SUPPORTING INFORMATION

Selectivity tuning over monometallic and bimetallic dehydrogenation catalysts: effects of support and particle size

Konstantinos A. Goulas, Yuying Song, Gregory R. Johnson, Justin P. Chen, Amit A. Gokhale, Lars C. Grabow, F. Dean Toste

We define selectivity S of component *i* as:

$$S_i = \frac{Y_i}{\sum Y_i}$$

Where Y_i is the yield of component *i*, as measured by GC.

The ratio of dehydrogenation to decarbonylation α in the context of the ABE reaction is defined as:

$$\alpha = \frac{S_{butyraldehyde} + S_{acetaldehyde} + S_{pentanone} + S_{heptanone} + S_{undecanone}}{S_{methane} + S_{propane}}$$

The condensation rate *r* is defined as:

$$r = \frac{\left(Y_{pentanone} + Y_{heptanone} + Y_{undecanone}\right)}{m_{catal}} F_{ABE}$$

Where m_{catal} is the total mass of the catalyst in the reactor and F_{ABE} is the molar flow of ABE reactants.

In the context of butyraldehyde reactions over $PdCu/SiO_2$ catalysts, we define the selectivity *S* of component *i* as:

$$S_i = \frac{Y_i}{\sum Y_i}$$

Where Y_i is the yield of component *i*, as measured by GC.

The ratio of decarbonylation to hydrogenation β is defined as:

$$\beta = \frac{S_{propane}}{S_{butanol}}$$

The rate of decarbonylation is defined as

$$r_{decarb} = \frac{Y_{propane}}{m_{catal}} F_{butyraldehyde}$$

Where $F_{butyraldehyde}$ is the molar flow of butyraldehyde.

Similarly, the rate of hydrogenation is defined as:

$$r_{hyd} = \frac{Y_{butanol}}{m_{catal}} F_{butyraldehyde}$$

The turnover frequency of reaction j is defined as:

$$TOF_j = \frac{r_j}{Dn_{metal}}$$

Where D is the dispersion and n_{metal} are the moles of metal per gram of catalyst.

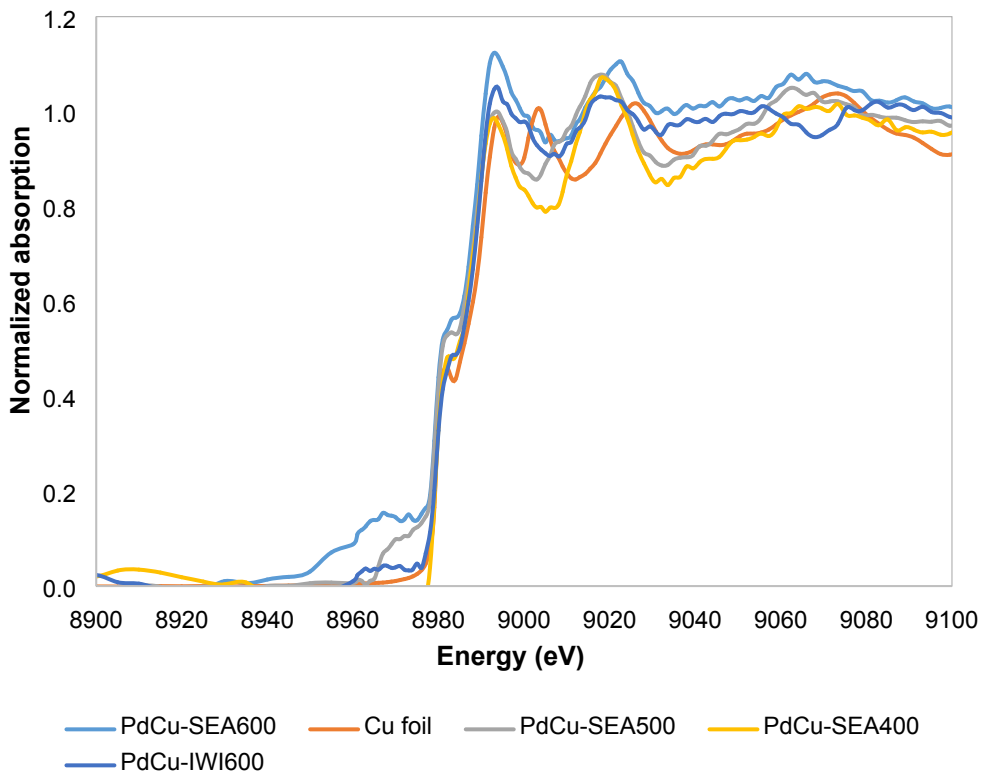

Figure S 1: Cu K edge XANES data for PdCu/SiO2 catalysts (reaction conditions).

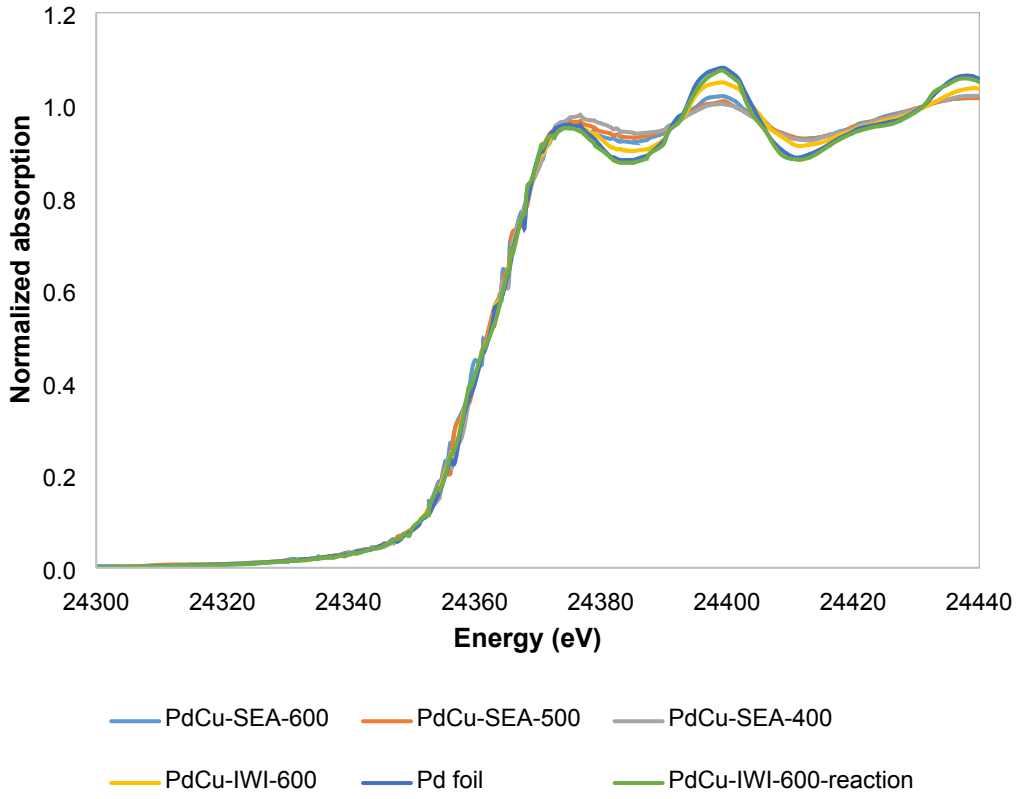

Figure S 2: Pd K edge XANES spectra of PdCu/SiO_2 catalysts.

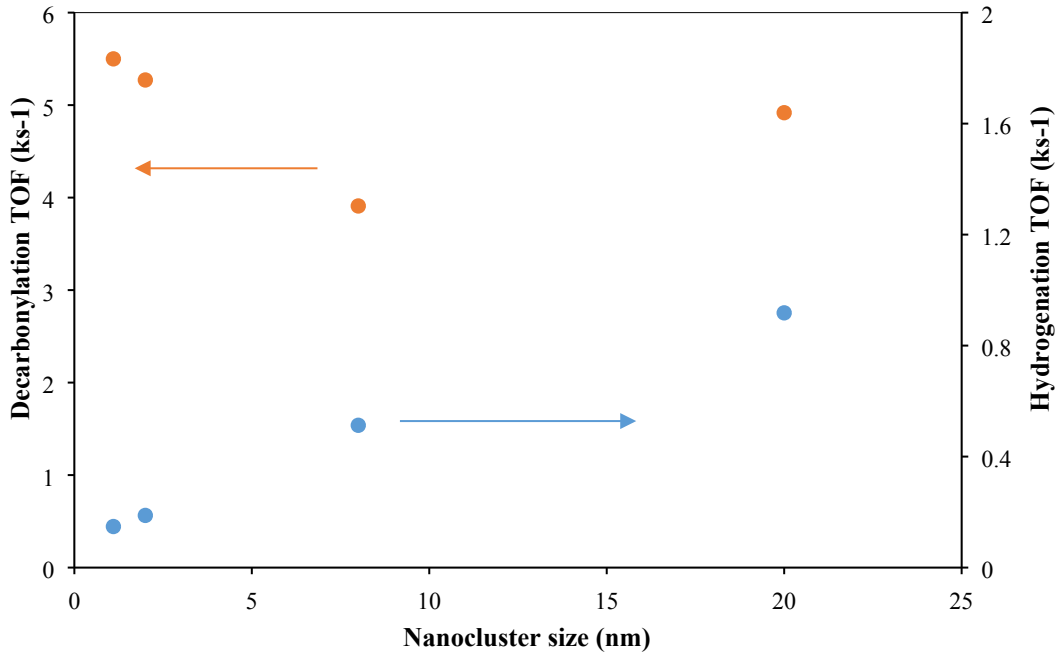

Figure S 3: TOF for hydrogenation and decarbonylation reactions over Pd/SiO_2 catalysts.

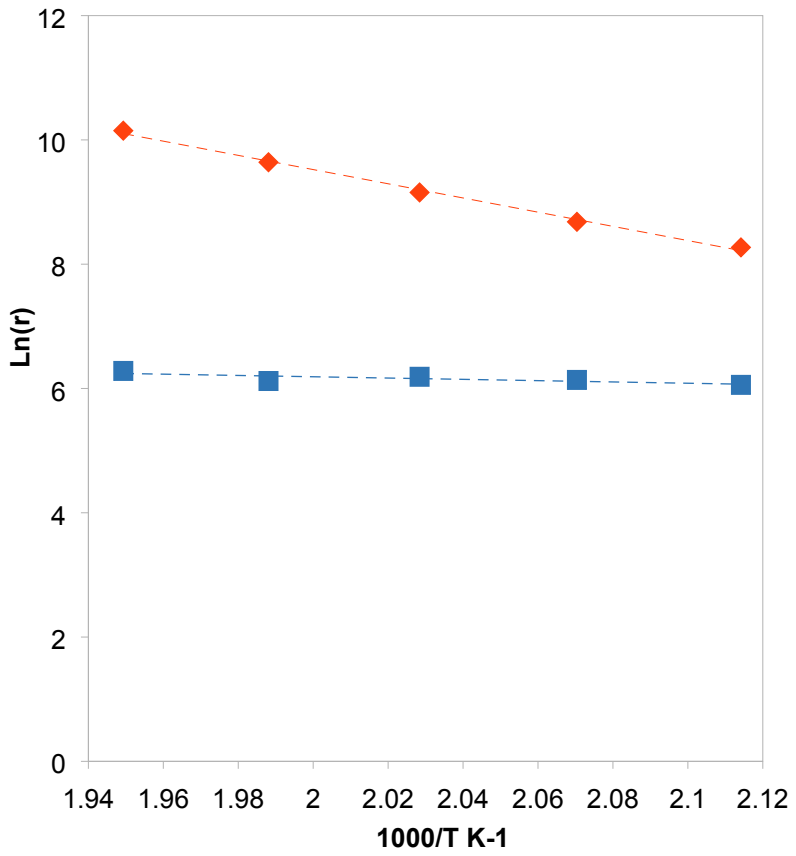

Figure S 4: Arrhenius plot for reactions over Pd/SiO2 catalyst (8 nm nanocluster size). Orange points: Decarbonylation, blue points: hydrogenation.

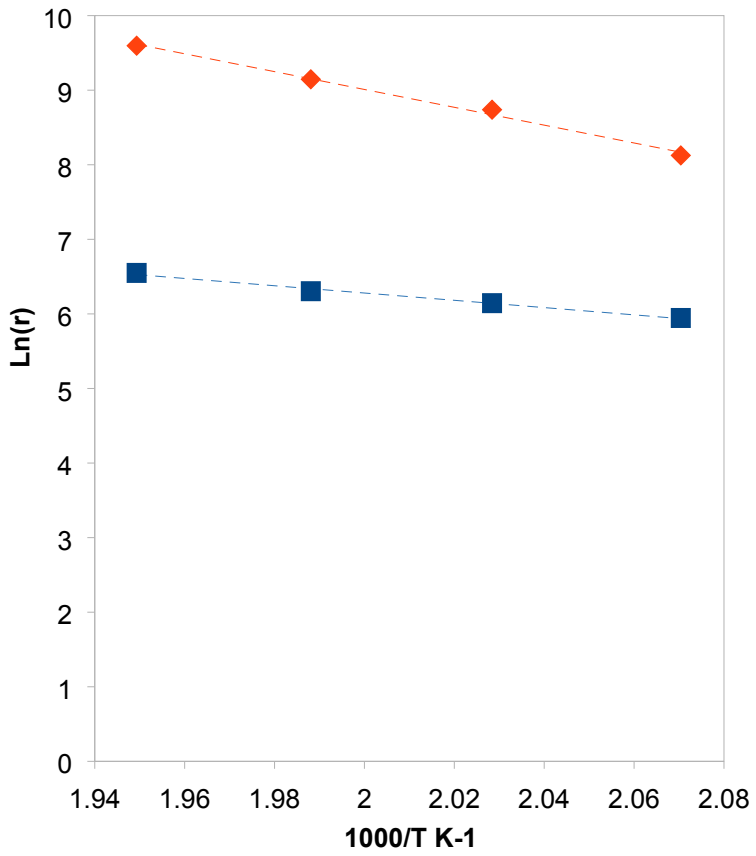

Figure S 5: Arrhenius plots for reactions over PdCu catalysts (5.9 nm nanoparticles): Orange points: Decarbonylation, blue points: hydrogenation.

Table S 1. The degrees of rate control for (A) hydrogenation pathway and (B) decarbonylation pathway on Pd(111) and 4CO+PdCu$_3$/Pd$_3$Cu(111) surfaces under the reaction condition of 473 K, 0.069 bar propanal and 0.931 bar H_2 with 0 % conversion.

	Pd(111)	4CO+PdCu$_3$/Pd$_3$Cu(111)
(III) $RCH_2CHO^{**} + H^* \rightleftharpoons RCH_2CHOH^{**} + *$	0.0	0.0
(IV) $RCH_2CHOH^{**} + H^* \rightleftharpoons RCH_2CH_2OH^* + 2^*$	0.8	0.0
(V) $RCH_2CHO^{**} + H^* \rightleftharpoons RCH_2CH_2O^* + 2^*$	0.1	0.9
(VI) $RCH_2CH_2O^* + H^* \rightleftharpoons RCH_2CH_2OH^* + *$	0.0	0.0

(A) Hydrogenation pathway

(B) Decarbonylation pathway

	Pd(111)	4CO+$PdCu_3/Pd_3Cu$(111)
(VIII) $RCH_2CHO^{**} + * \rightleftharpoons RCH_2CO^{**} + H^*$	0.0	0.0
(IX) $RCH_2CO^{**} \rightleftharpoons RCH_2^* + CO^*$	1.0	1.0
(X) $RCH_2^* + H^* \rightleftharpoons RCH_3(g) + 2^*$	0.0	0.0

Table S 2. Microkinetic modeling input files and their corresponding pathway in SI.zip.

File Name	**File Pathway**
Energetic Inputs for Pd(111)	MKM/energies-Pd.txt
Energetic Inputs for $PdCu_3/Pd_3Cu$(111)	MKM/energies-Alloy.txt
Energetic Inputs for 4CO+$PdCu_3/Pd_3Cu$(111)	MKM/energies-CO+Alloy.txt
Microkinetic Model Setup	MKM/MKM_setup.mkm

Table S 3. The file pathway in SI.zip for the most favorable structures of adsorbates on Pd(111), $PdCu_3/Pd_3Cu$(111), 4CO+ $PdCu_3/Pd_3Cu$(111), Pd(211), CO+Pd_sCu_3/Pd_3Cu(211) and CO+Pd_tCu_3/Pd_3Cu(211) surfaces.

Surface	**Adsorbate**	**File Pathway**
Pd(111)	Propanol	structures/Pd(111)/adsorbate/Propanol
	alkoxy	structures/Pd(111)/adsorbate/alkoxy
	hydroxyalkyl	structures/Pd(111)/adsorbate/hydroxyalkyl
	Propanal	structures/Pd(111)/adsorbate/Propanal
	ethylacylium	structures/Pd(111)/adsorbate/ethylacylium
	ethyl	structures/Pd(111)/adsorbate/ethyl
$PdCu_3/Pd_3Cu$(111)	Propanol	structures/Alloy(111)/adsorbate/Propanol
	alkoxy	structures/Alloy(111)/adsorbate/alkoxy
	hydroxyalkyl	structures/Alloy(111)/adsorbate/hydroxyalkyl
	Propanal	structures/Alloy(111)/adsorbate/Propanal
	ethylacylium	structures/Alloy(111)/adsorbate/ethylacylium
	ethyl	structures/Alloy(111)/adsorbate/ethyl
4CO+$PdCu_3/Pd_3Cu$(111)	Propanol	structures/4CO+Alloy(111)/adsorbate/Propanol
	alkoxy	structures/4CO+Alloy(111)/adsorbate/alkoxy
	hydroxyalkyl	structures/4CO+Alloy(111)/adsorbate/hydroxyalkyl
	Propanal	structures/4CO+Alloy(111)/adsorbate/Propanal
	ethylacylium	structures/4CO+Alloy(111)/adsorbate/ethylacylium
	ethyl	structures/4CO+Alloy(111)/adsorbate/ethyl
Pd(211)	Propanol	structures/Pd(211)/adsorbate/Propanol
	hydroxyalkyl	structures/Pd(211)/adsorbate/hydroxyalkyl
	Ethylacylium	structures/Pd(211)/adsorbate/ethylacylium
	ethyl	structures/Pd(211)/adsorbate/ethyl
CO+Pd_sCu_3/Pd_3Cu(211)	alkoxy	structures/CO+Alloy(211)/Pd-step/adsorbate/alkoxy
	Propanal	structures/CO+Alloy(211)/Pd-step/adsorbate/Propanal
	ethylacylium	structures/CO+Alloy(211)/Pd-step/adsorbate/ethylacylium
	ethyl	structures/CO+Alloy(211)/Pd-step/adsorbate/ethyl
CO+Pd_tCu_3/Pd_3Cu(211)	alkoxy	structures/CO+Alloy(211)/Pd-terrace/adsorbate/alkoxy
	Propanal	structures/CO+Alloy(211)/Pd-terrace/adsorbate/Propanal

	ethylacylium	structures/CO+Alloy(211)/Pd-terrace/adsorbate/ethylacylium
	ethyl	structures/CO+Alloy(211)/Pd-terrace/adsorbate/ethyl

Table S 4. The file pathway in SI.zip for transition state structures of each reaction on Pd(111), $PdCu_3/Pd_3Cu(111)$, 4CO+ $PdCu_3/Pd_3Cu(111)$, Pd(211), CO+$Pd_sCu_3/Pd_3Cu(211)$ and CO+$Pd_tCu_3/Pd_3Cu(211)$ surfaces.

Surface	**Reaction**	**File Pathway**
Pd(111)	(III) Propanal+H→hydroxyalkyl	structures/Pd(111)/TS/III
	(IV) hydroxyalkyl+H→Propanol	structures/Pd(111)/TS/IV
	(V) Propanal+H→alkoxy	structures/Pd(111)/TS/V
	(VI) alkoxy+H→Propanol	structures/Pd(111)/TS/VI
	(VIII) Propanal→ethylacylium+H	structures/Pd(111)/TS/VIII
	(IX) ethylacylium→ethyl+CO	structures/Pd(111)/TS/IX
	(X) ethyl+H→Ethane	structures/Pd(111)/TS/X
$PdCu_3/Pd_3Cu(111)$	(III) Propanal+H→hydroxyalkyl	structures/Alloy(111)/TS/III
	(IV) hydroxyalkyl+H→Propanol	structures/Alloy(111)/TS/IV
	(V) Propanal+H→alkoxy	structures/Alloy(111)/TS/V
	(VI) alkoxy+H→Propanol	structures/Alloy(111)/TS/VI
	(VIII) Propanal→ethylacylium+H	structures/Alloy(111)/TS/VIII
	(IX) ethylacylium→ethyl+CO	structures/Alloy(111)/TS/IX
	(X) ethyl+H→Ethane	structures/Alloy(111)/TS/X
4CO+$PdCu_3/Pd_3Cu(111)$	(III) Propanal+H→hydroxyalkyl	structures/4CO+Alloy(111)/TS/III
	(IV) hydroxyalkyl+H→Propanol	structures/4CO+Alloy(111)/TS/IV
	(V) Propanal+H→alkoxy	structures/4CO+Alloy(111)/TS/V
	(VI) alkoxy+H→Propanol	structures/4CO+Alloy(111)/TS/VI
	(VIII) Propanal→ethylacylium+H	structures/4CO+Alloy(111)/TS/VIII
	(IX) ethylacylium→ethyl+CO	structures/4CO+Alloy(111)/TS/IX
	(X) ethyl+H→Ethane	structures/4CO+Alloy(111)/TS/X
Pd(211)	(IV) hydroxyalkyl+H→Propanol	structures/Pd(211)/TS/IV
	(IX) ethylacylium→ethyl+CO	structures/Pd(211)/TS/IX
CO+$Pd_sCu_3/Pd_3Cu(211)$	(V) Propanal+H→alkoxy	structures/CO+Alloy(211)/Pd-step/TS/V
	(IX) ethylacylium→ethyl+CO	structures/CO+Alloy(211)/Pd-step/TS/IX
CO+$Pd_tCu_3/Pd_3Cu(211)$	(V) Propanal+H→alkoxy	structures/CO+Alloy(211)/Pd-terrace/TS/V
	(IX) ethylacylium→ethyl+CO	structures/CO+Alloy(211)/Pd-terrace/TS/IX