



# Hydrogenation of benzaldehyde *via* electrocatalysis and thermal catalysis on carbon-supported metals



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## ABSTRACT

Selective reduction of benzaldehyde to benzyl alcohol (model reaction for low-temperature stabilization of bio-oil) on C-supported Pt, Rh, Pd, and Ni in aqueous phase was conducted using either H<sub>2</sub> (thermal catalytic hydrogenation, TCH) or hydrogen generated in situ electrocatalytically (electrocatalytic hydrogenation, ECH). In TCH, the intrinsic activity of the metals at room temperature and 1 bar H<sub>2</sub> increased in the sequence Pt/C < Rh/C ≤ Pd/C, while Ni/C is inactive. At these conditions, the coverage of benzaldehyde is high while the coverage of adsorbed H is low and the reaction follows a Langmuir–Hinshelwood mechanism. All tested metals were active in ECH of benzaldehyde above the onset potentials of the H<sub>2</sub> evolution reaction (HER). Thus, hydrogenation competes with HER. The relative rates of H reacting to H<sub>2</sub> and H addition to benzaldehyde determines the selectivity to ECH and HER. Accordingly, the selectivity of the metals towards ECH increases in the order as follows: Ni/C < Pt/C < Rh/C < Pd/C. The latter having ECH selectivity around 99%. In ECH, the intrinsic activities of all tested metals were higher and the activation energies of benzaldehyde hydrogenation were lower than in TCH.

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## 1. Introduction

Producing bio-fuels from renewable lignocellulosic biomass has the potential to substantially reduce the anthropogenic carbon footprint. Hydrogenation of biomass-derived carbon resources is the most capital and energy intensive step which significantly increases the cost in the biomass conversion to fuels. Electrocatalytic hydrogenation (ECH) is a new promising route for this step as adsorbed hydrogen, or reduction equivalents for hydrocarbon conversion, are produced in situ on the cathode [1–6]. With the ECH approach, the required electric energy can be provided from renewable energy resources such as solar radiation and wind making it a truly renewable process. However, current catalysts and fundamental understanding of the kinetics is lacking. Developing suitable catalysts requires understanding of the catalytic properties of the metal and the reaction mechanisms in condensed phase in the presence of electric potential.

In ECH, noble metals have been found to be active for the reduction of carbonyl groups to alcohols [7,8], hydrogenation of phenolic rings, and hydrogenation and C–O bond cleavage of diaryl ethers [9,10]. For the latter two examples, Pd showed much lower activity than Pt and Rh. Faradaic efficiency (selectivity for the electrons to participate in the desired reaction) on noble metals is usually low and seems controlled by reaction parameters rather than by the nature of the metal. Metals with high overpotentials for the H<sub>2</sub> evolution reaction (HER), i.e., base metals and post-transition metals have also been tested for reduction of carbonyl groups showing dissimilar activities and Faradaic efficiencies to each other and to noble metals, which indicates stronger dependence on the nature of the metal. Pb cathodes, for instance, are efficient for the reduction of levulinic acid, whereas Cu is inactive [11]. Ni and Ni-containing alloys have been active for ECH of conjugated substrates such as benzene, acetophenone and styrene, while not active for ECH of non-conjugated olefins such as cyclohexene and geraniol [12,13]. Raney Ni has been reported to be active for ECH of phenolic and aromatic compounds, as well as of β-O-4 lignin models, including hydrogenolysis of phenolic β-arylethyl-aryl ethers [14,15].

Despite being abundant in bio-oils (up to 18% in carbon yield) and being prone to polymerization [16–18], comparably little work

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has been done on the reduction of aromatic aldehydes. The stability of the treated bio-oil is especially improved when reducing the carbonyl content, which distributes among sugars, ketones, and aldehydes [19]. Thus, benzaldehyde is an ideal model compound for low temperature hydrogenation aiming to stabilize lignin-derived bio-oils.

Based on previous results [9,10], we hypothesize that below the electric potential required for direct reduction of the aldehydes, ECH and thermal catalytic hydrogenation (TCH) follow the same reaction mechanism, and that the competition between HER and ECH is a specific property of the metal. To test these hypotheses, we explored the hydrogenation of benzaldehyde on Pt/C, Rh/C, Pd/C and Ni/C under ECH and TCH conditions. The results showed that the carbonyl functionality is quantitatively hydrogenated, which suggest that reactive carbonyl groups in bio-oil could be converted to stable alcohols at mild conditions. The study further elucidated the dependences of intrinsic activity of the metals on temperature and electric potential and provided insight into the mechanisms for hydrogenation of the target functionality in aqueous phase.

## 2. Experimental

### 2.1. Chemicals and catalytic materials

Chemicals were purchased from Sigma Aldrich and used as received: benzaldehyde ( $\geq 99.0\%$ ), acetate buffer solution (pH 4.6), ethyl acetate ( $\geq 99.9\%$ , HPLC),  $\text{Na}_2\text{SO}_4$  ( $\geq 99.9\%$ ),  $\text{NaCl}$  ( $\geq 99.9\%$ ), and  $\text{KCl}$  ( $\geq 99.9\%$ ).  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (99.999%), and activated carbon powder were used as received to prepare the Ni/C catalyst. High purity water, obtained with a Milli-Q water purification system with a resistivity of at least  $18.2 \text{ M}\Omega \text{ cm}$ , was used for all experimental procedures.  $\text{H}_2$  (Air Liquide,  $>99.99\%$ ) was used for thermal hydrogenation,  $\text{N}_2$  (Air Liquide,  $>99.99\%$ ) was used as protection gas to remove  $\text{O}_2$  from the electrolyte before ECH and Ar (Air Liquide,  $>99.99\%$ ) was used to change the partial pressure for determination of reaction partial orders in TCH.

### 2.2. Catalyst preparation

The noble metal catalysts used in this study were Pt/C, Rh/C and Pd/C with a metal content of 5 wt.%, purchased from Sigma Aldrich. Ni/C, with 5 wt.% metal, was prepared by impregnating activated carbon powder with an aqueous solution of  $\text{Ni}(\text{NO}_3)_2$ . After drying at 383 K, the impregnated material was heated at a rate of  $2 \text{ K min}^{-1}$  in flowing  $\text{H}_2$  and treated in flowing  $\text{H}_2$  at 723 K for 5 h.

### 2.3. Catalyst characterization

The metal loadings of the catalysts were verified by atomic absorption spectroscopy (AAS) carried out on a UNICAM 939 AA-Spectrometer equipped with a GF 95 graphite furnace. The specific surface area and pore diameter of the catalysts were derived (according to BET and BJH models) from  $\text{N}_2$  physisorption isotherms, which were measured at 77 K on a PMI automated BET sorptometer. The samples were outgassed before measurements at 523 K for 2 h. The metal dispersion was determined by  $\text{H}_2$  chemisorption. Prior to the measurements, the materials were treated in vacuum at 588 K for 1 h and then cooled to 313 K. A first set of adsorption isotherms were measured from 1 to 40 kPa. Afterwards, the samples were outgassed at 313 K for 1 h and a second set of isotherms was measured, which corresponded to physisorbed  $\text{H}_2$ . The concentrations of chemisorbed  $\text{H}_2$  were determined by extrapolating the difference isotherms to zero  $\text{H}_2$  pressure. The dispersion was estimated from the concentration of chemisorbed hydrogen assuming a stoichiometry of 1:1 metal to hydrogen atoms. The catalysts were also exam-

ined by transmission electron microscopy (TEM). Samples of the catalysts were ground, and ultrasonically dispersed in ethanol. Drops of the suspensions were applied on a copper-carbon grid and the measurements were carried out in a JEOL JEM-2011 electron microscope with an accelerating voltage of 120 keV. Statistical treatment of the metal particle size was done by counting at least 300 particles detected in several places of the grid. The morphology of the working electrode (activated carbon felt) before and after incorporating the catalysts was investigated by a scanning electron microscope (JSM-7500F from JEOL).

### 2.4. Electrocatalytic hydrogenation

Electrocatalytic hydrogenation (ECH) experiments were carried out in a two-compartment batch electrolysis cell described in Ref. [10]. A detailed drawing of the cell is shown in the supporting information (Fig. S1). Cathodic and anodic compartments were separated by a Nafion 117 proton exchange membrane (Ion Power, Inc.), which was treated in a  $\text{H}_2\text{O}_2$  solution (3 vol.%) and in sulfuric acid (2 M) before reaction. The working electrode was located in the cathode compartment and consisted of a carbon felt (Alfa Aesar  $>99.0\%$ ) connected to a graphite rod (Sigma Aldrich, 99.99%). The carbon felt was  $3 \times 1.5 \times 0.6 \text{ cm}$ . A platinum mesh (Alfa Aesar, 99.9%) was used as counter electrode in the anodic compartment. The reference electrode was a Ag/AgCl electrode (Ametek) with a double junction for protection. The cathode compartment was filled with 60 mL of acetate buffer solution at pH 5. 10 mg of the Rh/C, Pt/C, Pd/C or Ni/C catalyst powder were added into the cathode compartment. Prior to ECH, the electrolyte with catalyst powder in the cathode compartment was stirred at 500 rpm for infiltration of the powder into the carbon felt. The stirring at 500 rpm was maintained throughout the test. Polarization of the catalyst was performed under a constant current of  $-40 \text{ mA}$  for 30 min. Benzaldehyde was typically added into the cathode compartment to obtain a final concentration of  $20 \text{ mmol L}^{-1}$ . This concentration was varied  $\pm 25\%$  to determine reaction orders in benzaldehyde. ECH experiments were performed at atmospheric pressure and constant applied potential while a flow of  $\text{N}_2$  was kept through the reactant solution. Temperature was controlled with a cooling/heating circulator (Julabo F25-ED). All electrochemical procedures were performed with a workstation VSP-300, Bio Logic.

Control experiments showed increasing rates of benzaldehyde ECH with increasing stirring speed up to 400 rpm. Thus, all experiments were performed keeping the stirring at 500 rpm. The reaction rates increased linearly with increasing catalyst amount during the reaction. These tests allow discarding external mass diffusion limitation. The possible diffusion limitations in the pores was addressed by applying the Weisz-Prater criterion, which gave us confidence that the observed kinetics were not influenced by diffusion limitations (supporting information). The uncompensated resistance ( $iR$  drop) was determined by potentiostatic electrochemical impedance spectroscopy (PEIS). The applied potentials were corrected using the value obtained therein. The large size of the cathode and its porosity may lead to inhomogeneous  $iR$ -drops, where the measured values correspond to the smallest resistances between reference and working electrodes. However, in preliminary experiments we observed that the incorporation of catalyst to the felt is reproducible and hardly affects the measured impedance and rate. Thus, the results reported in this work are reproducible and the different catalytic performances can be accurately discussed.

### 2.5. Thermal catalytic hydrogenation

Thermal catalytic hydrogenation (TCH) was carried out in a glass batch reactor with 10 mg samples of Pt/C, Rh/C, Pd/C and

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