



Aqueous phase electrocatalysis and thermal catalysis for the hydrogenation of phenol at mild conditions



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ABSTRACT

The electrocatalytic hydrogenation (ECH) of phenol on Pt/C, Rh/C, and Pd/C was explored in an H-type two-compartment cell with respect to the impact of electrolyte, pH, current, and catalyst concentration. In all cases, the electric efficiencies increased with increasing phenol conversions. Rh/C exhibited the highest hydrogenation rate normalized to the concentration of accessible metal (TOF) followed by Pt/C in terms of mass of metal and intrinsic activities. Therefore, the effect of temperature on ECH and of mild thermal hydrogenation (TH) of phenol was explored on these catalysts. The activation energies for ECH were ca. 23 kJ/mol and 29 kJ/mol on Rh/C, and Pt/C, respectively. TH is much faster than ECH, although both pathways have the same activation energy. Cyclic voltammetry of bulk Pt and Pt/C in the presence of phenol indicated that phenol is adsorbed on the metal and reacted with hydrogen radicals. Hence, ECH was concluded to proceed *via* a Langmuir-type mechanism where the surface hydrogen is produced by reduction of protons (which occurs when the catalyst contacts the electrode) instead of H₂ dissociation as in TH. Although competitive reactions evolve H₂ during ECH, the involvement of this H₂ in phenol hydrogenation was minor. Thus, ECH and TH are independent processes and do not exhibit any synergy. In both pathways, the reaction path is phenol → cyclohexanone → cyclohexanol. C–O bond cleavage was not observed.

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1. Introduction

Reductive biomass conversion and electricity generation from renewable sources (e.g., photovoltaics, wind power, and hydropower) are essential to secure a sustainable supply of energy, fuels, and chemicals [1–4]. Most of the techniques that are emerging for producing biofuels from biomass-derived feedstocks require H₂ to remove oxygen from the biogenic material [5–7]. Whereas, H₂ may not be available in the decentralized locations, excess electricity generated from renewable resources may be stored supplying the reduction equivalents. Thus, coupling electrochemical water reduction with the reduction of biomass-derived feedstocks would help to improve the utilization of wind and solar energy by storing energy *via* reduction of the locally available feedstock.

The electrocatalytic hydrogenation (ECH) of biomass is beginning to emerge as a conceptually attractive alternative for thermal upgrading bio-oil at mild conditions using reduction equivalents

generated by electricity [8,9]. During ECH, H[•] is formed on the surface of the catalyst *via* reduction of protons supplied by the electrolyte, hydrogenating organic substrates. The conversions are ideally achieved at mild conditions and the overpotential required for ECH can be minimized by adapting the electrocatalyst [10].

Lignocellulosic biomass deconstructed *via* thermal or chemical methods is easily available at a local level, stimulating substantial efforts in the catalytic reduction of complex mixtures to fuels and chemicals [11,12]. Exploring the conversion of compounds, representative of deconstructed biomass, on well-defined materials is critical to elucidate structure-activity correlations needed for the development of better catalysts, which must be stable in the presence of substantial concentrations of water associated with the treatment of bio-oils [13]. Stimulating efforts on the conversion of representative compounds in aqueous phase have been reported in literature [14,15]. However, classical electrochemical mechanisms have been given for granted and the involvement of thermal pathways is a question that is not addressed. Conversion routes accessed by thermal catalysis might be relevant at mild conditions over metals that offer the highest activity and stability in electrochemical processes performed in aqueous solutions. Comparing thermal catalysis and electrocatalysis is of prime importance as H₂

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produced from water electrolysis can be used as external H₂ supply to maximize hydrogenation efficiency.

Thus, the present work investigates the performance of a series of C-supported noble metal catalysts (Pt, Pd, and Rh) integrated in an electrolytic cell for the cathodic transformation of phenol in aqueous phase. The effects of electrolyte, current, pH and temperature on selectivity, intrinsic activity (TOF) and electrical efficiency of the catalysts are described. ECH is compared with thermal catalysis at the same mild conditions in order to understand the reaction mechanisms.

2. Experimental

2.1. Chemicals and catalytic materials

All chemicals were obtained from Sigma–Aldrich and used as received, i.e., phenol ($\geq 99.0\%$), acetate buffer solution (pH 4.6), phosphoric acid ($\geq 99.9\%$), acetic acid ($\geq 99.0\%$), sulfuric acid ($\geq 99.9\%$), toluene ($\geq 99.9\%$, HPLC), ethyl acetate ($\geq 99.9\%$, HPLC), NaOH ($\geq 99.9\%$, HPLC), and KCl ($\geq 99.0\%$). High purity water, obtained with a Milli-Q water purification system with a resistivity of 18.2 M Ω cm, was used for all experiments. The supported noble metal catalysts used in this study were purchased from Sigma–Aldrich: Pt/C, Pd/C, and Rh/C. All these materials had a metal content of 5 wt.%.

2.2. Catalyst characterization

The surface areas and pore diameters of the catalysts were determined by N₂ adsorption at 77 K on a PMI automated BET sorptometer. The samples were outgassed before measurements at 523 K for 20 h. The surface areas and pore distributions were calculated according to BET and BJH models.

The dispersion of the metal phase was determined by H₂ chemisorption. Prior to the measurements, the materials were treated under vacuum at 588 K for 1 h and then cooled to 313 K. Hydrogen adsorption isotherms were measured at 1–40 kPa H₂. After equilibration with H₂, the samples were outgassed at 313 K for 1 h and a second set of isotherms was measured. The concentrations of chemisorbed H₂ on the metal were determined by extrapolating the difference isotherms to zero hydrogen pressure. The dispersion of the supported metals was estimated from the concentration of chemisorbed H₂ assuming a stoichiometry of 1:1 metal to hydrogen atoms.

The dispersion of the metal was also explored 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 200 particles detected in several places of the grid.

2.3. Electrocatalytic hydrogenation (ECH)

Electrolysis was carried out at atmospheric pressure in an H-type two-compartment electrochemical cell with a jacket for temperature control. Typically, the temperature was kept at 296 K (room temperature), except during a series of experiments performed at temperatures up to 353 K. The two compartments of the cell were separated by a Nafion 117 proton exchange membrane (Ion Power, Inc.), which was treated in sulfuric acid (2 M) before use. A piece of reticulated vitreous carbon (RVC, ERG Aerospace Corp., 100 pores per inch) shaped into a 20 mm \times 20 mm \times 12 mm cuboid, and connected to a graphite rod (Sigma–Aldrich), was used as working electrode in the cathode compartment. A Pt wire (Alfa

Aesar, 99.9%) was used as counter electrode in the anode compartment. The reference electrode was a home-made Ag/AgCl electrode with a double junction. The cathode compartment was filled with 58 mL of electrolyte solutions at defined pH (adjusted by adding small amounts of aqueous NaOH or the corresponding acid). A chosen amount of catalyst was added into liquid at the cathode compartment as powder, stirring the slurry at 500 rpm. Prior to ECH, polarization of the catalyst was performed under a constant current of -40 mA for 30 min. After polarization, 2 mL of phenol solution was added into the cathode compartment to obtain a final concentration of 17.7 mmol/L. ECH was then performed at galvanostatic (-40 mA) or potentiostatic (-0.72 V on Pt/C and -0.65 V on Rh/C) conditions, while a flow of N₂ was maintained through the cell. During all these described procedures, the anode compartment was filled with 40 mL of solution containing the corresponding electrolyte. All electrochemical procedures were performed with an electrochemical workstation (VSP-300, Bio Logic). Before each ECH test (and before the voltammetric experiments described below), the cell compartments and other materials were cleaned with concentrated H₂SO₄ and immersed in boiling water for 2 h several times. Prior to the reactions, the electrodes were alternatively immersed in H₂SO₄ (5 M) and KOH (5 M) for 15 min. After each immersion, the materials were thoroughly cleaned (Pt electrodes were further ultrasonically treated) in ultrapure water for 15 min.

2.4. Catalytic hydrogenation (CH) and additional electrochemical measurements

Catalytic hydrogenation (i.e., thermal, with and without the presence of any electric potential) was carried out at atmospheric pressure of H₂ at constant temperature. This was achieved by flowing 20 mL/h of H₂ through the solution in the cathode compartment. The concentration of phenol was kept at 17.7 mmol/L, whereas, different amounts of catalyst was used (to control the reaction rates) suspended in the solution and magnetically stirred at constant rate. Electrocatalytic hydrogenation in the presence of H₂ (20 mL/h) was performed following the procedure for the ECH process mentioned above.

Selected cyclic voltammetric experiments were performed using Pt wires as cathode and anode. An Ag/AgCl electrode was used as reference electrode, whereas, the electrolyte was an aqueous solution of acetic acid at pH 5. The potential window from -0.5 V to 0.9 V was applied with a scan rate of 20 mV/s. CVs were performed using a RVC cathode with a potential window from -1.4 V to 0.2 V and a scan rate of 20 mV/s.

2.5. Product analysis

The course of the ECH and CH experiments was followed by periodically withdrawing aliquots of 1 mL from the cathode compartment. The products were extracted with 3 mL of ethyl acetate. The organic phase (ethyl acetate) was separated from the aqueous phase by decantation and dried on Na₂SO₄. 1 mL of the dry organic phase was mixed with 0.5 mL of a solution containing toluene as standard. Quantitative analyses of those samples were performed by gas chromatography coupled with mass spectrometry (Shimadzu GC–MS–QP2010), equipped with a plot Q capillary column (30 m \times 250 μ m) and a thermal conductivity detector (TCD).

3. Results and discussion

3.1. Physicochemical properties of catalysts

The textural properties of the catalytic materials are compiled in Table 1. All materials exhibit comparably high specific surface areas and pore volumes. Microporosity, also comparable for all materials,

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