over various catalysts (Figure 2). Figure 2B shows the catalytic data of various catalysts. The CeO2supported monometallic Au and Pt catalysts (Au/CeO2 and Pt/CeO₂) exhibit low conversion (3.1-16.1%) and poor MMP selectivity (2.2-2.9%). In contrast, most bimetallic Au-Pt catalysts (Au-Pt/AC, Au-Pt/SiO₂, and Au-Pt/CeO₂) give significantly higher conversions (>31.0%) and selectivities (>70.0%) than the monometallic Au and Pt catalysts. Particularly, when Au-Pt/CeO₂ is used as the catalyst, the MMP selectivity can reach 99.8% at full conversion of vanillin, outperforming other Au-Pt catalysts with similar Au and Pt loadings on other supports (Tables S1 and S2). Additionally, when the sizes of Au-Pt nanoparticle on CeO₂ support were 2.5-6.0 nm via precipitation synthesis (Figures S4 and S5), the Au-Pt/CeO₂ still exhibited full conversion of vanillin but relatively low MMP selectivity at 80% (Table S3). These data suggest that the superior catalytic performance of Au-Pt/CeO2 is owing to the contribution of the alloy metals, small nanoparticles, and CeO₂ support.

Figure 2C shows the dependence of FA and vanillin conversion and MMP and HMP selectivity on the reaction time over the Au-Pt/CeO₂ catalyst. The pressure of the autoclave reactor increased significantly in the beginning of the reaction, indicating the formation of a large amount of gaseous product (H₂ and CO₂, by GC analysis). The conversion of FA is always higher than that of vanillin, which indicates that this reaction is a tandem of FA dehydrogenation and vanilline HDO. When the reaction time reaches 4.5 h, the vanillin is completely converted, by-products, such as HMP, are nearly undetectable, and MMP appears as the sole product during the reaction process, indicating that MMP is from the direct hydrolysis of

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Table 1 Catalytic data in FA dehydrogenation and WGS over various catalysts.

	Catalyst	FA dehydrogenation ^a		
Entry		TOF	Selectivity (%)	
		(h-1)	00 II	
			$CO_2 + H_2$	$CO + H_2O$
1	Au/SiO ₂	14	95.0	5.0
2	Au/CeO ₂	298	94.2	5.8
3	Pt/CeO ₂	370	32.9	67.1
4	Pt/C	340	20.0	80.0
5	Au-Pd/CeO2	842	>99.0	b
6	Au-Pt/CeO ₂	1637	>99.0	b
$^{\it a}$ Reaction conditions: 160 °C, 15 bar of N2, 10 mg of catalyst, 2 mmol				
of FA, 10 mL of water, and 25 min. ^b Trace.				

vanillin. Even if the amount of hydrogen source (FA) was significantly reduced, high selectivity to MMP at 99.0% was still obtained (Figure S6). This phenomenon is different from the HDO of vanillin with gaseous hydrogen, where HMP is obtained as a by-product from the uncompleted hydrogenolysis of vanillin.⁶

Based on the catalytic data for the HDO with FA, the superior performance of Au-Pt/CeO2 might be related to its high efficiency in the tandem catalysis of the individual steps, including dehydrogenation of FA and hydrogenolysis of C=O bond. Figure S7 shows the dependence of FA conversion on time over various catalysts, including Au/SiO₂, Au/CeO₂, Pt/CeO₂, Pt/C, and Au-Pt/CeO₂ at relatively high temperature (160 °C). The turnover frequencies (TOFs) were calculated based on the FA conversion of the starting reactions. As presented in Table 1, the monometallic Au catalysts (Au/CeO₂ and Au/SiO₂) catalyze the dehydrogenation of FA with high selectivity for CO₂ and H₂ (94.2-95.0%) but low TOFs (14-298 h⁻ ¹, entries 1 and 2 in Table 1). In contrast, the monometallic Pt catalysts (Pt/CeO₂ and Pt/C) exhibit higher activities (340-370 h⁻¹) but lower selectivities (20.0-32.9%, entries 3 and 4 in Table 1) than those of the monometallic Au catalysts. The lower selectivity is due to the side reaction of FA dehydration. When the bimetallic Au-Pt/CeO₂ is used as a catalyst, both high activity (1637 h⁻¹) and extraordinary selectivity (>99.0%, entry 6 in Table 1) are obtained. The bimetallic Au-Pd catalysts have been reported to be highly efficient catalysts for the conversion of FA to produce hydrogen;^{10,12} therefore, we also studied the catalytic performances of CeO2-supported Au-Pd catalyst (Au-Pd/CeO₂) in the dehydrogenation of FA at 160 °C. As presented in Table 1 (entry 5), the Au-Pd/CeO₂ gives good selectivity to H₂ with undetectable CO, but the TOF of Au-Pd/CeO₂ is much lower than that of Au-Pt/CeO₂. These results indicate the excellent performances of Au-Pt/CeO2 in dehydrogenation of FA. Despite the development of encouraging bimetallic catalysts for FA dehydrogenation in recent years, 10, 12, 13 it is still difficult to find an efficient bimetallic catalyst for FA dehydrogenation at higher temperature (e.g., 160 $^{\circ}$ C), where the relatively high temperature is favourable to tandem HDO because these

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Figure 3A shows the Raman spectra of CeO₂ and Au-Pt/CeO₂ before and after FA dehydrogenation, which are denoted as fresh and FA-treated samples, respectively. For CeO₂, there is no change in the Raman peak at 464 cm⁻¹ (F_{2g} mode) after treatment (Figure S8). However, the FA treatment of Au-Pt/CeO₂ leads to a shift of 4 cm⁻¹ for the F_{2g} peak, along with the appearance of a broad peak at 655 cm⁻¹ (insert in Figure 3A). The broad peak is attributed to the defect sites in the sample.¹⁴ Figure S9 shows the H₂-TPR curves of CeO₂ and Au-Pt/CeO₂. CeO₂ gives a wide peak at 120-350 ℃ and a narrow peak centralized at 443 °C, which are related to the reduction of weakly and strongly bonded oxygen species on CeO₂. In contrast, the reduction of very weakly bonded oxygen species occurs at 86 °C on Au-Pt/CeO2, which is due to the activation of the Ce-O bond associated with defects sites by strongly bound Au-Pt nanoparticles.¹⁵



Figure 3. (A) Raman spectra, (B) Ce3d and (C) O1s XP spectra of the (a) as-synthesized Au-Pt/CeO₂ and Au-Pt/CeO₂ after FA dehydrogenation treatment for (b) 0.5 h and (c) 1 h. (D) Acetone-adsorption IR spectra of (a) CeO₂, (b) Au-Pt/CeO₂ and (c) Au-Pt/CeO₂ after FA dehydrogenation treatment for 1 h.

Figures 3B and C give Ce3d and O1s XP spectra of fresh and FA-treated Au-Pt/CeO₂. For the Ce3d spectra, the fresh Au-Pt/CeO₂ exhibits bands at 883.1, 898.4, 901.1, and 917.3 eV. The doublets at 883.1 eV (Ce3d $_{5/2}$) and 901.1 eV (Ce3d $_{7/2}$) are assigned to the primary photoemission from Ce(IV)-O, and the doublets at 894.8 eV (Ce3d_{5/2}) and 917.3 eV (Ce3d_{7/2}) are from the transfer of one or two electrons from a filled O2p orbital to an empty Ce4f orbital. The treated Au-Pt/CeO2 has two additional peaks at 885.2 and 902.6 eV, which are assigned to the presence of Ce3+ species.¹⁶ This phenomenon indicates the partial reduction of Ce4+ cations during FA dehydrogenation, which is also evidenced by the O1s XP spectra of the sample. The fresh Au-Pt/CeO₂ gives two peaks at 529.4 and 531.6 eV in the O1s XP spectra, which are associated with the lattice oxygen and chemically adsorbed oxygen species on the catalyst surface, respectively. After FA treatment, these peak intensities are significantly decreased due to the reduction of the catalyst surface, in good agreement with the results obtained from the Ce3d XP and Raman spectra.

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To recognize the interaction between C=O group with the catalysts, FT-IR spectra of adsorbed molecules on the catalysts were studied using acetone as a probe molecule. Figure 3D shows the C=O stretching band of the adsorbed acetone at 1704 $cm^{\text{-}1}$ for CeO_2 and Au-Pt/CeO_2. The treated Au-Pt/CeO_2 has a band at 1669 cm⁻¹, with a shift of 35 cm⁻¹ from the C=O stretching band on CeO₂ (1704 cm⁻¹). This red shift indicates that the treated Au-Pt/CeO₂ interacts more strongly with the C=O group than the fresh catalysts. $^{\rm 17}$ Considering that the reactions were conducted in water solvent, the adsorption of acetone on various samples in the presence of water was also studied (Figure S10), similar results were also obtained to the water-free test. The strong interaction between C=O with the catalyst reasonably originates from the presence of oxygen defects on the treated Au-Pt/CeO2,18 which facilitates the cleavage of C=O bonds in HDO. After C=O cleavage, the oxygen was removed by hydrogenation to form water, thus leading to Au-Pd/CeO2 catalyst with oxygen defects, as proposed in Scheme S1.

We also tested the catalytic performance of Au-Pt/CeO₂ for HDO using gaseous hydrogen instead of FA as a hydrogen source. where more hydrogen molecule are used (hydrogen/vanillin ratio at 36) than that using FA (FA/vanillin ratio at 10). The vanillin conversion is 90%, which is obviously lower than that (nearly 100%) using FA (Table S4). This result indicates that FA has better capability than gaseous hydrogen in the HDO reaction, which might be related to the higher solubility of FA than gaseous hydrogen in a polar water solvent. The hydrogen from FA dehydrogenation on the catalyst surface could directly reduce vanillin, while the gaseous hydrogen has to be dissolved into the catalytic system for the reaction. Additionally, the MMP selectivity in the HDO with gaseous hydrogen is only 41.1%, much lower than that with FA (99.8%). Higher activities/selectivities in the HDO using FA than gaseous hydrogen should are important for potential application of FA.



Figure 4. (A) Catalytic data of $Au-Pt/CeO_2$ for the HDO of vanillin in the recyclability test.

Figure 4 shows the recyclability tests for the HDO of vanillin with FA over Au-Pt/CeO₂. The catalyst can be easily recycled by filtration. Notably, the recyclable catalyst gives an almost stable conversion of vanillin (65.5-68.4%) and a good selectivity to MMP (>98.7%), indicating the excellent recyclability of the Au-Pt/CeO₂ catalyst. The carbon balances in these reactions are greater than 98.5%. The leaching of Au and Pt is negligible during the recycling test, as confirmed by ICP analysis, which should be due to the strong interaction between the metal nanoparticles with CeO₂.^{11b}

In summary, an alternative process for the Aselective hydrogenolysis of C=O bonds using FA aslathydrogenCsource over the bimetallic Au-Pt/CeO₂ catalyst has been developed. The excellent performance of Au-Pt/CeO₂ is related to the catalyst synergy for both the dehydrogenation of FA to active hydrogen and the hydrogenolysis of C=O species. The strategy in this work would be helpful for developing green processes for selective hydrogenolysis in the future.

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