

Electrocatalytic conversion of biomass-derived oxygenated aromatics to cycloalkanes

Meheryar R. Kasad^{a,b}, James E. Jackson^c and Christopher M. Saffron^{*a,b}

^a *Department of Chemical Engineering and Materials Science, Michigan State University, East Lansing, Michigan 48824, USA.*

^b *Department of Biosystems and Agricultural Engineering, Michigan State University, East Lansing, Michigan 48824, USA. E-mail: saffronc@msu.edu*

^c *Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA.*

Electronic Supplementary Information

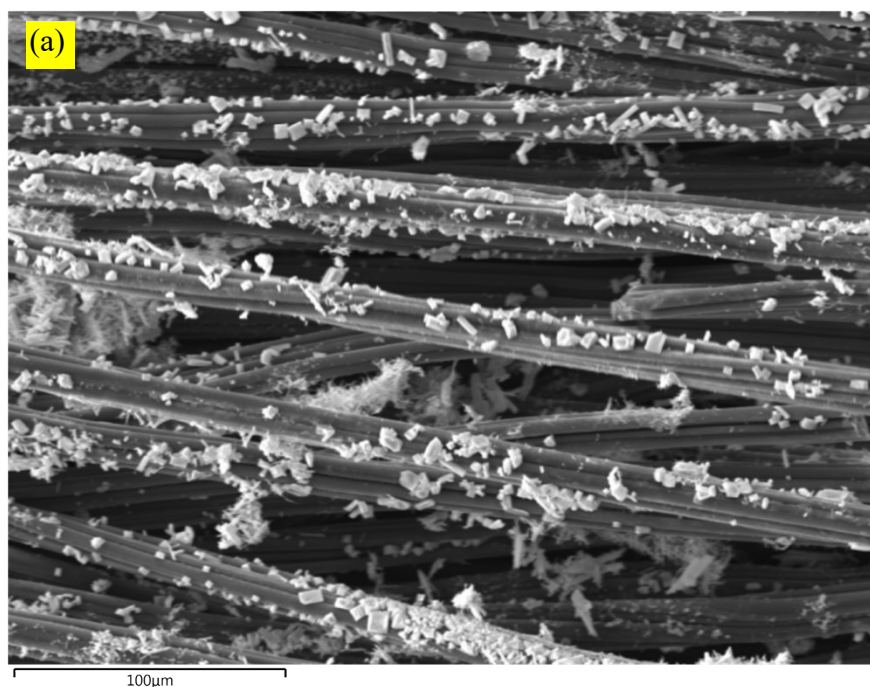
Materials

2-Methoxy-4-propylphenol (99%), eugenol (99%), 4-ethylguaiaicol (98%), 2-methoxy-4-methylphenol (98%), *p*-propyl anisole (99%), toluene (99.8%), ethylcyclohexane (99%), chloroplatinic acid solution (8 wt.% in H₂O), sulfuric acid (95%-98%), ammonium hydroxide solution (28%-30% NH₃ basis), dichloromethane (99.5%), 2-octanol (97%), 2-propanol (99.5%) [Sigma-Aldrich, St. Louis, MO]; sodium sulfate (99%) [Columbus Chemical Industries, Columbus, WI]; 4-propylphenol (99%), propylcyclohexane (98%) [TCI, Portland, OR]; di-*p*-tolyl ether (99%), 4-allyl-2,6-dimethoxyphenol (98%) [Thermo Fisher Scientific, Ward Hill, MA]; 2-methoxy-4-propylcyclohexan-1-ol (mixture of diastereomers) (95%) [Enamine]; cumene (99.9%) [Acros Organics, Geel, Belgium]; 1-methoxy-4-methylcyclohexane, 4-ethylcyclohexanol [AA Blocks, San Diego, CA]; 4-methylcyclohexanol (cis+trans) (98%), methylcyclohexane (99%) [Alfa Aesar, Ward Hill, MA]; 4-methylcyclohexanone [Aldrich Chemical Company, Milwaukee, WI]; sodium chloride (crystal), sulfuric acid (95%-98%) [Avantor Performance Materials, Center Valley, PA]; 4-propylcyclohexanol (98%) [BeanTown Chemical, Hudson, NH]; hexaammineruthenium(III) chloride (99%) [Strem Chemicals, Newburyport, MA] were used as received without purification. Deionized water from a NANOpure ultrapure water system was used for preparing aqueous solutions.

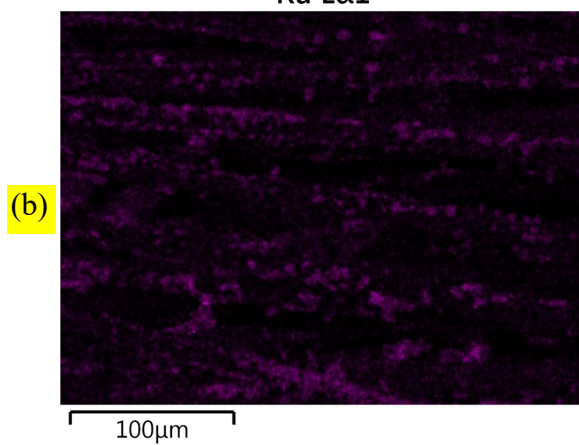
Electrocatalyst characterization

Table S1: Physical characteristics based on N₂ physisorption.

	S_{BET} (m² g⁻¹)	V_t (cm³ g⁻¹)	V_{μpore} (cm³ g⁻¹)	D_p (nm)
Washed and dried ACC	1,095	0.476	0.414	1.74
Ru_{1.0}Pt_{0.0}/ACC	874	0.409	0.332	1.87
Ru_{0.75}Pt_{0.25}/ACC	952	0.455	0.361	1.91
Ru_{0.50}Pt_{0.50}/ACC	903	0.416	0.344	1.84
Ru_{0.25}Pt_{0.75}/ACC	937	0.432	0.356	1.84
Ru_{0.0}Pt_{1.0}/ACC	1,017	0.448	0.386	1.76



Ru Lα1



Pt Mα1

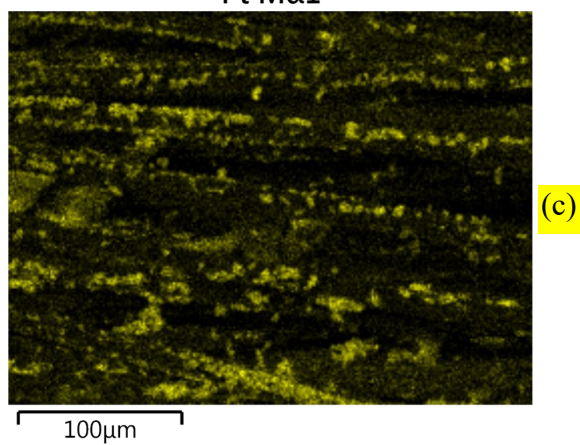


Figure S1: (a) SEM image of $\text{Ru}_{0.75}\text{Pt}_{0.25}/\text{ACC}$ and elemental maps of (b) Ru and (c) Pt collected by EDS.

Mole balance closure

The incomplete mole balance closure in various experiments of the present study indicates loss of material (reactants and products) from the ECH cell. The likely mechanisms for material loss include migration to the anode compartment, vaporization/stripping by the hydrogen gas produced at the cathode surface, and irreversible adsorption/reaction with the ACC support. Analysis of the anolyte extracts by GC-MS following the ECH trials suggests that migration of material to the anode compartment is not a major loss mechanism. Therefore, to investigate the loss of material by vaporization/stripping due to H₂ gas evolution at the cathode surface, control experiments were conducted whereby MeChH, EtChH, PrChH, 4-MeChOH and 4-PrGu substrates were subjected to electrolytic reduction on washed and dried ACC. The results provided in Figure S2 indicate that there is significant loss of material by this mechanism. The differences in substrate losses can be attributed to the differences in their boiling points as well as their solubility in the catholyte solution. For example, alkylcyclohexanes are insoluble in the catholyte solution and remain adsorbed to the ACC cathode (RuPt/ACC cathode in case of ECH); thus, they are more likely to be lost by gas stripping due to their proximal location to the site of hydrogen evolution. Future work would involve developing cell designs to condense the vapor phase materials exiting the cathode compartment. Finally, no product formation was observed in the 4-PrGu metal free trials confirming that the presence of Ru and/or Pt particles on the electrocatalyst was necessary to drive the HDO and aromatic ring saturation reactions. Moreover, the lack of product formation during 4-PrGu trials indicates that the hydrolysis pathway hypothesized for cleavage of ether linkages does not occur homogeneously in the catholyte solution used in the present study.

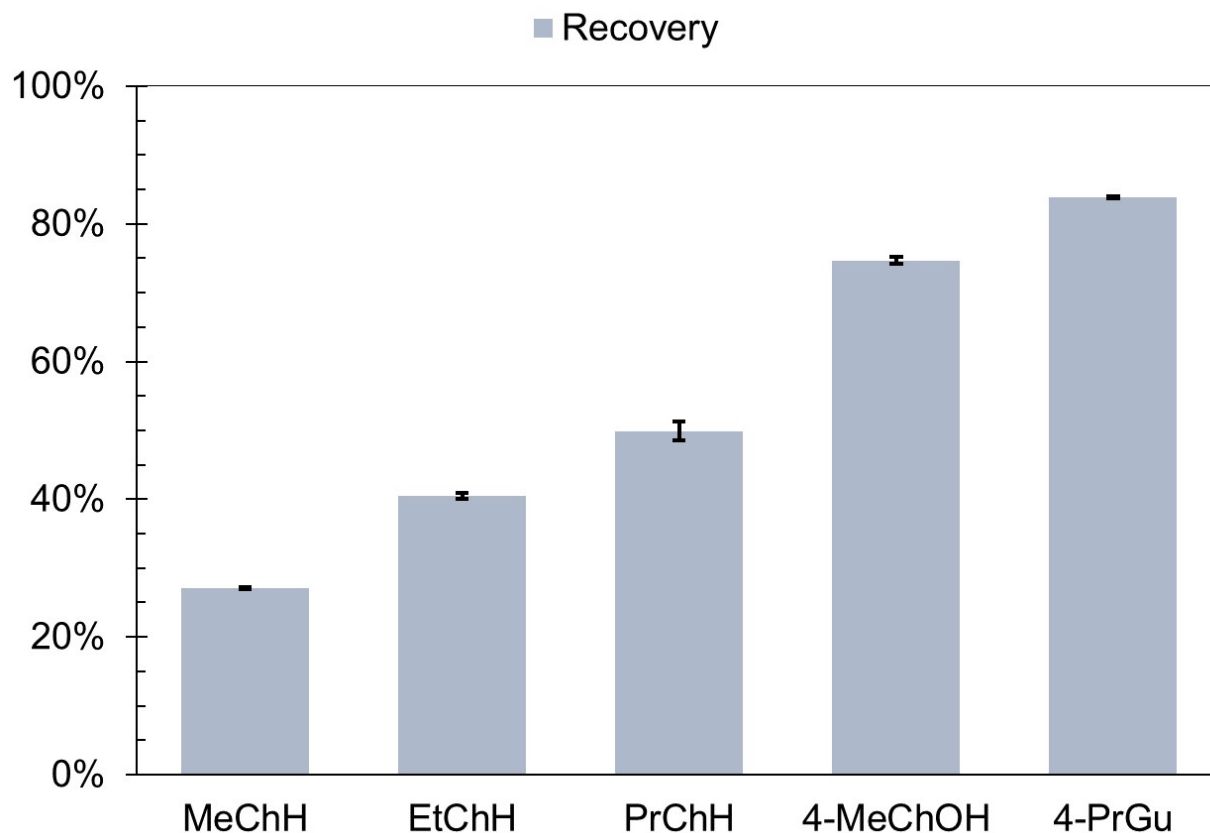


Figure S2: Electrolytic reduction of substrates on washed and dried ACC to estimate losses by vaporization/gas stripping due to H₂ evolution at the cathode. Experiment conditions: current=60 mA, (mol e⁻)/(mol substrate)=25, temperature=50 °C (MeChH and 4-MeChOH) and 60 °C (EtChH, PrChH and 4-PrGu), substrate concentration at the start of the trial (t=0): 0.012 M (MeChH, EtChH, PrChH and 4-MeChOH) and 0.020 M (4-PrGu).

C-O bond dissociation energies

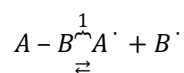
Table S2: Bond dissociation energy for C-O bonds in different substrates.

Bond (in Compound)	Bond dissociation energy (BDE) kcal/mol [phase]	Reference
C _{aryl} -OH (in phenol)	110.8 [gas]	1
	110.7 [aqueous]	2
	113.9 [gas]	#
	113.0 [aqueous]	#
C _{aryl} -OH (in guaiacol)	114.7 [gas]	2
	107.2 [gas]	3
	115.5 [gas]	4

$C_{\text{aryl}}-\text{OH}$ (in syringol)	111.3 [aqueous]	2	
	115.1 [gas]	#	
	112.6 [aqueous]	#	
	105.8 [gas]	5	
	114.7 [gas]	4	
	110.5 [gas]	#	
	106.7 [aqueous]	#	
$C_{\text{aryl}}-\text{OCH}_3$ (in anisole)	100.1 [gas]	1	
	99.4 [aqueous]	2	
	105.9 [gas]	#	
	103.8 [aqueous]	#	
	$C_{\text{aryl}}-\text{OCH}_3$ (in guaiacol)	102.4 [gas]	2
		92.2 [gas]	3
		105.7 [gas]	4
		99.8 [aqueous]	2
$C_{\text{aryl}}-\text{OCH}_3$ (in syringol)	90.5 [gas]	5	
	118.9 [gas]	4	
	$C_{\text{aryl}}\text{O}-\text{CH}_3$ (in anisole)	62.9 [gas]	1
67.2 [aqueous]		2	
66.8 [gas]		#	
63.8 [aqueous]		#	
$C_{\text{aryl}}\text{O}-\text{CH}_3$ (in guaiacol)		59.4 [gas]	2
		47.1 [gas]	3
		60.9 [aqueous]	2
$C_{\text{aryl}}\text{O}-\text{CH}_3$ (in syringol)	51.8 [gas]	5	
$C_{\text{cyclic}}-\text{OH}$ (in cyclohexanol)	95.3 [gas]	1	
	96.1 [gas]	#	
	95.7 [aqueous]	#	

C _{cyclic} O—CH ₃ (in methoxycyclohexane)	72.5 [gas]	*
	82.6 [gas]	#
	81.2 [aqueous]	#
C _{cyclic} —OCH ₃ (in methoxycyclohexane)	82.4 [gas]	*
	88.2 [gas]	#
	86.9 [aqueous]	#
C _{cyclic} —OH (in 2,4-cyclohexadien-1-ol)	79.8 [gas]	*
	73.0 [gas]	#
	71.2 [aqueous]	#
C _{cyclic} —OCH ₃ (in 5-methoxycyclohexa-1,3-diene)	69.3 [gas]	*
	64.3 [gas]	#
	62.3 [aqueous]	#
C _{cyclic} O—CH ₃ (in 5-methoxycyclohexa-1,3-diene)	82.6 [gas]	*

*Bond dissociation energies were computed as the difference of the sum of heats of formation of the products and the heat of formation of the reactant for homolytic cleavage at the site indicated. Mathematically, for the homolytic cleavage of a compound A-B the relationship is expressed as:



$$\Delta H_1^0 = [\Delta H_f^0(A \cdot) + \Delta H_f^0(B \cdot)] - \Delta H_f^0(A - B)$$

The heats of formation of the reactants and product radicals were computed by the law of bond additivity using the values provided in the tables by Benson⁶.

#The heat of formation of a compound or radical in the gas phase was computed using the G3(MP2) theory.⁷ To estimate solvation energies, structures were gas-phase optimized using the ω B97X-D functional⁸ with the 6-311+G** basis set.^{9, 10} Single-point energies (again ω B97X-D/6-311+G**) were then computed in “water” simulated via the CPCM continuum method.¹¹ These calculations were implemented in Spartan’20 (Wavefunction Inc., Irvine, CA).

ECH experimental results

Table S3: Summary of substrate conversion, product (2-MeO-4-RChOH, 4-RChOH and RChH) yields and faradaic efficiency. The standard errors are reported in parentheses. The experimental conditions are provided in the figure captions in the article.

Substrate	Electrocatalyst	Conversion	Yield 2-MeO-4-RChOH	Yield 4-RChOH	Yield RChH	Faradaic efficiency
4-PrGu	Ru _{1.0} Pt _{0.0} /ACC	33.1% (±1.3%)	1.9% (±0.1%)	4.0% (±0.8%)	2.6% (±0.5%)	1.7% (±0.3%)
	Ru _{0.75} Pt _{0.25} /ACC	97.3% (±0.9%)	3.3% (±0.6%)	24.0% (±0.6%)	47.6% (±0.4%)	27.6% (±0.2%)
	Ru _{0.5} Pt _{0.5} /ACC	91.4% (±3.7%)	4.2% (±0.9%)	27.6% (±2.4%)	37.4% (±2.8%)	24.9% (±2.1%)
	Ru _{0.25} Pt _{0.75} /ACC	92.6% (±1.4%)	5.2% (±0.7%)	25.8% (±0.6%)	38.9% (±1.9%)	25.2% (±1.1%)
	Ru _{0.0} Pt _{1.0} /ACC	80.9% (±5.5%)	4.4% (±0.4%)	22.3% (±0.9%)	24.1% (±3.1%)	17.9% (±1.1%)
4-MeGu	Ru _{0.75} Pt _{0.25} /ACC	94.1% (±0.1%)	-	29.3% (±0.4%)	37.8% (±0.4%)	22.6% (±0.1%)
4-EtGu		94.7% (±0.1%)	-	26.4% (0.0%)	37.3% (±1.2%)	23.4% (±0.5%)
Eugenol		100% (0.0%)	5.1% (±0.5%)	25.3% (±0.3%)	30.1% (±1.1%)	22.8% (±0.4%)
4-PrPhOH		98.3% (±0.6%)	-	44.4% (±2.5%)	32.7% (±1.1%)	26.4% (±0.3%)
4-PrPhOMe		85.3% (±6.7%)	-	7.5% (±0.4%)	45.5% (±2.2%)	21.1% (±1.0%)
4-PrCh=O		100% (0.0%)	-	71.2% (±2.5%)	-	14.3% (±0.5%)
Toluene		100% (0.0%)	-	-	49.1% (±0.8%)	19.6% (±0.3%)
4-AySy		100% (0.0%)	4.7% (±0.1%)	13.1% (±1.3%)	17.8% (±0.3%)	14.6% (0.0%)

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