





Structure Sensitivity in Hydrogenation Reactions on Pt/C in Aqueous-phase

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Hydrogenation of phenol and of the benzaldehyde carbonyl group catalyzed by Pt are structure sensitive in aqueous phase. The intrinsic reaction rates are directly proportional to the average size of the Pt particles. This trend is indifferent of the genesis of the reduction equivalents, i.e., dissociation of H₂ or proton reduction under cathodic potential. It is concluded that the structure sensitivity is caused by the ensemble size

Introduction

Hydrogenation of hydrocarbons in gas phase is commonly accepted to be a structure-insensitive reaction for a wide range of metals and reaction conditions. [1],[2] Structure sensitivity in heterogeneous catalysis is generally attributed to stabilization of adsorbed or transition states of substrates. That is, the substrate will adsorb and be activated only on specific ensembles of atoms.^[3] The fraction of such catalytically active sites may vary with the particle size or the chemical composition.^[4,5,6] If single atoms act as active sites, the reaction rate normalized to the concentration of active metal will be insensitive to changes in metal particle size, i.e., it is structureinsensitive.^[7]

Early work on hydrogenation of unsaturated hydrocarbons suggested that it is also structure insensitive in liquid phase, albeit with lower rates than in gas phase reactions.^[8,9] The lower rates were attributed to the competition of solvent and substrate for adsorption. Few examples, however, of significant particle size effects for the hydrogenation of polar molecules in liquid phase were reported.[10,11,12,13,14] Strong attractive or

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sensitivity of the adsorption of the aromatic molecules, which is favored on (100) and (111) surfaces of larger particles. For electrocatalytic reduction, this structure sensitivity implies that hydrogen evolution increases in rate relative to hydrogen addition to reacting substrates as the size of Pt particles decreases.

repulsive interactions of the polar group in the molecule with the solvent stabilize the adsorbed state(s) and the activated complex to different degrees. The resulting weaker interaction may induce sensitivity to specific adsorption structures or an overall nonlinear impact of the competitive adsorption.

We wish to probe, therefore, the generality of sensitivity to particle size for hydrogenation in aqueous phase. In particular, we would like to probe, whether and how such particle size effect impacts reductive electrocatalytic conversions.

Electrochemical hydrogenation (ECH) conceptually allows low-temperature hydrogenation with the cathodic potential providing the reduction equivalents.^[15,16,17,18,19,2021] The potential problem with this approach is that the H_2 evolution reaction (HER) competes with ECH.^[22] It has been shown that the former reaction was not structure or size sensitive.^[23] If the ECH would be structure sensitive, the size of the active metal particles at the cathode could be used to control the relative rates of H₂ evolution and catalytic hydrogenation.

We have chosen the hydrogenation of phenol and benzaldehyde, because the two molecules present the possibility to compare structure sensitivity for a carbonyl compound versus an aromatic ring. The size of the catalyst particles is varied indirectly by varying the concentration of Pt on a carbon support. The kinetics of reduction is explored either by providing the reduction equivalents with cathodic potential or with molecular H_2 in an open circuit potential mode.

Results and Discussion

Structural Characterization of Pt/C Catalysts and Quantifying the Concentration of Exposed Pt

Pt/C catalysts with Pt loadings of 1, 3, 5 and 10 wt.% were used in the present study. The average Pt particle size was evaluated by TEM analysis. Representative TEM images and corresponding particle size distributions are shown in Figure 1.





Figure 1. Representative TEM images and the corresponding size distribution histograms of different metal wt.% Pt/C catalysts: a) Pt/C-1; b) Pt/C-3; c) Pt/C-5; d) Pt/C-10

Table 1. Metal loading and fractional exposure of Pt particle size of Pt catalysts							
Catalyst	Pt [wt.%]	Fractional exposure [a]	Particle size [nm] [b]	Particle size [nm] [c]	Exposed metal surface [µmol·g ⁻]		
Pt/C-1 Pt/C-3 Pt/C-5 Pt/C-10	1 3 5 10	0.37 0.34 0.26 0.11	3.1 3.5 4.5 12.1	2.9 3.2 4.3 10	18 50 65 53		

[a] Determined from H₂ chemisorption; [b] The average Pt particle size calculated based on the fractional exposure determined by H₂ chemisorption and assuming a cuboctahedron shape of the particles; [c] The average Pt particle size calculated from the TEM micrograph.

The fractional exposure of Pt varied from 0.37 to 0.11 while the metal loading of the Pt/C catalysts varied from 1 wt.% to 10 wt.% (Table 1). Pt fractional exposures and average particle size were also determined by H₂ chemisorption. The average particle diameters obtained by H₂ chemisorption were in good agreement with those estimated by TEM analysis as shown in Table 1. The fractional exposure estimated by TEM and H₂ chemisorption for calculating intrinsic rates has also been verified by in situ titration with poisons.

In order to titrate the metal sites accessible under reaction conditions, the hydrogenation of benzaldehyde was performed while adding small aliquots of butanethiol with concentrations increasing up to the concentrations of available metal sites as determined by H_2 chemisorption. We hypothesize that butanethiol reacts stoichiometrically with the metal sites according to the following reaction:

$$Pt(s) + C_4H_9$$
-SH $\rightarrow PtS(s) + C_4H_{10} \Delta G^{\circ} \sim -103 \text{ kJ/mol}$ (i)

The intrinsic activity of the catalysts decreased proportionally to the amount of butanethiol added to the reaction medium. It blocked catalytic activity nearly completely, once the amount of butanethiol equaled the amount of surface metal atoms measured by H_2 chemisorption (Figure 2). The same proportional deactivation was observed, when the titration with thiol was carried out under cathodic potential (Figure S1 and Table S1).

The small residual activity is attributed either to an underestimation of the exposed metal surface by H_2 chemisorption or to a less than complete adsorption of the butanethiol aliquots added. These results confirm the fraction of surface metal atoms determined by H_2 chemisorption are identical to the fraction of



Figure 2. Rates of benzaldehyde hydrogenation (turnover frequency, TOF) on different Pt/C catalysts in the presence of varying concentrations of butanethiol in the reaction media. -SH/Pt_{surface} denotes the molar ratio of thiol added in the reaction to surface Pt determined by H₂ chemisorption. The reactions were performed under 1 bar flowing H₂ at room temperature. TOF values are calculated against the surface Pt determined by H₂ chemisorption

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available metal under both experimental conditions in aqueous phase.

Hydrogenation of Phenol on Pt/C Catalysts with Varying Pt Particle Size

The rate normalized to the number of surface Pt atoms, i.e., the turnover frequency (TOF), for phenol hydrogenation decreased with increasing fractional exposure of Pt. The same result was observed, when the reaction was performed in the presence of H_2 (thermal catalytic hydrogenation, TCH) and when a cathodic potential (electrocatalytic hydrogenation, ECH) was used to generate the reductive environment (Figure 3a, mass-normal-



Figure 3. (a) Rates of phenol hydrogenation (turnover frequency, TOF) at different cathodic potentials (vs Ag/AgCl) under 1 bar N₂ (ECH) or 1 bar H₂ (TCH) along with the fractional exposures of the Pt/C catalysts. (b) Added current efficiencies for cyclohexanone and cyclohexanol observed during electrocatalytic hydrogenation of phenol at different cathodic potentials along with the fractional exposure of Pt. The reactions were performed at room temperature. The particle size corresponding to fractional exposure represented in bottom x-axis are shown at the top of the figure.

ized rates are presented in Figure S2 and Table S2). Cyclohexanone and cyclohexanol were the primary and secondary products, respectively (Figures S3 shows selected concentration profiles). Thus, the dependence of TOF on fractional exposure shows a marked particle size effect on aromatic ring hydrogenation under the conditions explored. The hydrogenation rates increased with increasing cathodic potentials on all Pt/C catalysts as reported for Rh/C.^[24] However, varying cathodic potential did not influence the product selectivity (Figure S4).

The hydrogenation of phenol on the metal is hypothesized to proceed as a Langmuir Hinshelwood type mechanism with the reaction of surface hydrogen atoms with the aromatic ring being the rate determining step (Scheme 1).^[25] Cyclohexanone

$$H^+ + e^- \rightleftharpoons H^*$$
 Electrochemical; Volmer step (1)
 $H_2 + 2^* \rightleftharpoons 2H^*$ Thermal (1 bar H_2 pressure) (2)

Hydrogenation reaction

$$\bigcup^{OH} + * \rightleftharpoons \left(\bigcup^{OH} \right)^*$$
(3)

$$\left(\bigcup_{i}^{OH} \right)^{*} + 4H^{*} \Longrightarrow \left(\bigcup_{i}^{O} \right)^{*} + 4^{*}$$

$$(4)$$

$$\begin{pmatrix} \circ \\ \bigcirc \end{pmatrix}^* \rightleftharpoons \bigcirc \qquad (5)$$

Hydrogen evolution reaction

H* + ŀ	H⁺ + e⁻	$ \rightarrow H_2 + *$	Heyrovsky step	(6)
2H*	+	H ₂ + 2*	Tafel step	(7)

Scheme 1. Elementary reaction steps towards phenol hydrogenation and $\rm H_{2}$ evolution reaction.

is the first observed hydrogenated product in measurable equilibrium with the mobile phase (Reactions 3 and 4 in Scheme 1 and desorption Reaction 5). The elementary steps for hydrogenation are concluded to be identical in the presence or absence of an external electric field.^[26] When the hydrogenation is performed under cathodic potential, the H₂ evolution reaction (HER) is the major competing pathway (Reactions 6 and 7 in Scheme 1). The current efficiency is defined here as the fraction of the current utilized to hydrogenate the organic compounds relative to the total current passed. As shown in Figure 3b and Table S2, Pt particle size also impacts the efficiency of the overall electrocatalytic reaction. The larger particles with higher hydrogenation TOFs had a higher selectivity for ECH than for HER. The current efficiencies were not affected by the external potential in the relatively narrow range explored, i.e., ECH and HER were enhanced by the cathodic potential to the same extent for a given dispersion of Pt.

The apparent activation energies did not change significantly across different Pt/C catalyst particle sizes, which indicates that the mechanism and rate determining step of phenol hydrogenation are not influenced by the Pt particle size. Figures 4a and 4b show the Arrhenius plots for the hydrogenation of phenol on Pt/C-5 and Pt/C-10. The Arrhenius plots for Pt/C-1 and Pt/C-3 are shown in Figures S5a and S5b. The corresponding apparent activation energies are summarized in



Figure 4. Arrhenius plots for the hydrogenation of phenol on Pt/C-5 (a) or Pt/C-10 (b). The reactions were performed at 1 bar of flowing N_2 (ECH) or H_2 (TCH).

Table 2 (Pt/C-5 and Pt/C-10) and Table S3 (Pt/C-1 and Pt/C-3). Invariant activation energies allow us to conclude that only the concentrations of active sites have changed with the particle size. At the external potential for which the rate of TCH and ECH were identical $(-0.7 \text{ V vs. Ag/AgCl or 1 bar H}_2)$, the apparent activation barriers for phenol hydrogenation are both approximately 35 kJ mol⁻¹. The activation energies for the electrochemical hydrogenation decreased from 45 kJ mol⁻¹ to 26 kJmol^{-1} as the potential varied from -0.6 V to -0.8 V vs. Ag/ AgCl. Activation energies measured for Pt/C-5 and Pt/C-10 at different cathodic potentials are shown in Table 2. We hypothesize that this decrease originates from an increase in the interaction strength of hydrogen on the metal.^[27] Conversely, the interaction of phenol with the surface does not seem to be affected by potential. The concentration profiles for ECH and TCH suggest a low reaction order (Figure S6a and Figure S6b). Rates at varying initial phenol concentrations indicate reaction orders in phenol of 0.1 - 0.3 in case of TCH and ECH at -0.7 V (Figure S7). This indicates that the coverage of phenol is relatively high.

Hydrogenation of Benzaldehyde on Pt/C Catalysts with Varying Pt Particle Size

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For benzaldehyde only the carbonyl group is selectively hydrogenated to benzyl alcohol. The TOFs for benzaldehyde hydrogenation were higher than those of phenol hydrogenation, indicating that the reactivity of the carbonyl group was higher than that of aromatic rings, even when considering that only 1/2 of the hydrogen is needed for the first step of the reaction. Despite the different functionality being reduced, the TOF for benzaldehyde hydrogenation decreased linearly with decreasing Pt particle size for both ECH and TCH (Figure 5a), just as observed for phenol. Larger Pt particles showed also higher selectivity towards benzaldehyde hydrogenation than towards HER. In parallel, the current efficiency increased from 8% to 50% (Figure 5b). Thus, the hydrogenation of both the aromatic carbonyl group and aromatic ring of phenol are concluded to depend on an active site that varies in concentration with the particle size. Details of benzaldehyde hydrogenation rates (mass specific rate and TOF), current, current efficiencies obtained under both electrochemical and thermal condition are compiled in Table S4.

Structure-Activity Correlations

Particle size effects are usually correlated with the fractions of surface atoms with varying coordination.[28] The fraction of metal atoms with low coordination (located at edge and corner sites) is over-proportionally reduced with increasing particle size and the surface becomes dominated by low index surfaces sites. According to cuboctahedra based geometric models ^[29,30,31,32] of the metal particles used in this study, the fraction of surface atoms in low index plane sites (such as (111) and (100) planes) increases from 0.63 at 3 nm particles to 0.9 for 10 nm particles (for details see supporting information). The rates of phenol and benzaldehyde hydrogenation scaled linearly with the calculated fraction of the sum of (111) and (100) planes of the different catalysts (Figure 6). As we have concluded that varying particle size does not affect the reaction mechanism or rate limiting step, we attribute the observed particle size effects to ensemble requirements towards the adsorption and hydrogenation of aromatic oxygenates. The increasing fraction of planar sites with increasing particle size is concluded to lead to a higher fraction of surface sites preferring the multiple

Table 2. Activatsponding to plpotentials.	able 2. Activation energies obtained from the Arrhenius plots corre- ponding to phenol hydrogenation on Pt/C-5 and Pt/C-10 at varying otentials.					
Pt/C-5 Cathodic Po- tential (V vs Ag/AgCl)	Activation Energy [kJ·mol ⁻¹]	Pt/C-10 Cathodic Po- tential (V vs Ag/AgCl)	Activation En- ergy [kJ·mol ⁻¹]			
-0.6 -0.7 -0.8 TCH	47 37 26 35	0.6 0.7 0.8 TCH	44 35 26 33			



Figure 5. Intrinsic activity (TOF) for benzaldehyde hydrogenation as a function of fractional exposure under electrochemical hydrogenation (ECH) and catalytic thermal hydrogenation (TCH) (a); Current efficiency obtained during ECH of benzaldehyde as a function of Pt fractional exposure (b). ECH was performed at -0.7 V vs Ag/AgCl. All reactions were performed at ambient temperature under 1 bar of flowing N₂ (ECH) or H₂ (TCH). The particle size corresponding to fractional exposure represented in bottom x-axis are shown at the top of the figure.



Figure 6. Correlation of rates of phenol and benzaldehyde hydrogenation with the fraction of terrace sites, determined from the calculated number of atoms in the (100) and (111) planes, using a geometric model for the catalyst particles. TOF indicated herein corresponds to ECH reaction performed at -0.7 V vs Ag/AgCl.

adsorption of the aromatic compounds. This enhances TCH and ECH rates, while leaving the energetics during the catalytic process unchanged.

It should be noted at this point that the total activity followed linearly the exposure to butanethiol. If a relatively large ensemble of metal atoms would suffice to serve as active site, one would tend to observe a nonlinear decay of catalytic activity upon increasing exposure to butanethiol, as the probability to reduce large ensemble by stochastic irreversible adsorption of a thiol molecule is higher than for a single site at corners and edges of particles.^[33,34,35]

The linear decay upon fractional poisoning could be, however, caused by two effects. The active sites could decrease in strict proportion to the fraction of exposed metal atoms. This could, for example, be the case if the low index surfaces dominate the particles. It could also be observed, if the adsorption of thiol was not irreversible, but equilibrated in aqueous phase.^[36]

The extrapolations of the hydrogenation TOFs to zero show that different thresholds of sizes exist for the Pt particles to be active towards phenol and benzaldehyde hydrogenation (Figure 6). The minimum requirement of planar site is higher for phenol hydrogenation (55%) than for benzaldehyde hydrogenation (40%), i.e., phenol hydrogenation benefits more from larger Pt particles than benzaldehyde hydrogenation.

In situ XANES Characterization

As outlined above, the fact that fractions of the Pt-surface exist and that the organic compounds cannot successfully access implies that the ratio of adsorbed molecules to metal surface sites change with particle size. In specific, it is hypothesized that small particles accommodate less organic molecules at saturation coverage than large particles, because the latter have higher fractions of surface available for hydrogenation. The hypothesis that larger metal particles accommodate a higher density of organic molecules at the surface than small particles was tested by measuring the XANES of the Pt L_3 edge of selected Pt/C catalysts in aqueous phase during the application of cathodic potential.

Despite XANES being a bulk technique (the spectra being an average of all Pt atoms), for small particles (<3 nm), the fraction of surface sites is sufficient to observe surface species such as adsorbed H.^[37] Upon adsorption of H₂ the intensity above the Pt L₃ edge at 11572 eV increased and the difference spectra of a Pt catalyst with and without adsorbed hydrogen shows this increase clearly.^[38,39,40] Figure 7 shows the difference in situ XANES spectra of two Pt/C catalysts synthesized by strong electrostatic adsorption (Pt/C Darco, 3 nm and Pt/C Vulcan 1.5 nm).^[41] When a 0.1 M phenol solution was passed through the cell (at -0.55 V vs Ag/AgCl), this peak decreased. This is attributed to adsorption of phenol and its competition with H for adsorption sites. The decrease of intensity of the Pt-H signal is shown in Figure 7a for a ~3 nm Pt/C catalyst. For the smaller particles, ~1.5 nm, there was little or no decrease in the Pt-H signal as phenol was admitted (Figure 7b). This difference between small and larger particles points to the fact that on smaller particle size phenol blocks the adsorption of H₂ less effectively than on larger particles. We conclude, therefore, that on the smaller Pt/C particles a smaller fraction of surface



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Figure 7. XANES difference spectra of Pt L₃ edge for Pt/C with Pt particles of: a) ~3 nm and; b) ~1.5 nm as determined by EXAFS. The spectra were recorded in the presence and the absence of 0.1 M phenol in acetate buffer, pH 4.6, room temperature and atmospheric pressure. The cathodic potential applied herein was -0.55 V vs Ag/AgCl. The data shown in (b) are reproduced from reference.^[37]

atoms exists that can accommodate aromatic rings, while $\rm H_2$ can dissociatively adsorb on all metal sites.

Conclusions

Aqueous phase hydrogenation of both phenol and benzaldehyde on Pt/C is structure-sensitive. The intrinsic reaction rates are inversely proportional to Pt fractional exposure, i.e., the averaged hydrogenation activity of accessible Pt increases with increasing particle size. This trend is identical for hydrogenation of aromatic rings and carbonyl groups. It is indifferent of the genesis of the reduction equivalents, i.e., dissociation of H₂ or proton reduction under cathodic potential.

The structure sensitivity is concluded to be caused by the ensemble size sensitivity of the adsorption of the aromatic molecule. Thus, the increasing intrinsic rates with increasing metal particle size are attributed to increasing fractions of (100) and (111) planes, which permit adsorption of the aromatic ring. This conclusion is supported by in situ XANES that showed a higher fraction of sites capable of phenol adsorption on larger particles. It is notable that the hydrogenation of the carbonyl group in benzaldehyde requires a smaller ensemble than the hydrogenation of the aromatic ring.

Overall, the existence of the structure sensitivity allows one to guide the design of Pt based electrocatalysts that can have a precisely tailored selectivity to hydrogenation (of polar organic molecules) compared to H_2 evolution. It is to be explored, however, whether such selectivity changes are specific to Pt based catalysts or a much broader phenomenon, as well as the contribution of solvation effects on the appearance of structure sensitivity.

Experimental Section

Chemicals and catalytic materials. All chemicals were obtained from Sigma-Aldrich and used as received: Phenol (\geq 99.0%), benzaldehyde (\geq 99.0%), acetate buffer solution (pH 4.6), ethyl acetate (\geq 99.9%, HPLC), NaOH (> 99.9%, HPLC), Na₂SO₄ (> 99.9%), NaCI (> 99.9%), KCl (\geq 99.9%), and butanethiol (98%). Water was purified with a Milli-Q system up to a resistivity of 18.2 M Ω -cm. H₂ (Air Liquide, >99.99%) was used for catalytic thermal hydrogenation, Ar (Air Liquide, >99.99%) was used to remove O₂ from the electrolyte before ECH and N₂ (Air Liquide, >99.99%) was used to adjust the partial pressure of H₂.

Catalyst preparation. Pt/C catalysts with different loadings (1, 3, 5 and 10 wt.%) were purchased from Sigma-Aldrich. Two catalysts were prepared for XANES experiments. These catalysts were synthesized following the strong electrostatic adsorption procedure reported by Regalbuto et al.^[41] Aqueous solutions of tetraamine platinum nitrate were mixed with samples of XC-72 C (Vulcan) and Darco carbons allowing ion-exchange for 12 h. After the metal deposition, the catalysts were dried in air and reduced in H2 at 375 °C for 4 h. The catalysts were designated as Pt/C Vulcan and Pt/C Darco, respectively.

Catalyst characterization. The metal loadings of the catalysts were verified by atomic absorption spectroscopy (AAS) carried out on an UNICAM 939 AA-Spectrometer equipped with a GF 95 graphite furnace. Specific surface areas and pore diameters of the catalysts were derived, according to BET and BJH models, from N₂ physisorption isotherms measured at 77 K on a PMI automated BET sorptometer. The samples were outgassed before measurements at 523 K for 2 h.

For H_2 chemisorption measurements, the materials were initially reduced at 573 K for 1 h under H_2 atmosphere followed by treatment in vacuum at 573 K for 1 h. The samples were 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 were measured, which corresponded to physisorbed H_2 . The concentrations of chemisorbed H_2 were determined by extrapolating the difference isotherms to zero H_2 pressure. The fractional exposures of the supported metals were estimated from the concentration of chemisorbed hydrogen assuming a stoichiometry of 1:1 surface metal to hydrogen atoms.

Volume-area mean Pt particle sizes were calculated from the metal fractional exposure assuming a cuboctahedron geometry for the particles. The corresponding equations are [Equation (1) and (2)]:^[32]

$$d = \frac{5.01}{D} \times d_{at} \quad \text{for } D < 0.2 \tag{1}$$



$$d = \frac{3.32}{D^{1.23}} \times d_{at} \text{ for } 0.2 \le D \le 0.92$$
 (2)

where *d* is volume-area mean particle size, *D* is the dispersion or fractional exposure obtained from hydrogen chemisorption, and d_{at} is the atomic diameter of Pt (0.275 nm).

The Pt particle sizes can also be calculated from the metal fractional exposure using the Equation (3) wherein the spherical geometry was assumed^[43]

$$d = \frac{6A}{\rho\sigma LD} \tag{3}$$

where *d* is the mean particle size, *D* is the fractional exposure, A = Pt atomic mass (195.1 g/mole), $\rho =$ density (21.45×106 g/m³), $\sigma =$ average surface area occupied by Pt atom (0.81×10⁻¹⁹ m²), and *L* is the Avogrado's constant

For titration with butanethiol, increasing amounts of thiol were added to suspensions containing the Pt/C catalysts in acetate buffer. After stirring for 30 minutes, TCH or ECH experiments were performed following the protocols described below.

Characterization by transmission electron microscopy (TEM) was performed after the samples of the catalysts were ground and ultrasonically dispersed in ethanol. Drops of the suspensions were applied on carbon coated copper grids 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. The volume-area mean particle size was calculated by using the Equation (4):^[43]

$$d_{\text{TEM}} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{4}$$

where d_{TEM} is the volume-area mean diameter of the particle, d_i is the diameter of the particle measured from TEM images and n_i is the number of particles with diameter d_i .

Electrocatalytic hydrogenation (ECH). The two-compartment batch electrolysis cell was used to perform ECH experiments.^[22] Cathodic and anodic compartments were separated by a Nafion 117 proton exchange membrane (Ion Power, Inc.), which was treated 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), connected to a graphite rod (Sigma Aldrich, 99.99%), was used as working electrode in the cathode compartment. The typical size of the carbon felt used for the electrode preparation was 3 cm X1.5 cm (geometric surface area 4.5 cm²). A platinum mesh (Alfa Aesar, 99.9%) was used as counter electrode in the anodic compartment. An Ag/AgCl electrode (saturated KCl) (Ametek) with a double junction protection was used as reference electrode. The cathode compartment was filled with 60 mL acetate buffer solution at pH 4.6 and added with 10 mg of the catalysts. Prior to ECH, stirring at 500 rpm allowed complete infiltration of the powder into the carbon felt. Polarization of the catalyst was performed at -40 mA for 30 min. Phenol and benzaldehyde were typically added into the cathode compartment to obtain a final concentration of 20 mM although the concentration of phenol was varied $\pm 25\%$ to determine reaction orders. The anode compartment contained acetate buffer (pH 4.6) as the electrolyte. ECH experiments were performed at fixed potential while a flow of N₂ was kept through the reactant solution. All reactions were performed at atmospheric pressure and constant potential. Temperature was controlled with a

cooling/heating circulator (Julabo F25-ED). All procedures were performed with an electrochemical workstation VSP-300, Bio Logic

Thermal catalytic hydrogenation (TCH). A glass batch reactor was used to perform TCH experiments. Typical measurements were performed at atmospheric pressure with H_2 (10 mL·min⁻¹) flowing through the reactant solution at 296 K with 10 mg of catalyst and stirring at 500 rpm. The concentration of phenol and benzaldehyde was 20 mM.

Control experiments. Series of control experiments were performed by varying the amount of catalyst and stirring rates. As shown in Figure S9a, the conversion of phenol increased proportionally with the amount of catalyst while the corresponding TOF remained the same (Figure S9b). The current did not change beyond 400 rpm (Figure S9c). Thus, all experiments were performed at stirring of 500 rpm. These observations allowed us to discard external mass transport limitations. The calculated effectiveness factor (1) and Weisz modulus (0.005) indicated that the measured kinetics were not limited by internal mass transport (Supporting information, Figure S10). Disappearance of the reactant or product formation were not observed in the absence of cathodic potential, H₂, or a material containing Pt.

Product analysis. The course of the reaction was followed by periodically withdrawing aliquots of 1 mL from the cathode compartment of the electrochemical cell (ECH) or from the batch reactor (TCH). The organic phase was separated from the aqueous phase by extraction with ethyl acetate and dried on Na₂SO₄. A sample of the dry organic phase was mixed with a solution containing acetophenone as external standard. Quantitative analyses of the samples were performed by gas chromatography coupled with mass spectrometry (Shimadzu GCMS-QP2010). The GC was equipped with a plot Q capillary column (30 m × 250 μ m) and a thermal conductivity detector.

In-situ XANES measurements. To prepare the working electrode, a suspension containing the catalyst powder was passed through a carbon felt (Alfa Aesar, 3.1 mm thick). In this process, more than 95% of the suspended powder was infiltrated into the felt. Finally, the carbon felt was punched to a diameter suitable for the electrochemical XAFS cell, which was described in detail elsewhere.^[37] The XANES and EXAFS of the Pt L₃ edge was taken under flow conditions in the electrochemical cell with applied potential at Sector 20 of the APS. Prior to the spectra, the Pt/C catalysts were reduced for ~15 minutes to ensure a metallic Pt (rather than surface oxide). XANES difference spectra were taken by comparing the spectra under reaction conditions to a bulk Pt foil (which does not show any surface effects from adsorbed species). EXAFS fitting was done in Artemis as described elsewhere.^[37]

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Conflict of Interest

The authors declare no conflict of interest.

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Structure sensitivity: Intrinsic hydrogenation rates of phenol and benzaldehyde in aqueous phase are directly proportional to average size of Pt particles with hydrogen being supplied by both, molecular H₂ and in situ by a cathodic potential. In the latter case, it is possible to control the relative rates of hydrogen addition to organics and of H₂ evolution using renewable electricity.



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Structure Sensitivity in Hydrogenation Reactions on Pt/C in Aqueousphase

