

## Supporting Information

# Single step hydrogenolysis of furfural to 1, 2-pentanediol using a bifunctional Rh/OMS-2 catalyst

*Devendra S. Pisal<sup>+</sup> and Ganapati D. Yadav<sup>+\*</sup>*

<sup>+</sup>Department of Chemical Engineering,  
Institute of Chemical Technology,  
Nathalal Parekh Marg, Matunga,  
Mumbai-400 019, India.

E-mail address: [gd.yadav@ictmumbai.edu.in](mailto:gd.yadav@ictmumbai.edu.in)

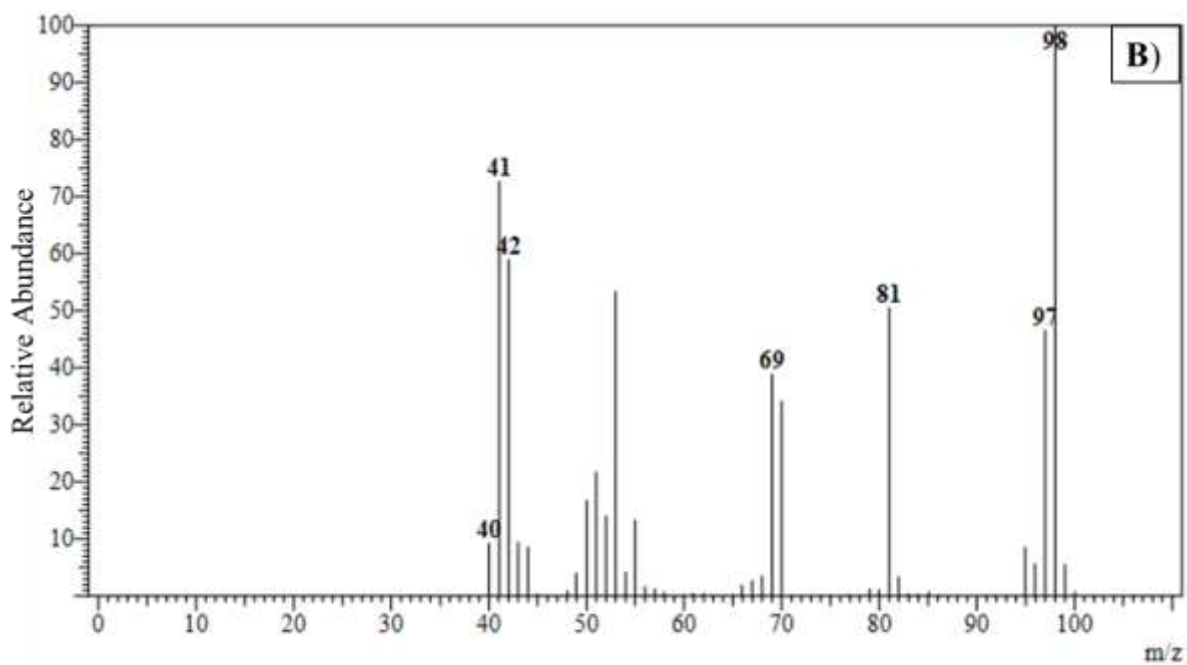
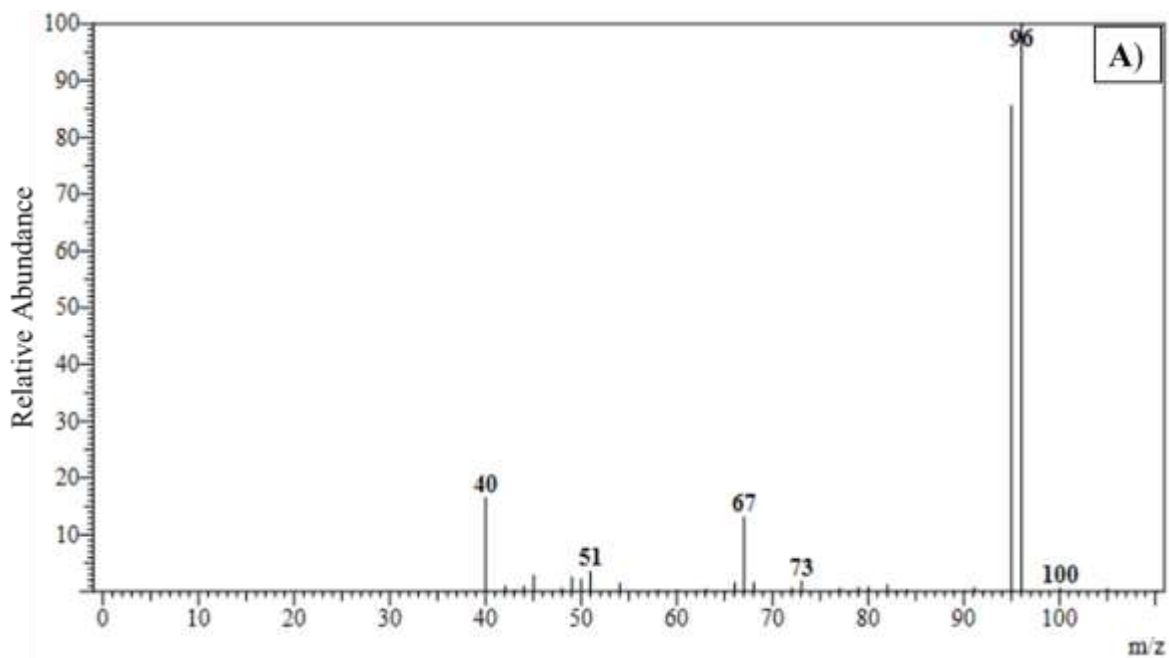
Tel.: +91-22-3361-1001, Fax: +91-22-3361-1020, +91-22 3361-1002.

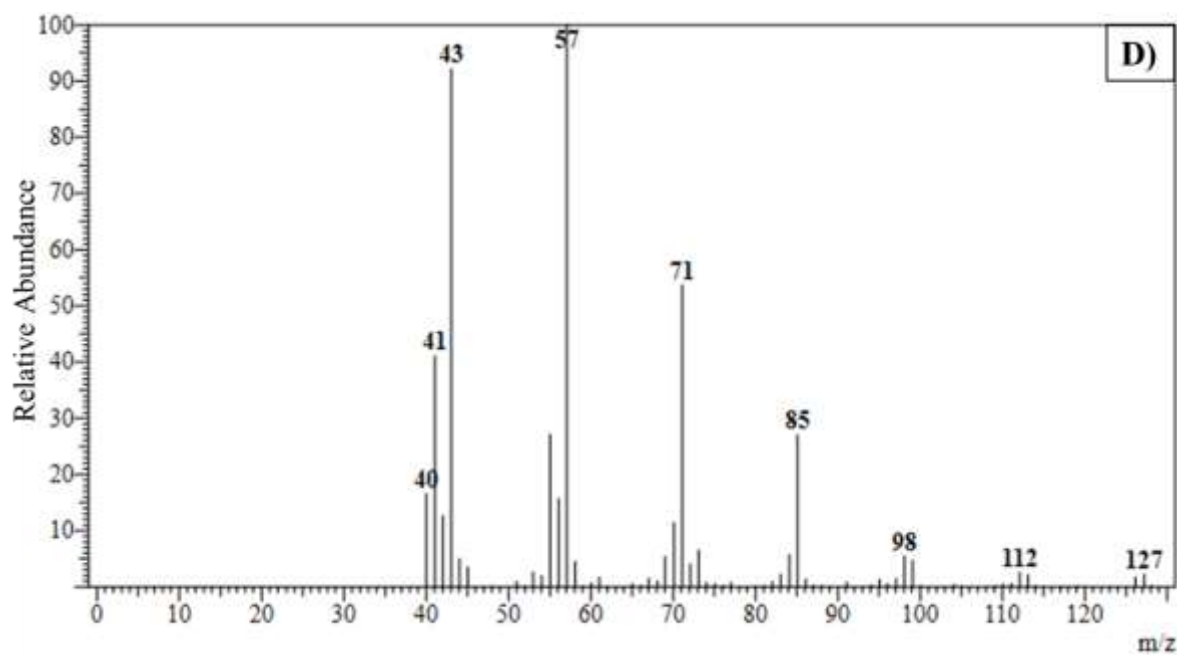
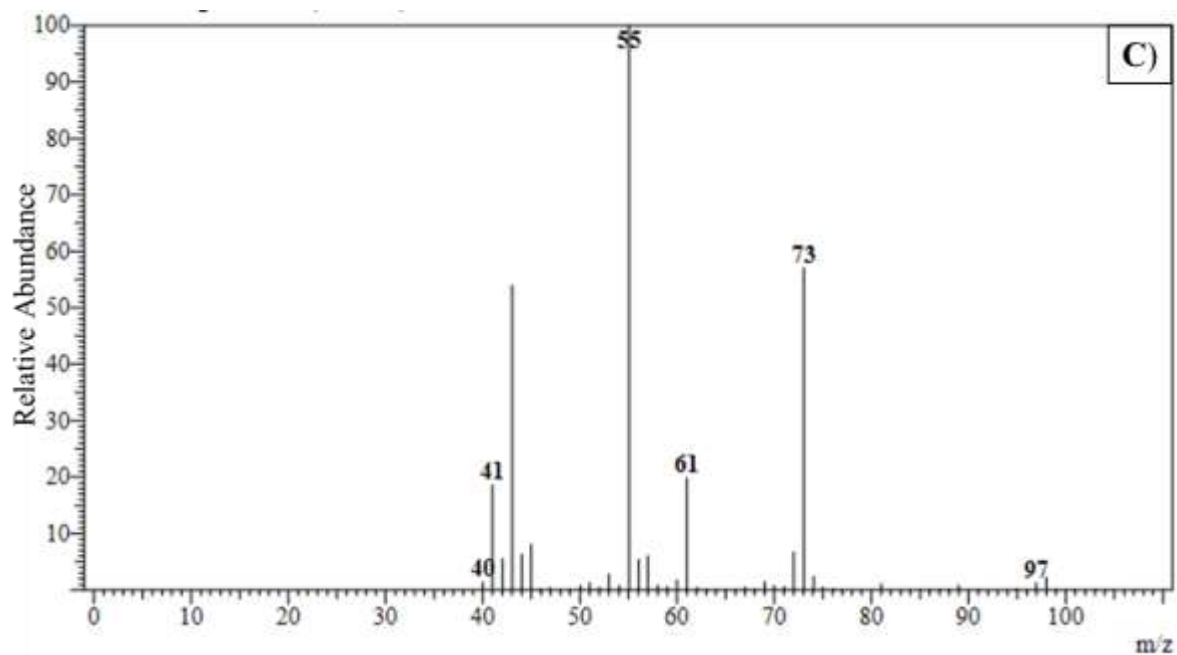
\*Author to whom correspondence should be addressed

*ORCID ID: 0000-0002-8603-3959*

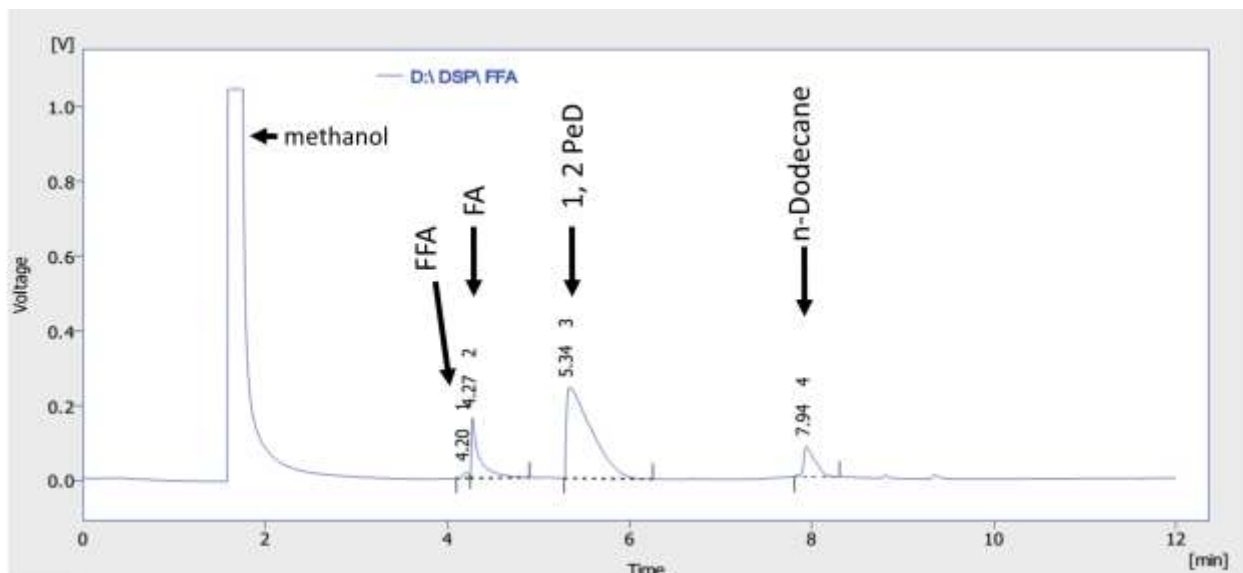
## GCMS analysis

The GC-MS analysis was done for the confirmation of the product. Following were the MS spectra's for all the GC peaks including A) Furfural, B) Furfuryl alcohol, C) 1, 2 pentanediol, and D) n-dodecane.





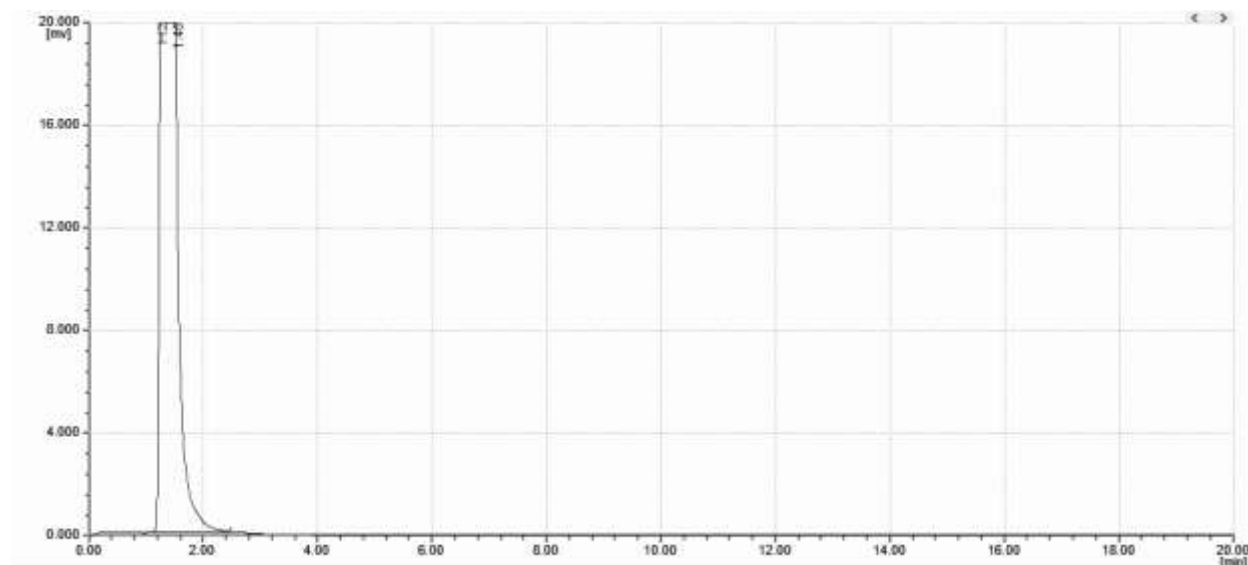
**Figure S1.** GCMS spectra of A) Furfural, B) Furfuryl alcohol, C) 1, 2 pentanediol, and D) n-Dodecane



**Figure S2.** Typical GC chromatogram of reaction mass.

### Gas phase analysis

The gas phase analysis was performed using GC 8610 unit equipped with Hayesep DB packed column. TCD was used for detecting H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, CO, and C<sub>2</sub>H<sub>6</sub>, etc. Nitrogen was used as a carrier gas. It was observed that except hydrogen, there was no peak of any other gas in the gas sample. The hydrogen peak intensity was significant (SI, Fig S3). The lower detection limit for CO, CO<sub>2</sub> CH<sub>4</sub> and C<sub>2</sub>H<sub>6</sub> was 10-15 ppm. Therefore it clearly indicates that CO<sub>x</sub> is not formed in the reaction within detection limit.



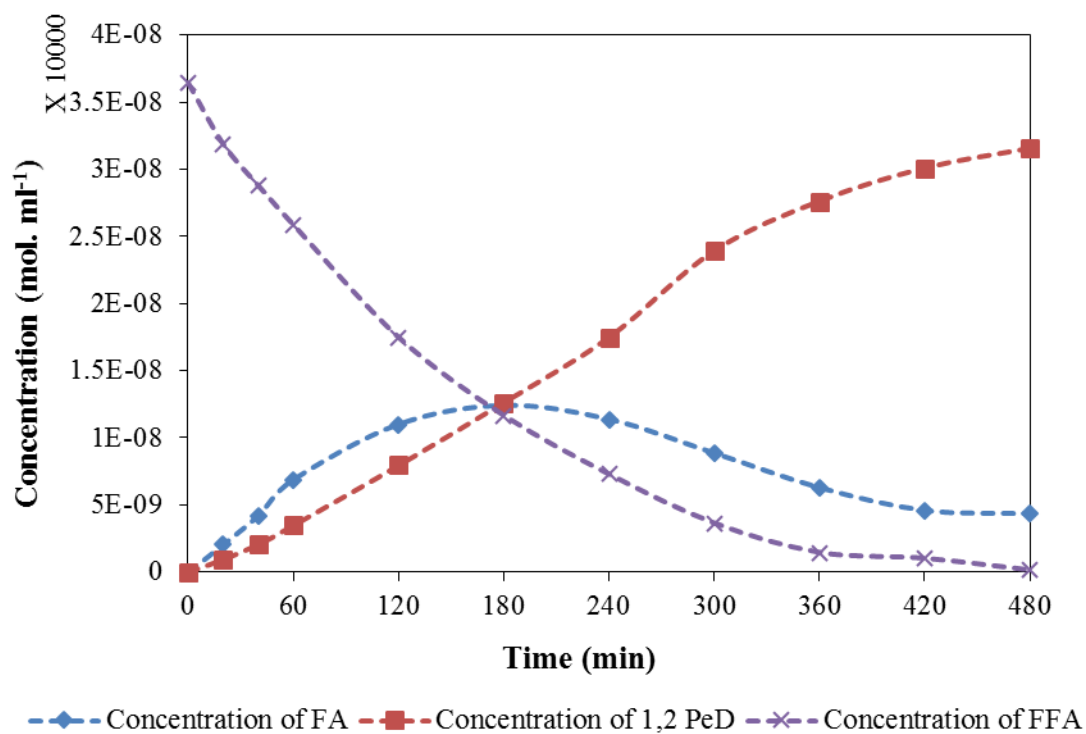
**Figure S3.** Typical GC chromatogram of gas phase analysis.

### **Carbon balance**

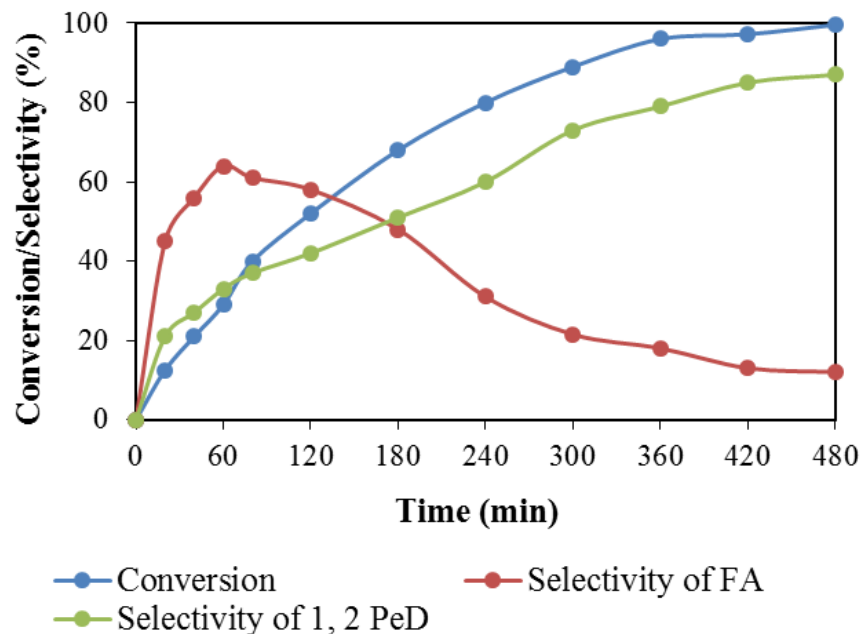
We have calculated the carbon balance as the sum of residual substrate and products. Carbon at inlet includes the feedstock furfural and was found to be 0.403 g while carbon at outlet from 1, 2 pentanediol and furfuryl alcohol, corresponds to 0.43 g. The values are within experimental limits.

### **Concentration profile of conversion of FFA to FA and 1, 2 PeD**

The concentration profiles for the formation of products FA and 1, 2 PeD are shown in Fig. S4. As this is a series reaction, the concentration profile with respect to reaction time was studied in order to get maximum conversion and selectivity.

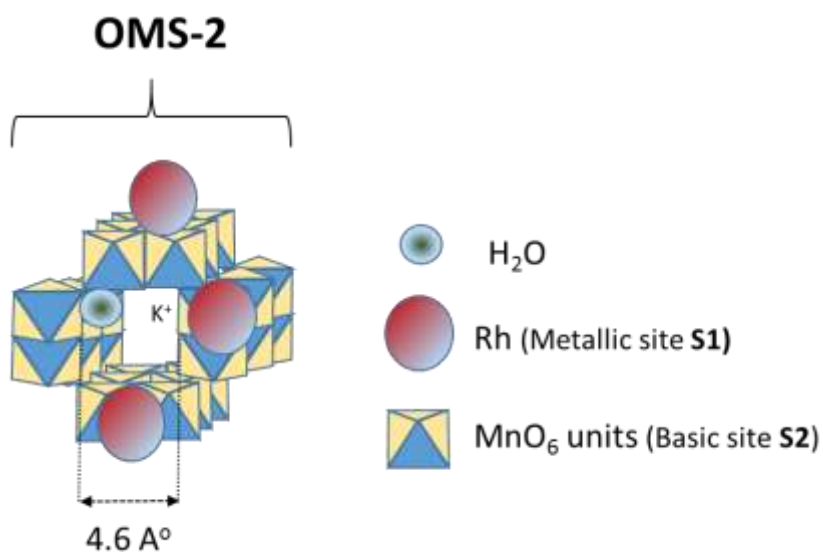


**Figure S4.** Concentration profile of conversion of FFA to FA and 1, 2 PeD; FFA, 0.0073 mol; catalyst wt., 0.25 g; hydrogen pressure, 30 atm; temperature, 160 °C; solvent, methanol; reaction time, 8 h; total volume, 20 cm<sup>3</sup>.



**Figure S5.** Selectivity of products FA and 1, 2 PeD in the wide range of conversion of FFA.

FFA, 0.0073 mol; catalyst wt., 0.25 g; hydrogen pressure, 30 atm; temperature, 160 °C; solvent, methanol; reaction time, 8 h; total volume, 20 cm<sup>3</sup>.



**Figure S6.** Demonstration of structure of active sites present over 1% Rh/OMS-2 catalyst.

## Mathematical model for hydrogenolysis of FFA

With increase in catalyst loading the conversion of furfural also increases, hence we used LHHW approach for the development of mathematical model. As the catalyst is bifunctional so the hydrogen will adsorb on site  $S_1$  while the furfural will be adsorbed on basic site  $S_2$ .

Assuming dissociative adsorption of hydrogen on metallic site  $S_1$



The rate of reaction for above equation can be written as

$$r_{HD} = k_h p_{H_2} C_{S_1}^2 - k'_h C_{H.S_1}^2 \quad (2)$$

$$\therefore r_{HD} = k_h \left( p_{H_2} C_{S_1}^2 - \frac{C_{H.S_1}^2}{K_H} \right) \quad (3)$$

Chemisorption of FFA on basic site  $S_2$  can be shown as



The rate is given by

$$r_{AD} = k_a C_A C_{S_2} - k'_a C_{A.S_2} \quad (5)$$

$$\therefore r_{AD} = k_a \left( C_{S_2} C_A - \frac{C_{A.S_2}}{K_A} \right) \quad (6)$$

It is a multistep reaction in which, first  $-CHO$  group of furfural (FFA) is hydrogenated into hydroxyl group and we get FA as an intermediate.

Then FA further undergoes hydrogenolysis by series of steps into final product i.e 1, 2 PeD.





As shown in the reaction profiles the concentration of D is not detected on GC analysis which indicates that the formation of E from D is very fast reaction and hence we can couple the above equations to write a single step.



Where  $k_2 = k_2' * k_2''$

The rate of reaction for equ<sup>n</sup> (3), (9) and (10) can be written as

$$-r_1 = \frac{-dC_A}{dt} = k_1 C_{A.S_2} C_{H.S_1} \quad (11)$$

$$r_2 = \frac{dC_B}{dt} = k_1 C_{A.S_2} C_{H.S_1} - k_2 C_{B.S_2} C_{H.S_1} \quad (12)$$

$$r_3 = \frac{dC_E}{dt} = k_3 C_{B.S_2} C_{H.S_1} \quad (13)$$

Assuming the adsorption and desorption steps to be very fast, we have values of intermediates

$$C_{A.S_2} = K_A C_A C_{S_2} \quad (14)$$

$$C_{H.S_1} = \sqrt{K_H p_{H_2}} C_{S_1} \quad (15)$$

$$C_{B.S_2} = K_B C_B C_{S_2} \quad (16)$$

$$C_{E.S_2} = K_E C_E C_{S_2} \quad (17)$$

The total balance for the catalytic sites can be written as follows:

For metallic sites  $S_1$

$$C_{T_1} = C_{S_1} + C_{H.S_1} \quad (18)$$

$$C_{T_1} = C_{S_1} + \sqrt{K_H P_{H_2}} C_{S_1} \quad (19)$$

$$C_{S_1} = \frac{C_{T_1}}{[1 + \sqrt{K_H P_{H_2}}]} \quad (20)$$

For basic sites  $S_2$ ,

$$C_{T_2} = C_{S_2} + C_{A.S_2} + C_{B.S_2} + C_{E.S_2} \quad (21)$$

$$C_{T_2} = C_{S_2} + K_A C_A C_{S_2} + K_B C_B C_{S_2} + K_E C_E C_{S_2} \quad (22)$$

$$C_{S_2} = \frac{C_{T_2}}{[1 + K_A C_A + K_B C_B + K_E C_E]} \quad (23)$$

$$\frac{-dC_A}{dt} = \frac{k_1 K_A C_A \sqrt{K_H P_{H_2}} w}{[1 + K_A C_A + K_B C_B + K_E C_E][1 + \sqrt{K_H P_{H_2}}]} \quad (24)$$

$$\frac{dC_B}{dt} = \frac{[k_1 K_A C_A - k_2 K_B C_B] \sqrt{K_H P_{H_2}} w}{[1 + K_A C_A + K_B C_B + K_E C_E][1 + \sqrt{K_H P_{H_2}}]} \quad (25)$$

$$\frac{dC_E}{dt} = \frac{k_2 K_B C_B \sqrt{K_H p_{H_2}} w}{[1 + K_A C_A + K_B C_B + K_E C_E] [1 + \sqrt{K_H p_{H_2}}]} \quad (26)$$

Where  $w$  is catalyst loading  $\text{g.L}^{-1}$

Using the above equations rate constants ( $k$ ) and adsorption constant ( $K$ ) were calculated and are mentioned in Table S1.

Table S1. Adsorption constants of different species at different temperatures

#.	T(K)	$K_A \times 10^3$ (L/mol)	$K_H$ (L/mol)	$K_B \times 10^3$ (L/mol)	$K_E \times 10^6$ (L/mol)
1	403	0.11	58.8	0.013	1.24
2	413	0.091	46.1	0.008	0.95
3	423	0.083	31.20	0.007	0.82
4	433	0.076	20.9	0.006	0.73
5	443	0.062	16.6	0.002	0.59

The control experiment with THFA as a starting material (SI, Table S2) was conducted to validate the proposed reaction mechanism (Scheme 2).

**Table S2.** Reaction of THFA over 1% Rh/OMS-2 catalyst at different concentrations

#	THFA Conc. (mol)	Conversion (%)	Selectivity of 1, 2 PeD (%)
1.	0.0073 <sup>a</sup>	-	-
2.	0.0036 <sup>a</sup>	5	100

<sup>a</sup> catalyst wt., 0.25 g; hydrogen pressure, 30 atm; temperature, 160 °C; solvent, methanol; reaction time, 8 h; total volume, 20  $\text{cm}^3$ .