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Au/CNTs catalyst for highly selective hydrodeoxygenation of vanillin at the water/oil interface†

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Au/CNTs assembled at the interfaces of a Pickering emulsion are reported, for the first time, exhibiting good catalytic activity and 100% selectivity for the hydrodeoxygenation of vanillin to *p*-creosol under mild reaction conditions. Simultaneous reaction and separation of the target products are achieved, which leads to substantial simplification of the separation and purification process for bio-oil upgrading.

With increasing environmental concerns, the development of highly selective reaction systems using heterogeneous catalysts is greatly desired. In selective hydrogenation reactions, gold nanoparticle catalysts have recently drawn considerable interest owing to their fascinating unique properties compared with those of conventional hydrogenation catalysts based on Pt group metals.[1] These reactions involve hydrogenations of unsaturated carbonyl compounds to unsaturated alcohols,[2–6] nitroaromatics to amines,[7,8] alkynes to alkenes,[9–11] deoxygenation of epoxides to alkenes[12–15] and so on. Therefore, it is important to explore new applications of gold catalysts for high efficiency liquid-phase organic transformations.

Bio-oil, produced by fast pyrolysis of biomass, is a promising second-generation renewable energy carrier. However, due to its high oxygen content and instability, the direct use of bio-oil as a liquid fuel is currently not feasible. Hydrodeoxygenation is considered to be the most important and promising method for bio-oil upgrading.[16–19] Conventional hydrogenation catalysts are sulfided NiMo and CoMo catalysts.[20] However, the process conditions are rather severe, which leads to the low energy efficiency. Therefore, there is a strong incentive to develop catalysts that operate under mild reaction conditions while still producing a modified bio-oil with improved properties. Owing to the high catalytic activities of noble metal catalysts, a series of noble metal catalysts have been employed recently to investigate their hydrogenation effects on bio-oil upgrading, such as Pt,[21–23] Ru,[24–28] and Pd[29–33] catalysts. However, the catalytic properties of gold nanoparticles for the hydrodeoxygenation of bio-oil compounds have been somewhat neglected. Bio-oil is a complex liquid formed by two immiscible phases (aqueous and organic) and diffusion limitations between aqueous phase and organic phase reduce the catalytic activity and selectivity of the employed catalysts. On the other hand, the separation and recycling issues of products and reagents increase the cost of operation. Therefore, the development of methods that allow a convenient separation and recycling of catalysts, products and reagents is a key issue in this research area.

In emulsion catalysis, reactions are carried out in a biphasic mixture of two immiscible solvents, and emulsifiers were added to enhance the interfacial surface area by emulsification, which could enhance the mass transfer of molecules between different phases. Surfactants were conventionally used as emulsifiers, which are difficult to separate and recover from the final mixtures. It has been reported that solid particles can be used to stabilize aqueous-oil emulsions, which are called Pickering emulsions.[34–40] The catalytic properties of Pickering emulsions catch the eyes of researchers in recent years.[41–52] Carbon nanotube supported metal nanohybrids have been proved that they could act as both recoverable emulsifiers and catalysts in our previous work.[43,44] The novel catalytic applications of carbon nanotube supported metal nanohybrids are waiting for exploring.

Vanillin, one typical oxygen-containing phenolic compound of bio-oil, was selected as the model compound to explore the catalytic properties of carbon nanotube supported gold catalyst for bio-oil upgrading because of its three different types of oxygenated functional groups (aldehyde, ether, and hydroxyl) and its partial solubility in both the organic and aqueous

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phases just as bio-oil. Herein we report for the first time that carbon nanotube supported gold catalyst, assembled at the interfaces of water-oil biphase, show excellent activity and especially 100% selectivity for the hydrodeoxygenation of vanillin to the target product of *p*-creosol under mild reaction conditions. Simultaneous reaction and separation of the target products are achieved, which leads to a substantial simplification of the separation and purification process.

The Au/CNT and Au/AC catalysts were prepared by a sol immobilization method.[53,54] Details of the preparation process can be found in the ESI.† A typical TEM image and the particle size distribution of the Au/CNT catalyst (Fig. 1) show that gold particles with an average size of 3.8 nm are highly dispersed on the surface of CNTs, which is consistent with the XRD result (Fig. S1†). According to a typical TEM image and the particle size distribution of the Au/AC catalyst (Fig. S2†), the average size of gold particles is 5.3 nm and the sintering of gold nanoparticles could be found giving a broad particle size distribution from 2.25 nm to 12.75 nm. ICP analysis shows that the actual loading of gold in the Au/CNT and Au/AC catalysts are 0.44 wt% and 0.48 wt%, respectively.

The hydrodeoxygenation of vanillin to *p*-creosol was used as a probe reaction to explore the catalytic application of the Au/CNT catalyst to phenolic hydrodeoxygenation, as illustrated in Scheme 1. The effect of catalyst supports, solvents, and bi-solvents on the catalytic activity of Au/CNTs for the hydrodeoxygenation of vanillin was studied, as summarized in Table 1. The catalytic activity of CNT supported Au catalyst is higher than the AC supported one (Entries 4 and 5), indicating that CNT is a suitable support for the Au catalyst for the vanillin hydrodeoxygenation reaction. According to the TEM images and the particle size distributions of the Au/CNT and Au/AC catalysts, a narrow particle size distribution and small average size of gold particles are obtained using CNT as catalyst support compared with AC, which could be one possible reason for the higher catalytic activity of Au/CNTs. Under the identical reaction conditions, the catalytic activity of Au/CNTs in water is higher than that in decalin (Entries 1 and 6). To explore the catalytic activity of the Au/CNTs catalyst in the aqueous and organic bi-phase reaction system of bio-oil, bi-solvents of decalin and water were employed and the proportion of bi-solvents on the effect of the catalytic activity was investigated. It should be noted that the target product selectivity to *p*-creosol reaches up to 100% and it is independent on the solvent system, indicating that Au/CNTs is a highly selective catalyst for the hydrodeoxygenation of vanillin to *p*-creosol. Results show that the proportion of bi-solvents has effect on the conversion of vanillin. When 20 mL of decalin and 20 mL of H_2O are used as bi-solvents, the highest yield of the target product of *p*-creosol is achieved. With the further increase of the water proportion in the bi-solvents, the yield of *p*-creosol begins to decrease, which implies that there is a proper solvent proportion to obtain the highest yield of the target product in the aqueous and organic bi-phase reaction system. According to our experimental results, it can be found that highly efficient hydrodeoxygenation of vanillin over Au/CNTs are achieved with a nearly full conversion of vanillin and the *p*-creosol selectivity of 100% under mild reaction conditions (1 MPa, 150 °C). In order to rule out the possibility that residual metal traces in CNTs catalyze the reaction itself, the blank reactions were performed, where the catalytic activity of the modified CNTs was tested for the hydrodeoxygenation reaction of vanillin. The conversion of vanillin is not detected, which reveals that gold nanoparticles instead of residual metal traces are active for the hydrodeoxygenation reaction.

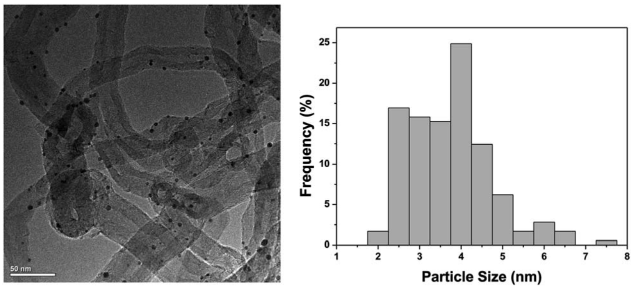
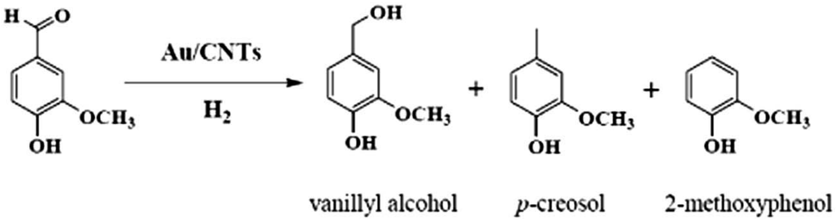


Fig. 1 TEM image and particle size distribution of the Au/CNT catalyst *via* sol immobilization method.

The effect of reaction temperature on the catalytic activity of Au/CNTs for the hydrodeoxygenation of vanillin is shown in Table 2. Results show that reaction temperature has a significant impact on chemoselectivity. At 50 °C, the product is vanillyl alcohol. At 100 °C, the selectivity of *p*-creosol increases to 19%, which is due to the hydrogenolysis of vanillyl alcohol. At 150 °C, hydrogenolysis becomes the dominant reaction path, giving the selectivity of *p*-creosol of 100%. The turnover number measured at 150 °C after the first 0.5 h of reaction is about 150 h^{-1}. Though the catalytic activity of Au/CNTs is lower than the best-performing ones reported in the literature,[42] but the hydrodeoxygenation selectivity of Au/CNTs is excellent. At 200 °C, the selectivity of *p*-creosol decreases to 75%, and the decarbonylation of the aldehyde group is detected which gives the selectivity of 2-methoxyphenol of 25%, indicating that the decarbonylation of the aldehyde group is promoted at high temperature.

Evolution of reactant and products concentration with reaction time at 150 °C is shown in Fig. 2a. Vanillyl alcohol has a concentration peaking after about 0.5 h of reaction, and meanwhile the concentration of *p*-creosol increases gradually. The results imply that vanillyl alcohol is an intermediate product and subsequently it is consumed by hydrogenolysis to form *p*-creosol. The partition of reactant and products in the organic and aqueous phases after 0.5 h of reaction is given in Fig. 2b. The GC analysis results show that vanillin alcohol is highly soluble in the aqueous phase, and the target product of *p*-creosol is much more soluble in the oil phase. Therefore, the formed *p*-creosol migrates to the organic phase upon formation. In contrast, vanillin alcohol remains in the aqueous phase and continues reacting. The results illustrate that the simultaneous reaction and separation of the products are achieved in the formed Pickering emulsions, which leads to drastically simplify the isolation and purification stages.



Scheme 1 Hydrogenation of vanillin over Au/CNTs.

Table 1 Effect of catalyst supports, solvents, and bi-solvents on the catalytic activity of the supported Au catalysts for the hydrodeoxygenation of vanillin[a]

Entry	Decalin/H_2O (mL/mL)	Conversion (%)	Selectivity (%)	
			p-Creosol	Vanillyl alcohol
1	40/0	89	100	0
2	30/10	94	100	0
3	20/20	98	100	0
4	10/30	89	97	3
5[b]	10/30	74	100	0
6	0/40	97.5	97	3

[a] Reaction conditions: vanillin (0.1 mmol), Au/CNTs (Au: 0.68 mol%), 150 °C, $p(H_2) = 1$ MPa, 8 h. [b] Reaction conditions: vanillin (0.1 mmol), Au/AC (Au: 0.74 mol%), 150 °C, $p(H_2) = 1$ MPa, 8 h.

Table 2 Effect of reaction temperature on the catalytic activity of Au/CNTs for the hydrodeoxygenation of vanillin[a]

T (°C)	Conversion (%)	Selectivity (%)		
		Vanillyl alcohol	*p*-Creosol	2-Methoxyphenol
50	41	100	0	0
100	75	81	19	0
150	94	0	100	0
200	100	0	75	25

[a] Reaction conditions: vanillin (0.1 mmol), Au/CNTs (Au: 0.68 mol%), solvent (decalin 20 mL, H_2O 20 mL), $p(H_2) = 1$ MPa, 6 h.

After each reaction period, the emulsion was broken by filtering out the Au/CNTs catalyst. The filtered Au/CNTs catalyst was washed with ethanol and dried at 70 °C under vacuum. The recycling experiment was performed to test the stability of the prepared Au/CNTs catalyst at 150 °C for 6 h. The recycled Au/CNTs catalyst shows that the conversion of vanillin slightly decreases from 94% to 87%, the selectivity of *p*-creosol decreases from 100% to 88%, and the selectivity of vanillyl alcohol increases to 12%, respectively. With the increase of reaction time, the conversion of vanillin and the selectivity of *p*-creosol will further increase using the recycled Au/CNTs catalyst. Therefore the prepared Au/CNTs catalyst is a convenient separation and recycling catalyst.

The process and mechanism of the catalytic reactions were studied in detail. Fluorescence microscopy can be used to determine the distribution of the amphiphilic catalysts in the emulsion system.[44,55,56] Herein, fluorescently labeled probes (Au/CNTs-P) was prepared to investigate the dispersion of Au/CNT nanoparticles in the multiphase reaction system. The preparation procedures are given in the ESI.† Fluorescence microscope image of the reaction system shows that Au/CNT nanoparticles are mainly distributed on the surfaces of the emulsion droplets forming a Pickering emulsion, as shown in Fig. 3a. The formed Pickering emulsion provides higher interfacial surface area where the reaction takes place to eliminate the limitation of the mass transfer, which has been justified by the theoretical study of the reference.[51] Meanwhile, the formed Pickering emulsion enhances hydrogen concentration at the interface because hydrogen has higher solubility in organic phase than in water. Vanillin and vanillin alcohol are highly soluble in the aqueous phase and the target product of *p*-creosol resulting from hydrogenolysis of vanillin alcohol is much more soluble in the organic phase. As a result, the oil-soluble compound, which is valuable as fuel component, can be readily migrated to the product system upon formation. Schematic

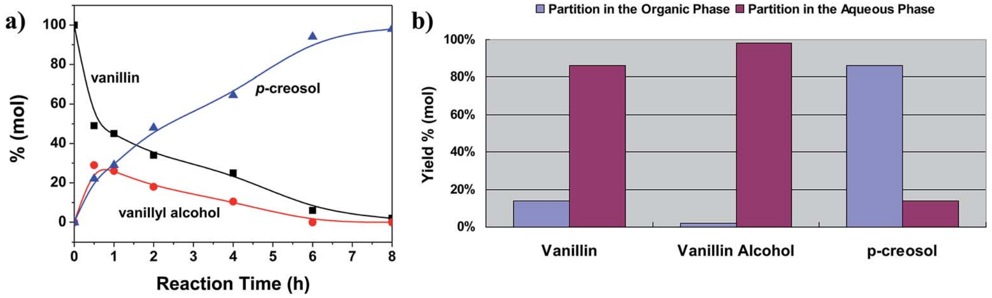


Fig. 2 (a) Evolution of reactant and products concentration with reaction time and (b) partition of reactant and products in the organic and aqueous phases after 0.5 h of reaction. Reaction conditions: vanillin (0.1 mmol), Au/CNTs (Au: 0.68 mol%), solvent (decalin 20 mL, H_2O 20 mL), 150 °C, $p(H_2) = 1$ MPa.

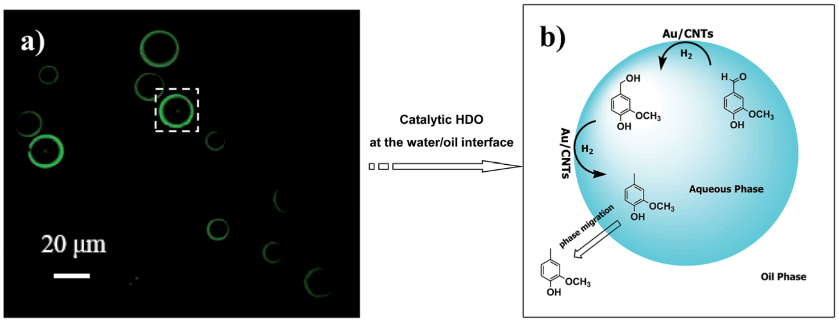


Fig. 3 (a) Fluorescence microscope image of the Pickering emulsion stabilized by Au/CNT nanoparticles and (b) schematic illustration of the hydrodeoxygenation of vanillin over Au/CNTs at the water/oil interface of the Pickering emulsion.

illustration of the hydrodeoxygenation of vanillin over Au/CNTs at the water/oil interface of the Pickering emulsion was shown in Fig. 3b. Similar studies on the unique properties and functions of Pickering emulsion stabilized by solid catalysts have been conducted.[42–44] The study presented here will provide new eyesight on the unique properties of gold nanoparticles and expand the catalytic applications of Pickering emulsion stabilized by solid catalysts.

In conclusion, effective catalytic hydrodeoxygenation of vanillin to *p*-creosol under mild reaction conditions has been realized, in which carbon nanotube supported gold nanoparticles function both as efficient catalysts and recoverable emulsifying agents. According to the direct fluorescence image of the reaction system, the Au/CNT catalyst is distributed mainly on the surface of the emulsion droplets, forming a Pickering emulsion. Simultaneous reaction and separation of the products are achieved in the constructed emulsions, which has great potential in the simplifications of the isolation and purification stages for bio-oil refining. Further studies of the bio-oil hydrogenation performance of supported gold catalysts are currently in progress.

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