Electronic Supplementary Information (ESI): First-Principles Study on Gas Phase Decomposition of Bio-oil Oxygenated Compounds over Palladium Catalyst Surface

by

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Table S1: The literature survey in tabulated form including all major details.

S. No.	Author(s)	Title	Catalyst(s)	T	p_{H2} / flow rate	Major Product(s)	Remarks
2-Butenal							
1.	Coloma et al.[5]	Crotonaldehyde hydrogenation over alumina- and silica-supported Pt–Sn catalysts of different composition. In situ DRIFT study	$PtSn/SiO_2$ $PtSn/Al_2O_3$	673 & 773 K	50 cm^3/min, H_2:Crotonaldehyde = 26:1	crotyl alcohol	the presence of Sn lowers the catalytic activity
2.	Bailie et al.[6]	Hydrogenation of but-2-enal over supported Au/ZnO catalysts	Au/ZnO	548-698 K	60 ml/min, H_2:but-2-enal = 14:1	Butanal, but-2-en-1-ol, 2-ethyl hexanal	Au particle size plays a significant role in the hydrogenation of C=O to alcohol
3.	Ruiz-Martínez et al.[7]	Ru–Ti intermetallic catalysts for the selective hydrogenation of crotonaldehyde	Ru/SiO_2 $RuTi/SiO_2$	773 K	50 ml/min (H_2)	crotyl alcohol	no selectivity of crotonaldehyde towards its alcohol using monometallic Ru catalyst while high selectivity using RuTi catalyst
4.	Delbecq et al.[8]	Metal–support interaction effects on chemo–regioselectivity: Hydrogenation of crotonaldehyde on Pt_{13}/CeO_2 (111)	Pt/CeO_2	0 K (electronic structure calculation)		Butanal, 2-butanol	hydrogenation of C=O double bond is less energy demanding at the metal-support interface compared to bare Pt(111) catalyst
5.	Zeinalipour-Yazdi et	Impact of co-adsorbed oxygen on crotonaldehyde adsorption over gold	Au_{13} and Au_{38} nanoclusters	0 K (electronic structure calculation)		---	surface coverage plays an important role in the prediction of adsorption

	al.[9]	nanoclusters: a computational study					energy
Butan-2,3-diol							
1.	Zheng et al.[10]	Conversion of 2,3-butanediol to butenes over bifunctional catalysts in a single reactor	Cu/ZSM-5	498-598 K	1 atm.	Butenes,	observed the conversion of 70% over CuO/ZSM-5 and high yield of butenes
2.	Zheng et al.[11]	Mechanistic study of the catalytic conversion of 2,3-butanediol to butenes	Cu/ZSM-5	548 K	1 atm.	Butenes, methyl ethyl ketone, 2-butanol	hydrogenation and dehydrogenation reactions prefer over Cu sites of the catalyst while dehydration mainly prefers the acid site of zeolite
3.	Duan et al.[12]	Dehydration of 2,3-butanediol into 3-buten-2-ol catalyzed by ZrO_2	CeO_2, La_2O_3, Yb_2O_3, ZrO_2, Al_2O_3, TiO_2, ZnO, Fe_2O_3, NiO, and Cr_2O_3	623 K	45 cm^3/min (H_2)	3-buten-2-ol, 3-hydroxy-2-butanone	the dehydration of butan-2,3-diol to 3-buten-2-ol prefers over monoclinic ZrO_2 along with a few ketones as the side products
4.	Zeng et al.[13]	Transformation of 2,3-butanediol in a dual bed catalyst system	Sc_2O_3 in first bed; and Al_2O_3, SiAl, zirconia doped calcium and ceria in	591-673 K	46-80 mL/min (H_2)	1,3-butadiene, 2,5-dimethylphenol	better selectivity of 1,3-butadiene using acidic oxides, e.g., Al_2O_3 and SiAl while basic sites led to the production of phenols

			second bed				
Butan-2,3-dione							
1.	Carrara et al.[14]	Hydrogenation of diacetyl over composite-supported egg-shell noble metal catalysts	Pt-BTAl Pt-UTAl Ru-BTAl Ru-UTAl Pd-BTAl Pd-UTAl	353 K	20 bar (H_2)	acetoin	Pd as most suitable towards hydrogenation of butan-2,3-dione among three metal catalysts

Table S2. The activation free barriers and forward reaction rate constants of all considered reaction steps under the conversion of bio-oil model compounds.

R. No.	$\Delta^{\ddagger}G$ (cal/mol)					k_f at 1 atm (sec-1)				
	298	398	498	598	698	298	398	498	598	698
2-Butenal										
R1	9.09E+03	9.06E+03	9.03E+03	9.01E+03	9.00E+03	1.37E+06	9.08E+07	1.17E+09	6.57E+09	2.29E+10
RA	2.41E+04	2.37E+04	2.33E+04	2.29E+04	2.24E+04	1.34E-05	7.79E-01	6.17E+02	5.61E+04	1.46E+06
R2	1.27E+04	1.22E+04	1.17E+04	1.12E+04	1.06E+04	3.19E+03	1.66E+06	7.70E+07	1.05E+09	6.97E+09
R3	2.09E+04	2.09E+04	2.10E+04	2.12E+04	2.13E+04	3.20E-03	2.77E+01	6.38E+03	2.39E+05	3.17E+06
Butan-2-3-diol										
R1	3.53E+04	3.59E+04	3.66E+04	3.72E+04	3.79E+04	8.91E-14	1.61E-07	9.49E-04	3.20E-01	2.09E+01
R2	2.01E+04	1.99E+04	1.97E+04	1.94E+04	1.90E+04	1.13E-02	9.98E+01	2.54E+04	1.08E+06	1.63E+07
R3	1.74E+04	1.80E+04	1.86E+04	1.93E+04	1.99E+04	1.20E+00	1.18E+03	7.42E+04	1.19E+06	8.63E+06
R4	7.30E+03	6.66E+03	5.98E+03	5.29E+03	4.58E+03	2.86E+07	1.89E+09	2.54E+10	1.50E+11	5.52E+11
Butan-2-3-dione										
R1	3.79E+04	3.80E+04	3.81E+04	3.82E+04	3.82E+04	1.06E-15	1.11E-08	1.96E-04	1.40E-01	1.59E+01
RA	1.78E+04	1.81E+04	1.83E+04	1.86E+04	1.89E+04	5.52E-01	1.03E+03	9.65E+04	2.01E+06	1.77E+07
R2	4.80E+03	4.58E+03	4.39E+03	4.21E+03	4.05E+03	1.94E+09	2.60E+10	1.28E+11	3.74E+11	8.10E+11
RB	2.47E+04	2.54E+04	2.61E+04	2.68E+04	2.76E+04	5.19E-06	1.00E-01	3.81E+01	2.03E+03	3.49E+04
RB1	1.54E+04	1.55E+04	1.56E+04	1.58E+04	1.60E+04	3.54E+01	2.77E+04	1.52E+06	2.22E+07	1.52E+08
RC	6.77E+03	6.71E+03	6.67E+03	6.64E+03	6.64E+03	6.98E+07	1.77E+09	1.27E+10	4.80E+10	1.25E+11

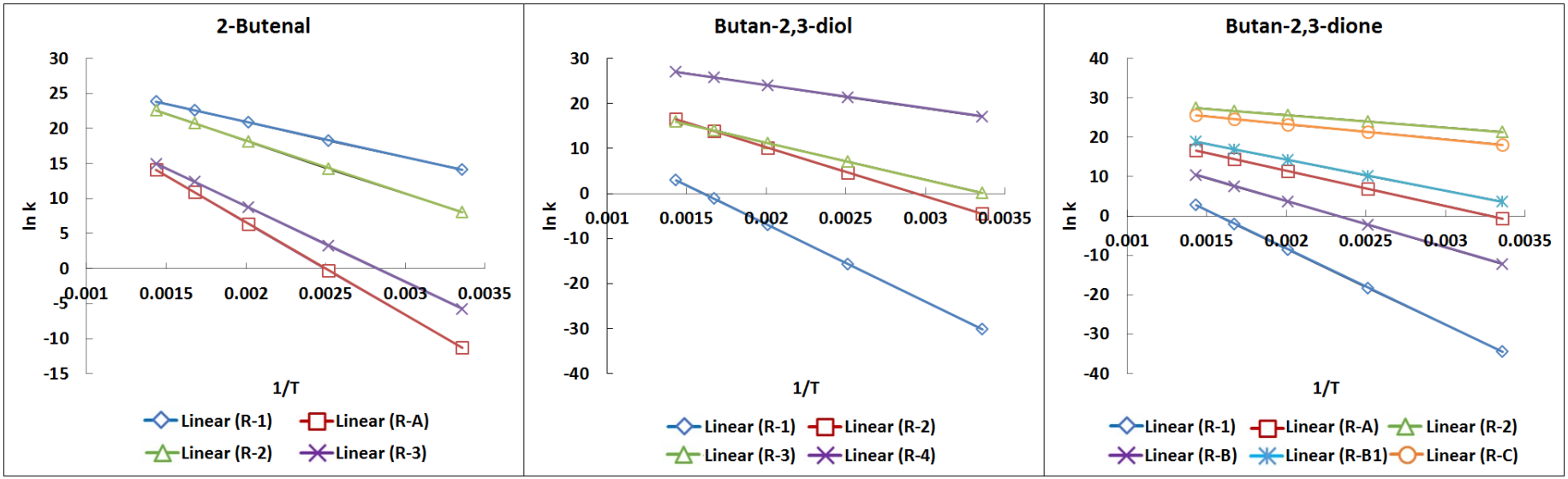

Figure S1. ln k vs. 1/T (K^{-1}) relations of all reaction schemes under the decomposition of each model compound.

Table S3. Arrhenius constants (A) and equilibrium constants of all considered reaction steps under the conversion of bio-oil model compounds.

R. No.	A					K at 1 atm				
	298	**398**	**498**	**598**	**698**	**298**	**398**	**498**	**598**	**698**
2-Butenal										
R-1	7.16E+12	9.72E+12	1.22E+13	1.46E+13	1.69E+13	1.78E+07	4.00E+05	4.27E+04	9.84E+03	3.50E+03
R-A	1.34E+13	2.34E+13	3.64E+13	5.23E+13	7.07E+13	5.59E-15	3.18E-11	5.90E-09	1.97E-07	2.44E-06
R-2	2.12E+13	3.75E+13	5.80E+13	8.19E+13	1.09E+14	5.01E+19	7.73E+14	1.06E+12	1.34E+10	5.98E+08
R-3	6.41E+12	7.94E+12	9.14E+12	1.01E+13	1.08E+13	2.01E+01	1.05E+01	6.76E+00	4.90E+00	3.81E+00
Butan-2,3-diol										
R-1	3.33E+11	4.02E+11	4.80E+11	5.62E+11	6.46E+11	3.67E-12	1.53E-09	5.68E-08	6.31E-07	3.51E-06
R-2	8.02E+12	1.31E+13	1.95E+13	2.71E+13	3.57E+13	1.00E-02	9.09E-02	3.61E-01	9.33E-01	1.87E+00
R-3	7.15E+11	7.73E+11	8.27E+11	8.76E+11	9.20E+11	6.62E-08	2.01E-06	1.49E-05	5.52E-05	1.38E-04
R-4	4.78E+13	8.66E+13	1.35E+14	1.90E+14	2.51E+14	7.22E+09	2.29E+08	2.98E+07	7.72E+06	2.96E+06
Butan-2,3-dione										
R-1	1.41E+12	2.26E+12	3.34E+12	4.61E+12	6.05E+12	4.88E-11	3.33E-08	1.76E-06	2.55E-05	1.75E-04
R-A	2.43E+12	3.02E+12	3.55E+12	4.02E+12	4.42E+12	2.47E+04	2.49E+03	6.40E+02	2.60E+02	1.37E+02
R-2	1.39E+13	2.00E+13	2.59E+13	3.12E+13	3.58E+13	6.78E+26	1.26E+20	1.14E+16	2.27E+13	2.64E+11
R-B	4.06E+11	4.46E+11	4.90E+11	5.32E+11	5.70E+11	2.96E+11	2.59E+08	4.03E+06	2.59E+05	3.70E+04
R-B1	4.19E+12	5.41E+12	6.44E+12	7.33E+12	8.10E+12	2.07E-12	1.11E-09	4.29E-08	4.49E-07	2.26E-06
R-C	7.50E+12	1.04E+13	1.30E+13	1.54E+13	1.76E+13	7.03E+07	1.60E+06	1.59E+05	3.27E+04	1.02E+04