

The influence of acidity of carbon nanofibre-supported palladium catalysts in the hydrogenolysis of hydroxymatairesinol

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The lignan hydroxymatairesinol (HMR, extracted from Norway spruce knots) was hydrogenolysed to matairesinol (MAT) over palladium supported by carbon nanofibres (Pd/CNF) in 2-propanol at 70 °C under hydrogen flow. The influence of support acidity on the activity and the selectivity to MAT was studied. The acidity of the Pd/CNF catalyst was varied by heat-treatment at different temperatures in nitrogen flow. The catalysts were characterized by transmission electron microscopy (TEM), inductively coupled plasma emission mass-spectrometry (ICP-MS, metal content), H₂-chemisorption (dispersion, metal particle size), and titration using NaOH. A more acidic support material was more active and selective to the desired product MAT. The major byproduct was 7-iso-propoxymatairesinol resulting from a reaction of the solvent with HMR over the acid sites on the support. The hydrogenolysis of HMR to MAT requires both the presence of metal and acidity.

KEY WORDS: Carbon nanofibres; palladium; acidity; hydrogenolysis.

1. Introduction

Precious metals on activated carbon supports are commonly used catalysts in fine chemical production. The main advantages using carbons as support materials are that they are relatively inert and inexpensive, they are stable in both acidic and basic media, and the precious metals supported on them can easily be recovered [1–4]. Activated carbon is produced from different kinds of raw materials, for example wood, coal, coconut shell, and peat are frequently used, but also synthetic polymers or petroleum processing residues can be utilized [1]. Commercial carbon-supported metal catalysts sometimes exhibit large batch-to-batch variations in performance which is, at least partially, due to natural variations in the starting materials [2]. To avoid this problem, synthetic carbon can be used as support material.

Carbon nanofibres (CNF) are such a material. They are grown by decomposition of carbon-containing gases on small metal particles. The material obtained is of high purity after the growth catalyst has been removed [5]. Reviews concerning CNF [6,7] describe the synthesis and properties of these materials in detail. Three common types of CNF are often described: ribbon-like (tubes), where the carbon layers are parallel to the growth axis, platelet, where the layers are perpendicular to the growth axis, and herringbone nanofibres, having

layers stacked obliquely with respect to the growth axis [7,8]. The CNF are pure, mechanically strong [9], and mesoporous, which makes them a perfect support material in liquid-phase reactions [5,7,10–12]. As the properties of activated carbons are difficult to control (poor reproducibility) and the microporous nature causes diffusion problems, CNF could replace their use [5].

The surface of the as-synthesized CNF support is hydrophobic and inert in nature, thus making the incorporation of metal challenging. By treating the surface with an oxidising agent, oxygen-containing surface groups are introduced thus increasing the hydrophilicity. The oxygen-containing surface groups are formed not only by reaction with oxidizing gases but also by treatment with aqueous solutions of, for example, nitric acid, sulphuric acid or hydrogen peroxide [11,12]. These treatments also increase the acidity of the CNF.

In this work, the natural lignan hydroxymatairesinol (HMR) was hydrogenolysed to matairesinol (MAT) over CNF-supported palladium catalysts. Lignans have anticarcinogenic [13] and antioxidative [14] effects and the lignan HMR can be found in unusually large amounts in Norway spruce (*Picea abies*) knots, i.e., the part of the branch that is embedded in the stem [15]. In our previous work [16], the hydrogenolysis was performed over palladium supported by activated carbon. The hydrogenolysis activity was correlated with the acidity of the activated carbon support; a more acidic

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support was more active. In this study, palladium was deposited on herringbone CNF after oxidation with nitric acid. The Pd/CNF catalyst was then subjected to heat-treatment at different temperatures in nitrogen flow, to remove acidic sites and receive catalysts with different acidities. This procedure has earlier been used by Toebe *et al.* for CNF-supported ruthenium [17] and platinum [18] catalysts.

2. Experimental

2.1. Synthesis of carbon nanofibre supported palladium catalysts

The Ni/SiO₂ growth catalyst was prepared as described in [19]. Silica (8.5 g, Degussa Aerosil 200) was suspended in de-ionised water (1 L) at 90 °C and under mechanical stirring. Nickel nitrate hexahydrate (10.55 g, Acros 99%) was added and the pH of the suspension was adjusted to a value between 3 and 4 using nitric acid (Merck p.a.) and thereafter urea (6.95 g, Acros p.a.) was introduced. After 16 h of reaction, the mixture was cooled to room temperature and filtered. The residue was washed three times with de-ionised water, followed by drying at 120 °C for 16 h. Finally, a sieve fraction of 425–850 µm of the catalyst precursor was calcined in static air at 600 °C (ramp 5 °C/min) for 3 h. The calcined samples were stored in static air for further use.

Carbon nanofibres (CNF) were grown as described in [19]. The Ni/SiO₂ catalyst (8.5 g), loaded in a quartz vessel in a tubular furnace, was reduced in a flow of hydrogen (182 mL/min) and nitrogen (715 mL/min) (2.2 bar over-pressure) at 700 °C (ramp 5 °C/min) for 2 h. The temperature was decreased to 550 °C and the CNF were grown for 24 h in a flow of N₂ (480 mL/min), H₂ (96 mL/min), and CO (266 mL/min) (2.2 bar over-pressure). This resulted in 41 g CNF combined with growth catalyst. The product was refluxed for 1 h in 1 M potassium hydroxide (500 mL) and, after filtration and washing, refluxed for 2 h in concentrated nitric acid (Merck, 65%) and then filtered. The residue was washed three times with deionised water and dried overnight at 120 °C.

The deposition of palladium on CNF was performed via an ion adsorption method according to [20]. The oxidised CNF (25.00 g) were suspended in de-ionised water (100 mL). The pH of the suspension was adjusted at a value between 5 and 6 by adding ammonium hydroxide solution (Acros, 25%). Subsequently, 5.0 g of Pd(NH₃)₄(NO₃)₂-solution (Johnson Matthey; 5.04 wt% Pd) was added and the resulting suspension was stirred for 20 h at room temperature under nitrogen atmosphere. The catalyst was filtered under nitrogen flow, washed and dried at 80 °C for 20 h (ramp 5 °C/min) under nitrogen flow. The Pd/CNF catalyst was reduced in hydrogen flow (96 mL/min) and nitrogen flow (480 mL/min) at 250 °C (ramp 5 °C/min) and 1.33 bar

for 2 h. The catalyst was sieved (25–90 µm) and stored in static air for further use. The Pd/CNF (21.81 g) obtained will be indicated as Pd/CNF-ox.

To vary the acidity of the support material, some of the acidic groups on the Pd/CNF-ox catalyst were removed by heat-treatment in nitrogen flow at 300 °C, 400 °C or 500 °C for 2 h (ramp 5 °C/min). The resulting products will be indicated as Pd/CNF-300, Pd/CNF-400, and Pd/CNF-500. The acidity of the catalysts decreased in the order Pd/CNF-ox > Pd/CNF-300 > Pd/CNF-400 > Pd/CNF-500.

2.2. Characterization of catalysts

The catalysts were characterized by transmission electron microscopy (TEM), inductively coupled plasma emission mass-spectrometry (ICP-MS, metal content), H₂-chemisorption, and titration (acidity). ICP-MS measurements were performed using an Agilent 7500a. Each sample was destructed with aqua regia (1:3 mixture of HNO₃: HCl) before ICP-MS analysis.

Hydrogen-chemisorption measurements were performed using a Micromeritics ASAP 2010C. The samples were dried in He at 373 K for 30 min, and reduced in flowing H₂ at 473 K for 2 h, heating rate 5 K/min. After reduction the samples were degassed for 30 min at 3–4 Pa at the reduction temperature in order to remove chemisorbed hydrogen and water. The isotherms were measured at 343 K. The dispersions (H/Pd ratio) are based on the amounts adsorbed at zero pressure found by extrapolation of the linear part of the isotherm. Calculations have been made with the total amount of adsorbed hydrogen. The average Pd particle size, *d*, was calculated using following formula (adsorption stoichiometry H/metal = 1)

$$d = \frac{6v_m}{a_m D} \quad (1)$$

where *d* is the particle diameter, *D* dispersion (H/Pd), *v_m* the volume occupied by an atom in bulk metal (14.7·10⁻³ nm³), *a_m* the area occupied by a surface atom (7.93·10⁻² nm²) [21].

Acid-base titrations were performed using a Titralab TIM 880 apparatus. The CNF catalysts with and without palladium were titrated. The CNF support was treated in hydrogen flow (96 mL/min) and nitrogen flow (480 mL/min) at 250 °C (ramp 5 °C/min) and 1.33 bar for 2 h prior to the titration to have the same treatment as for the Pd/CNF catalysts. 60 ml of 0.1 M KCl was slowly added to the catalyst sample (the amount of sample varied with the acidity to keep the amount of consumed titrant approximately constant; for example 0.05 g of Pd/CNF-ox and 0.2 g of Pd/CNF-500 were used). A solution containing 0.01 M NaOH and 0.1 M KCl was used as titrant. The amount of titrant consumed to reach pH 7.5 was used to calculate the amount of acidic groups.

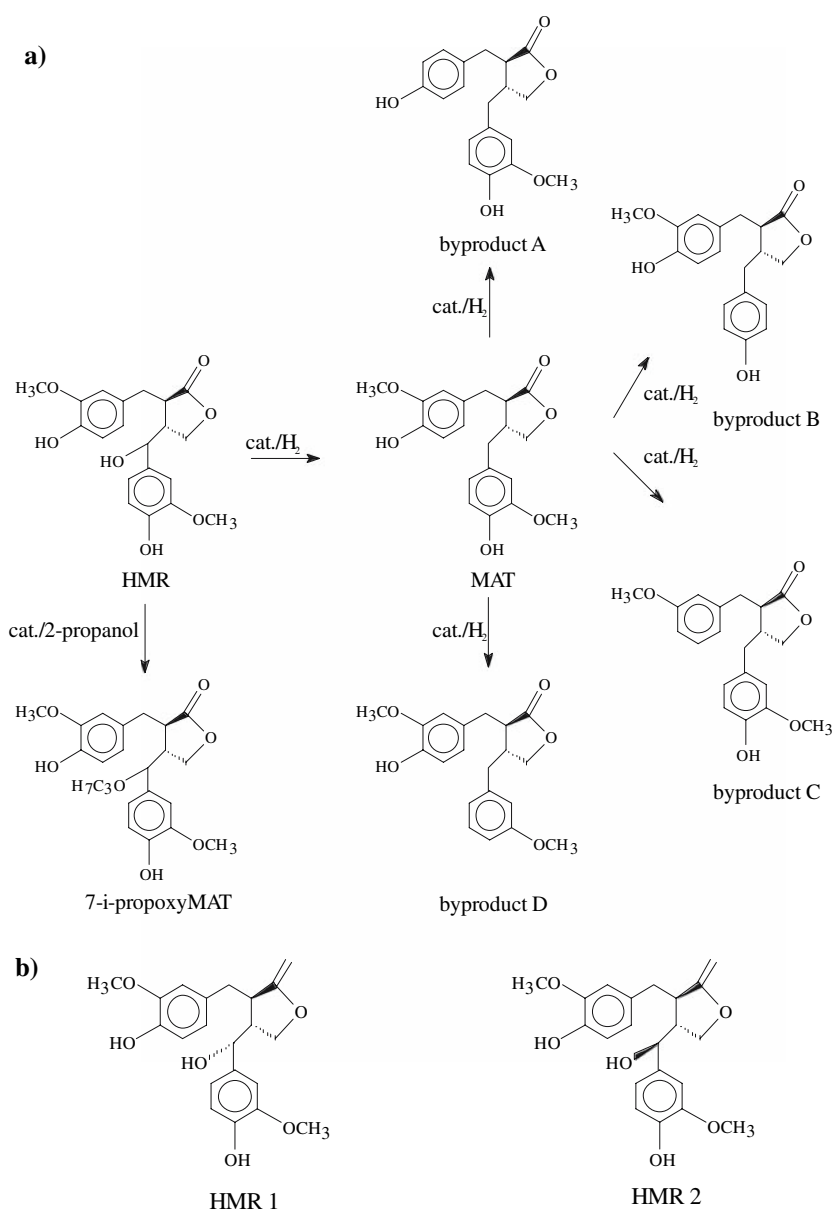


Figure 1. (a) Reaction scheme, (b) isomers of HMR.

2.3. Hydrogenolysis of hydroxymatairesinol

Hydroxymatairesinol was isolated from Norway spruce knots as described in [16]: the knots were ground and extracted in acetone–water mixture. The extract was concentrated in a rotary evaporator and then purified by flash chromatography. The purity of the material was determined by gas chromatography to be 90%. The major impurity was the lignan conidendrin. There are two diastereomers of hydroxymatairesinol, (7*R*,8*R*,8'*R*)-(-)-7-*allo*-hydroxymatairesinol (HMR 1) and (7*S*,8*R*,8'*R*)-(-)-7-hydroxymatairesinol (HMR 2), the ratio between HMR 1 and HMR 2 was approximately 1:2. The reaction scheme is visualized in Figure 1a and the difference between the isomers is presented in Figure 1b.

Hydrogenolysis experiments were performed at atmospheric pressure in a 200 mL glass reactor equipped with a heating jacket, a re-flux condenser, oil lock, pitched-blade turbine, and stirring baffles. In a typical experiment 500 mg of the catalyst was pre-activated *in-situ* in a hydrogen (AGA, 99.999%) flow (100 mL/min) at 100 °C for 1 h (including heating time), after which the reactor was cooled down to the reaction temperature 70 °C in a nitrogen (AGA, 99.999%) flow (100 mL/min). The reactant solution, consisting of 100 mg hydroxymatairesinol dissolved in 78 g 2-propanol (J.T. Baker, 99.5%), was deoxygenated by nitrogen gas flow (100 mL/min) for 10 min in a glass tube. After pouring the reactant solution into the reactor, the stirring was started at reaction time set to zero, the gas flow was

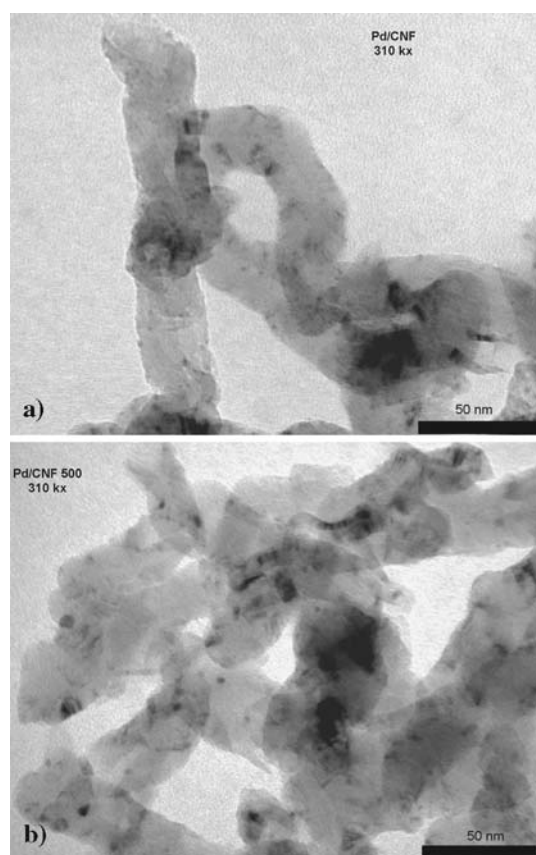


Figure 2. TEM images of reduced (a) Pd/CNF-ox and (b) Pd/CNF-500

changed to hydrogen (100 mL/min) and the first sample was withdrawn.

Samples were taken at different time intervals and analysed by a gas chromatograph (GC) as described in [22]. The samples were silylated prior to analysis using *N,O*-bis(trimethylsilyl)trifluoro-acetamide (BSTFA, 98%, Fluka), trimethylchlorosilane (TMCS, 98%, Acros Organics), and pyridine (99.0%, J.T. Baker).

3. Results and discussion

3.1. Catalyst characterization

The catalyst heat-treated at the highest temperature, Pd/CNF-500, and Pd/CNF-ox were investigated using TEM to verify whether the heat-treatment had affected the metal particle size. The dark dots in Figure 2 correspond to the palladium particles. The metal particle size determined by TEM was for Pd/CNF-ox 2–3 nm and for Pd/CNF-500 2–8 nm (mainly 2–5 nm), indicating that the heat-treatment increased the particle size slightly (TEM cannot identify metal particles below 2 nm). The metal content, the H/Pd (dispersion), metal particle size, and the acidity for CNF with and without metal are displayed in Table 1. When the metal particle size was calculated using equation (1) and the H/Pd

Table 1
Properties of the catalysts.

Catalyst	Metal content ¹ (wt%)	H/Pd ratio ²	Metal particle size ³ (nm)	Acidity ⁴ (mmol/g _{cat})
CNF	0	—	—	0.0932
Pd/CNF-ox	0.99	0.83	1.3	0.0246
CNF-300	0	—	—	0.0841
Pd/CNF-300	0.99	0.69	1.6	0.0221
CNF-400	0	—	—	0.0503
Pd/CNF-400	0.99	0.71	1.6	0.0177
CNF-500	0	—	—	0.0192
Pd/CNF-500	0.99	0.31	3.6	0.0078

¹Determined by ICP-MS.

²Dispersion determined by H₂-chemisorption.

³Calculated from the dispersion obtained from H₂-chemisorption measurements.

⁴Titration using NaOH.

ratios (dispersion) in Table 1, it is clear that the metal particle size was larger for the Pd/CNF-500 than for the others, which indicates that some sintering took place at the highest temperature. The acidity of the CNF decreased when metal was incorporated, which is logical since acidic sites are used as anchoring sites for the metal. Moreover the presence of Pd might increase the degree of reduction of the oxygen functionalities on the support.

3.2. Activity and selectivity

As Fig. 3a shows, the MAT yield increased when the acidity of the support material was increased; the least acidic material Pd/CNF-500 (heat-treated in nitrogen at 500 °C) gave the lowest yield while Pd/CNF-ox (the most acidic material) was the most active in the hydrogenolysis of HMR to MAT. This is in accordance with the results obtained in hydrogenolysis of HMR over Pd/C catalysts [16]. Protonation of the hydroxyl group was suggested to be the explanation to why a more acidic support is preferred in the hydrogenolysis reaction [16]. In general, when the influence of support acidity has been studied in different reactions, mainly two theories have been discussed: the metal-support interactions and the support polarity. The acidic sites on the support surface could affect the electronic properties of the metal, which has been proposed for zeolites [23,24]. However, Toebes *et al.* [18] did not find any change in the electronic properties of platinum particles deposited on CNF possessing different acidity. For zeolites the difference in acidity can be varied from alkaline to strong acidic, while for CNF the range of acidity is much smaller, which could explain why no changes in electronic properties were noticed for CNF [18]. The polarity of the CNF changes when the support acidity varies. As-synthesized CNF is hydrophobic, but becomes hydrophilic after treatment with nitric acid. The CNF changes from polar towards nonpolar as the

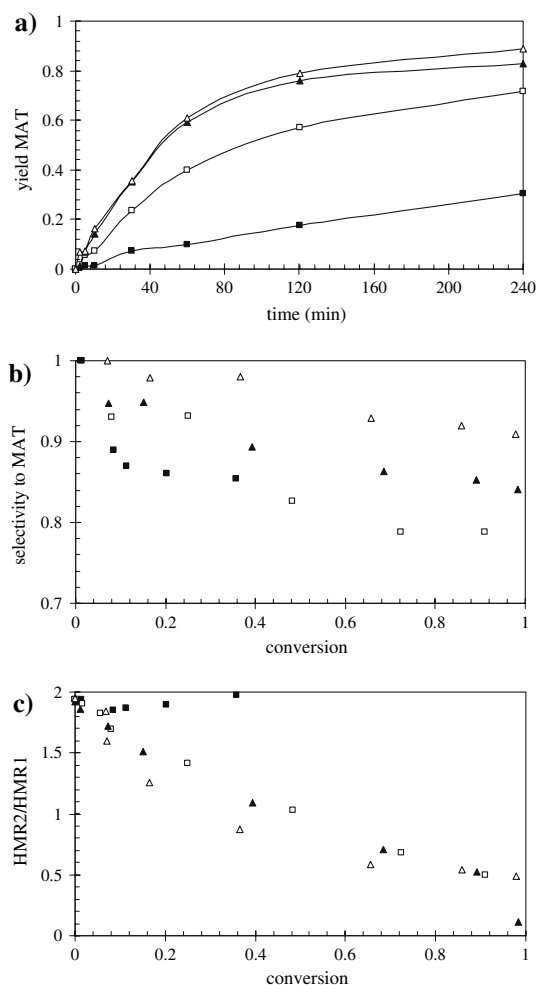


Figure 3. Hydrogenolysis of HMR over CNF supported palladium catalysts, \triangle = no treatment, \blacktriangle = treatment in nitrogen flow at 300 °C, \square = treatment in nitrogen flow at 400 °C, and \blacksquare = treatment in nitrogen flow at 500 °C: (a) yield MAT versus time, (b) selectivity to MAT versus conversion, and (c) HMR 2-to-HMR 1 ratio versus conversion

acidic groups are removed by heat-treatment in nitrogen. The change in surface polarity may change the adsorption mode of the reactants.

The selectivity (Figure 3b) was highest for the most acidic Pd/CNF-ox, and the selectivity decreased when the acidity was decreased. The major byproduct was 7-isopropoxymatairesinol (7-i-propoxyMAT, two isomers) as a result from interactions with the solvent. An experiment using CNF material without metal incorporated was performed and 7-i-propoxyMAT was observed as a product, meaning that the major byproduct can be formed using CNF without metal. No products were obtained when the reactant mixture was heated without any metal or CNF. The acidic groups on the CNF support may go into the solvent and the reaction between HMR and 2-propanol takes place in the solvent or then the other possibility is that HMR needs to adsorb on the CNF support before it can react with 2-propanol to form 7-i-propoxyMAT.

The ratio between the two HMR isomers can vary from tree to tree [15]. In our previous publications [16,22] the HMR 2/HMR 1 ratio was 3, but in this study it was 2. The ratio between the isomers can vary with pH [15] and also the solvent may have an important effect on the stabilities of various HMR conformers [25]. It is noticeable from Figure 3c that the HMR2/HMR1 ratio decreased with conversion for all catalysts except for Pd/CNF-500. The fastest decrease was obtained for the most acidic material. The isomerisation from HMR 2 to HMR 1, which was observed with more acidic Pd/CNF, changes the ratio between the isomers. Moreover, it was concluded in our previous studies [16,22] that HMR 1 reacts more slowly than HMR 2, which also changes the ratio between the isomers.

4. Conclusions

The lignan hydroxymatairesinol (extracted from Norway spruce knots) was hydrogenolysed to matairesinol over carbon nanofibre supported palladium catalysts. The acidity of the support material was varied by heat-treatment at different temperatures in nitrogen flow. Both the activity and the selectivity to the desired product matairesinol increased when the acidity of the support was increased. The major byproduct was 7-isopropoxymatairesinol resulting from interactions with the solvent 2-propanol. The formation of matairesinol requires both palladium and acidity, while the byproduct was also formed when acidic support material without palladium was used.

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