Integrated catalytic and electrocatalytic conversion of substituted phenols and diaryl ethers

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Abstract

Electrocatalytic hydrogenation and catalytic thermal hydrogenation of substituted phenols and diaryl ethers were studied on carbon-supported Rh. The rates of electrocatalytic hydrogenation increase with increasingly negative potentials, which have been related with the coverage of adsorbed hydrogen. The lowest and highest negative potentials in electrocatalytic hydrogenation correspond to the onset of H₂ evolution and to the onset of reactions involving the electrolyte, respectively. For electrocatalytic and catalytic thermal hydrogen addition reactions, the dominant reaction pathway is hydrogenation to cyclic alcohols and cycloalkyl ethers. The presence of substituting methyl or methoxy groups led to lower rates compared to unsubstituted phenol or diphenyl ether. Methoxy or benzyloxy groups, however, undergo C-O bond cleavage *via* hydrogenolysis and hydrolysis (minor pathway). The surface chemical potential of hydrogen can be increased also by generating a H₂ atmosphere above the reaction media, supporting the conclusion that thermal and electrochemical routes share the same reaction pathways.

Keywords: Hydrogenation, electrocatalysis, biomass conversion, mild reaction conditions.

Introduction

Electrocatalytic hydrogenation of biomass feedstocks is a promising approach for the synthesis of zero-carbon-footprint energy carriers by coupling electrocatalytic H^+ reduction using renewable energy with reductive processing of biomass-derived intermediates to fuels. In order to realize such a pathway, the synthesis has to occur decentralized, as the renewable electric energy is generated decentralized and with relatively low power. The local, small-scale reductive conversions must be performed under milder conditions than typical hydrotreating processes [1-8].

Formally, electrocatalytic hydrogenation consists of integrating the reduction of protons (Reaction I) and the hydrogenation of organic compounds at the cathode. The reduction at the cathode occurs, while O_2 (Reaction II) is formed or another oxidation reaction occurs at the anode.

Mechanistically, electrocatalytic hydrogenation (ECH) could proceed through two main different pathways, i.e., stepwise proton/electron addition or simultaneous electron-proton (neutral) hydrogenation. In turn, the stepwise hydrogenation may consist of electron addition followed by protonation of the oxygenated hydrocarbon, or by direct protonation of the hydrocarbon followed by electron transfer. Direct electron addition to an aromatic hydrocarbon followed by proton addition is not likely, because higher negative overpotentials are required for the direct reduction of aromatic molecules than for proton reduction, as shown, e.g., for the reduction of benzene in Reaction III [9]. A pathway started by protonation of the aromatic would depend on the strength of the acid present in the environment and the proton affinity of the hydrocarbon in solution. We can rule out such a pathway for phenolic compounds (model molecules used in this study), because the pK_a of, e.g., protonated phenol and protonated benzene are -6 and -24, respectively. Thus, very high activation barriers are expected in stepwise hydrogenation mechanisms, compared to neutral pathways [10].

The mechanistic steps for the cathode reaction in water electrolysis comprise of the formation of adsorbed H (Volmer step, Reactions IV and V), the combination of H to H_2 (Tafel step, Reaction VI) and the concerted reductive H_2 production (Heyrovsky steps, Reactions VII and VIII).

The simultaneous electron-proton transfer to the hydrocarbon as hydrogenation mechanism may proceed *via* concerted electron-proton transfer or *via* H-atom transfer [11,12]. Reaction IX exemplifies a first concerted hydrogenation step to adsorbed phenol, whereas Reaction X shows the hydrogenation of phenol to cyclohexanone by H atoms. It is difficult to determine unequivocally the nature of the hydrogenation step. However, phenol can be hydrogenated at the metal surface with adsorbed H in the absence of electric potential [13]. Thus, under our conditions, the hydrogenation pathway is hypothesized at this point to be equivalent to the thermally induced catalyzed reaction between H_2 and the reactant thermal hydrogenation (thermal catalytic hydrogenation, TCH). In this instance, the (reversible) Volmer step, would establish the surface chemical potential of H that drives the hydrogenation and product desorption.

Therefore, the ECH in this case is equivalent to the metal catalyzed hydrogenation of hydrocarbons in aqueous phase with the adsorbed hydrogen generated *in situ*. ECH of phenol has been reported on Pd-, Ni-, and Rh-based catalysts [13-15]. C-O bond cleavage has been observed for the electrochemical conversion of benzophenone, diaryl ethers, and hydroxymethylfurfural [15,16]. However, the reaction pathways, mechanisms that operate at such mild conditions and the impact of the molecular structure on the pathways have hardly been explored. A detailed molecular level understanding of the reaction pathways is required to advance this important reaction step in an overall concept of a decentralized synthesis of carbon-neutral fuels.

As a step in this direction, we report here on the catalytic hydrogenation of increasingly complex aromatic molecules containing oxygen, ranging from phenol to substituted di-aryl ethers on carbon-supported Rh (Rh/C). We compare reaction pathways and kinetic parameters obtained when the adsorbed hydrogen is formed from proton reduction (ECH) or H_2 dissociation (TCH).

Methods

A comprehensive list of chemical and materials used in our experiments is provided in the supporting information. The characterization of the catalytic material, Rh supported on C is also described in the supporting information. In the following we describe the experimental methods for electrocatalytic hydrogenation (ECH), and thermal catalytic hydrogenation (TCH). The geometrical surface area of the carbon felt electrode (30 mm·15 mm·6 mm) was 9.54 cm². However, we considered the real electrode area as the metal surface area determined by H₂ chemisorption measurements (supporting information). That is, 88 m²·g or 880 cm² of Rh in 20 mg catalyst, typically used in the experiments.

Electrocatalytic hydrogenation (ECH)

In a previous contribution, ECH was slower than TCH by one order of magnitude [10]. The reason for the low rates of was the particular experimental configuration in which the large distance between electrodes and the concomitant resistance to ion transport led to significant voltage losses. In order to minimize internal Ohmic resistance, in this work all experiments were carried out in a two-compartment galvanostatic cell with very short distance between electrodes and the membrane. A diagram of the cell used to perform the reactions is shown in Figure S1. Cathodic and anodic compartments of the cell were separated by a Nafion 117 proton exchange membrane (Ion Power, Inc.), which was pretreated in a H₂O₂ solution (3 vol.%) and in sulfuric acid (2 M) before reaction. A piece of carbon felt (Alfa Aesar >99.0%, 3.2 mm thickness, shown in Figure S2) connected to a graphite rod (Sigma Aldrich) was used as working electrode in the cathode compartment. A platinum wire (Alfa Aesar, 99.9 %) was used as counter electrode in the anodic compartment. The reference electrode was a home-made Ag/AgCl electrode with a double junction. For ECH of phenol, methylphenol and methoxyphenol, the cathode compartment was filled with acetate buffer at pH 5. 20 mg of the Rh/C catalyst were added into the cathode compartment. All reactions were performed at atmospheric pressure at 296 K. The stirring at 500 rpm allowed complete incorporation of the powder into the carbon felt. Prior to ECH, polarization of the catalyst was performed under a constant current of -40 mA for 30 min. For ECH, phenolic solution was added into the cathode compartment to obtain a final concentration of 16 mmol/L. Owing to the poor solubility of di-aryl ethers in water at room temperature a mixture of acetate buffer (30 vol.%) in isopropanol was used as solvent for ECH of diphenyl ether, p-tolyl ether, and benzyl phenyl ether. For the ECH of these compounds, solutions with 5·10⁻⁴ mol reactants were mixed with 50 mg of Rh/C. ECH experiments were performed at constant potential while a flow of He was kept through the cell. During all described procedures, the anode compartment contained mixtures of acetate buffer (pH 5) as the electrolyte. All electrochemical procedures were performed with an electrochemical workstation (VSP-300, Bio Logic). Before each ECH test, 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 H_2SO_4 (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. ECH with recycling hydrogen were performed in the cell depicted in as Figure S1. The cell was closed gas-tight and equipped with a recycling gas pump on top of the cathodic chamber to recycle the hydrogen produced via hydrogen evolution reaction during ECH.

Thermal catalytic hydrogenation (TCH)

Catalytic thermal reactions were carried out at atmospheric pressure with H_2 (20 mL/min) flowing through the reactant solution in the cathode compartment at 296 K. The preparation of the different reactant solutions and their concentrations were the same as those described for ECH. For coupled ECH and TCH experiments, a recycling pump was connected to the cell in order to feed in the H_2 produced by the hydrogen evolution reaction, whereas the cell was closed to allow building up of the pressure.

Product analysis

The course of the ECH and TCH experiments was followed by periodically withdrawing aliquots of 1 mL from the cathode compartment. The products were extracted with 3 mL of ethyl acetate. A 2 mL of 1 mol/L Na_2SO_4 solution was needed for the extraction of diaryl ethers, owing to the presence of ethanol in the solution. The organic phase was separated from the aqueous phase by decantation and dried on Na_2SO_4 . A sample of the dry organic phase was mixed with a solution containing a standard. Quantitative analyses of those samples were performed by gas chromatography coupled with mass spectrometry (Shimadzu GCMS-QP2010), equipped with a plot Q capillary column (30m x 250 μm) and a thermal conductivity detector (TCD).

Results and discussion

The catalyst used in this work was carbon-supported Rh with a metal loading of 5 wt.% and average Rh particle size of 3.4 nm. During the experiments, this catalyst was infiltrated in an activated carbon felt. Experimental procedures (Figures S1), calculation details, and catalyst characterization (Figures S2) are described in the supporting information. In the following the Faradaic efficiencies (FE) is defined as the percentage of the current producing the adsorbed hydrogen that reacts with oxygenates, i.e., reactant and intermediates of ECH. The turnover frequencies (TOF) correspond to the moles of ECH reactant converted per surface metal atom per hour. ECH and rates of the hydrogen evolution reaction (HER) are defined as the moles of organic reactant converted and moles of molecular H_2 produced, respectively, per second and gram of Rh. Adsorbed hydrogen (H_{ads}) consumption rates of ECH, TCH, and

HER are defined as the moles of adsorbed H that react with organic compounds *via* ECH or TCH or that produce molecular H₂ in HER, respectively, per second and gram of Rh.

Manipulating the electrocatalytic hydrogenation of phenol with potential

In the conversion of phenol at varying potentials, the cathodic current increased linearly from 18 mA to 220 mA with potentials varying from -0.4 V to -0.9 V (vs Ag/AgCl) (Table 1). In this potential range, the sum of hydrogen reacted with oxygenates and evolved as H₂ (only product detected in the gas phase) equaled the measured currents. Thus, electrons were only consumed in the reduction of protons, which solely participate in ECH as well as in HER. The ohmic loss was 1.8 Ohm as determined by impedance measurements. Upon taking into account this loss, the current showed an exponential increase with increasingly negative HFR-free potentials as shown in Table S2 and Figure S3.

Table 1. Measured current, current density, rate of electrocatalytic hydrogenation (ECH), TOF, Faradaic efficiency (FE), and rates of hydrogen evolution (HER) observed during the catalytic hydrogenation of phenol at varying potentials. The reactions were performed in mixtures of water and acetic acid at room temperature and atmospheric pressure on Rh/C.

Potential (V vs Ag/AgCl)	-0.4	-0.5	-0.6	-0.7	-0.8	-0.9
Current (mA)	-18	-50	-100	-140	-175	-220
Current density ^a (mA·cm ⁻²)	0.02	0.06	0.11	0.16	0.20	0.25
ECH (·10 ⁻⁵ mol·s ⁻¹ ·g _{Rh} ⁻¹)	0.81	7.5	16	26	28	34
TOF (h ⁻¹)	15	138	296	475	538	629
FE (%)	20	58	68	70	68	66
HER (·10 ⁻⁵ mol·s ⁻¹ ·g _{Rh} ⁻¹)	7.5	11	16	22	29	38

^a The electrode area is defined as the metal surface as determined *via* H₂ chemisorption.

For comparison, the rates of hydrogen equivalents consumed during ECH (converting the reactant and intermediate) and during HER are shown in Figure 1 (for values see Table S3). The low rates of ECH and HER at -0.4 V are caused by the overpotential needed for generating surface hydrogen at pH of 4.6 (-0.45 V vs Ag/AgCl). Between -0.4 V and -0.9 V, the changes of HER and ECH rates with potential increased linearly with 3 μmolH_{ads}·s⁻¹·g_{Rh}⁻¹ of H consumed in HER and 1.2 μmolH_{ads}·s⁻¹·g_{Rh}⁻¹ of H consumed in ECH (0.61 μmol·s⁻¹·g_{Rh}⁻¹ of H₂ evolved and 0.68 μmol·s⁻¹·g_{Rh}⁻¹ of phenol converted), per 1 mV of negative potential. ECH rates increasing faster than HER rates with increasing negative potentials suggesting a surprisingly stronger dependence of phenol hydrogenation than HER on concentration of adsorbed hydrogen.

Figure 1. Dependence of electrocatalytic phenol hydrogenation (ECH) and hydrogen evolution rates (HER), expressed as rate of adsorbed hydrogen consumed, on potential. The reactions were performed in a water-acetic acid mixture at room temperature and atmospheric pressure on Rh/C.

The rate of H addition to oxygenates in TCH was $10 \cdot 10^{-4} \text{ mol H}_{ads} \cdot (\text{s} \cdot \text{g}_{Rh})^{-1}$ (TOF of 385 h^{-1}) at 298 K and 1 bar H_2 (Figure 2). In ECH, the conversion of the organic compounds was controlled by potential and could reach rates, which were up to 1.6 times higher than TCH at a H_2 pressure of 1 bar, i.e., $15 \cdot 10^{-4} \text{ mol H}_{ads} \cdot (\text{s} \cdot \text{g}_{Rh})^{-1}$ (TOF of 629 h^{-1}) at -0.9 V.

The reaction order in phenol from -0.4 V to -0.9 V was zero (Figure 2). Thus, the coverage of reactive hydrogen on the metal surface determines the ECH rates. In turn, faster ECH than TCH implies that the concentration of adsorbed H under ECH is higher than the equilibrium value corresponding to 1 bar H_2 .

Figure 2. Decrease in phenol concentration during thermal catalytic hydrogenation (TCH), and electrocatalytic hydrogenation under varying potentials (from -0.4 V to -0.9 V vs Ag/AgCl). The reactions were conducted in a water-acetic acid mixture at room temperature and atmospheric pressure on Rh/C.

At conditions where only HER occurs (Reaction I), the hydrogen coverage at the metal surface at -0.23 V (or -0.52 V at pH 5), vs Ag/AgCl is equivalent to 1 bar of H₂ gas. However, the ECH conditions are far from ideal, as protons must compete with hydrocarbons for adsorbing at the metal, where H recombination occurs in parallel to hydrogenation. This has to require high over potentials to sustain hydrogen coverages. Follow this rationale, if the role of the potential in ECH is to provide the adsorbed hydrogen that reacts with phenol, a potential must exist (more negative than that required for ideal HER) at which the hydrogen coverage is identical to that corresponding to 1 bar of H₂ in the presence of the hydrocarbon. We identified -0.7 V as that potential, because all rates of TCH and ECH of the reaction of intermediates were similar at that point (Figure 2). Figure 3 shows that the concentration profiles of TCH and ECH at -0.7 V were equivalent. In contrast, the concentration profiles of TCH and ECH at e.g., -0.6 V are clearly different. The cyclohexanol to cyclohexanone molar ratio at, e.g., ~20% phenol conversion, increased from 0.31 to 0.4 with increasingly negative potentials. This shows that increasing hydrogen coverage enhances the production of cyclohexanol, which is formed after addition of 6 H to the initial reactant phenol.

Figure 3. Concentration profiles observed during thermal catalytic hydrogenation (TCH) and electrocatalytic hydrogenation (ECH) of phenol. a) Comparison between TCH and ECH at -0.7 V, b) comparison between TCH and ECH at -0.6 V (vs Ag/AgCl).

Electrocatalytic hydrogenation and catalytic thermal hydrogenation of substituted phenolic compounds

The conversion rates of methylphenol and methoxyphenol were lower than that of phenol under identical TCH and ECH conditions (Table 2). In ECH, the FEs of methylphenol and methoxyphenol were lower than the ones observed of phenol at the same potential, whereas the observed currents did not vary significantly. This indicates that the surface concentration of the hydrocarbons decreased with increasing substitutions, allowing for the rates of HER to increase twofold compared to the HER parallel to the ECH of phenol (Table 2). Indeed, the presence of a methyl or methoxy group decreases the adsorption energy of the aromatic compound on noble metals by 10-30 kJ·mol⁻¹ [17]. This effect is caused by repulsive interactions between the substituent groups and the metal surface, whereas their induction effect on the adsorption of the ring is minor. In agreement with this, we observed that the position of the substituents (*o*, *m*, or *p*) had a small influence on the hydrogenation rates (Table S4 and Figure S4 of the supporting information).

Table 2. Potential, current, current density, reaction rate, TOF, and Faradaic efficiency observed during the conversion of phenol, 4-methylphenol, and 4-methoxyphenol during ECH and TCH. The reactions were performed in a water-acetic acid mixture at room temperature and atmospheric pressure on Rh/C.

	Phenol		4-Methylphenol		4-Methoxyphenol	
	ECH	TCH	ECH	TCH	ECH	TCH
Potential (V vs Ag/AgCl)	-0.6	-	-0.6	-	-0.6	-
Current (mA)	-100	-	-105	-	-95	-
Current density ^a (mA·cm ⁻²)	0.11		0.12		0.11	
Reaction rate ($\cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$)	16	20	8.1	10	7.4	11
TOF (h ⁻¹)	296	374	151	191	138	212
FE (%)	68	-	31	-	35	-
HER rate ($\cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$)	17	-	38	-	32	-

^a The electrode area is defined as the metal surface as determined *via* H₂ chemisorption.

Complete removal of O from hydroxyl groups at room temperature was not observed. This concluded to be absent, because the energy of activation to cleave the C-O bond is too high for secondary alcohols [18, 19]. Thus, the conversion of phenol and methylphenol is limited to hydrogenation to cyclohexanones and cyclic alcohols (Figure S5, and Figure 4a and 4c). The concentrations of cyclohexanones pass through maximum values indicating that they are primary and intermediate products. In contrast, the concentration of alcohols increased exponentially with time indicating that these are stable products [20-22]. Note that the concentration profiles in TCH and ECH are not identical, because coverages of adsorbed hydrogen in TCH and ECH differ under the experimental conditions. At sufficiently long reaction time, complete conversion of reactant and intermediates was achieved.

The ECH and TCH of methoxyphenol produced hydrogenated products, (i.e., methoxy cyclohexanone and methoxy cyclohexanol), as well as phenol, cyclohexanone, cyclohexanol, and methanol (Figure 4b and 4d). Thus, the presence of the methoxy group opened a C-O hydrogenolysis pathway, yielding methanol (not reacting under these conditions) and phenol, which reacts further along the hydrogenation pathway described before. The selectivity was 90 % to hydrogenation, and 10 % to hydrogenolysis under ECH and TCH.

Figure 4. Concentration profiles observed during thermal catalytic hydrogenation (TCH, upper panels) and electrocatalytic hydrogenation (ECH bottom panels) of 4-methylphenol (a, c) and 4-methoxyphenol (b, d). The reactions were performed in water at room temperature and atmospheric pressure on Rh/C. The potential in ECH was -0.6 V (vs. Ag/AgCl).

Scheme 1 shows the reaction networks for the conversion of phenolic compounds by ECH and TCH. The only pathway for phenol, and methyl phenol, and main pathway for methoxyphenol is the consecutive 4- and 2-hydrogen additions to the corresponding cyclohexanones and cyclic alcohols, respectively. 4-Methoxyphenol undergoes C-O bond hydrogenolysis as a minor pathway. We hypothesize that the C-O bond was cleaved between the methoxy group and phenol in 4-methoxyphenol due to its lower strength ($410 \text{ kJ}\cdot\text{mol}^{-1}$) compared to the bond between the hydroxyl group and the aromatic ring ($480 \text{ kJ}\cdot\text{mol}^{-1}$). Cleavage of the methoxy group in the hydrogenated products was not observed.

Scheme 1. Reaction networks of the conversion of phenol ($R=H$) 4-methylphenol ($R=CH_3$) (up) and 4-methoxyphenol (bottom) under catalytic thermal hydrogenation and electrocatalytic hydrogenation.

Electrocatalytic hydrogenation and catalytic thermal hydrogenation of di-aryl ethers

The conversion of the aryl ethers (representative of lignin-derived bio-oils): diphenyl ether (DPE), *p*-tolyl ether (PTE), and benzyl phenyl ether (BPE), was performed *via* TCH and ECH. The supporting information describes the effect of the solvent on rates and the choice of isopropanol-water mixtures as solvent. Under TCH and ECH modes, the reactivities of the aryl ethers increased following the ranking $PTE < DPE < BPE$ (Table 3 and Figure S6 of the supported information). PTE is the least reactive, because of the steric repulsion induced by the methyl groups, decreasing the adsorption enthalpy by $75 \text{ kJ}\cdot\text{mol}^{-1}$ compared to DPE [23]. In contrast, the high reactivity of BPE is related to the relatively low dissociation energy of the α -O-4 bond ($218 \text{ kJ}\cdot\text{mol}^{-1}$), compared to, e.g., that of the 4-O-5 bond in DPE ($314 \text{ kJ}\cdot\text{mol}^{-1}$).

In TCH and ECH, the conversion of di-aryl ethers was slower than the conversion of phenolic compounds (Tables 2, 3, and S5). This was caused by the fact that the conversion of di-aryl ethers was carried out in the presence of large concentrations of isopropanol (needed to dissolve the ether), which is expected to strongly solvate the ethers and strongly adsorb on the metal reducing the aryl ether coverage [24]. In line with this conclusion, the conversion of aryl ethers in TCH and ECH followed a first order dependence on the hydrocarbon (Figure S6), reflecting their low coverage. The conversion rates during TCH were higher than during ECH by factors of up to 1.7 (Table 3), which is attributed to differences in hydrogen coverage as shown for phenol.

Although usage of organic solvents has profound effects on ECH rates (detail studies regarding the effect of solvent has been discussed in the supporting information), it does not affect HER strongly. Similarly, HER rates during the ECH of di-aryl ethers (performed in isopropanol-electrolyte mixtures) were between 33 and 42·10⁻⁵ mol·s⁻¹·g_{Rh}⁻¹, while the HER rate in phenol was 38·10⁻⁵ mol·s⁻¹·g_{Rh}⁻¹ at a potential of -0.9 V (vs Ag/AgCl) (Tables 1 and 3).

Table 3. Current, current density, reaction rate, TOF, and Faradaic efficiency of the conversion of di-aryl ethers via electrocatalytic hydrogenation (ECH) and thermal catalytic hydrogenation (TCH). The reactions were performed in water-isopropanol mixtures at room temperature and atmospheric pressure on Rh/C.

	Diphenyl ether		<i>p</i> -Tolyl ether		Benzyl phenyl ether	
	ECH	TCH	ECH	TCH	ECH	TCH
Potential (V vs Ag/AgCl)	-0.9	-	-0.9	-	-0.9	-
Current (mA)	-100	-	-100	-	-100	-
Current density ^b (mA·cm ⁻²)	0.11		0.11		0.11	
Reaction rate (·10 ⁻⁵ mol·s ⁻¹ ·g _{Rh} ⁻¹)	3.2	4.5	2.3	2.8	4.7	8.2
Initial TOF (h ⁻¹)	60	85	43	50	88	155
FE (%)	25	-	18	-	36	-
HER rate (·10 ⁻⁵ mol·s ⁻¹ ·g _{Rh} ⁻¹)	39	-	42	-	33	-

^a C-O cleavage TOF was estimated from the sum of the selectivities to hydrolysis and hydrogenolysis.

^b The electrode area is defined as the metal surface as determined *via* H₂ chemisorption.

In the conversion of DPE *via* ECH or TCH (Figure 5), the concentrations of cyclohexyl phenyl ether, phenol, cyclohexanone, and benzene passed through maxima, which indicate that they are intermediates and reactive products. Dicyclohexyl ether, cyclohexanol, and cyclohexane are secondary and stable products. The product profiles observed in the ECH and TCH of PTE (Figure 6) indicate that 4-methylphenyl 4-methylcyclohexyl ether, 4-methylphenol, 4-methylcyclohexanone, and toluene are primary and intermediate products, whereas di 4-methylcyclohexyl ether, 4-methylcyclohexanol, and methylcyclohexane are final products.

Figure 5. Concentration profiles observed during catalytic thermal catalytic hydrogenation (TCH) and electrocatalytic hydrogenation (ECH) of diphenyl ether. The reactions were performed in water-isopropanol-acetic acid mixtures at room temperature and atmospheric pressure on Rh/C.

The products identified in the conversion of DPE and PTE point to three reaction pathways, i.e., hydrogenation (yielding hydrogenated ethers), hydrogenolysis, and hydrolysis (both yielding oxygenated as well as O-free hydrocarbons with only one aliphatic or aromatic ring). Hydrolysis was inferred by mass balances applied to the concentrations of the compounds with only one ring. The selectivity to the different pathways was similar for the conversions of DPE and PTE in ECH and TCH (Figure S7). This is attributed to the similarity of the structure and bond energies of both molecules and to identical elemental steps occurring on the metal surface under either ECH or TCH.

Scheme 2 shows the reaction network for DPE and PTE and the selectivity to the different reaction pathways. In the hydrogenation route (selectivity of ~70%) both rings are hydrogenated in consecutive steps, each of them involving the addition of six hydrogen atoms. C-O bond cleavage does not occur on this route, which yields ethers as final products. In the hydrogenolysis route (selectivity of 7-13%), a C-O bond is cleaved to produce phenolic and phenyl compounds as primary products, which are hydrogenated in subsequent parallel routes. The hydrolysis pathway (selectivity of 15-25%) leads to phenolic compounds, which undergo consecutive hydrogenation yielding cyclic alcohols as final products (as shown for

phenol and methylphenol in Scheme 1). Additional experiments using cyclohexyl phenyl ether, and 4-methylphenyl 4-methylcyclohexyl as starting reactants showed that the C-O bond between benzyl and ether groups are cleaved yielding O-free aromatics and cyclic alcohols (indicated in Scheme 2 with the dotted red line). The selectivity towards complete hydrogenation, however, from those partially hydrogenated ethers is higher than 90% (Figure S8 supporting information).

Figure 6. Concentration profiles observed during thermal catalytic hydrogenation (TCH) and electrocatalytic hydrogenation (ECH) of p-tolyl ether during of diphenyl ether. The reactions were performed in water-isopropanol-acetic acid mixtures at room temperature and atmospheric pressure on Rh/C.

Scheme 2. Reaction network of the conversion of diphenyl ether ($R=H$) and p-tolyl ether ($R=CH_3$) under catalytic thermal hydrogenation and electrocatalytic hydrogenation.

The product profiles observed during the TCH and ECH of benzyl phenyl ether (BPE) are shown in Figure 7. The hydrogenated ethers, methyl cyclohexyl phenyl ether, cyclohexyl benzyl ether were primary and reactive products, whereas cyclohexyl methyl cyclohexyl ether was a stable product. Within the products with one functionalized ring, phenol, cyclohexanone, and benzyl alcohol, were secondary intermediates, whereas cyclohexanol, and cyclohexylmethanol were final products. The oxygen-free hydrocarbons toluene and methylcyclohexane were intermediate and final products, respectively.

Figure 7. Concentration profiles observed during catalytic thermal hydrogenation of benzyl phenyl ether. The reactions were performed in a water-ethanol mixture at room temperature and atmospheric pressure on Rh/C.

The concentrations profiles and structure of the products allowed us to conclude that the conversion of BPE follows a reaction network that includes hydrogenation, hydrogenolysis, and hydrolysis as in the case of the symmetric ethers (Scheme 3). The selectivities to these three pathways in ECH and TCH are similar (Figure S7). The hydrogenation pathway (selectivity of ~38%) yields partially and fully hydrogenated ethers in consecutive steps. Cyclohexyl benzyl ether is the dominant primary product (over methyl cyclohexyl phenyl ether) suggesting that the phenyl ring is more facile to hydrogenate than the benzyl ring. This is because the sp^3 hybridized $-CH_2-$ group induces looser bonding of the aromatic ring to the surface. Hydrogenolysis (selectivity of 59-63%) yields phenol and toluene on the cleavage of the α -O-4 bond. The same bond is cleaved by hydrolysis (selectivity of ~2%) yielding phenol and benzyl alcohol. The primary products of hydrogenolysis and hydrolysis undergo hydrogenation of the aromatic ring and carbonyl groups without further C-O bond cleavage (as shown in Scheme 1 for phenol). Neither benzene nor cyclohexane were observed, indicating that the $C_{sp^2}-O$ bond in BPE was not cleaved. This is attributed to the large difference in bond energies, i.e., $218 \text{ kJ}\cdot\text{mol}^{-1}$ for $C_{sp^3}-O$ and $334 \text{ kJ}\cdot\text{mol}^{-1}$ for $C_{sp^2}-O$.

Scheme 3. Reaction network of the conversion of benzyl phenyl ether under catalytic thermal catalytic hydrogenation and electrocatalytic hydrogenation.

Let us analyze the particular initial conversion rates of the selected di-aryl ethers by ECH and TCH (Table 4). Comparisons between the rates of DPE and PTE conversion shows that the strong impact of the methyl groups on the adsorption of PTE is reflected in the rates of all pathways, which decreased by 20-50%. BPE was converted much faster than DPE and PTE, mainly via hydrogenolysis, which proceeded at $4.7 \cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH ($2.1 \cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH). That is, from 4 to 8 times faster than the hydrogenolysis of DPE ($6 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and $5 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH) and from 5 to 19 times faster than the hydrogenolysis of PTE ($2.5 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and $4 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH). In contrast, the hydrogenation rate of BPE was identical to that of DPE ($\sim 3.3 \cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and $\sim 2.5 \cdot 10^{-5} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH). Hence, the hydrogenation of the aromatic rings is not influenced by the presence of the methylene bridge group. The rates of BPE hydrolysis ($1 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and ECH) are lower than those of DPE ($7 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and $3 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH) and even lower than those of PTE ($6 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in TCH and $2 \cdot 10^{-6} \text{ mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$ in ECH). This is attributed to the preference of a $\text{PhCH}_2\cdot$ fragment to combine with $\text{H}\cdot$ but not $\text{OH}\cdot$ [25]. We note in passing that hydrolysis did not occur in the absence of adsorbed hydrogen (via H_2 dissociation or H^+ reduction). Thus, the C-O cleavage for hydrolysis appears to be related to that in hydrogenolysis, whereas the difference relates to the probability of $\text{H}\cdot$ or $\text{OH}\cdot$ being added to the adsorbed hydrocarbon moiety [25].

Table 4. Reaction rate ($\text{mol} \cdot \text{s}^{-1} \cdot \text{g}_{\text{Rh}}^{-1}$) of di-aryl ethers *via* different pathways in electrocatalytic hydrogenation. The reactions were performed in a water-isopropanol-acetic acid mixture at room temperature and atmospheric pressure on Rh/C.

	Hydrogenation		Hydrolysis		Hydrogenolysis	
	ECH	TCH	ECH	TCH	ECH	TCH
DPE	$2.4 \cdot 10^{-5}$	$3.2 \cdot 10^{-5}$	$3 \cdot 10^{-6}$	$7 \cdot 10^{-6}$	$5 \cdot 10^{-6}$	$6 \cdot 10^{-6}$
PTE	$1.6 \cdot 10^{-5}$	$1.9 \cdot 10^{-5}$	$2 \cdot 10^{-6}$	$6 \cdot 10^{-6}$	$4 \cdot 10^{-6}$	$2.5 \cdot 10^{-6}$
BPE	$2.5 \cdot 10^{-5}$	$3.4 \cdot 10^{-5}$	$1 \cdot 10^{-6}$	$1 \cdot 10^{-6}$	$2.1 \cdot 10^{-5}$	$4.7 \cdot 10^{-5}$

Coupling electrocatalytic and catalytic conversion.

We have established that the rates of ECH increase with increasingly negative potentials due to changes in the concentration of adsorbed hydrogen. At potentials less negative than -0.9 V, the hydrogen coverages are low (-0.7 V equals to only 1 bar H₂ pressure). Thus, we hypothesized that the Tafel step could be reverted even with small H₂ pressure increases in order to increase the concentration of adsorbed hydrogen. In order to test this hypothesis, ECH was performed at optimum conditions keeping the H₂ ex HER in the reaction media, while monitoring the associated pressure increase. Namely, combined ECH/TCH experiments of phenol and PTE (the most reactive compound and the least reactive compound, respectively, used in this study) at -0.7 and -0.9 V, respectively, while recycling the evolved H₂ into the reactor.

Under normal ECH conditions, the conversion of phenol increased linearly, which leads to a constant TOF along the whole experiment. In contrast, with increasing H₂ pressure the conversion increases with time because the TOF increases as the coverage of H increases (Figure 8). As the reaction is zero order in phenol, we could directly correlate the increase in rates in the ECH/TCH experiments with the pressure of H₂ accumulated in the reactor. The increases in rate exhibited a reaction order of 1.5 on H₂ pressure (Figure S9), which confirms that the coverage of hydrogen is low under ECH conditions (at -0.7 V). In the case of ECH of PTE at normal conditions, the conversion decreased with time due to deactivation and the TOF rapidly decreased. In the presence of increasing H₂ pressure, the increases in rate also exhibited a reaction order of 1.5 on H₂ pressure, whereas the conversion followed first order kinetics with an apparent rate constant of 17 h⁻¹. This indicates that increasing the coverage of hydrogen at the surface compensates the effect of low hydrocarbon coverages for the hydrogenation rates.

Figure 8. Comparison of electrocatalytic reduction of phenol and p-tolyl ether (PTE) (at -0.7 V and -0.9 V, respectively). Orange columns, lines and symbols represent results obtained at normal ECH conditions. Blue columns, lines and symbols represent results obtained when recycling the evolved H₂.

Conclusions

The rates of electrocatalytic hydrogenation (ECH) of functionalized aromatic molecules on carbon supported Rh are proportional to the negative potential of the electrode at ambient reaction conditions. Reaction rates of ECH rise with increasing cathodic potentials (above the potential needed for H₂ evolution) up to values that trigger the formation of compounds that adsorb strongly on the metal. ECH rates were higher than those of thermal catalytic hydrogenation (TCH). The concentration of adsorbed hydrogen can be sustained at values above that corresponding to 1 bar H₂ by employing higher cathodic potentials. This coverage, however, seems low and can be increased by keeping H₂ (ex-H₂ evolution reaction) in the reaction media favoring the inverse Tafel step to aid the oxygenate transformation instead of competing with it.

Electrocatalytic and thermal hydrogenation of phenolic compounds and diaryl ethers follow identical routes, i.e., hydrogenation, hydrogenolysis, and hydrolysis, with similar selectivity. Comparison with high temperature hydrodeoxygenation studies allows concluding that the

presence of substituents in the aromatic rings reduces ECH and TCH rates due to repulsion with the metal, whereas the rate of C-O bond cleavage is inversely proportional to the corresponding bond energy. Hydrogenation, the dominant route (the only one for phenol and methylphenol), yields cyclic alcohols and cycloalkyl ethers as final products. Hydrogenolysis and hydrolysis (minor pathway) allow C-O bond cleavage of methoxy groups and ether bonds. This allows obtaining O-free hydrocarbons in a reaction path, which can reach significant selectivities.

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Graphical Abstract

Electrocatalytic hydrogenation (ECH) of phenolic compounds and diaryl ethers was explored on Rh/C at room temperature and atmospheric pressure in the absence of external H_2 . The dominant reaction pathway is hydrogenation of the aromatic rings, although methoxy and benzyloxy groups can undergo C-O bond cleavage. Increasing cathodic potentials favors the rates of ECH over H_2 evolution. The coverage of adsorbed H is further increased by generating a H_2 atmosphere enhancing hydrogenation rates.