Electronic Supporting Information

Kinetic Modelling of Hydrogen Transfer Deoxygenation of a Prototypical Fatty Acid over a bimetallic $Pd_{60}Cu_{40}$ catalyst: An Investigation of the Surface Reaction Mechanism and Rate Limiting Step

Kin Wai Cheah, Suzana Yusup*, Martin J. Taylor, Bing Shen How, Amin Osatiashtiani,
Daniel J. Nowakowski, Anthony V. Bridgwater, Vasiliki Skoulou,
Georgios Kyriakou and Yoshitmitsu Uemura

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1. **Materials and methods**

1.1. Catalyst preparation

In our previous work [1], we reported a simple, cheap and commercially relevant method namely incipient wetness impregnation for the synthesis of a series of bimetallic Pd-Cu based catalysts supported on activated carbon. The most efficient catalyst in the batch configuration with a nominal total metal loading of 5 wt. % and Pd to Cu molar ratio of 3:2 was selected for this kinetic modelling study. The same method was used to prepare the bimetallic $Pd_{60}Cu_{40}/C$ catalyst. Briefly, 0.95 g mesoporous activated carbon Norit® D10 (Alfa Aesar) was impregnated with 0.72 mL of Pd(NH3)4(NO3)2 (99%, Sigma-Aldrich), and 124 mg of Cu(NO3)2.3H2O (99%, Acros Organics). Subsequently, the solution was heated to 80 °C and aged for 24 h. Then, the resulting solid was collected by filtration and annealed under flowing He at 500 °C for 2 h, and thereafter reduced under flowing H_2 at 450 °C for 2 h.

1.2. Catalyst characterisation

Elemental analysis was performed using a Thermo Scientific iCAP 7000 series ICP-OES. Samples were prepared using ~10 mg of the catalyst, 100 mg ammonium fluoride (Sigma-Aldrich), 5 mL HNO_3 (68%, VWR Chemicals), 2 ml H_2SO_4 (>95%, Fisher), and 2 mL of deionized water. The mixture was stirred and digested for 0.5 h at 175 °C using a CEM Discover-S microwave system. Subsequently, the reactively-formed HF was neutralized using with 1 mL HCl (37%, VWR Chemicals) and 1 mL of boric acid solution (4%, Fluka). Finally, the samples were diluted 10 times with deionized water before being analysed on ICP-OES.

Surface areas and pore sizes were measured by N_2 physisorption on a Quantachrome Nova 4000 instrument, after sample outgassing at 120 °C for 4 h prior to analysis at -196 °C.

Surface areas were calculated using the Brunauer–Emmett–Teller (BET) method over the range $P/P_0 = 0.03–0.18$, where a linear relationship was maintained. Pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) model applied to the desorption branch of the isotherm.

Table S1. Physicochemical properties of $Pd_{60}Cu_{40}/C$ catalyst

Catalyst	Nominal molar ratio (Pd:Cu)	Metal loading[a] / wt.%			Surface area[b]	Pore diameter[c]	Particle size[d]
		Pd	Cu	Total	/ m^2 g^{-1}	/ nm	/ nm
$Pd_{60}Cu_{40}$	3:2	3.1	1.2	4.4	596	3.9	8.1

[a] ICP-OES, [b] BET, [c] BJH, [d] TEM

1.3. Development and fitting of mathematical kinetic equations

Power law or better known as differential rate law is a simple kinetic expression used extensively for quick determination of kinetic parameters without taking in the surface mechanistic steps into account. It expresses the rate of a reaction in terms of the concentration of reactants (oleic acid, tetralin and adsorbed H atoms) raised to an experimentally determined exponents. The power law kinetic expressions for Reaction 1 and 2 are expressed as follow:

Reaction 1: $r_1 = k_{rxn,1} [TET]^{\alpha}$

Reaction 2: $r_1 = k_{rxn,1} [OA]^{\propto} [H_2]^{\beta}$

Where r_1 is tetralin dehydrogenation rate, r_2 is oleic acid deoxygenation rate, $k_{rxn,1}$ is the forward rate constant, [TET] is molar concentration of tetralin, [OA] is molar concentration of oleic acid, $[H_2]$ is the molar concentration of molecular hydrogen, α and β are experimentally determined exponents.

For L-H kinetic model, it depicts a bimolecular surface reaction between two adsorbed reactant species. Regardless of the type of L-H model aforementioned, it generally involves a sequence of three similar steps: 1.) Adsorption of reactants, 2.) Surface reaction, 3.) Desorption of products. In order to derive L-H kinetic models for Reaction I and Reaction II, one of the individual reaction steps was initially assumed as irreversible rate-limiting step, while adsorption and desorption steps were considered to be rapid and at equilibrium state.

To further simplify the kinetic models, the following assumptions are taken into considerations: (1) an irreversible rate-controlling step with other elementary steps in a quasi-equilibrium state, (2) concentration of all mediums on the catalyst surface are in steady state, (3) identical catalytic sites are distributed homogenously on the catalyst surface, and (4) the adsorption constant for stearyl alcohol was disregarded in the denominator since such intermediate species are typically less strongly adsorbed on the catalyst surface, as compared to acid species [2].

As an example, the elemental sequence of dehydrogenation of tetralin (Reaction 1) involved are expressed into three individual steps as follows:

1.) Adsorption of tetralin: $TET + S \leftrightarrow TET \cdot S$

2.) Surface reaction: $TET \cdot S \rightarrow NAP \cdot S + 4H$

3.) Desorption of byproduct: $NAP \cdot S \leftrightarrow NAP + S$

where TET is tetralin molecule, H is hydrogen atom liberated from tetralin, NAP is naphthalene byproduct ,S is the active site and $X \cdot S$ is any reactant species adsorbed on a single active site.

In the interest of conciseness, only certain selected L-H kinetic models are derived herein. Considering the proceeding assumption of both adsorption and desorption steps were non-rate limiting, the L-H rate expression model for catalytic dehydrogenation of tetralin with surface reaction as the rate limiting step can be developed as follow:

$$r_1=K_{rxn,1}\,[TET \cdot S] \qquad (1)$$

where $r_1$is tetralin dehydrogenation rate, $K_{rxn,1}$ is the forward rate constant of reaction 1 and [TET ˙ S] is the molar concentration of tetralin molecules occupied the active site, S.

The molar concentration of tetralin adsorbed on the active site, [TET ˙ S] can be expressed as follow:

$$[TET \cdot S] = k_{TET}\,[TET]\,[S] \tag{2}$$

where k_{TET} is the equilibrium adsorption constant of tetralin, [TET] is molar concentration of tetralin, [S] is the concentration of free active sites.

By substituting Eq (2) into Eq (1), the L-H rate expression model for catalytic dehydrogenation of tetralin with surface reaction as the rate limiting step is showed as follow:

$$r_1 = K_{rxn,1}\,k_{TET}\,[TET]\,[S] \tag{3}$$

The total concentration of free active sites on the surface of catalysts can be given by the following simple expression:

$$[S_{Total}] = [S] + [TET \cdot S] \tag{3}$$

where $[S_{Total}]$ is the concentration of total active site on the catalysts surface, [TET·S] is the concentration of tetralin molecules occupied the active site, and [S] is the concentration of free active site, S

By substituting Eq (2) into Eq (3),

$$[S_{Total}] = [S] + k_{TET}[TET]\,[S] \tag{4}$$

$$[S] = \frac{[S_{Total}]}{1 + k_{TET}} \tag{5}$$

By taking Eq (5) into Eq (3) and lumping the concentration of total active site, $[S_{Total}]$ and forward reaction constant together as an apparent reaction constant denoted as $K_{rxn,\,1}$, giving the rate expression as:

$$r_1 = \frac{K_{rxn,1}\ k_{TET}\ [TET]}{1 + k_{TET}} \qquad (6)$$

To derive L-H competitive reaction model with non-dissociative adsorption of hydrogen for Reaction 2, the elemental sequence of deoxygenation of oleic acid involved are divided into four individual steps as follows:

1.) Adsorption of oleic acid: $OA + S \leftrightarrow OA \cdot S$

Adsorption of molecular hydrogen: $H_2 + S \leftrightarrow H_2 \cdot S$

2.) Surface reaction 1: $OA \cdot S + H_2 \cdot S \rightarrow SA \cdot S + S$

3.) Surface reaction 2: $SA \cdot S \rightarrow C17 \cdot S + CO_2$

4.) Desorption of product: $C17 \cdot S \leftrightarrow C17 + S$

where OA is oleic acid molecule, H_2 is molecular hydrogen, SA is stearic acid intermediate, C17 is the heptadecane product, S is the active site and $X \cdot S$ is any reactant species, X adsorbed on a single active site.

By assuming surface reaction 1 is rate limiting step, the L-H rate expression model for catalytic deoxygenation of oleic acid with surface reaction 1 as the rate limiting step can be developed as follow:

$$r_2 = K_{rxn,2}\ [OA \cdot S]\ [H_2 \cdot S] \qquad (7)$$

where r_2 is oleic acid deoxygenation rate, $K_{rxn,2}$ is the forward rate constant of reaction 2, $[OA \cdot S]$ and $[H_2 \cdot S]$ is the molar concentration of oleic acid and molecular hydrogen occupied on the active site, S respectively.

The molar concentration of tetralin and oleic acid adsorbed on the active site can be expressed as follow:

$$[OA \cdot S] = k_{OA}\,[OA]\,[S] \quad (8)$$

$$[H_2 \cdot S] = k_{H2}\,[H_2]\,[S] \quad (9)$$

where k_{OA} and k_{H2} are the equilibrium adsorption constant of oleic acid and molecular hydrogen, respectively, [OA] is molar concentration of oleic acid, $[H_2]$ is molar concentration of molecular hydrogen and [S] is the concentration of free active site.

By substituting Eq (8) ad Eq (9) into Eq (7),

$$r_2 = K_{rxn,2}\,k_{OA}\,k_{H2}\,[OA]\,[H_2]\,[S]^2 \quad (10)$$

The total concentration of free active sites on the surface of catalysts can be given by the following simple expression:

$$[S_{Total}] = [S] + [OA \cdot S] + [H_2 \cdot S] + [SA \cdot S] + [C17 \cdot S] \quad (11)$$

where $[S_{Total}]$ is the concentration of total active site on the catalysts surface, $[X{\cdot}S]$ is the concentration of chemical species occupied the active site, S and [S] is the concentration of free active site.

As surface reaction 1 is assumed to be rate limiting, the concentration of resulting stearic acid and heptadecane occupied the active sites can be considered as negligible.

$$[SA \cdot S] = [C17 \cdot S] = 0 \quad (12)$$

$$[S_{Total}] = [S] + [OA \cdot S] + [H_2 \cdot S] \quad (13)$$

By substituting Eq (8) and Eq (9) into Eq (13),

$$[S_{Total}] = [S] + k_{OA}\,[OA]\,[S] + k_{H2}\,[H_2]\,[S] \quad (14)$$

$$[S] = \frac{[S_{Total}]}{1 + k_{OA}[OA] + k_{H2}[H_2]} \quad (15)$$

By taking Eq (15) into Eq (10) and lumping the concentration of total active site, $[S_{Total}]$ and forward reaction constant together as an apparent reaction constant denoted as $K_{rxn,2}$, giving the rate expression as:

$$r_2 = \frac{K_{rxn,2}\ k_{OA}\ k_{H2}[OA]\,[\,H_2]}{\left(1 + k_{OA}[OA]\ + k_{H2}[H_2]\right)^2} \tag{16}$$

For the E-R kinetic mode is, we assume the adsorption of oleic acid with non-adsorbed hydrogen molecules from the liquid phase and non-adsorption of oleic acid with dissociative adsorption of hydrogen molecules. By using the similar derivation method showed above, the rate expression can be written as follow:

$$r_2 = \frac{K_{rxn,2}\ k_{OA}[OA]\,[\,H_2]}{\left(1 + k_{OA}[OA]\right)} \tag{17}$$

$$r_2 = \frac{k_{rxn,2}\, k_{H_2}[OA][H_2]}{\left(1 + \sqrt{k_{H_2}[H_2]}\right)^2} \tag{18}$$

Based on the proposed mechanistic schemes in Table 3, different kinetic mathematic equations were derived based on the similar derivation steps aforementioned, considering each surface reaction as a rate-limiting step. As the conversion values of oleic acid and tetralin in these kinetic studies were higher than 10 %, an integral reactor method was used to find the dependence of the reaction rates on reaction temperatures. The consumption of oleic acid and tetralin in a continuous fixed bed reactor were expressed through measurable process parameters and are given by the following equations:

$$\frac{dF_{OA,out}}{dw} = r_{OA} \tag{19}$$

$$\frac{dF_{TET,\,out}}{dw} = r_{TET} \tag{20}$$

where F_{OAout} and F_{TETout} are the outlet molar flow rate of oleic acid and tetralin respectively, r_{OA} and r_{TET} are the reaction rate of oleic acid and tetralin and w is the mass of $Pd_{60}Cu_{40}/C$ catalyst used. $F_{OA,out}$ and $F_{TET,out}$ can be calculated by multiplying the outlet concentration of oleic acid and tetralin (C_{OA} or C_{TET}) with the liquid flow rate. With negligible heat and mass transfer limitations determined from the mass transportation and heat transfer studies, the reaction rates were assumed to be constant radially and varied axially along the reactor due to changes in reactant concentrations. Therefore, a series of experiments were carried out in the fixed bed reactor with the variation of WHSV (change in catalyst mass) instead of measuring the reactant concentration locally along the reactor. Liquid samples were withdrawn in hourly intervals to monitor the reaction equilibrium condition. With a total of 7 h reaction, all experiment runs achieved steady state condition after the 3rd h with less than 10% deviation from the average reactant conversion. Thus, the outlet molar concentration of unreacted oleic acid, tetralin and molecular hydrogen obtained from the 3rd h to the 7th h were taken as the raw experimental data for the fitting of derived rate equations.

MATLAB software R2018a (provided by Universiti Teknologi PETRONAS, Malaysia) was used to fit the raw experimental data into the rate equation. In order to estimate the kinetics constants, each rate equation was subjected to a non-linear regression analysis by minimizing the objective function of the root mean square difference between experimental rate and calculated rate. The integrity of the model was further described by the residual of experimental and estimated results in square and the residual of experimental and mean experimental values in square given the degree of explanation, R^2. In this work, the regression analysis on the experimental data was performed purely based on mathematical basis without taking thermodynamic significance of the kinetics constants into account. Rate constants from the developed model were estimated using experimental data at four different temperatures, 300 °C, 330 °C, 360 °C and 390 °C by using a non-linear regression curve fitting algorithm (Levnberg-Marquardt) built into the MATLAB software.

The rate constants obtained must satisfy the following conditions, which are derived from thermodynamics and optimization considerations. These constraints include (1) Rate and adsorption equilibrium constant must be positive, (2) the activation energy should be positive, and (3) $R^2 > 95\%$. Based on the all the criteria/constraints above, the rate equation(s) with the best fitted experimental data (the highest R^2 and the lowest root-mean-square error (RMSE) values) will be further considered for the calculation of activation energy, E_a and pre-exponential factor, A. Activation energy and pre-exponential factor were calculated by plotting ln(k) against 1/T (Arrhenius plot) using the estimated rate constants from the best fitted rate equation at different temperatures.

2. **Effect of superficial flow velocity**

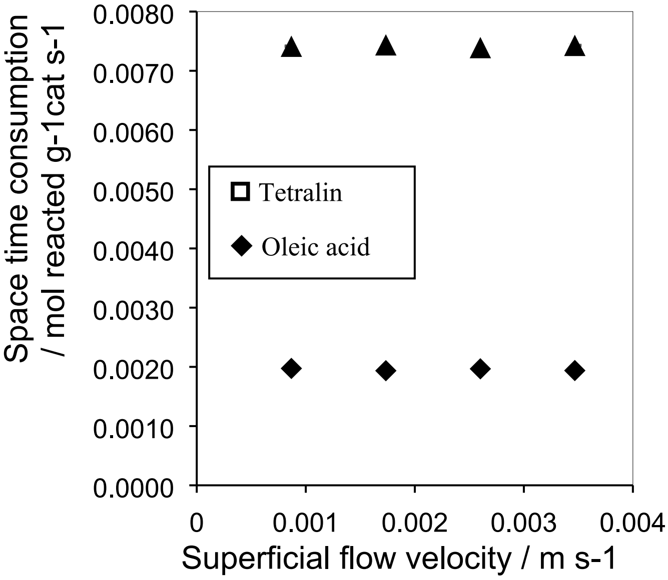


Figure S1. Effect of superficial flow velocity on space time consumption of oleic acid and tetralin. (Reaction conditions: oleic acid concentration = 3.6 mol/L , oleic acid:tetralin ratio = 1, 300 °C, 1 MPa bar of N_2, WHSV 10 h^{-1}, N_2 pressure = 1 MPa)

3. Catalyst stability in term of tetralin conversion

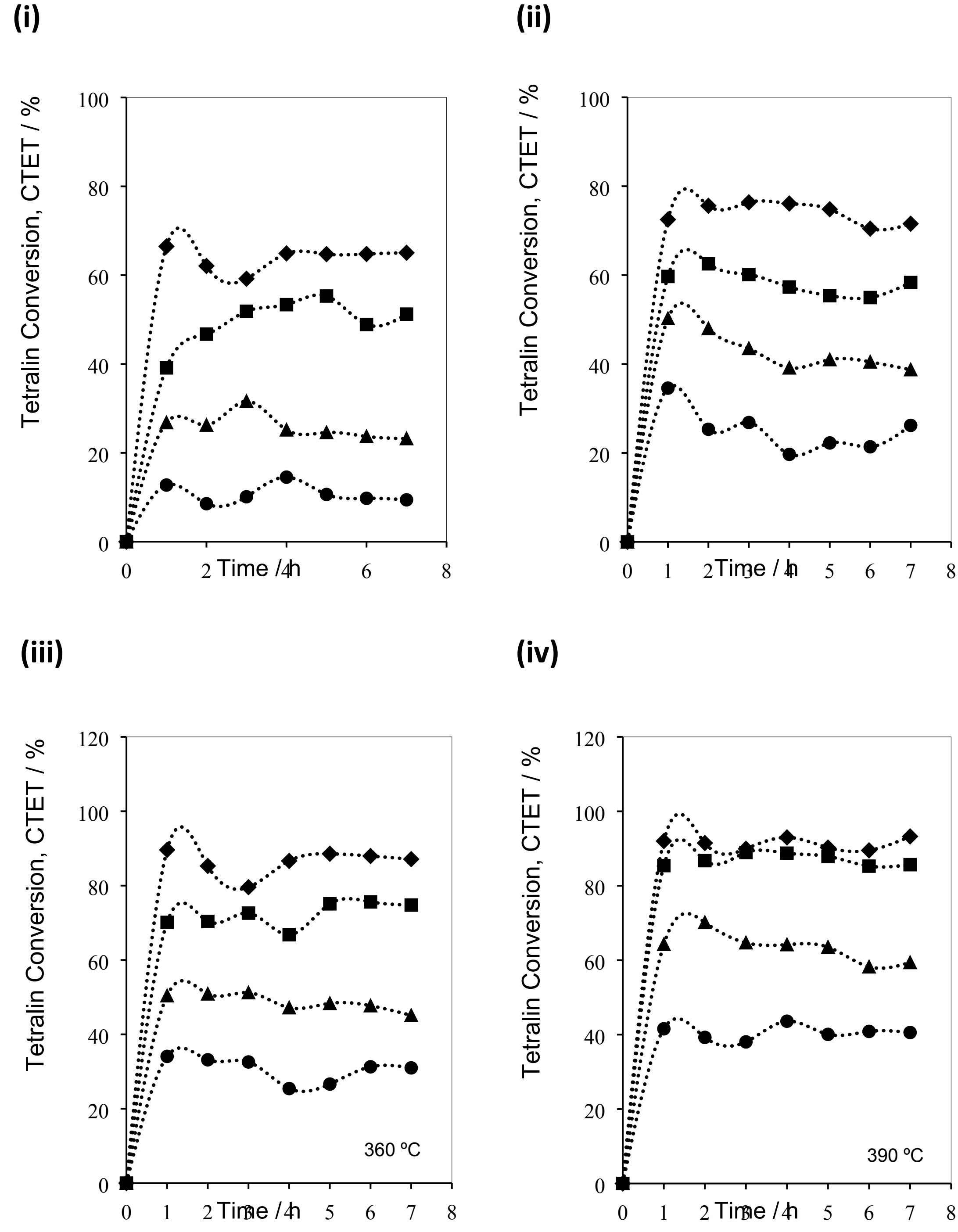
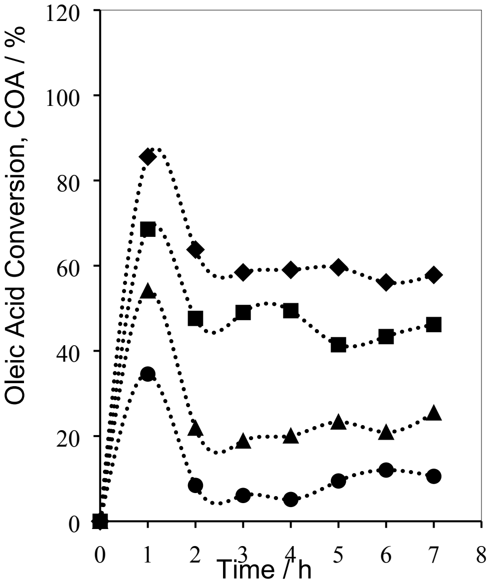
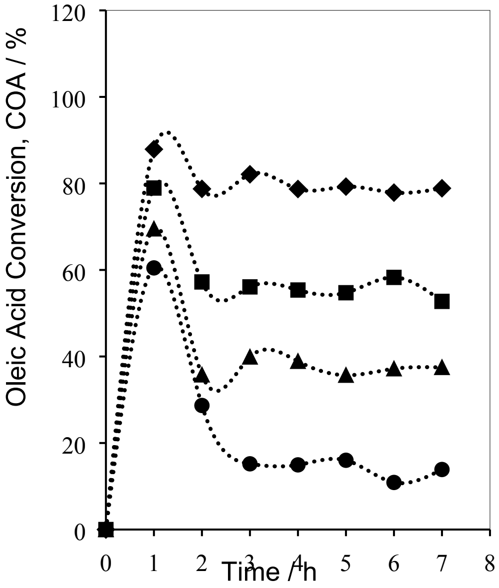


Figure S2. Profiles of tetralin conversion over $Pd_{60}Cu_{40}/C$ catalyst at reaction temperatures of (i) 300 ºC, (ii) 330 ºC, (iii) 360 ºC and (iv) 390 ºC, where the symbol (♦), (■), (▲), (●) refers to WHSV = 1 h^{-1}, 2.5 h^{-1}, 5 h^{-1} and 10 h^{-1} respectively. (Reaction conditions: oleic acid concentration = 3.6 mol/L , oleic acid:tetralin mass ratio = 1, catalyst mass = 0.5 - 3.6g , N_2 pressure =1 MPa)

4. **Catalyst stability in terms of oleic acid conversion.**

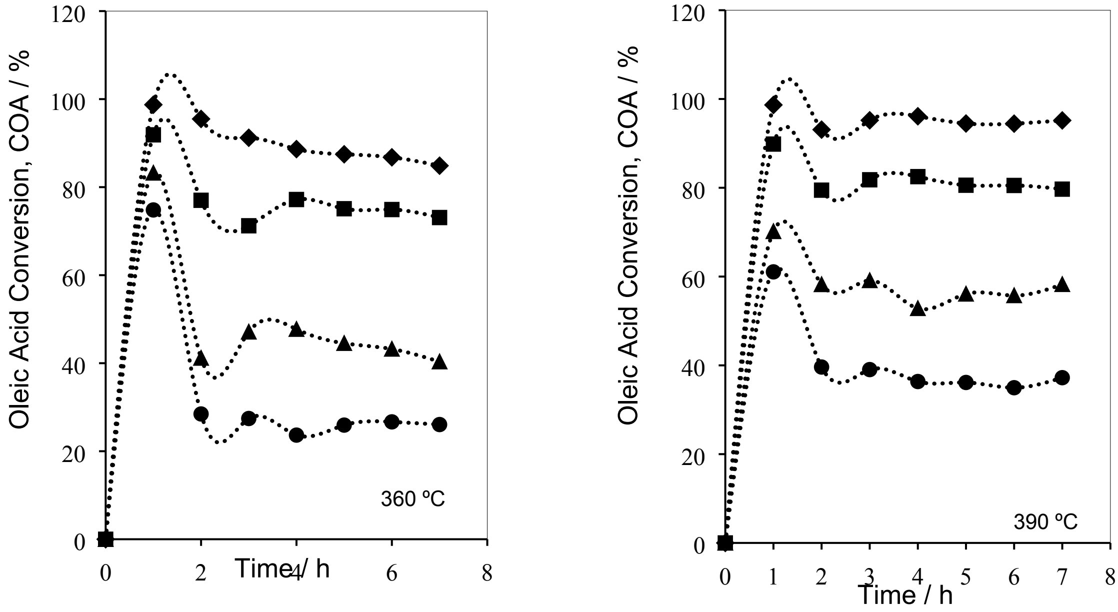
(ii)





(i)

(iv)



(iii)

Figure S3. Conversion of oleic acid over $Pd_{60}Cu_{40}$ catalyst over 7 h at reaction temperatures of (i) 300 ºC, (ii) 330 ºC, (iii) 360 ºC and (iv) 390 ºC, where the symbol (♦), (■), (▲), (●) refers to WHSV = 1 h^{-1}, 2.5 h^{-1}, 5 h^{-1} and 10 h^{-1} respectively. (Reaction conditions: oleic acid concentration = 3.6 mol/L , oleic acid:tetralin mass ratio = 1, catalyst mass =0.5 - 3.6g , N_2 pressure =1 MPa)

5. Kinetic and statistical parameters for tetralin dehydrogenation reaction

Surface Reaction 1 - Catalytic dehydrogenation of tetralin

Model	Temperature / ºC	$k_{rxn,\,I}$ / s^{-1}	γ	R_2	RSME
Power Law $r_1 = k_{rxn,1[TET]^{\alpha}}$	300	4.195×10^{-7}	1.087	0.8736	1.58×10^{-7}
	330	5.839×10^{-7}	1.107	0.8860	1.53×-10^{-7}
	360	9.128×10^{-7}	1.060	0.8881	9.59×10^{-6}
	390	5.778×10^{-7}	1.658	0.7712	1.32×10^{-6}

Model	Temperature / ºC	$k_{rxn,\,I}$ / mol s^{-1} g_{cat}^{-1}	K_{TET} / L mol^{-1}	R_2	RSME
L-H model with single site adsorption of tetralin $TET * S \rightarrow Nap * S + 4H_{ads}$ $r_1 = \frac{k_{rxn,1}k_{TET}[TET]}{(1 + k_{TET}[TET])}$	300	0.1552	3.149×10^{-6}	0.9931	7.86×10^{-8}
	330	0.3550	1.992×10^{-6}	0.9957	1.72×10^{-8}
	360	0.5160	1.925×10^{-6}	0.9991	8.10×10^{-8}
	390	1.120	1.260×10^{-6}	0.9987	9.97×10^{-8}

Table S2: Kinetic and statistical parameters of Power Law and L–H model determined from regression analysis of tetralin dehydrogenation data.

6. **Kinetic and statistical parameters for oleic acid deoxygenation reaction**

Table S3: Kinetic and statistical parameters of Power Law, L–H and E–R models determined from regression analysis of oleic acid deoxygenation kinetic data.

Surface Reaction 2- Catalytic deoxygenation of oleic acid							
Type of model/Rate Equations	Temperature / ºC	$k_{rxn,II}$ / s^{-1}	α	β		R_2	RSME
Power Law $r_2 = k_{rxn,2}[OA]^{\propto}[H_2]^{\beta}$	300	1.633×10^{-7}	0.8909	-0.3685		0.7941	1.33×10^{-8}
	330	1.299×10^{-5}	0.8677	0.3300		0.5223	7.20×10^{-7}
	360	7.468×10^{-6}	0.7553	0.6559		0.7074	8.79×10^{-7}
	390	3.362×10^{-5}	0.4699	0.5192		0.4647	1.48×10^{-7}
Model/Rate Equations	Temperature / ºC)	$k_{rxn,II}$ / mol s^{-1} g_{cat}^{-1}	K_{OA} / L mol^{-1}	K_{H_2} / L mol^{-1}	K_{SA} / L mol^{-1}	R_2	RSME
L-H model with single site adsorption of oleic acid with H₂ $OA*S + H_2*S \rightarrow SA*S + S$ $r_2 = \frac{k_{rxn,2}\, k_{OA}[OA]\, k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + k_{H_2}[H_2]\right)^2}$	300	2.854	6.978×10^{-7}	511.5	-	0.8624	5.03×10^{-7}
	330	2.342	1.348×10^{-6}	542.0	-	0.7832	1.27×10^{-7}
	360	2.356	1.962×10^{-6}	687.9	-	0.8167	1.34×10^{-7}
	390	2.497	2.453×10^{-6}	637.1	-	0.8391	8.06×10^{-8}
L-H model with single site adsorption of stearic acid with H₂ $SA*S \rightarrow C17*S + CO_2$	300	30.66	5.849×10^{-10}	9884	28.50	0.9923	2.55×10^{-5}
	330	43.80	4.485×10^{-10}	1.258×10^{4}	41.24	0.9794	2.24×10^{-4}

$r_2 = \frac{k_{rxn,2}\, k_{SA} k_{OA}[OA] k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + k_{H_2}[H_2] + k_{SA} k_{OA}[OA] k_{H_2}[H_2]\right)}$	360	48.71	5.293×10^{-10}	1.546×10^{4}	45.53	0.9908	2.43×10^{-4}
	390	89.89	1.907×10^{-10}	1.661×10^{4}	87.01	0.9879	4.93×10^{-4}
L-H model with single site adsorption of oleic acid with H atoms $OA * S + 2H * S \rightarrow SA * S + 2S$ $r_2 = \frac{k_{rxn,2}\, k_{OA}[OA]\, k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + \sqrt{k_{H_2}[H_2]}\right)^3}$	300	0.1142	2.940×10^{-5}	1843	-	0.9931	3.37×10^{-8}
	330	0.1869	2.870×10^{-5}	1953	-	0.9871	9.97×10^{-8}
	360	0.4281	1.810×10^{-5}	2073	-	0.9952	7.99×10^{-8}
	390	0.9431	1.110×10^{-5}	2120	-	0.9992	3.96×10^{-8}
L-H model with single site adsorption of stearic acid with H atoms $SA * S \rightarrow C_{17} * S + CO_2$ $r_2 = \frac{k_{rxn,2}\, k_{SA} k_{OA}[OA] k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + \sqrt{k_{H_2}[H_2]} + k_{SA} k_{OA}[OA] k_{H_2}[H_2]\right)}$	300	36.86	1.021×10^{-10}	11310	36.11	0.5871	1.36×10^{-3}
	330	43.40	1.234×10^{-10}	9771	42.32	0.8073	2.09×10^{-3}
	360	44.87	1.668×10^{-10}	9949	43.32	0.8904	2.89×10^{-3}
	390	76.76	5.554×10^{-11}	11390	75.67	0.8761	5.05×10^{-3}
L-H model with dual site adsorption of oleic acid with H_2 $OA * S_1 + H_2 * S_2 \rightarrow SA * S_1 + S_2$ $r_2 = \frac{k_{rxn,2}\, k_{OA}[OA]\, k_{H_2}[H_2]}{\left(1 + k_{OA}[OA]\right)\left(1 + k_{H_2}[H_2]\right)}$	300	12.96	3.942×10^{-8}	9894	-	0.9923	5.05×10^{-7}
	330	31.58	2.515×10^{-8}	21840	-	0.9797	1.49×10^{-7}
	360	89.70	1.271×10^{-8}	87130	-	0.9924	1.42×10^{-7}
	390	142.10	1.028×10^{-8}	81020	-	0.9895	2.07×10^{-7}
L-H model with dual site adsorption of stearic acid with H_2 $SA * S_1 \rightarrow C_{17} * S_1 + CO_2$	300	1.169	5.990×10^{-5}	1.551	1.764	0.2794	5.26×10^{-4}
	330	0.507	1.445×10^{-3}	0.619	0.889	0.4935	5.49×10^{-4}

$r_2 = \frac{k_{rxn,2}\, k_{SA} k_{OA}[OA] k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + k_{SA} k_{OA}[OA] k_{H_2}[H_2]\right)}$	360	2.111	6.163×10^{-5}	2.073	2.167	0.7293	8.06×10^{-4}
	390	1.498	1.911×10^{-4}	1.473	1.303	0.7038	7.69×10^{-4}
L-H model with dual site adsorption of oleic acid with H atoms	300	0.0972	4.913×10^{-6}	0.683	-	0.9884	6.18×10^{-7}
$OA * S_1 + 2H * S_2 \rightarrow SA * S_1 + 2S_2$	330	0.128	6.022×10^{-6}	0.937	-	0.9387	1.49×10^{-7}
$r_2 = \frac{k_{rxn,2}\, k_{OA}[OA]\, k_{H_2}[H_2]}{\left(1 + k_{OA}[OA]\right)\left(1 + \sqrt{k_{H_2}[H_2]}\right)^2}$	360	0.188	6.016×10^{-6}	0.554	-	0.9927	1.39×10^{-7}
	390	0.641	2.267×10^{-6}	0.169	-	0.9899	2.03×10^{-7}
L-H model with dual site adsorption of stearic acid with H atoms	300	1.169	5.990×10^{-5}	1.551	1.764	0.2794	5.26×10^{-4}
$SA * S_1 \rightarrow C_{17} * S_1 + CO_2$	330	0.507	1.445×10^{-3}	0.619	0.889	0.4935	5.49×10^{-4}
$r_2 = \frac{k_{rxn,2}\, k_{SA} k_{OA}[OA] k_{H_2}[H_2]}{\left(1 + k_{OA}[OA] + k_{SA} k_{OA}[OA] k_{H_2}[H_2]\right)}$	360	2.111	6.163×10^{-5}	2.073	2.167	0.7293	8.06×10^{-4}
	390	1.498	1.911×10^{-4}	1.473	1.303	0.7038	7.69×10^{-4}
E-R model with adsorbed oleic acid and non-adsorbed H_2	300	1.234×10^{-4}	-0.254	-	-	0.9766	6.22×10^{-8}
$OA * S + H_2 \rightarrow OA * S$	330	2.076×10^{-4}	-0.262	-	-	0.9657	1.36×10^{-7}
$r_2 = \frac{k_{rxn,2}\, k_{OA}[OA][H_2]}{\left(1 + k_{OA}[OA]\right)}$	360	2.622×10^{-4}	0.316	-	-	0.9823	1.53×10^{-7}
	390	2.336×10^{-4}	-0.372	-	-	0.9992	4.06×10^{-8}
E-R model with non-adsorbed oleic acid and adsorbed H atoms.	300	1.219×10^{-5}	-	0.131	-	0.7344	2.09×10^{-7}
$2H * S + OA \rightarrow SA * 2S$	330	1.895×10^{-5}	-	0.219	-	0.8679	2.68×10^{-7}
$r_2 = \frac{k_{rxn,2}\, k_{H_2}[OA][H_2]}{\left(1 + \sqrt{k_{H_2}[H_2]}\right)^2}$	360	2.774×10^{-5}	-	0.361	-	0.9233	3.18×10^{-7}
	390	3.192×10^{-5}	-	0.842	-	0.9119	4.24×10^{-7}

7. **Sample calculations to compute reaction rate of tetralin dehydrogenation and oleic acid deoxygenation at different temperatures.**

a.) Rate of reaction for tetralin dehydrogenation (Reaction I)

For Langmuir Hinshelwood model with single adsorption of tetralin:

At reaction temperature of 300 ºC, the outlet concentrations of tetralin, F_{tetout} were recorded and plotted against varies catalysts mass, as shown in Figure 2.

The corresponding exponential function at reaction temperature of 300 ºC was obtained as below:

$$F_{TET,out,\ 300} = 0.000012e^{-0.297w} \tag{1}$$

By differentiating Eq (1), the instantaneous reaction rate at different catalyst mass is computed using the equation below:

$$\frac{dF_{TET,out}}{dw} =- 0.00000356e^{-0.297w} \tag{2}$$

By substituting catalyst mass, w of 0.53g, 1.1g, 2.15g and 3.58g into Eq (2), the instantaneous experimental reaction rate are calculated to be -3.0449E-06 mol/s g_{cat}^{-1}, -2.5707e-06 mol s^{-1} g_{cat}^{-1}, -1.882E-06 mol s^{-1} g_{cat}^{-1} and -1.2308E-06 mol s^{-1} g_{cat}^{-1} respectively.

With the outlet [TET] and reaction rates obtained from the experiments, the rate constant, $k_{rxn.I}$ and tetralin adsorption constant, k_{tet} in Eq(3) were estimated at four different reaction temperatures of 300 °C, 330 °C, 360 °C and 390 °C, by using using non-linear regression curve fitting algorithm (Levnberg-Marquardt) built in MATLAB software R2018a.

$$r_1 = \frac{k_{rxn,1}k_{TET}[TET]}{(1 + k_{TET}[TET])} \tag{3}$$

From the MATLAB optimization results, $k_{rxn.1}$ and tetralin adsorption constant, k_{tet} at reaction temperature of 300°C were estimated to be 0.1552mol s^{-1} g_{cat}^{-1} and 3.149E-06 L mol^{-1} with the R^2 of 0.9931 and RMSE of $7.86x10^{-8}$.

b.) Rate of reaction for oleic acid dehydrogenation (Reaction II)

For Langmuir Hinshelwood model with single adsorption of oleic acid:

At reaction temperature of 300 ºC, the outlet concentrations of oleic acid, F_{OAout} were recorded and plotted against varies catalysts mass, as shown in Figure 3.

The corresponding exponential function at reaction temperature of 300 ºC was obtained as below:

$$F_{OA,out,\ 300} = 0.0000053e^{-0.286w} \tag{4}$$

By differentiating Eq (4), the instantaneous reaction rate at different catalyst mass is computed using the equation below:

$$\frac{dF_{OA,out}}{dw} = - 0.000001516e^{-0.286w} \tag{5}$$

By substituting catalyst mass, w of 0.53g, 1.1g, 2.15g and 3.58g into Eq (5), the instantaneous experimental reaction rate of oleic acid deoxygenation at 300 ºC are calculated to be -1.303E-06 mol/s g_{cat}^{-1}, -1.107E-06 mol s^{-1} g_{cat}^{-1}, -8.196E-067mol s^{-1} g_{cat}^{-1} and -5.445E-07 mol s^{-1} g_{cat}^{-1} respectively.

With the outlet [OA], [H_2] and reaction rate obtained from the experiments, the rate constant, $k_{rxn.I}$ and tetralin adsorption constant, k_{tet} in Eq(6) were estimated at four different reaction temperatures of 300 °C, 330 °C, 360 °C and 390 °C, by using using non-linear regression curve fitting algorithm (Levnberg-Marquardt) built in MATLAB software R2018a.

$$r_2 = \frac{k_{rxn,2}\, k_{OA}[OA]\, k_{H_2}\, [H_2]}{\left(1 + k_{OA}[OA] + k_{H_2}[H_2]\right)^2} \tag{6}$$

From MATLAB optimization results, the reaction constant of reaction 2, $k_{rxn.2}$, oleic acid adsorption constant, k_{OA} and hydrogen adsorption constant, K_{H2} at reaction temperature of 300°C were estimated to be 0.1142mol s^{-1} g_{cat}^{-1} 2.945e-05 L mol^{-1} and 1843 L mol^{-1} respectively with the R^2 of 0.9931and RMSE of $3.37x10^{-8}$.