Supporting information

Selective production of 2,3 pentanedione from bio-derived lactic acid over polymorph ZrO$_2$

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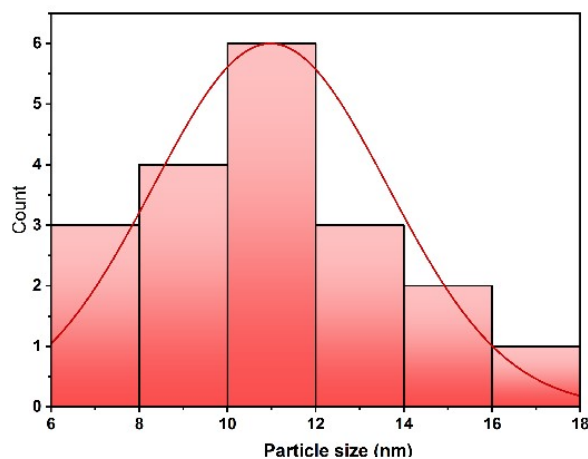
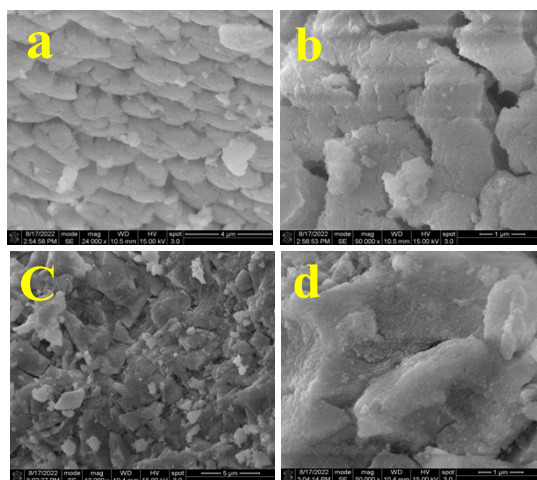Figure S1. average particle size profile of ZrO2 catalyst calcined at 550°C.

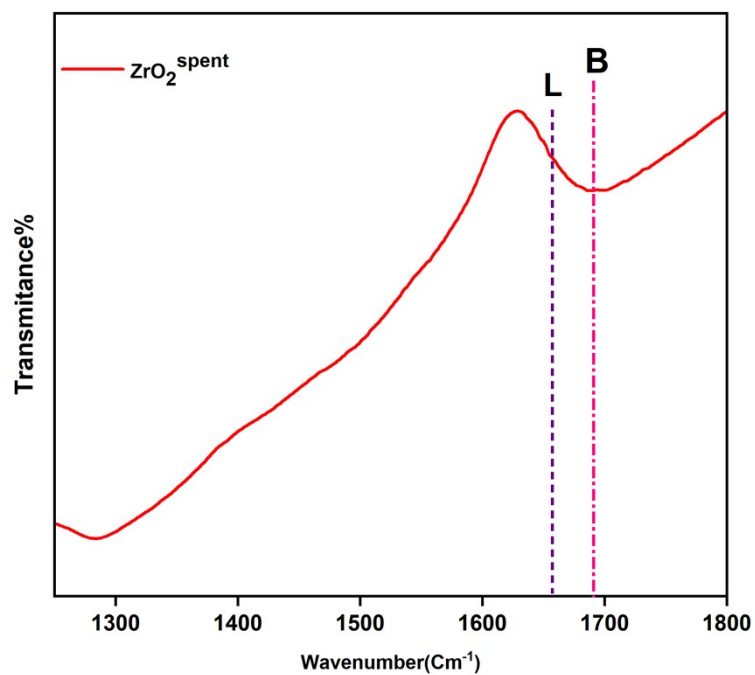Figurex S2: SEM image fresh (a,b)and spent(c, d) Zirconium oxide catalyst

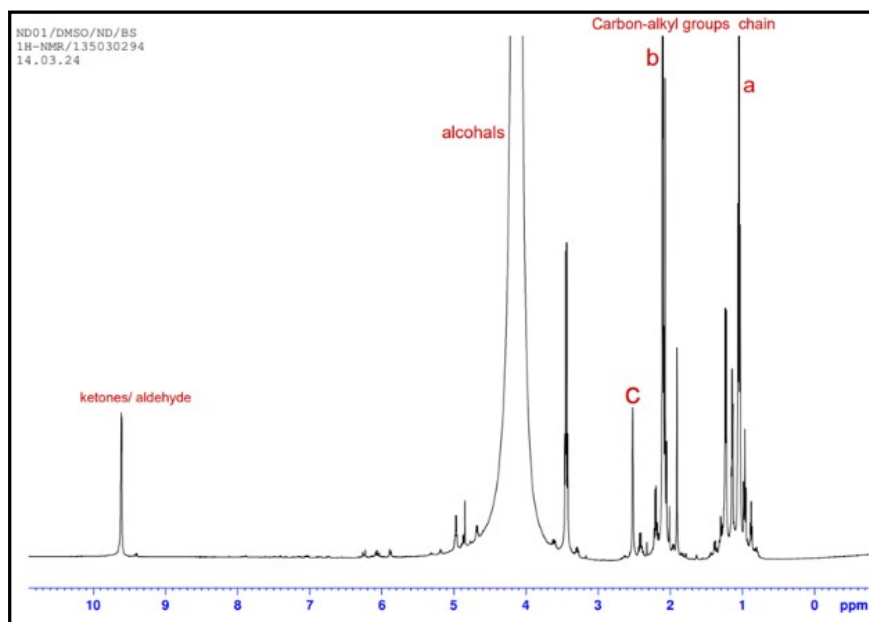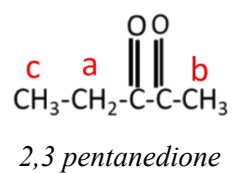Figure S3: pyridine FTIR spectra of spent Zirconium oxide catalyst

2,3 pentanedione

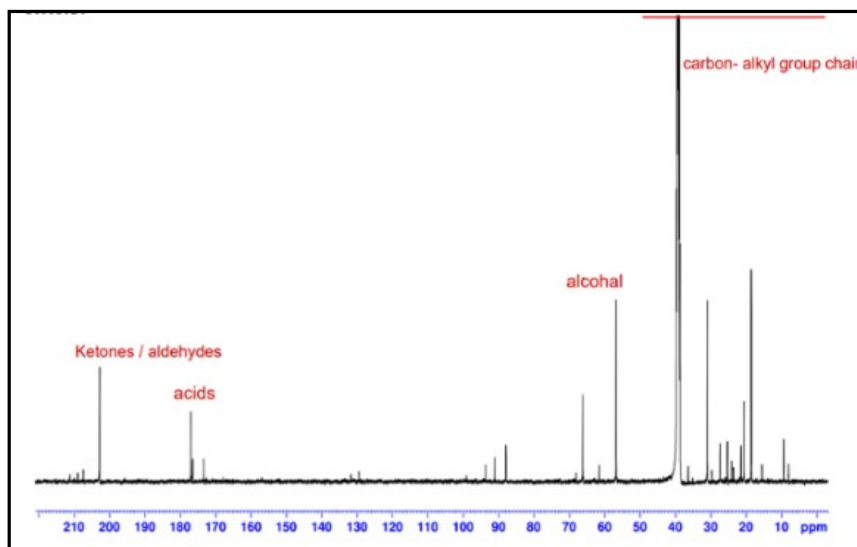Figure S4. ^{1}H NMR of products of mixture

Figure S5. ^{13}C NMR of products of mixture

Figure S3 shows 1H- NMR of 2-3 pentane dione. The peak at chemical shifts 2.77, 2.33, and 1.09 ppm were attributed to the –CH2(a), –CH3 (b), and –CH3 (c) groups due to pentanedione moiety. It was evident that the synthesis of 2-3 pentane dione was successful because there was a ketone group region present at about 10 ppm. Similarly, 13C -NMR has shown (Figure S4) mainly two types of peak at the range 0-38 and 200-210 ppm corresponding to the carbon alkyl group chain of pentanedione and ketone and aldehyde groups. The peak at 170-180 ppm confirms the presence of an acid group present as a by-product in a mixture of products.

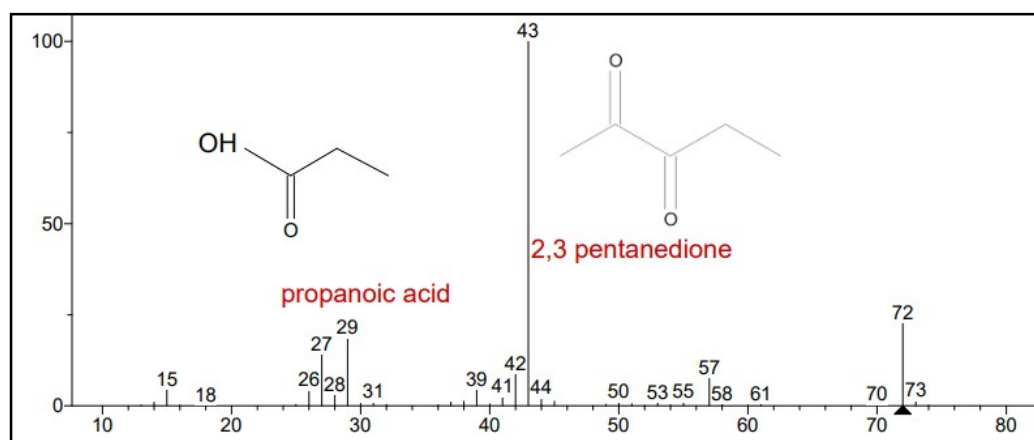Figure S6: GC-MS data of products of mixture

The GC-MS of the product stream in Figure S5 clearly shows the presence of 2,3 pentanedione and propanoic acid at 43 and 29 retention times. The other groups of acids do not show any peak in spectra due to the lower amount of product and lower detection limit of the instrument. NMR and GC-ms give clear evidence of the selective presence of 2,3 pentanedione.
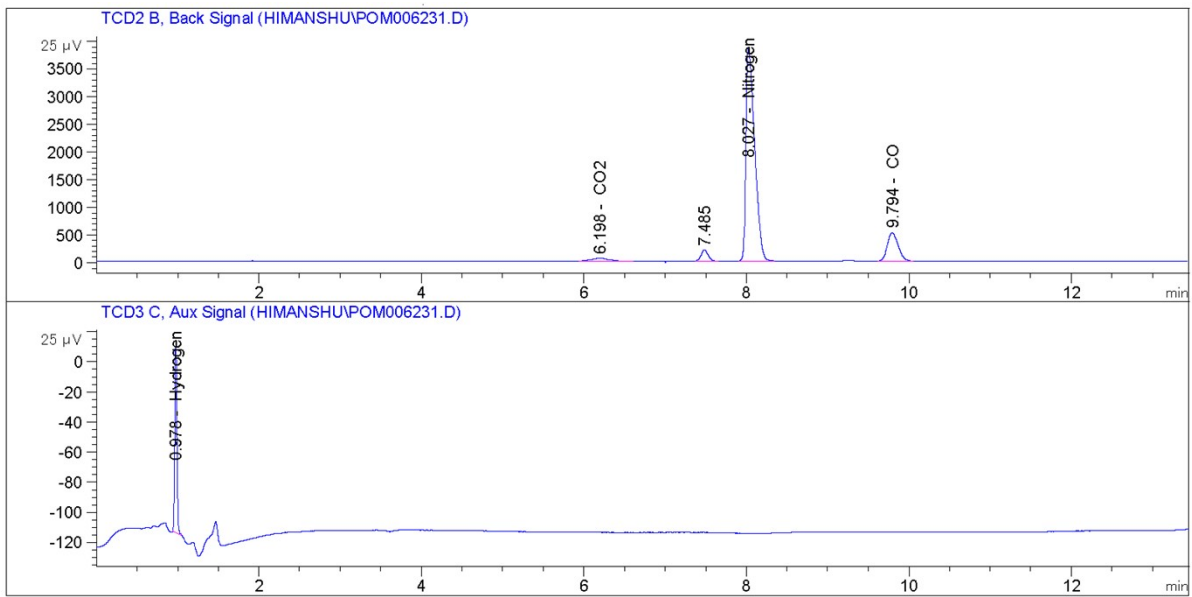
Figure S7 : GC profile of gas from condensation of LA to 2,3-pentanedione on the ZrO2 calcined at 550°C
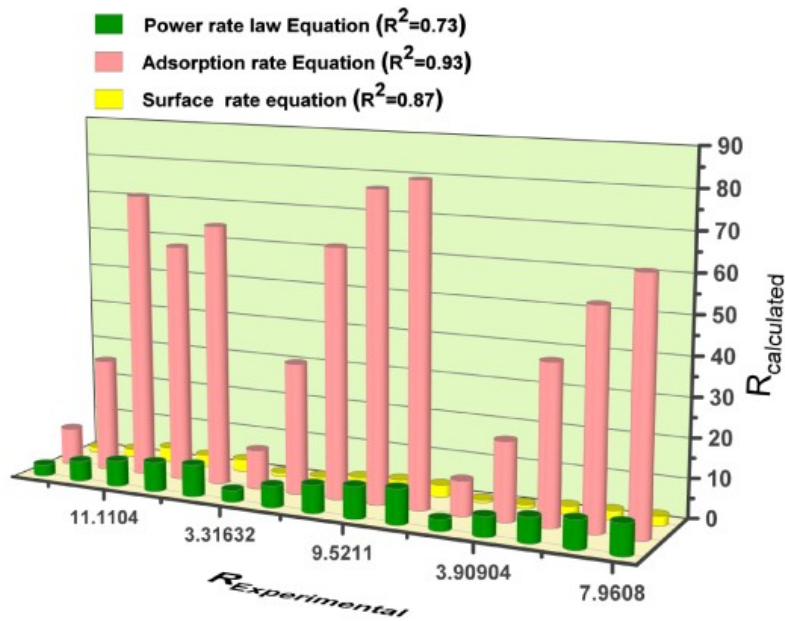
Figure S8. The plot of R $_{calculated}$ Vs R$_{observed}$ of the data taken between 300-350°C

Furthermore, a few hypotheses were taken into account to simplify the reaction rate equations. The initial kinetics can, therefore be taken into account, and the partial pressure of the products can be assumed to be zero, i.e., $p_{(C5 H8O2)}$, p_{CO2}, and $p_{(H2 O)}$ = 0. Additionally, the experiments were carried out with conversion and low PhE pressure (0.06 to 0.11 atm). It was determined from the aforementioned hypotheses that the desorption processes could not be the rate-limiting phase. When taking into account the initial kinetics, the rate expressions of the EQs-C (in SI) tend towards infinity, which implies that these fundamental reactions occur very quickly. So, it is possible to consider one of the aforementioned equations as the step that determines the rate.
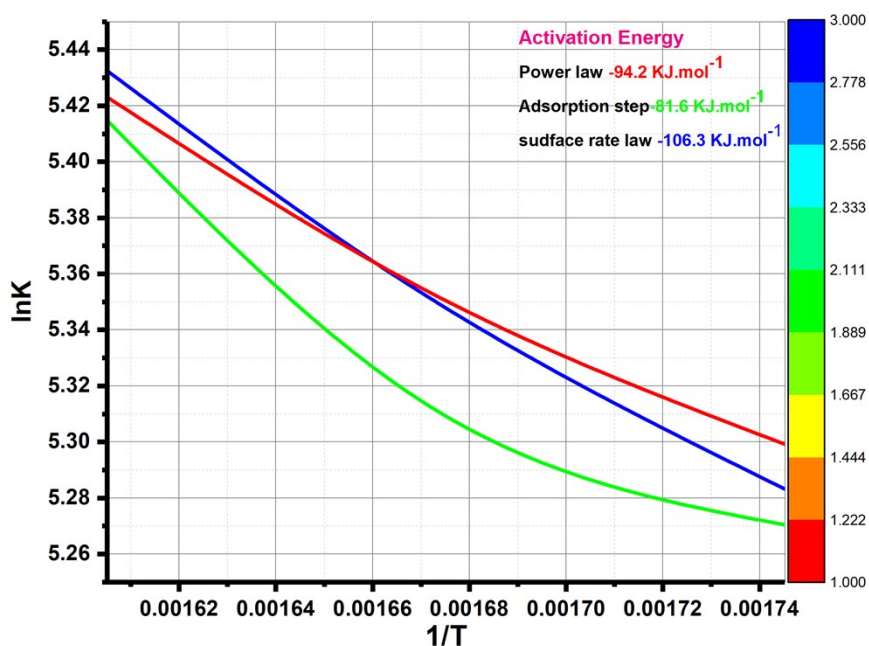
Figure S9. Arrhenius plot for the different reaction and their corresponding activation energy

Table S1. Comparison studies of our catalyst with reported catalysts.

Catalyst	Conversion (%)	Selectivity (%)	Yield (%)	Reference
Caesium-Doped Hydroxyapatite	90	72.3	65.1	*1*
CsOH/silica	74	81	60	*2*
CsNO3/SiO2	99	80	54.1	*3*
Ba2P2O7 doped with Cs	92	61.1	56.2	*4*
Polymorphic ZrO2	99.7	99.5	95.3	This work
Commercial - ZrO2	79.4	66.1	52.4	

Scherrer's Formula to Estimate average particle size

Scherrer equation (also referred to as the Debye–Scherrer equation) has been applied to estimate the size of particle size measurement or analysis. It is used to measure the size of crystals in the form of powder. The Scherrer equation can be written as:

$t = [K \lambda]/\beta Cos\Theta$

Where,
t = mean size of the crystalline domains
K = dimensionless shape factor (0.9)
λ = X-ray wavelength (1.54Å)
β = FWHM (full width at half max)
Θ = Bragg angle

Example

For $2\Theta = 30.3$
$Cos(30.2/2) = 0.96547$
β = FWHM = 0.90425 degree(from XRD data)

$$= (2\pi \times degree/\ 180)\ S$$
$$= 2 \times 3.14 \times 0.90425/180$$
$$= 0.03155\ (radian)$$
Therefore, t= [0.9 x 1.54]/[0.03155 x .96547]
$$= 1.386/0.0305$$
$$= 45.44\text{Å}$$
$$= 4.5\ nm$$
$$t = 4.5\ nm$$
For $2\Theta = 30.1$
$Cos(30.1/2) = 0.96569$
$\beta = FWHM = 0.8331$ degree(from XRD data)
$$= (2\pi \times degree/\ 180)$$
$$= 2 \times 3.14 \times 0.8331/180$$
$$= 0.02906\ (radian)$$
Therefore, t= [0.9 x 1.54]/[0.02906 x 0.96569]
$$= 1.386/0.0281$$
$$= 49.32\text{Å}$$
$$= 4.9\ nm$$
$$t = 5\ nm$$

For $2\Theta = 60$
$Cos(30) = 0.866025$
$\beta = FWHM = 1.9828$ degree(from XRD data)
$$= (2\pi \times degree/\ 180)$$
$$= 2 \times 3.14 \times 1.9828\ /180$$
$$= 0.06918\ (radian)$$
Therefore, t= [0.9 x 1.54]/[0.06918 x 0.866025]
$$= 1.386/0.0599$$
$$= 23.13\text{Å}$$
$$t = 2.3\ nm$$
For $2\Theta = 60$
$Cos(30) = 0.866025$
$\beta = FWHM = 1.56485$ degree(from XRD data)
$$= (2\pi \times degree/\ 180)$$
$$= 2 \times 3.14 \times 1.56485\ /180$$
$$= 0.05459\ (radian)$$
Therefore, t= [0.9 x 1.54]/[0.05459 x 0.866025]
$$= 1.386/0.0472$$
$$= 29.36\text{Å}$$
$$= 2.9\ nm$$
$$t = 3\ nm$$

Catalyst	Phase	Bragg angle (Θ)	β (radian)	Particle size (nm)
ZrO_2	Tetragonal	30.2/2	0.03155	4.5
ZrO_2^{Spent}	Tetragonal	30.1/2	0.02906	5
ZrO_2	Monoclinic	60	0.06918	2.3
ZrO_2^{Spent}	Monoclinic	60	0.05459	3

Derivation of kinetic rate expressions of condensation of bio-deroived lactic acid overZrO$_2$

$$2C_3H_6O_3 \longrightarrow C_5H_8O_2 + CO_2 + 2H_2O$$

$$2C_3H_6O_3 + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2C_3H_6O_3.S \text{ (LA adsorption step)}$$

$$2C_3H_6O_3.S + S \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} 2C_3H_5O_{2.5}.S + H_2O \text{ (surface reaction)}$$

$$2C_3H_5O_{2.5}.S + 2S \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} C_5H_8O_2.S + H_2O.S + CO_2 \text{ (surface reaction)}$$

$$C_5H_8O_2.S \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} C_5H_8O_2 + S \text{ (PON desorption step)}$$

$$CO_2.S \underset{K_{-5}}{\overset{K_5}{\rightleftharpoons}} CO_2 + S \text{ (CO}_2 \text{ desorption step)}$$

$$2H_2O.S \underset{K_{-6}}{\overset{K_6}{\rightleftharpoons}} 2H_2O + S \text{ (H}_2O \text{ desorption step)}$$
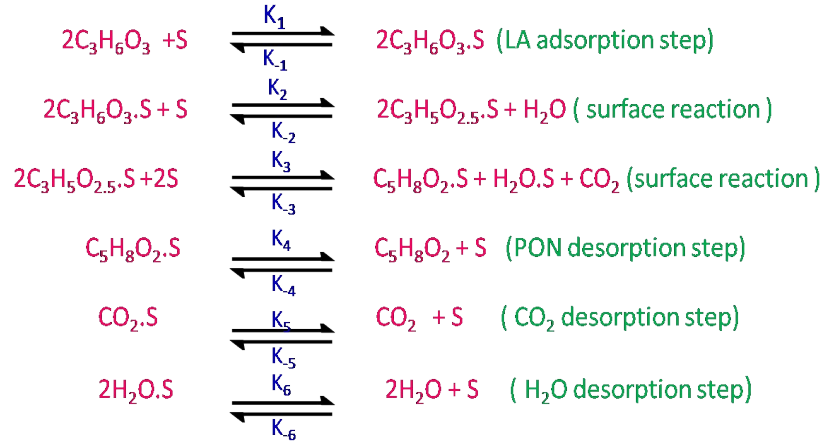
1. Adsorption as a rate-determining step:

$$2C_3H_6O_3 + S \underset{K_{-1}}{\overset{K_1}{\rightleftharpoons}} 2C_3H_6O_3.S \text{ (LA adsorption step)}$$
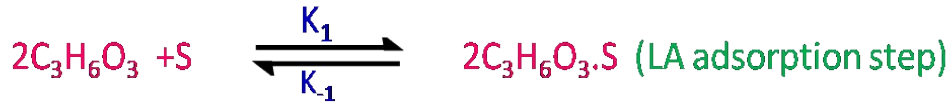
$$R_A = K_1.p_{C_3H_6O_3}^2 . \theta_S - K_{-A}.\theta_{C_3H_6O_3.S}^2$$

$$R_A = K_1\left[p_{C_3H_6O_3}.\theta_S - K_{-1}.\frac{\theta_{C_3H_6O_3.S}}{K_1} \right]$$

$$R_A = K_1\left[p_{C_3H_6O_3}.\theta_S - .\frac{\theta_{C_3H_6O_3.S}}{K_A} \right] \text{where, } \{K_A = K_1/K_{-1}\} \quad (1)$$

By consideringother elementary reaction steps to be very fast

$$R_{S1} = 0; \; R_{S2} = 0; R_{D1} = 0; R_{D2} = 0 \; ; R_{D3} = 0$$

$$\theta_{C_3H_6O_3S}^2 = \frac{\theta_{C_3H_5O_{2.5}S}^2 . \theta_{H_2OS}}{K_{S1}.\theta_S} \quad (3)$$

$$\theta_{C_3H_5O_{2.5}S} = \left(\theta_{C_5H_8O_2S}.\theta_{H2O}.\frac{\theta_{CO_2}}{K_{S2}.\theta_S} \right) \quad (4)$$

$$\theta_{C_5H_8O_2S} = \frac{p_{C_5H_8O_2}.\theta_S}{K_{D1}} \quad (5)$$

$$\theta_{HS} = \left(\frac{p_{CO_2}}{K_{D2}}\right).\theta_S \tag{6}$$

$$\theta_{HS} = \left(\frac{p_{H_2O}}{K_{D3}}\right).\theta_S \tag{7}$$

Total coverage sites

$$\theta_t = \theta_{C_3H_6O_3}^2 {}_{.S} + \theta_{C_3H_5O_{2.5}}^2 {}_{.S} + \theta_{C_5H_8O_2.S} + \theta_{CO_2.S} + \theta_{H_2O.S} + \theta_S \tag{8}$$

$$\theta_S = \theta_t / \left[\left(\frac{p_{C_5H_8O_2}.p_{CO_2}.p_{H_2O}^2}{K_{S1}.K_{S2}.K_{D1}.K_{D2}.K_{D3}}\right) + \frac{\left[p_{C_5H_8O_2}.p_{H_2O}.p_{CO_2}\right]}{K_{S2}.K_{D1}.K_{D2}.K_{D3}} + \frac{p_{C_5H_8O_2}}{K_{D1}} + \left(\frac{p_{CO_2}}{K_{D2}}\right) + \left(\frac{p_{H_2O}}{K_{D3}}\right) + 1 \right] \tag{9}$$

From eqs (1), (2),
(10)

$$R_A = K_1.\theta_S \left(p_{C_3H_6O_3}^2 - \frac{p_{C_5H_8O_2}.p_{H_2O}^2.p_{CO_2}}{K_{S1}.K_{S2}.K_{D1}.K_{D2}} \right)$$

Putting the value of θ_S in equ(10)

$$R_A$$
$$= \theta_t / \left[\left(\frac{p_{C_5H_8O_2}.p_{CO_2}.p_{H_2O}^2}{K_{S1}.K_{S2}.K_{D1}.K_{D2}.K_{D3}}\right) + \frac{\left[p_{C_5H_8O_2}.p_{H_2O}.p_{CO_2}\right]}{K_{S2}.K_{D1}.K_{D2}.K_{D3}} + \frac{p_{C_5H_8O_2}}{K_{D1}} + \left(\frac{p_{CO_2}}{K_{D2}}\right) + \left(\frac{p_{H_2O}}{K_{D3}}\right) + 1 \right] \left(p_{C_3H_6O_3}^2 \right. \tag{11}$$

Initial kinetics is considered then partial pressure of the products can be assumed as zero, i.e., $p_{C_5H_8O_2}=0$, $p_{H_2O} = 0$ and $p_{CO_2} = 0$. Then,

$$R_A = k_1.\theta_t.p_{C_3H_6O_3}^2$$

$$R_A = k_A.p_{C_3H_6O_3}^2$$

2a. Surface Reaction as Rate determining step

$$2C_3H_6O_3.S + S \underset{K_{-2}}{\overset{K_2}{\rightleftharpoons}} 2C_3H_5O_{2.5}.S + H_2O \ (\text{surface reaction})$$

$$R_{S1} = k_2.\theta_{C_3H_6O_3.S}^2.\theta_S - k_{-2}.\theta_{C_3H_5O_{2.5}.S}^2.\theta_{H_2OS} \tag{12}$$

$$R_{S1} = k_2 \left[\theta_{C_3H_6O_3.S}^2.\theta_S - \frac{\theta_{C_3H_5O_{2.5}.S}^2.\theta_{H_2OS}}{K_{S1}} \right] \tag{12}$$

Total coverage sites:

$$\theta_S = \theta_t / [K_A \cdot p_{C_3H_6O_3} + \frac{[p_{C_5H_8O_2} \cdot p_{H_2O} \cdot p_{CO_2}]}{K_{S2} \cdot K_{D1} \cdot K_{D2} \cdot K_{D3}} + \frac{p_{C_5H_8O_2}}{K_{D1}} + \left(\frac{p_{CO_2}}{K_{D2}}\right) + \left(\frac{p_{H_2O}}{K_{D3}}\right) + 1]$$

(13)

From solve the above eqs (12), (13) and considered to be at initial kinetics the partial pressure of the products can be assumed as zero, $p_{C_5H_8O_2} = 0$, $p_{H_2O} = 0$ and $p_{CO_2} = 0$.

$$R_{S1} = \frac{K_2 \cdot \theta_t^2 \cdot K_A \cdot p_{C_3H_8}^2}{\left[1 + K_A p_{C_3H_8}^2\right]^2}$$

$$R_{S1} = \frac{k \cdot K_A \cdot p_{C_3H_8}^2}{\left[1 + K_A p_{C_3H_8}^2\right]^2} \quad \text{where,} \quad K_2 \cdot \theta_t^2 = K$$

(14)

2b. Surface Reaction as Rate determining step

$$2C_3H_5O_{2.5}.S + 2S \underset{K_{-3}}{\overset{K_3}{\rightleftharpoons}} C_5H_8O_2.S + H_2O.S + CO_2 \text{ (surface reaction)}$$

$$R_{S2} = k_3 \cdot \theta_{C_3H_5O_{2.5}S}^2 \cdot \theta_S^2 - k_{-3} \cdot \theta_{C_3H_8O_2S} \cdot \theta_{H_2OS} \cdot \theta_{CO_2S}$$

(15)

$$R_{S2} = k_3 \left[\theta_{C_3H_5O_{2.5}S}^2 \cdot \theta_S^2 - \frac{\theta_{C_3H_8O_2S} \cdot \theta_{H_2OS} \cdot \theta_{CO_2S}}{K_{S2}} \right]$$

(16)

After solving for total coverage sites, the rate expression of the 2nd surface reaction step is found that **The rate expression will tend towards infinity**, which 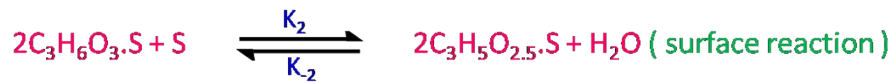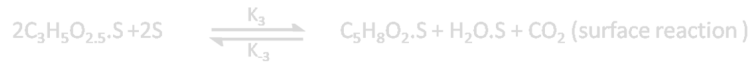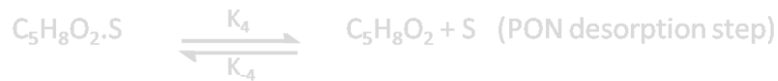implies that this step can never be rate limiting step. When initial kinetics is considered and partial pressure of the products can be assumed as zero, i.e., $p_{C_5H_8O_2} = 0$, $p_{H_2O} = 0$ and $p_{CO_2} = 0$.

3a. Desorption as Rate determining step:

$$C_5H_8O_2.S \underset{K_{-4}}{\overset{K_4}{\rightleftharpoons}} C_5H_8O_2 + S \text{ (PON desorption step)}$$

$$R_{D1} = k_4 \cdot \theta_{C_5H_8O_2S} \cdot \theta_S - k_{-4} \cdot p_{C_5H_8O_2} \cdot \theta_S$$

(17)

$$R_{D1} = k_4 \left[\theta_{C_5H_8O_2S} - \frac{p_{C_5H_8O_2} \cdot \theta_S}{K_{D1}} \right]$$

(18)

After solving for total coverage sites, the rate expression of the 3rd surface reaction step is found that **The rate expression will tend towards infinity**, which implies that PON desorption step will not be very fast and will not affect the reaction kinectics . When initial kinetics is considered and partial pressure of the products can be assumed as zero, i.e., $p_{C_5H_8O_2} = 0$, $p_{H_2O} = 0$ and $p_{CO_2} = 0$.

### 3b. Desorption as Rate determining step:

$$CO_2.S \underset{K_{-5}}{\overset{K_5}{\rightleftharpoons}} CO_2 + S \text{ (CO}_2 \text{ desorption step)}$$

$$R_{D2} = k_5.\theta_{CO_2.S}.\theta_S - k_{-5}.p_{CO_2}.\theta_S \tag{19}$$

$$R_{D2} = k_5\left[\theta_{CO_2.S} - \frac{p_{CO_2}.\theta_S}{K_{D2}}\right] \tag{20}$$

When initial kinetics is considered and partial pressure of the products can be assumed as zero, i.e., $p_{C_3H_6}$ and $p_{H_2} = 0$. After solving for total coverage sites, the rate expression of the 3rd desorption reaction step is found that ,The overall rate expression will be infinity thus implies that the hydrogen desorption will be very fast and will not affect the reaction kinetics.

3C. Desorption as Rate determining step:

$$2H_2O.S \underset{K_{-6}}{\overset{K_6}{\rightleftharpoons}} 2H_2O + S \quad (H_2O \text{ desorption step})$$
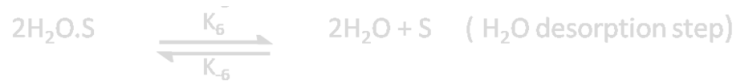
$$R_{D3} = k_6.\left(\theta_{H_2O}^2\right) - k_{-6}.p_{H_2O}.(\theta_S)^2 \tag{21}$$

$$R_{D3} = k_6\left[\left(\theta_{H_2O.S}^2\right) - \frac{p_{H_2O}^2.(\theta_S)^2}{K_{D3}}\right] \tag{22}$$

When initial kinetics is considered and partial pressure of the products can be assumed as zero, i.e., $p_{C_3H_6}$ and $p_{H_2} = 0$. The overall rate expression after solving the above equation rate will be infinity thus implies that the water desorption will be very fast and will not affect the reaction kinetics.

Calculation of activation energy and pre-exponential factor of the reactions

Arrhenius rate eqaution,

$$K = A.e^{\frac{-E_a}{RT}} \tag{15}$$

The above equation was solved for simplified rate expression of the reactions, and the activation energy and Arrhenius constant were calculated as slope and intercept of 1/T versus ln(k).

Table S2. The rate and partial pressure at 300°C

LAflow rate (ml/hr)	Partial Pressure of LA (atm)	LA flow rate(micromole/sec)	fractional conversion of LA	Rate of LA consumption micromole /gm	LA (R$_{LA}$)
1	0.065845847	3.76	0.882	3.31632	
2	0.089301762	7.46	0.806	6.01276	
3	0.101334361	11.2	0.792	8.8704	
4	0.108654461	14.9	0.639	9.5211	
5	0.113577151	18.6	0.485	9.021	

Table S3. The rate and partial pressure at 325°C

| LAflow rate (ml/hr)	Partial Pressure of LA (atm)	LA flow rate(micromole/sec)	fractional conversion of LA	Rate of consumption micromole /gm	LA (R_{LA})
1	0.065845847	3.76	0.872	3.27872	
2	0.089301762	7.46	0.752	5.60992	
3	0.101334361	11.2	0.992	11.1104	
4	0.108654461	14.9	0.542	8.0758	
5	0.113577151	18.6	0.439	8.1654	

Table S4. The rate and partial pressure at 350°C

LAflow rate (ml/hr)	Partial Pressure of LA (atm)	LA flow rate(micromole/sec)	fractional conversion of LA	Rate of consumption micromole /gm	LA (R_{LA})
1	0.065845847	3.76	0.814	3.06064	
2	0.089301762	7.46	0.524	3.90904	
3	0.101334361	11.2	0.559	6.2608	
4	0.108654461	14.9	0.502	7.4798	
5	0.113577151	18.6	0.428	7.9608	

TableS5 .$R_{observed}$ and $R_{calculated}$ using different elementary reaction steps

$R_{Experimental}$	$R_{calculated}$(Power rate law equation)	$R_{calculated}$(Adsorption rate equation)	$R_{calculated}$(Surface rate equation)
3.27872	2.88559	9.46104	1.38292
5.60992	5.16087	28.95209	2.14952
11.1104	6.5685	72.97865	3.79711
8.0758	7.50345	60.59637	3.05332
8.1654	8.1654	66.67376	3.15448
3.31632	3.0287	10.04413	0.9598
6.01276	5.57422	33.51643	1.23037
8.8704	7.17938	63.684	2.50568
3.14366	8.25523	78.59891	3.15184
3.422844	9.021	81.37844	3.18512

1.003104	2.9403	8.9992	0.80191
1.239414	5.13052	20.05541	1.02243
1.898578	6.46335	40.46574	2.03135
2.44816	7.34174	54.91475	2.37385
2.485968	7.9608	63.37434	2.45794

Table S6. Heats of reaction for the conversion of La into chemicals
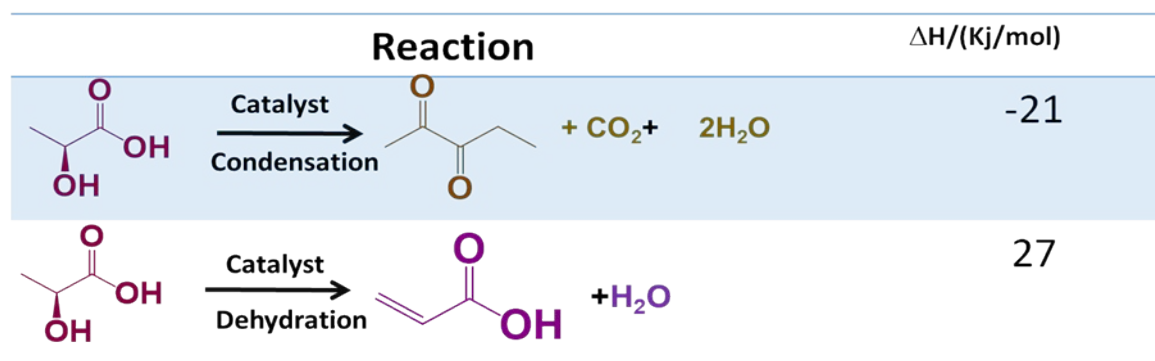
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1. X. Li, L. Sun, W. Zou, P. Cao, Z. Chen, C. Tang and L. Dong, *ChemCatChem*, 2017, **9**, 4621-4627.
2. M. S. Tam, J. E. Jackson and D. J. Miller, *Industrial & engineering chemistry research*, 1999, **38**, 3873-3877.
3. L.-W. SUN, X.-L. LI and C.-M. TANG, *Acta Physico-Chimica Sinica*, 2016, **32**, 2327-2336.
4. X. Li, Y. Zhang, Z. Chen, P. Cao, W. Zou, C. Tang, L. Dong and Y. Wang, *Industrial & Engineering Chemistry Research*, 2017, **56**, 14437-14446.