



Short Communication

Hydrodeoxygenation of vanillin over carbon nanotube-supported Ru catalysts assembled at the interfaces of emulsion droplets

Xiaomin Yang^a, Yu Liang^a, Yanyan Cheng^a, Wei Song^a, Xiaofeng Wang^{a,c,*}, Zichen Wang^{a,**}, Jieshan Qiu^b^a College of Chemistry, Jilin University, Changchun 130012, China^b Carbon Research Laboratory, State Key Lab of Fine Chemicals, Dalian University of Technology, Dalian 116023, China^c State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, College of Chemistry, Jilin University, Changchun 130012, China

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ABSTRACT

Carbon nanotube supported ruthenium catalysts, assembled at the water/oil interfaces, show excellent activity and selectivity for the hydrodeoxygenation of the bio-oil model compound of vanillin under mild conditions (1 MPa, 150 °C). Based on a direct fluorescence image, the Ru/CNT catalysts are mainly distributed 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 have great potential in the simplifications of the isolation and purification stages for bio-oil refining.

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1. Introduction

Bio-oil, a liquid fuel from fast pyrolysis of lignocellulosic biomass, is one of the most promising renewable fuels to replace fossil fuels. It is crucial to upgrade bio-oil to accomplish this goal. Via the thermal processing, lignin breaks down to produce high concentrations of phenolic molecules (phenol, guaiacol, syringol and their derivatives), most of which are already in the gasoline range and require a deoxygenation process to improve the fuel properties [1]. Phenolic compounds represent a significant fraction of the biomass pyrolysis bio-oil and remain a challenge for upgrading [2]. It has been proposed that the studies of model compound are of crucial importance to establish the conditions for conversion of phenolic-rich compounds [3].

Hydrodeoxygenation is considered to be the most effective method for bio-oil upgrading [2]. Conventional hydrogenation catalysts are sulfided NiMo and CoMo catalysts [4]. The process conditions for the hydrogenation of bio-oil are rather severe, which leads to the formation of substantial amounts of gases and char. As a result, the energy efficiency is relatively low. Therefore, it is an important theme to develop catalysts that operate under mild conditions while still producing a modified bio-oil with improved properties. A series of noble metal catalysts have been employed recently to investigate their hydrogenation effects on bio-oil upgrading, such as Pd [5–9], Ru [10–12], and Pt [13–15] heterogeneous

and homogeneous catalysts. However, bio-oil is a complex liquid only partially soluble in either water or hydrocarbon solvents (i.e. bio-oil is a water–oil biphasic system). The catalysts employed are either hydrophilic or hydrophobic, which cannot disperse uniformly in bio-oil. The diffusion limitations of reactants between aqueous phase and organic phase will reduce the catalytic activities of the employed catalysts. Meanwhile, the separation and recycling issues increase the cost of homogeneous catalysts. Therefore, how to enhance the mass transfer of molecules between different phases in bio-oil, and realize the convenient separation and recycling of catalysts is key problems.

In conventional phase-transfer catalysis, reactions are carried out in a biphasic mixture of two immiscible solvents, and surfactants were added to enhance the interfacial surface area by emulsification, which could enhance the mass transfer of molecules between different phases. However, the surfactants are difficult to separate and recover from the final mixtures. Therefore, the development of bifunctional solid materials serving as both emulsifiers and catalysts to achieve the simple separation and the efficient recycling is highly desirable. Solid particles can be used to stabilize aqueous–oil emulsions, which are called Pickering emulsions [16–22]. In recent years, these solid particle-stabilized emulsions catch the eyes of researchers in the field of catalysis [23–32]. Our previous work have revealed that CNTs could act as such kind of bifunctional material serving as both recoverable emulsifier and catalyst support in the aerobic oxidation of alcohols [25], and it is believed that carbon nanotube supported metal catalysts will be of wide use in the field of emulsion catalysis.

Vanillin (4-hydroxy-3-methoxybenzaldehyde), one typical oxygen-containing phenolic compound of pyrolysis oil derived from the lignin

* Correspondence to: X. Wang, College of Chemistry, Jilin University, Changchun 130012, China. Tel./fax: +86 431 85155358.

** Corresponding author. Tel./fax: +86 431 85155358.

E-mail addresses: wangxf103@jlu.edu.cn (X. Wang), wangzc@jlu.edu.cn (Z. Wang).

fraction, was appealing for study because of its three different types of oxygenated functional groups (aldehyde, ether, and hydroxyl) and its partial solubility in both the organic and aqueous phases as bio-oil. Therefore, the vanillin was commonly used as a model compound to explore the catalytic application of catalysts to bio-oil upgrading. Herein we report that CNT-supported ruthenium catalysts, assembled at the interfaces of emulsion droplets, show excellent activity and selectivity for the hydrodeoxygenation of vanillin under mild conditions. Simultaneous reaction and separation of the target products are achieved, which leads to a substantial simplification of the separation and purification process.

2. Experimental

2.1. Materials

CNTs with a diameter of 10–20 nm, a length of 1–2 μm , and a N_2 surface area of 151 m^2/g were purchased from Shenzhen Nanotech Port Co., Ltd. (Shenzhen, China). Before use, pristine CNTs were refluxed in a mixture of HNO_3 , H_2SO_4 , and deionized water (volume ratio of 2:1:1) at 120 $^\circ\text{C}$ for 4 h, then filtered and washed with deionized water until the pH value of the filtrate reached 7, then dried under vacuum. All reagents used in this work were of analytical grade.

2.2. Catalyst preparation and characterization

The Ru/CNT catalysts were prepared by a wetness impregnation method. The oxidized CNTs were impregnated in an aqueous solution of RuCl_3 under ultrasonic conditions for 30 min, and then the mixture was incubated at room temperature for 12 h. The CNT-supported RuCl_3 samples were dried at 110 $^\circ\text{C}$ for 12 h under vacuum, and reduced at 400 $^\circ\text{C}$ in flowing hydrogen for 2 h, and then cooled to room temperature in Ar, obtaining Ru/CNT catalysts. Transmission electron microscopy (TEM) examination was conducted using a JEM-2100F equipped with a CCD camera operated at 200 kV.

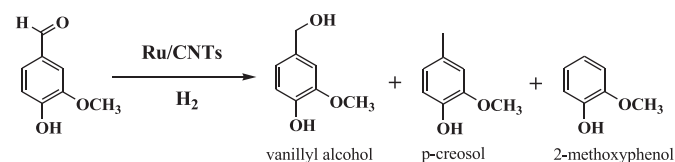
2.3. Preparation of fluorescently labeled probes (Ru/CNTs-P)

Procedures for the preparation of FITC-labeled Ru/CNTs are as follows. The Ru/CNT catalysts were reacted with hexamethylenediamine in the presence of EDC (1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride) and NHS (N-hydroxysuccinimide) to afford a linker between the CNTs and the subsequent fluorescent probe. Briefly, 2 mg Ru/CNTs was mixed with 5 mg hexamethylenediamine and 10 mg NHS/100 mg EDC in 100 mM 2-(N-morpholino)ethanesulfonic acid (MES buffer, pH = 5.5). The mixed solution was stirred at room temperature for 2 h. The Ru/CNTs conjugated with hexamethylenediamine (Ru/CNTs- $\text{CONH}(\text{CH}_2)_6\text{NH}_2$) were obtained by centrifuging at 25,000 rpm to remove the excess reagents. Subsequent reaction of the Ru/CNTs- $\text{CONH}(\text{CH}_2)_6\text{NH}_2$ with fluorescein isothiocyanate (FITC) resulted in the formation of fluorescently labeled Ru/CNTs. Excess FITC was removed by rinsing with 500 μL phosphate-buffered saline (PBS) and centrifuging three times at 25,000 rpm.

2.4. Hydrodeoxygenation of vanillin

The vanillin hydrodeoxygenation reactions were performed in a 100 mL autoclave under stirring. Hydrodeoxygenation of vanillin was used to probe the catalytic hydrogenation activities of the Ru/CNT catalysts, as illustrated in Eq. (1). For a typical run, the reaction was carried out with 5.9 mmol vanillin, 0.2 mol% Ru/CNTs, 20 mL decalin and 20 mL water as bi-solvents, and 1 MPa H_2 at 100 $^\circ\text{C}$ for 3 h. After each reaction, the emulsion was broken by filtering out the catalyst particles. The two liquid phases were separated and analyzed individually by means of GC (2014C, SHIMADZU) and GC-MS (QP 2010 Plus, SHIMADZU).

Eq. (1). Hydrodeoxygenation of vanillin over Ru/CNTs.



3. Results and discussion

The oxidation of CNTs by mixed acid aims to remove amorphous carbon and to increase the number of surface oxygen-containing functional groups that are useful for the metal deposition and dispersion. A typical TEM image and the particle size distribution of the Ru/CNT sample show that Ru particles with an average size of 3.5 nm are highly dispersed on the surface of CNTs, as shown in Fig. 1.

The hydrodeoxygenation of vanillin was used to explore the catalytic application of the Ru/CNT nanohybrids to phenolic hydrodeoxygenation. The effect of solvents on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin was studied, as shown in Table 1. Under identical reaction conditions, the catalytic activity of Ru/CNTs in water is much higher than in decalin. With decalin as solvent, the conversion of vanillin is 24%, and the selectivity of the target product of p-cresol is 11%. When some amount of water is added, substantial increases in the conversion of vanillin and the selectivity of the target product of p-cresol are obtained. 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-cresol is achieved. With the further increase in the water proportion in the bi-solvents, the yield of p-cresol begins to decrease, which implies that there is a proper decalin/water proportion to obtain the highest yield of the target product.

The effect of reaction pressure on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin is shown in Table 2. The Ru/CNT catalysts exhibit good catalytic activities for the hydrodeoxygenation of vanillin even under very mild reaction conditions (100 $^\circ\text{C}$, 0.4 MPa). With the increase of the hydrogen pressure from 0.4 to 1 MPa, the conversion of vanillin increases from 50% to 97%. The selectivity of vanillyl alcohol decreases slightly and meanwhile the selectivity of p-cresol increases correspondingly, which implies that the hydrogenolysis of vanillyl alcohol is promoted at higher reaction pressure.

The effect of reaction temperature on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin is shown in Table 3. Results show that the selectivity of products changes significantly with the increasing of reaction temperature. At 50 $^\circ\text{C}$, the dominant product is vanillyl alcohol. At 100 $^\circ\text{C}$, the selectivity of p-cresol increases to 26%, which might be due to the hydrogenolysis of vanillyl alcohol. At 150 $^\circ\text{C}$, p-cresol becomes the dominant product, and the decarbonylation of the aldehyde group is detected which gives the selectivity of 2-methoxyphenol of 2%. The turnover number measured at 150 $^\circ\text{C}$ after the first 0.5 h of reaction was about 455 h^{-1} . At 200 $^\circ\text{C}$, the selectivity of 2-methoxyphenol increases to 7%, which implies that the decarbonylation of the aldehyde group is promoted at high temperature. According to experimental results, it can be found that high efficient hydrodeoxygenation of vanillin over Ru/CNTs is achieved with a full conversion of vanillin and the p-cresol selectivity of 96% under mild conditions (1 MPa, 150 $^\circ\text{C}$).

The variation of products and reactant distribution with reaction time at 150 $^\circ\text{C}$ is shown in Fig. 2a. Vanillyl alcohol has a concentration peaking after about 0.5 h of reaction, and meanwhile the concentration of p-cresol increases gradually. The results imply that vanillyl alcohol is an intermediate product and subsequently it is consumed by hydrogenolysis to form p-cresol. The partition of the various 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

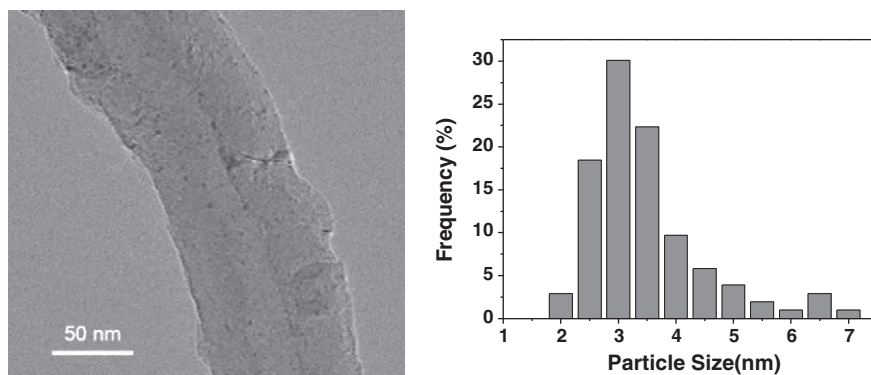


Fig. 1. TEM image and particle size distribution of 6.0 wt.% Ru/CNTs via impregnation method.

highly soluble in the aqueous phase, and the products of *p*-creosol and 2-methoxyphenol are much more soluble in the oil phase. Therefore, the formed *p*-creosol and 2-methoxyphenol will migrate to the organic phase upon formation, preventing further conversion. 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, which have great potential in the simplifications of the isolation and purification stages.

To unravel the nature behind the high catalytic activity of Ru/CNT catalysts for the hydrodeoxygenation of vanillin under the water–oil bi-phasic reaction system, 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. [33,34] Herein, fluorescently labeled probes (Ru/CNTs-P) were prepared to investigate the dispersion of Ru/CNT nanoparticles in the multiphase reaction system. Fluorescence microscope image of the reaction system shows that Ru/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. Meanwhile, the formed Pickering emulsion enhances hydrogen concentration at the interfaces because hydrogen has higher solubility in organic phase than in water. In the Pickering emulsion stabilized by Ru/CNTs, oil/water ratio is a crucial factor in determining the properties and states of emulsion droplets, which would further affect the catalytic performance of the emulsion. Therefore, it is reasonable why there is a proper decalin/water proportion to obtain the highest yield of the target product of *p*-creosol, as shown in Table 1. Vanillin and vanillin alcohol are highly soluble in the aqueous phase and the products of *p*-creosol and 2-methoxyphenol resulting from both hydrogenolysis and decarbonylation are much more soluble in the organic phase. As a result, the oil-soluble compounds, which are valuable as fuel components, can be readily migrated to the product system upon formation. Schematic illustration of the hydrodeoxygenation

of vanillin over Ru/CNTs at the water/oil interface was shown in Fig. 3b. Similar studies on the unique properties and functions of Pickering emulsion stabilized by solid catalysts have been conducted [24,25]. The study presented here will expand the catalytic applications of a Pickering emulsion stabilized by solid catalysts in important processes such as bio-oil refining or fine chemical synthesis.

4. Conclusions

Effective catalytic hydrodeoxygenation of vanillin under mild conditions has been realized, in which carbon nanotube supported ruthenium particles function both as recoverable emulsifying agents and efficient catalysts. According to the direct fluorescence image of the reaction system, the Ru/CNT catalysts are 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 emulsion system, which has great potential in the simplifications of the isolation and purification process for bio-oil refining. Further studies of bio-oil hydrodeoxygenation over Ru/CNTs are currently in progress.

Table 2

Effect of reaction pressure on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin^a.

P (MPa)	Conversion (%)	Selectivity (%)	
		Vanillyl alcohol	<i>p</i> -Creosol
0.4	50	86	14
0.6	66	85	15
0.8	82	77	23
1	97	74	26

^a Reaction conditions: vanillin (5.9 mmol), Ru/CNTs (Ru: 0.2 mol%), solvent (decalin 20 mL, H₂O 20 mL), 100 °C, 3 h.

Table 1

Effect of solvents on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin^a.

Decalin/H ₂ O (mL/mL)	Conversion (%)	Selectivity (%)	
		Vanillyl alcohol	<i>p</i> -Creosol
40/0	24	89	11
30/10	86	74	26
20/20	97	74	26
10/30	99	76	24
0/40	95	87	13

^a Reaction conditions: vanillin (5.9 mmol), Ru/CNTs (Ru: 0.2 mol%), *p* (H₂) = 1 MPa, 100 °C, 3 h.

Table 3

Effect of reaction temperature on the catalytic activity of Ru/CNTs for the hydrodeoxygenation of vanillin^a.

T (°C)	Conversion (%)	Selectivity (%)		
		Vanillyl alcohol	<i>p</i> -Creosol	2-Methoxyphenol
50	100	98	2	0
100	100	74	26	0
150	100	2	96	2
200	100	0	93	7

^a Reaction conditions: vanillin (1.2 mmol), Ru/CNTs (Ru: 1 mol%), solvent (decalin 20 mL, H₂O 20 mL), *p* (H₂) = 1 MPa, 3 h.

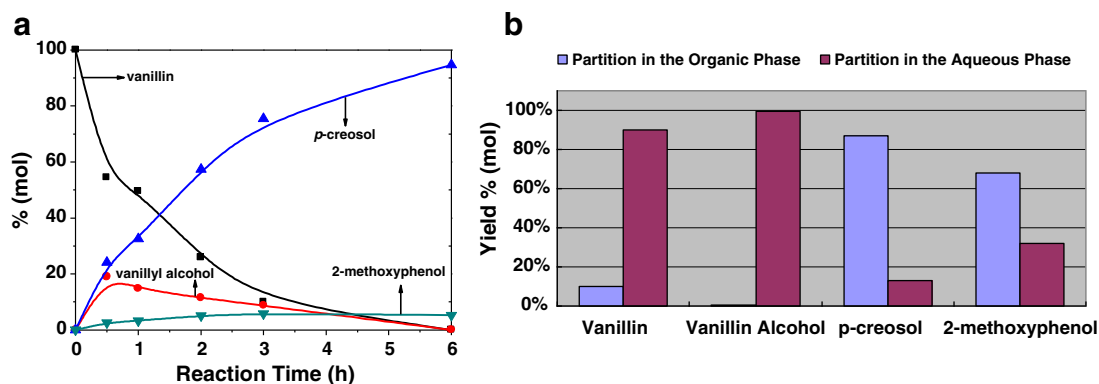


Fig. 2. a) Evolution of reactant and products concentration with reaction time and b) partition of the various products in the organic and aqueous phases after 0.5 h of reaction. Reaction conditions: vanillin (5.9 mmol), Ru/CNTs (Ru: 0.2 mol%), solvent (decalin 20 mL, H₂O 20 mL), 150 °C, p (H₂) = 1 MPa.

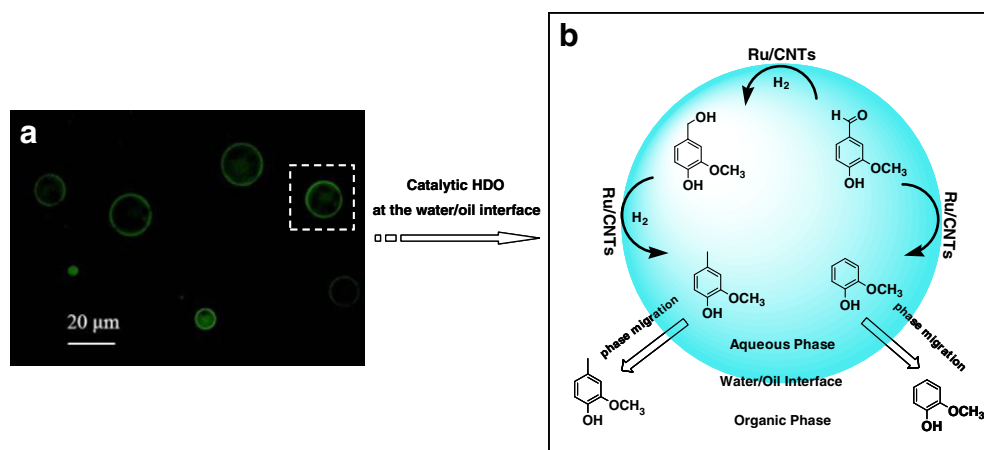


Fig. 3. a) Fluorescence microscope image of the Pickering emulsion stabilized by Ru/CNT nanoparticles and b) schematic illustration of the hydrodeoxygenation of vanillin over Ru/CNTs at the water/oil interface.

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