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Mild electrocatalytic hydrogenation and hydrodeoxygenation of bio-oil derived phenolic compounds using ruthenium supported on activated carbon cloth

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Electrocatalytic hydrogenation (ECH) is an option for stabilizing or upgrading bio-oil that employs mild conditions (≤80 °C and ambient pressure) compared to hydrotreatment. In this study, phenol, guaiacol (2-methoxyphenol), and syringol (2,6-dimethoxyphenol) were chosen as model lignin-like substrates because of their abundance in bio-oil and their high resistance to hydrogenation relative to the carbonyl compounds. Cathodic reduction was catalyzed by ruthenium supported on activated carbon cloth (Ru/ACC), a novel electrocatalyst. Incipient wetness impregnation and cation exchange methods were employed to prepare the electrocatalyst using three different ruthenium precursors. Scanning electron microscopy revealed that ruthenium nanoparticles within the range of 10 to 20 nm were deposited on the support by both catalyst synthesis methods. Catalysts prepared by cation exchange were more active than those prepared using incipient wetness impregnation, presumably because of support surface functionalization by the oxidation pretreatment. When using incipient wetness impregnation, catalysts synthesized with precursor hexaammineruthenium(III) chloride showed the best activity and electrochemical efficiency, followed by catalysts prepared with ruthenium(III) chloride and ruthenium(III) nitrosyl nitrate. The Ru/ACC electrocatalyst reduced guaiacol, phenol and syringol with similar electrochemical efficiencies, but temperature was an important variable; the electrochemical efficiency for guaiacol reduction increased from 8% at 25 °C to 17% at 50 °C, but then dropped back to 10% at 80 °C. Solution pH also affected catalyst activity and product selectivity, with acidic conditions favoring guaiacol conversion, electrochemical efficiency and cyclohexanol selectivity.

Introduction

Bio-oil, the liquid product from fast pyrolysis of biomass, is a promising sustainable material for transportation fuel production. However, the raw bio-oil is not ready for end use because of its tendency to polymerize and to corrode metal containers and pipes. This reactivity is largely due to the presence of unsaturated oxygenates such as aldehydes, ketones, carboxylic acids and phenols.^{1,2} Thus, for long-term storage and any further upgrading, bio-oil must first be stabilized in order to minimize downstream coke formation, catalyst deactivation and carbon loss to the gas phase.³

Catalytic hydrogenation has been shown to be a good method for bio-oil stabilization, converting most aldehydes, ketones, phenols and sugars to saturated alcohols and polyols.3,4 However, such hydrogenation is typically run at temperatures over 100 °C, 3,5,6 high enough to cause accelerated bio-oil polymerization.7 We propose instead electrocatalytic hydrogenation (ECH) which operates at less than 80 °C and ambient pressure; these mild conditions minimize both polymerization and catalyst deactivation by coke formation. During ECH, reduction of protons from solution forms atomic hydrogen in situ on the catalytic electrode surface where it is needed to hydrogenate organic substrates. This strategy simplifies processing and avoids the need for externally supplied, fossil-based hydrogen gas and associated handling equipment. Ideally, the needed electricity would come from carbon-free sources such as solar, wind, or even nuclear power. Electrocatalytic hydrogenation thus represents a green, carbon-retentive pathway for stabilization (and potentially further upgrading) of biomass-derived bio-oil to produce fuels and chemicals.

Lignin-derived phenolic compounds account for 25-30% of the raw bio-oil,^{8,9} but have a lower oxygen content (22–30 *vs.* 33–40 wt% for raw bio-oil, dry basis).¹⁰ Compared to other bio-oil components such as aldehydes and ketones, phenolics are

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Sample name	Preparation method	Precursor	BET surface area $(m^2 g^{-1})$	Micropore area $(m^2 g^{-1})$	Micropore volume $(cm^3 g^{-1})$	
Blank ACC 3-IW-Cl 3-IW-NH3 3-IW-NO 6.6-CE-NH3	DI water wash H ₂ reduction at 220 °C and 500 psi Incipient wetness Incipient wetness Incipient wetness Cation exchange	— Ru(NH ₃) ₆ Cl ₃ Ru(NO)(NO ₃) ₃ Ru(NH ₃) ₆ Cl ₃	1010 904 800 879 341	685 599 551 612 139	0.30 0.27 0.26 0.28 0.06	

Table 1 BET surface area, micropore area and micropore volume of the blank ACC and the catalysts

more resistant to hydrogenation.¹¹ Therefore, successful ECH of phenol is a significant step towards its application for raw bio-oil stabilization.

Previous research^{12–17} on ECH of phenolic compounds has shown that large cathode surface areas are usually necessary to achieve high reaction rates. Electrodes made with pressed metallic powder particles have been successfully used,^{18,19} but their mechanical strength is weak without addition of a binding material²⁰ and much surface area is lost in the powder pressing step. To overcome the disadvantages of pressed electrodes, Menard and co-workers developed a new electrode by entrapping catalytic powders into reticulated vitreous carbon (RVC).^{12,21–23} This is an effective system to test different classical catalytic hydrogenation catalysts using electrochemistry.^{12,24} However, the catalyst powders are mobile, so the amount of active catalysts involved in the actual hydrogenation is difficult to measure and the mechanically fragile electrode may be destroyed by strong stirring.

To develop a well-defined catalytic cathode, we immobilized ruthenium onto activated carbon cloth (ACC) using incipient wetness impregnation and cation exchange methods. As a catalyst support, the advantages of ACC include high rates of adsorption, high surface area (1000 to 2100 m² g⁻¹)²⁵ and potential for easy *in situ* regeneration.²⁶ Ruthenium supported on carbon has been shown to be an efficient catalyst for classical chemical hydrogenation of various organics such as phenols,²⁷ organic acids,^{28,29} amino acids³⁰ and bio-oil itself.³¹

In this investigation, ECH of guaiacol was assessed in terms of reactivity, product selectivity and electrochemical efficiency (E.E.) as functions of catalyst parameters (*e.g.* preparation methods, precursor types, ruthenium content, type of support) and reaction conditions (temperature and pH). In order to demonstrate chemical reduction on a range of phenolic compounds, the ECH of phenol and syringol were also investigated using the same conditions as for guaiacol ECH.

Results and discussion

Characterization of catalysts

As mentioned in the introduction, a high surface area cathode is necessary for the efficient reduction of guaiacol. The catalytic cathodes' BET surface area, micropore area and micropore volume were analyzed (Table 1). In order to assess the underlying support properties of the catalyst supports, ACC was pretreated in the same manner (designated the "blank ACC") as the catalyst, by washing with DI water and reducing with hydrogen

at 220 °C and 500 psi. The blank ACC has a surface area of 1010 m² g⁻¹, very similar to the value reported in the literature.³² Compared with other supports used for cathodes,¹² this kind of support has much larger surface area. The majority of the pores are micropores and the volume is $0.30 \text{ cm}^3 \text{ g}^{-1}$ (Table 1). Upon loading with different ruthenium precursors, the supports' micropore volumes decreased, suggesting that some of the micropores were blocked by ruthenium. As shown in Table 1, catalyst 6.6-CE-NH3,† prepared by cation exchange, has a very different surface area and micropore volume than the other catalysts because the support was pretreated in 1 mol dm⁻³ boiling nitric acid for 24 h. According to Pradhan and Sandle,³³ oxidation with nitric acid generates surface oxygen moieties at the entrance of the pores, restricting access of N₂ molecules to the micropores. Thus this type of catalyst shows reduced surface area and micropore volume.

Fig. 1 shows a SEM image of the blank ACC FM100. With its carbon fibers knitted together, the conductivity is very high,³⁴ making it a good electrocatalyst support. Because it is monolithic, filtration or decantation is not needed after the reaction. This flexible support can conveniently be cut and shaped to fit into different kinds of reactors.

SEM images of the catalysts (IW series) prepared by incipient wetness impregnation with precursor Ru(NH₃)₆Cl₃ are shown in Fig. 2(a) and (b). As seen in Fig. 2(a), most of the ruthenium was distributed into white spots larger than 100 nm. Fig. 2(b) shows that the white spots were made of accumulated ruthenium particles. For the cation exchange (CE series) preparations, the HNO₃ pre-oxidation of the ACC fiber surface forms oxygenated functional groups such as carboxylic acid, lactone, phenolic hydroxyl and quinone groups.³³ When loading the ACC in the ruthenium salt solution, metal cations ion pair with the surface anionic sites. After catalyst reduction under hydrogen, white spots are observed on the ACC fiber (Fig. 2(c)). Magnification of these white spots reveals nanoparticles in the 10-20 nm range. Compared with the IW preparation, these nanoparticles tend to be isolated from each other as opposed to forming a continuous sheet (Fig. 2(d)).

 $[\]dagger$ Catalyst codes are used to refer to each type of catalyst and catalyst preparation method. In 6.6-CE-NH3, the number "6.6" is the ruthenium weight percent, "CE" is the method cation exchange and "NH3" means the precursor is Ru(NH₃)₆Cl₃. For incipient wetness impregnation, "IW" is used to indicate the method. Designations for the other two precursors, RuCl₃ and Ru(NO)(NO₃)₃, are "Cl" and "NO" respectively. For the catalysts (3 wt% Ru) prepared on HCl-washed ACC with RuCl₃ as precursor, the code 3-IW-Cl-AW was used, where "AW" stands for acid washed.

Mechanism of guaiacol electrocatalytic hydrogenation with Ru/ACC

According to Sergeev and Hartwig,³⁵ a detailed reaction mechanism remains unclear, even for an aryl ether hydrogenolysis catalyzed by a well-defined nickel complex. For the present guaiacol cleavage, effected by heterogeneous Ru/ACC catalysts, we follow the lead of Dabo *et al.*²¹ and simply outline the transformation in a manner analogous to that of pi-bond hydrogenation (Scheme 1). Reactions involved in ECH of guaiacol



Fig. 1 SEM image of the blank ACC FM100. Scale bar: 500 µm.

include: formation of adsorbed atomic hydrogen (eqn (1)), adsorption of guaiacol (eqn (2)), reactions between adsorbed guaiacol and adsorbed hydrogen (eqn (3)), demethoxylation of guaiacol (eqn (4)), hydrogenation of phenol to cyclohexanone (eqn (5)) and cyclohexanol (eqn (6)), and desorption of the products (eqns (7) and (8)).^{28,36}

$$H_3O^+ + e^- + M \to M(H) + H_2O$$
 (1)



Scheme 1 Schematic representation of the electrocatalytic hydrogenation mechanism with Ru/ACC, where Y=Z is the unsaturated organic compound, YH–ZH is the hydrogenated product.



Fig. 2 (a) and (b) SEM images of 3-IW-NH3 prepared with incipient wetness impregnation using $Ru(NH_3)_6Cl_3$ as precursor; (c) and (d) SEM images of 5-CE-NH3 prepared with cation exchange method using $Ru(NH_3)_6Cl_3$ as precursor. Scale bar: (a) 100 nm; (b) 100 nm; (c) 1 μ m; (d) 100 nm.



$$2M(H) + \left(\bigcirc OCH_3 \right) M \longrightarrow \left(\bigcirc \right) M + \left(CH_3OH \right) M + M$$
(4)

~ . .

$$4M(H) + \left(\bigcirc H \right) M \longrightarrow \left(\bigcirc H \right) M + 4M$$
 (5)

$$2M(H) + \left(\bigcup_{i=1}^{O} \right)M \longrightarrow \left(\bigcup_{i=1}^{OH} \right)M + 2M$$
 (6)

$$(\bigcirc OH_3) M \longrightarrow OH_3 + M$$
 (7)

$$(\bigcup^{OH}) M \longrightarrow \bigcup^{OH} + M$$
 (8)

Here, M is the metal active site for hydrogen or organic compounds, M(H) is the chemisorbed atomic hydrogen. Besides the reactions listed above, hydrogen desorption *via* the Tafel (eqn (9)) or Heyrovsky (eqn (10)) processes competes with the desired hydrogenation (eqn (3)–(6)) decreasing its electrochemical efficiency (E.E.).^{37,38} As a practical matter, for bio-oil upgrading, this byproduct hydrogen could potentially be captured and used as a valuable reducing agent for further hydrotreatment.

$$M(H) + M(H) \rightarrow H_2 + 2M \tag{9}$$

$$M(H) + H^+ + e^- \to H_2 + M$$
 (10)

Control experiments

The first control experiment used only blank ACC as cathode material; at 80 °C and ambient pressure, no hydrogenation of guaiacol was observed. For this control experiment, there were no metal active sites for atomic hydrogen, and no catalyst for the hydrogenation reaction. Therefore, ACC alone cannot hydrogenate guaiacol.

The second control experiment used 3-IW-NH3 catalyst at 80 °C and ambient pressure, with no current passed. No guaiacol was converted, showing that hydrogen is essential for hydrogenation.

The third control experiment was performed on 3-IW-NH3, with no current passed through the electrochemical cell. However, H_2 gas was supplied by bubbling through the solution at 80 °C and ambient pressure. No conversion of guaiacol was observed either. Catalyst surface-bound atomic hydrogen forms

differently in chemical catalytic hydrogenation vs. ECH. For ECH, atomic hydrogen directly forms on the cathode surface (eqn (1)), so reduction can occur at ambient pressure. For catalytic hydrogenation, H_2 gas must dissolve first, but it is poorly soluble in water, so high pressure is usually needed for aqueous reactions. However, under ambient pressure, the H_2 concentrations in solution and on the catalyst surface would be low. Furthermore, the temperatures used here are much lower than the 125 °C reported by Vispute¹¹ as the lowest temperature where guaiacol starts to be chemically reduced.

ECH of guaiacol using different catalysts: preparation methods and precursor effects

ECH of guaiacol was studied with several different catalysts prepared using two methods (incipient wetness impregnation and cation exchange) with different precursors. Various conditions were employed, including different reaction temperatures, electrolytes and currents. The results were summarized in Table 2. The effects of these conditions on guaiacol conversion, electrochemical efficiency and product selectivities are discussed in detail in the following text.

Products detected using GC/MS include cyclohexanol, *cis*-2-methoxycyclohexanol, *trans*-2-methoxycyclohexanol and phenol (Table 2, Fig. 3). However, phenol only appeared in measurable quantities with 3-IW-NH3, 5-IW-NH3 and 3-IW-NO as cathodes, indicating that most of the catalysts efficiently hydrogenated phenol. The reaction pathway for ECH of guaiacol to the major products is shown in Scheme 2. While demethylation is one of the major reactions in traditional catalytic deoxygenation of guaiacol,³⁹ it is not observed during ECH; demethoxylation dominates instead. Thus ECH of bio-oil retains more carbon in the liquid products than conventional upgrading.

Deoxygenation of oxygenated compounds is one ultimate goal for bio-oil upgrading. Though deoxygenation is difficult at such mild conditions, partial deoxygenation of guaiacol was observed, resulting in two products, cyclohexanol and phenol. Cyclohexanol is a major product while phenol is only an intermediate. Among the catalysts studied, 5-IW-NO and 3-IW-Cl gave the greatest selectivity to cyclohexanol although their guaiacol conversion activities were relatively low (Fig. 4).

When we compared the catalysts with the same nominal ruthenium content (3 wt%), 3-CE-NH3 resulted in slightly higher guaiacol conversion than 3-IW-NH3 (Fig. 4) even though the metal dispersions (measured from hydrogen chemisorption) are very similar. The pretreatment in the cation exchange method functionalizes the support surface by increasing acidic groups, which likely enhances guaiacol adsorption⁴⁰ and thus, electrocatalytic activity.

Ru/ACC catalysts prepared from different precursors using incipient wetness impregnation showed different activities toward ECH of guaiacol. Ru(NH₃)₆Cl₃ exhibited the highest activity among the three precursors, followed by RuCl₃ and Ru(NO)(NO₃)₃. The presence of residual nitrogen on the catalyst and an uneven ruthenium distribution could be responsible for the reduced performance of the catalyst prepared with Ru(NO)-(NO₃)₃.⁴¹ This notion is supported by the blocky accumulations of ruthenium seen in Fig. 5. Similarly, Nurunnabi *et al.*⁴²

Product selectivity (%) Cis-2-Temp. Electrolyte Current Conversion Trans-2- $0.2 \text{ (mol dm}^{-3}\text{)}$ E.E. (%) Catalysts $(^{\circ}C)$ (mA)(%) CH MCH MCH Р 65 ± 7.1 3-IW-Cl 80 100 52 ± 0.4 10 ± 2.1 4.4 ± 2.3 1 HC1 31 ± 4.8 2 3-IW-NH3 80 **HCl** 100 69 ± 1.3 31 ± 2.9 58 ± 3.1 25 ± 3.2 12 ± 0.3 3.7 ± 0.4 3 29 ± 3.1 5-IW-NH3 80 48 ± 8.7 59 ± 11 2.4 ± 2.8 HC1 100 19 ± 4.3 9.8 ± 6.4 4 47 ± 0.9 36 ± 0.0 3-IW-NO 80 HC1 100 38 ± 0.5 9.8 ± 0.5 12 ± 1.0 5.9 ± 0.1 5 5-IW-NO 5.2 ± 0.8 80 HCl 100 53 ± 1.6 19 ± 0.4 72 ± 1.3 22 ± 0.4 6 7 48 ± 2.3 1-CE-NH3 80 HCl 100 52 ± 6.2 19 ± 3.5 37 ± 5.0 14 ± 2.7 80 100 75 ± 3.9 11 ± 2.0 3-CE-NH³ HC1 30 ± 4.3 53 ± 1.4 36 ± 2.3 8 3-IW-Cl 25 **HCl** 100 13 ± 0.4 7.7 ± 1.8 26 ± 0.3 62 ± 6.5 12 ± 6.9 9 3-IW-Cl 50 14 ± 0.0 HC1 100 36 ± 12 17 ± 1.6 30 ± 1.4 56 ± 1.4 10 1.5-CE-NH3 25 HC1 100 51 ± 0.8 19 ± 6.6 25 ± 8.4 59 ± 9.3 16 ± 0.9 50 100 31 ± 4.9 38 ± 0.5 47 ± 2.8 11 1.5-CE-NH3 HC1 60 ± 13 15 ± 2.2 12 3-CE-NH3 80 NaCl 100 64 ± 8.8 20 ± 2.2 42 ± 3.3 42 ± 1.3 17 ± 2.0 13 3-CE-NH3 80 NaOH 100 62 ± 2.4 28 ± 1.0 48 ± 0.2 38 ± 0.5 13 ± 0.6 6.6 ± 0.4 14 3-IW-NH3 80 NaOH 100 45 ± 2.3 20 ± 1.2 46 ± 3.8 36 ± 2.3 11 ± 1.9 15 3-IW-NH3 80 **HCl** 40 71 ± 3.3 27 ± 0.1 61 ± 1.9 28 ± 1.2 11 ± 0.7 16 70 69 ± 0.0 57 ± 0.5 3-IW-NH3 80 HCl 28 ± 3.9 30 ± 0.4 13 ± 0.1 17 3-IW-NH3 80 HC1 130 65 ± 4.2 23 ± 0.6 45 ± 1.3 38 ± 0.8 14 ± 0.5 2.1 ± 0.0 18 3-IW-NH3 80 $60\pm{<}0.01$ $22 \pm < 0.01$ $49 \pm < 0.01$ $14 \pm < 0.01$ HCl 160 $37 \pm < 0.01$

Table 2 Guaiacol conversion, electrochemical efficiency and product selectivities for ECH of guaiacol at various conditions

CH: cyclohexanol; Cis-2-MCH: Cis-2-methoxycyclohexanol; Trans-2-MCH: Trans-2-methoxycyclohexanol; P: phenol.







Scheme 2 Reaction pathway for ECH of guaiacol to the major products; 2-methoxycyclohexanol includes both *cis* and *trans* isomers.

showed low CO conversion during Fischer-Tropsch synthesis with catalysts prepared from $Ru(NO)(NO_3)_3$. Diaz *et al.*⁴³ also reported that Pd/C prepared with a nitrate precursor $(Pd(NO_3)_2)$ showed a lower overall hydrogenation activity.

The electrochemical efficiencies of guaiacol ECH at 80 °C using different catalysts were compared as summarized in Fig. 4.



Fig. 4 Guaiacol conversion and electrochemical efficiency for ECH of guaiacol at 80 °C and ambient pressure using different catalysts with 0.2 mol dm^{-3} HCl as catholyte.



Fig. 5 Ruthenium accumulation for the catalyst 3-IW-NO prepared with incipient wetness impregnation using $Ru(NO)(NO_3)_3$ as precursor. Scale bar: (a) 10 μ m.

Both 3-IW-NH3 and 3-CE-NH3 catalysts show >30% electrochemical efficiency, higher than the 26.3% maximum reported E.E. for phenol ECH, obtained using a Pd catalyst.¹² One possible reason for these high E.E. values is that the present immobilization schemes achieve more intimate metal-support electrical contact.

Temperature effect

The effect of temperature on guaiacol ECH was studied with 0.2 mol dm⁻³ HCl as catholyte for 2 h under a constant current of 100 mA. Three different temperatures, 25, 50 and 80 °C, were studied, all much lower than those used in classical catalytic conversion of phenolic compounds.^{44,45}

The E.E. is a function of the competition between electrocatalytic hydrogenation and hydrogen desorption. Raising the temperature from 25 °C to 50 °C increased E.E. (Fig. 6) from 8% to 17% but further heating to 80 °C dropped it back to 10%. This indicates that electrocatalytic hydrogenation was favored from 25 °C to 50 °C, while hydrogen desorption rates accelerated as temperature increased from 50 °C to 80 °C. Similar E.E. changes on the ECH of indigo to leuco indigo were observed by Roessler et al.,⁴⁶ who found that E.E. rose as temperature was ramped up from 30 °C to 60-80 °C, but then dropped off above this range. However, Dabo et al.21 found continuous E.E. improvement from 25 °C to 75 °C during ECH of 4-phenoxyphenol to phenol over 5% Pd/C in 1 mol dm⁻³ NaOH. Amouzegar and Savadogo⁴⁷ also saw continuous E.E. increases from 5 °C to 40 °C to 60 °C during ECH of phenol to cyclohexanol on platinum dispersed on graphite particles; the E.E. increase from 40 °C to 60 °C, however, was much smaller than that from 5 °C to 40 °C.

Cation exchange prepared catalyst shows good activity toward guaiacol conversion at 25 °C, very similar to that at 50 °C (Fig. 7). However, guaiacol conversion for incipient wetness impregnation prepared catalyst decreased dramatically from 36% to 13% (Fig. 6). Again, catalysts prepared by cation exchange show better performance than those prepared by incipient wetness impregnation.

The effects of temperature on the product selectivities using 3-IW-Cl are shown in Fig. 6. At 80 °C, cyclohexanol was the dominant product, while *cis*-2-methoxycyclohexanol became the largest one at 25 °C and 50 °C. Though the *trans*-2-



Fig. 6 Product selectivities, guaiacol conversion and E.E. for ECH of guaiacol at different temperatures using 3-IW-Cl as cathode. Bars refer to product selectivities. G: guaiacol.

Temperature °C

methoxycyclohexanol isomer was expected to be more stable, the *cis* isomer was always the major product at these studied temperatures. Presumably, during hydrogenation, the aromatic ring lies down on the ruthenium active surface and atomic hydrogens are added to the one face, thus forming *cis*-2-methoxyclohexanol. This phenomenon was also observed when using catalyst prepared by the cation exchange method (Fig. 7). Solladié-Cavallo *et al.*⁴⁸ showed a similar result for hydrogenation of substituted phenols over Ru/Al₂O₃.

Catalyst support effect

Analysis by EDX reveals that there are other elements in the original ACC besides C and O, including Al, Zn and S (Table 3). Some elements, especially S, may have strong chemisorption with ruthenium, blocking active sites and moderating the hydrogenation reaction.⁴⁹ Thus catalyst performance was assessed based on original and demineralized ACC. ACC was demineralized by washing in boiling hydrochloric acid for 3 days, resulting in the decrease of the ash content from 5 wt% to around 0.1 wt%. Catalysts made from original and demineralized ACC supports were compared during ECH of guaiacol using 0.2 mol dm⁻³ HCl as catholyte at 25, 50 and 80 °C (Fig. 8). The trivial differences found indicate that the extra elements in the original ACC do not interfere with the Ru catalytic activity.

pH effect

All experiments discussed above were carried out in 0.2 mol dm^{-3} HCl solution. To probe pH effects, the performance of these



Fig. 7 Product selectivities, guaiacol conversion and E.E. for ECH of guaiacol at different temperatures using 1.5-CE-NH3.

Table 3Energy dispersive X-ray analyses of the original ACC andwashed ACC

	Weight (%)	Weight (%)			
Element	Original ACC	Washed ACC			
С	80.9 ± 0.48	92.0 ± 0.05			
0	12.1 ± 0.03	7.3 ± 0.05			
Cl	_	0.8 ± 0.01			
Al	2.6 ± 0.16	_			
S	0.3 ± 0.06	_			
Zn	4.1 ± 0.29	—			

catalysts in neutral (0.2 mol dm⁻³ NaCl as catholyte) and basic solution (0.2 mol dm⁻³ NaOH as catholyte) was examined here. All other conditions were the same as the runs with 0.2 mol dm^{-3} HCl as electrolyte. When using 3-CE-NH3 and 3-IW-NH3 as catalysts, guaiacol conversion was favored under acidic conditions (Fig. 9). Guaiacol adsorption onto catalyst sites (eqn (2)) is a key step in the hydrogenation reaction. The ionization state of guaiacol varies with solution pH, potentially affecting its adsorption characteristics. In acidic and neutral conditions, guaiacol $(pK_a = 9.9)^{50}$ is mainly a neutral molecule, while deprotonation of guaiacol to form phenolate anion occurs under alkaline conditions. As ionic forms prefer to remain in the polar solution and the carbon support preferentially adsorbs neutral species, adsorption onto the support is reduced. Furthermore, the resonance delocalization in the phenolate form shifts the thermodynamics and makes the ECH of guaiacol more difficult.¹² Thus, greater guaiacol conversion was observed in acidic than in alkaline solution. A similar effect on E.E. was observed, showing higher E.E. under acidic conditions. Likewise, selectivity to cyclohexanol was higher under acidic conditions, indicating a higher level of demethoxylation of guaiacol (Fig. 9).

Current density effect

Current density effects on guaiacol conversion, electrochemical efficiency and product selectivities were studied for guaiacol



Fig. 8 ECH of guaiacol using catalysts prepared on HCl washed ACC (3-IW-Cl-AW) and original ACC (3-IW-Cl) with 0.2 mol dm^{-3} HCl as electrolyte at different temperatures.

 \square CH \square Cis-2-MCH \square Trans-2-MCH \square P \neg G conversion \rightarrow E.E. 100% 80% 60% 40% 20% 0% 3-IW-NH3 3-IW-NH3 3-CE-NH3 3-CE-NH3 3-CE-NH3 acidic neutral alkaline acidic alkaline

Fig. 9 ECH of guaiacol using catalysts 3-CE-NH3 and 3-IW-NH3 under different pH conditions at 80 °C and ambient pressure. Bars refer to product selectivities.

ECH at 80 °C and ambient pressure with 0.2 mol dm⁻³ HCl as catholyte. Because it was difficult to measure the actual effective electrode surface area, current is directly used without calculating current density. As shown in Fig. 10, guaiacol conversion and electrochemical efficiency are invariant when current is in the range of 40 mA to 100 mA and above 100 mA, both decrease slightly. The current density effect on guaiacol conversion and E.E. is not very obvious for ECH of guaiacol using Ru/ACC as cathode because the surface area of the cathode is relatively high and the absolute change of the current density is very small. Additionally, product selectivities are only slightly affected. Selectivity for cyclohexanol formation is higher for the current range from 40 mA to 100 mA than 130 mA and 160 mA.

ECH of other phenolic compounds: phenol and syringol

In addition to guaiacol, both phenol and syringol served as lignin-derived model compounds. ECH of these two model compounds was carried out in 0.2 mol dm⁻³ HCl catholyte solution at 80 °C and ambient pressure. ECH of phenol generates two products, cyclohexanol and cyclohexanone (Table 4). Cyclohexanol is the major product, consistent with separate observations of rapid, efficient reduction of cyclohexanone to cyclohexanol. Five major products are obtained from ECH of syringol: cyclohexanol, *cis*-2-methoxycyclohexanol, *trans*-2-methoxycyclohexanol, 2-methoxycyclohexanone and guaiacol (Table 4); these products are similar to those obtained from ECH of guaiacol and point to demethoxylation as the first step from syringol.

Equal amounts of charge were passed for ECH of phenol and syringol, but ECH of phenol requires fewer electrons than ECH of syringol, resulting in higher conversion of phenol. The π -system's electron density increases as the methoxylation degree increases from phenol to syringol, so syringol should be more difficult to reduce. However, similar E.E. values were obtained for ECH of both model compounds.

Catalyst stability

Catalyst deactivation is an important concern during catalytic bio-oil upgrading. To evaluate the catalyst stability during ECH



Fig. 10 ECH of guaiacol using catalyst 3-IW-NH3 under different currents at 80 °C and ambient pressure. Bars refer to product selectivities.

			Product selectivity (%)					
Reactants	Conversion (%)	E.E. (%)	Cyclohexanol	Cyclohexanone	Cis-2- methoxycyclohexanol	Trans-2- methoxycyclohexanol	2- methoxycyclohexanone	Guaiacol
Phenol Syringol	89 58	29 29	99 35	1 0	27	9	13	16

Table 4 ECH of phenol and syringol using 1.5-CE-NH3 at 80 °C and ambient pressure with 0.2 mol dm⁻³ HCl as catholyte



Fig. 11 Time course of guaiacol conversion for the initial reaction, the first and the second reuse of the catalyst 3-IW-NH3 using 0.2 mol dm⁻³ HCl as catholyte at 80 °C and ambient pressure.

of phenolic compounds, the catalysts were reused two times. After each use of the catalytic cathode, it was washed overnight using DI water, followed by drying under vacuum in the dessicator. At the beginning of the next experiment, pre-electrolysis was carried out at 80 mA for 10 min. As shown in Fig. 11, guaiacol conversion did not change significantly with each reuse of the catalyst. Also, ICP-OES analysis of the solution showed that there was no significant ruthenium leaching into the solution. This observed stability of the Ru/ACC catalytic cathode is likely due to the mild conditions required for effective ECH of guaiacol.

Conclusions

This work shows that Ru/ACC is an efficient catalyst for electrocatalytic hydrogenation and partial hydrodeoxygenation of phenolic compounds under mild conditions compared to other catalytic reductions, including other ECH schemes. Catalyst comparisons demonstrated that Ru/ACC catalysts prepared via the cation exchange method show much better activity than those prepared by incipient wetness impregnation. When using incipient wetness impregnation, Ru(NH₃)₆Cl₃ showed the highest activity among the three precursors studied. Within the range 25-80 °C, higher temperature was found to favor guaiacol conversion and deoxygenation. Lower pH resulted in higher guaiacol conversion and electrochemical efficiencies. Furthermore, phenol and syringol can be hydrogenated using Ru/ACC catalysts, showing electrochemical efficiencies similar to those found for guaiacol. Based on the results from this investigation, electrocatalytic hydrogenation with Ru/ACC is a potential strategy for ambient pressure hydrogenation of phenolic compounds at low temperatures, and it may offer significant advantages for future bio-oil stabilization and upgrading.

Experimental

Reagents and materials

Guaiacol (98+%) and 2-methoxycyclohexanol (99%) were obtained from Alfa Aesar. 2,6-Dimethoxyphenol (syringol) (99%) was purchased from Sigma-Aldrich and cyclohexanol (99+%) was from Mallinckrodt. All of these compounds were used as received without further purification. Phenol, from Mallinckrodt, was purified by sublimation to remove moisture.

Zorflex® ACC FM100 was obtained from the Calgon Carbon Co. Ruthenium(III) chloride (RuCl₃) hydrate (99.9% PGM basis, Ru 38% min), hexaammineruthenium(III) chloride (Ru(NH₃)₆Cl₃, Ru 32.1% min) and ruthenium(III) nitrosyl nitrate (Ru(NO)(NO₃)₃, Ru 31.3% min) were bought from Alfa Aesar.

Catalyst preparation

Zorflex® ACC FM100 was chosen as the support for the ruthenium catalysts due to good conductivity and high surface area. For most of the experiments, ACC was washed in DI water; this material was labeled "original ACC." According to energy dispersive X-ray spectroscopy (EDX) analysis, there were some mineral impurities in the original cloth (Table 3). To probe the effects of the catalyst support, "washed ACC" was obtained by washing ACC in boiling concentrated HCl solution for three days, thoroughly rinsing with DI water to remove residual HCl, and then drying in the oven at 105 °C. EDX of this material only showed C, O and small amounts of Cl, presumably a residue from the HCl washing, as there was no Cl in the original ACC.

Two methods were used for the catalyst preparation: incipient wetness impregnation and cation exchange. For incipient wetness impregnation, three precursors were used, including Ru(NH₃)₆Cl₃, Ru(NO)(NO₃)₃ and RuCl₃. For Ru(NH₃)₆Cl₃ and Ru(NO)(NO₃)₃, two ruthenium loadings (nominal 3 wt% and 5 wt%) were prepared, while only 3 wt% (nominal) ruthenium content was used for RuCl₃ because of its relatively low solubility in water. A piece of ACC (1.3 cm \times 3.0 cm) was first soaked in ruthenium precursor solution to saturate the ACC pores. Kimwipes® were then used to remove the excess solution after the ACC was soaked. The wet ACC was dried under room conditions, then vacuum dried at room temperature, and finally reduced with H₂ in a Parr pressure reactor (model 452HC) at 500 psi and 220 °C for more than 12 h. During the reduction, hydrogen was supplied continuously and the reactor was purged occasionally to remove the product gases.

 $Ru(NH_3)_6Cl_3$ was used as the precursor for cation exchange preparation and five ruthenium loadings (nominal 1 wt%, 1.5 wt%, 3 wt%, 5 wt% and 6.6 wt%) were prepared. A piece of ACC was first pre-oxidized using boiling 1 mol dm⁻³ HNO₃ solution for 24 h.³³ The pretreated ACC was then washed thoroughly with DI water to remove the residual HNO₃ and dried under vacuum at room temperature. After drying, it was soaked in Ru(NH₃)₆Cl₃ solution with 1 mol dm⁻³ ammonia overnight to exchange Ru(NH₃)₆³⁺ onto the cloth.⁵¹ The ACC was removed, washed carefully with DI water, and then dried under vacuum at room temperature, and reduced as above with H₂ at 500 psi and 220 °C.

Catalyst characterization

Ruthenium contents of the catalysts were measured on a Varian 710-ES inductively coupled plasma optical emission spectrometer (ICP-OES). The catalysts were digested using aqua regia in a boiling water bath for 4 h, filtered and diluted with DI water. The standards prepared with $RuCl_3$ were used to quantify the ruthenium content over a concentration range of 0.08 ppm to 50 ppm.

Scanning electron microscopy (SEM) on a JEOL JSM-7500F and a JEOL 6400V were used to image the catalyst support and the morphology of ruthenium particles on the support. The catalysts were mounted onto the aluminum stubs with carbon paste and then dried under vacuum overnight. Secondary electron imaging was used to obtain the images. Surface chemical composition was characterized by EDX coupled with the JEOL 6400V SEM.

Brunauer–Emmett–Teller (BET) surface area, micropore area and micropore volume of the samples were measured on a Micromeritics® ASAP 2010 system using a static volumetric adsorption and desorption method. Nitrogen was used as the adsorptive gas and the measurement was made at 77 K. Nitrogen pressure was increased until 99% of the nitrogen saturation pressure was reached. The total surface area of the sample was calculated using the BET method from the adsorption isotherm from 0.06 to 0.20 relative pressures. The micropore volume was calculated from the desorption isotherm using the BJH (Barrett, Joyner and Hallender) method.

A method devised by NREL⁵² was used to analyze the ash content in the original ACC and in the HCl washed ACC. Samples of 0.5 to 2.0 g were weighed to the nearest 0.1 mg and transferred to dried crucibles. A muffle furnace set to 575 \pm 25 °C was used to ash the samples to constant weights. After cooling in a desiccator, the residue was weighed to determine the ash content.

Experimental setup

Electrochemical hydrogenation was carried out in a two-chamber glass H-cell,⁵³ separated with a DuPont® Nafion-117 membrane. Catholyte (30 mL) consisted of 0.2 mol dm⁻³ HCl, 0.2 mol dm⁻³ NaCl or 0.2 mol dm⁻³ NaOH, depending on the experiments. Ru/ACC prepared as described above was used as the working electrode (cathode). Anolyte (30 mL) consisted of 0.2 M phosphate buffer (pH = 7), and a Pt wire was used as the counter electrode (anode). The whole cell was placed in a water bath for experiments at controlled temperatures such as 50 °C and 80 °C. ECH was carried out under galvanostatic control (100 mA) with a dual channel potentiostat from Lambda (Model: LPD 422A FM). Before the electrochemical hydrogenation, 10 minutes of

pre-electrolysis (80 mA) was applied to activate the ruthenium catalyst. After the ruthenium was reduced, 1 mL 620 mmol dm⁻³ guaiacol solution in isopropanol was added to the cathode chamber to make an initial concentration of guaiacol equal to 20 mmol dm⁻³. For all the experiments, ECH was performed for 2 h.

Product analysis

Chemical analysis proceeded by withdrawing 1 mL sample aliquots at discrete time intervals from the cathode and the anode chambers. The samples were further saturated with NaCl, acidified to pH = 1 and then 1 mL chloroform was added to extract the organics.¹² After the experiments, the Ru/ACC catalyst was immersed in 5 mL chloroform and the solution was sonicated for 15 min to desorb any adsorbed organics into the solution. The solution was then filtered using a 0.22 µm syringe filter for GC/MS analysis.

All the samples were analyzed on a Shimadzu QP-5050A GC/MS. The GC used a Restek Rtx-1701 capillary column, 60 m × 0.25 mm with a 0.25 µm film thickness, a 1.0 ml min⁻¹ helium carrier gas flow rate, and a split ratio of 1 : 40. The injector temperature was set at 270 °C. The GC oven program started at 40 °C for 1 min, and then heated at 15 °C min⁻¹ to 260 °C. Mass spectrometry was operated in the electron ionization (EI) mode at an ionization energy of 80 eV, a *m/z* ranging from 28 to 400, and a sampling interval of 0.34 s. Species associated with each chromatographic peak were identified by comparing their observed mass spectrum with the NIST library and then confirmed by injection of authentic samples. External standards were also used to identify compounds and quantify the peaks.

Calculations

The conversion, selectivity and electrochemical efficiency were calculated according to the following equations:

Conversion = (moles reactant consumed/initial moles reactant)

$$\times 100$$

(11)

$$\label{eq:selectivity} \begin{split} \text{Selectivity} &= (\text{moles desired product}/\text{total moles products}) \\ &\times 100. \end{split}$$

Methanol was not accounted for the selectivity calculation.

E.E. = (Electrons used to generate products/Total electrons passed)(13)

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