## **Supporting Information**

## Pt Catalysts for Efficient Aerobic Oxidation of Glucose to Glucaric Acid in Water

Jechan Lee<sup>a</sup>, Basudeb Saha<sup>a\*</sup>, and Dionisios G. Vlachos<sup>a,b\*</sup>

<sup>a</sup>Catalysis Center for Energy Innovation (CCEI)

<sup>b</sup>Department of Chemical and Biomolecular Engineering, University of Delaware, Newark, DE 19716

Table S1. Glucose oxidation over the Pt/C catalyst in water as a function of reaction time.

Reaction time	Glucose		Carbon		
(h)	conversion (%)	Glucaric acid	Gluconic acid	Others <sup>a</sup>	balance <sup>b</sup> (%)
0.17	64	9	81	0	93
0.5	76	20	70	0	92
1	82	41	48	1	90
3	90	50	25	1	90
5	94	57	20	2	88
10	99	65	19	3	85

<sup>a</sup>Others include keto-glucose dialdehyde and keto-glucaric acid. <sup>b</sup>Carbon balance is the sum of carbon moles of products detected by HPLC and HPLC-MS and carbon moles of unconverted glucose. Reaction conditions: 80 °C, 6.2 bar O<sub>2</sub>, glucose/Pt (mol/mol) = 54.

	Table S2.	Physicoch	emical prop	erties of th	e Pt catalysts
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Catalyst	CO uptake	Pt particle size	BET surface	BJH pore	BJH pore
	(µmol/g)	<mark>(nm)</mark> a	area (m <sup>2</sup> /g)	volume (cm <sup>3</sup> /g)	size (nm)
Pt/C	62.6	<mark>4.2</mark>	1311.9	0.88	4.9
$Pt/Al_2O_3$	41.4	<mark>6.3</mark>	83.0	0.20	7.5
Pt/SiO <sub>2</sub>	82.4	<mark>3.2</mark>	125.1	0.94	9.3

<sup>a</sup>Pt particle size is calculated based on CO uptake of the catalysts after reduction in H<sub>2</sub> (300 °C, heating rate 5 °C /min, hold time 2 h). The following equation was used: Mean particle size =  $6(v_m/a_m)/D$  where  $v_m$  = volume occupied by an atom in bulk metal,  $a_m$  = area occupied by a surface atom, D = metal dispersion measured by CO chemisorption after H<sub>2</sub> reduction. The values of  $v_m$  and  $a_m$  are 15.10 Å<sup>3</sup> and 8.07 Å<sup>2</sup>,<sup>1</sup> respectively. The structure of Pt is assumed to be fcc.<sup>1</sup>

**Table S3.** Glucaric acid (5 wt% solution) stability in acidic and basic solutions in the presence of the Pt/C catalyst. Reaction conditions: 80 °C, 6.2 bar  $O_2$ , 1 h, glucaric acid/Pt (mol/mol) = 39.

Entry	Initial Fine	Final	Conversion - (%)	5	Carbon balanco		
	pH	pH		Tartronic acid	Oxalic acid	Keto-glucaric acid	(%)
1	2.5	3	24	0	0	30	84
2	8.5	7	46	52	22	22	98

Initial pH of 2.5 in entry 1 was adjusted with 0.04 mmol of  $H_2SO_4$ . Initial pH of 8.5 in entry 2 was adjusted with 0.08 mmol of NaOH.



Scheme S1. Proposed reaction pathways for glucose oxidation in water.



**Figure S1.** (a) Stack plots of HPLC chromatograms, showing glucaric and gluconic acids peaks, for glucose oxidation in water over the Pt/C catalyst. (b) Concentration of products from glucose

oxidation in water as a function of reaction time. Reaction conditions: 80 °C, 6.2 bar  $O_2$ , glucose/Pt (mol/mol) = 54.



**Figure S2**. Select conformations of adsorption of glucose, gluconic acid, and glucaric acid on Pt(111) along with free energies of adsorption at 298 K estimated using a first-principles group additivity scheme.<sup>2</sup> In this scheme, density functional theory is being used on a metal to estimate free energies of formation of various small compounds, unique groups are identified using graph theory, and their free energies are regressed to the estimates of the free energies of the compounds. Subsequently, the group values form a database which can be used to estimate the thermochemistry of complex molecules on the same catalyst. In this example, data from polyols, esters, ethers, acids, etc. are used<sup>2</sup> to estimate the free energies of the species depicted herein.



**Figure S3.** BJH pore volume and pore size of the Pt/C catalyst before and after five reactions (white patterned bars: pore volume; gray bars: pore size).

## **References**

- 1. G. Ertl, H. Knözinger, F. Schüth and J. Weiktamp, eds., *Handbook of Heterogeneous Catalysis*, Wiley-VCH, Weinheim, 2008.
- 2. M. Salciccioli, S. M. Edie and D. G. Vlachos, J. Phys. Chem. C, 2012, 116, 1873-1886.