Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Continuous Hydroxyketone Production from Furfural Using Pd-TiO_2 Supported on Activated Carbon Catalysts

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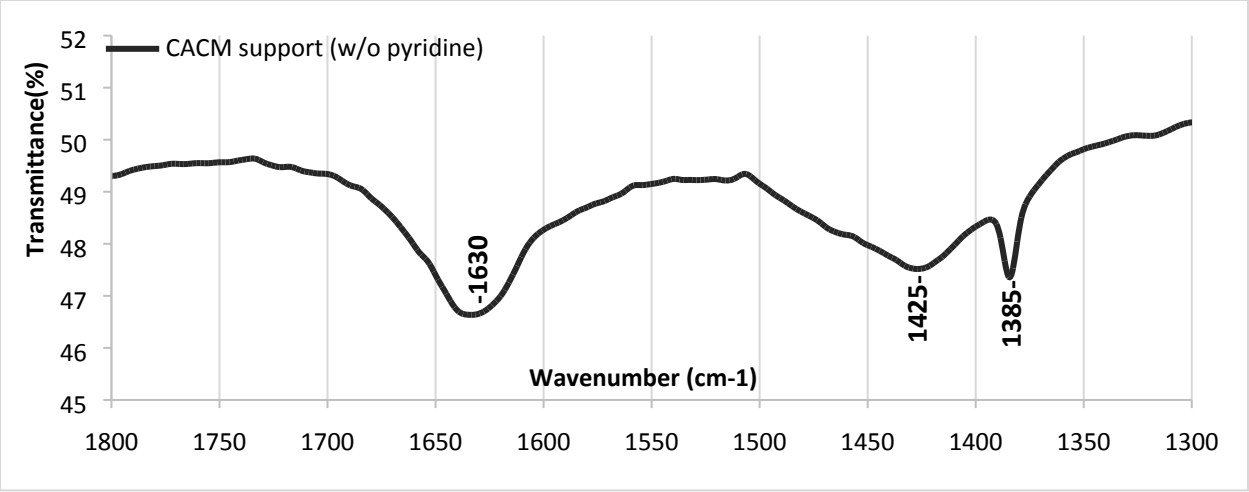
Supporting Information.

1. Kinetic Parameters
2. FTIR analysis of base material, activated carbon monolith
3. XRD analysis
4. Pore size distribution, BET, and t-plots
5. Effect of temperature and pressure on product selectivity and space time yield
6. Furfural conversion and carbon closure
7. Turnover frequency plots
8. Reaction pathway

Key kinetic parameters were calculated in the following manner. Conversion (X), yield (Y), selectivity (S), weighted hourly space velocity (WHSV), liquid hourly space velocity (LHSV), space time yield (STY) and the catalyst to mass rate ratio (W/F) were calculated using the following equations. $X_A = 1\text{-}F_{Aout}/F_{Ain}$, where F_A is the molar rate for species A (e.g., $F_{Aout} = C_{Aout} Q_{out}$; C_{Aout} is the measured concentration and is the measured volumetric flowrate). $Y_A = F_{Aout}/ F_{Tin}$, where $F_{Tin} = \sum F_i$ and i is species. $S_A = F_{Aout}/(F_{Tin}- F_{Tout})$. WHSV was calculated as $[MW_A* F_{Ain}]/W$, where W is catalyst mass and MW is the molecular weight. LHSV was calculated as $[Q_{in}*\rho_{cat}]/W$ and GHSV as $[Q_{gas,in}*\rho_{cat}]/W$, where ρ_{cat} is the bulk density of the catalyst. STY was calculated as $F_{Aout} \rho_{cat} MW_A / W$ (g/L-catalyst/h).



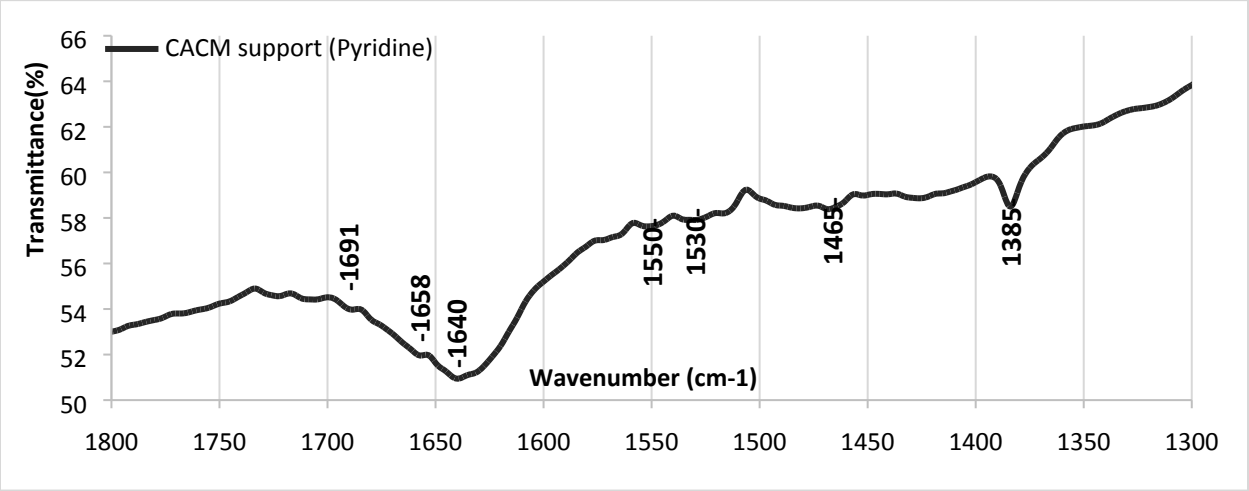
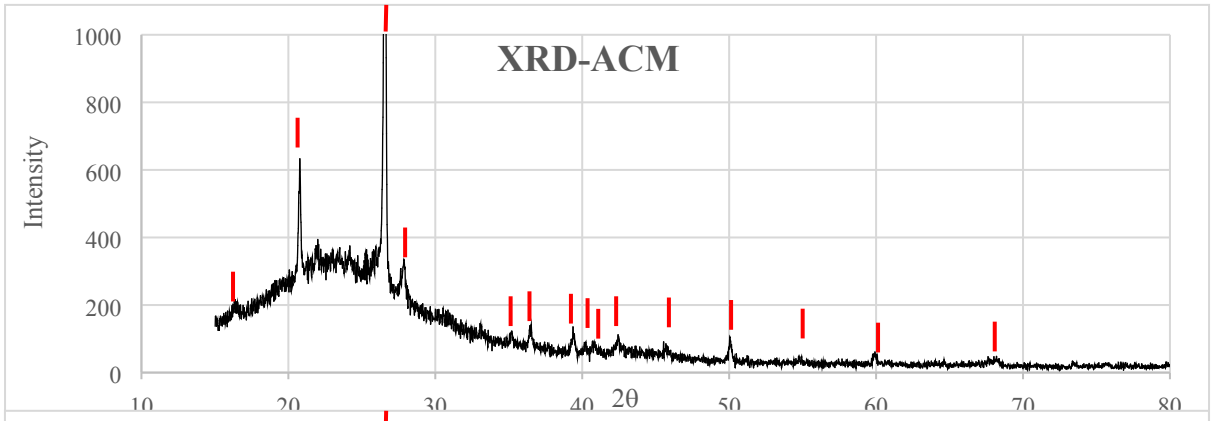
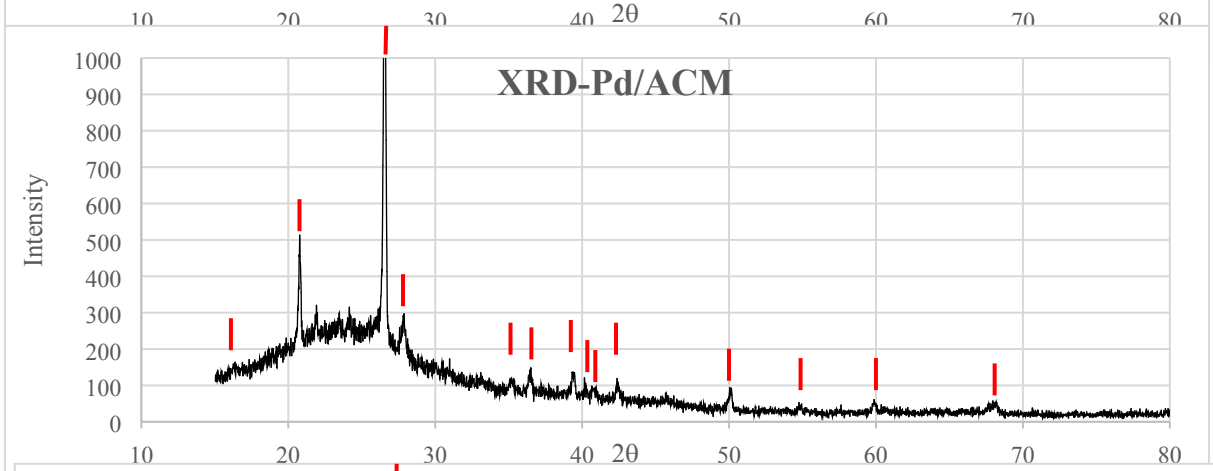
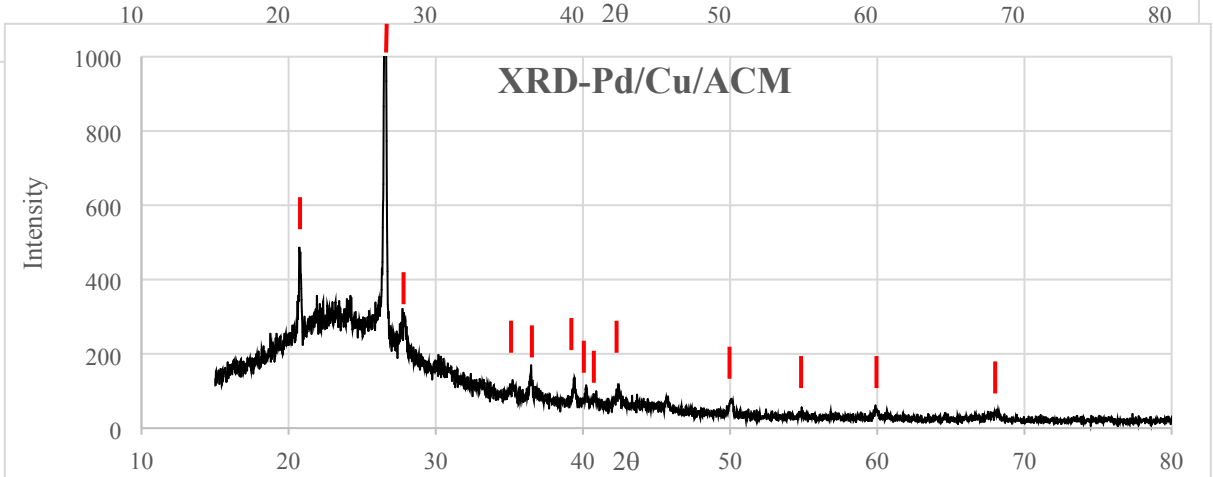
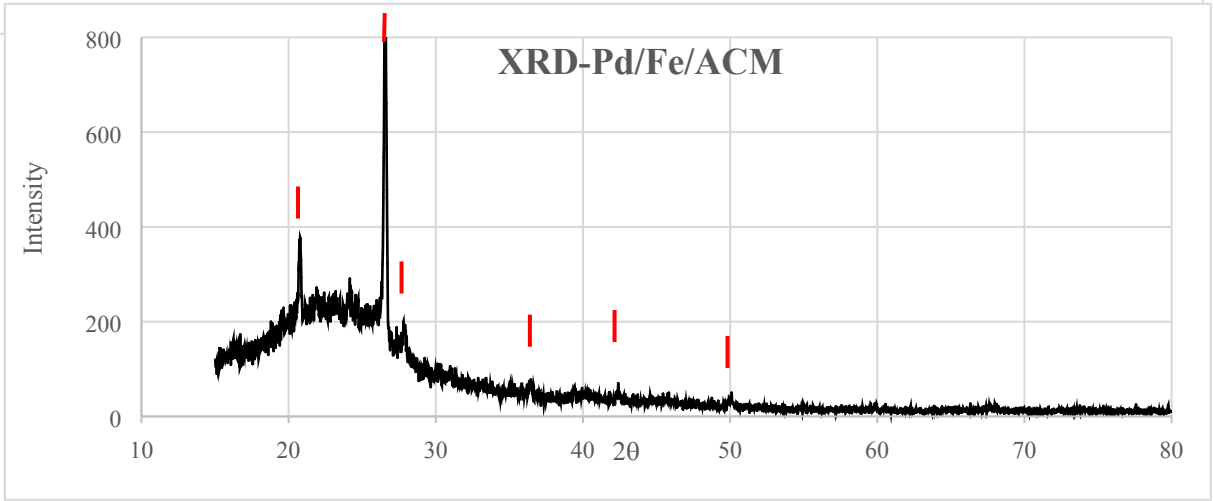


Figure SI-1: FTIR analysis of CACM support.


XRD-ACM
Intensity
2θ
0
200
400
600
800
1000
10
20
30
40
50
60
70
80


XRD-Pd/ACM
Intensity
2θ
0
100
200
300
400
500
600
700
800
900
1000
10
20
30
40
50
60
70
80


XRD-Pd/Cu/ACM
Intensity
2θ
0
200
400
600
800
1000
10
20
30
40
50
60
70
80


XRD-Pd/Fe/ACM
Intensity
2θ
0
200
400
600
800
10
20
30
40
50
60
70
80

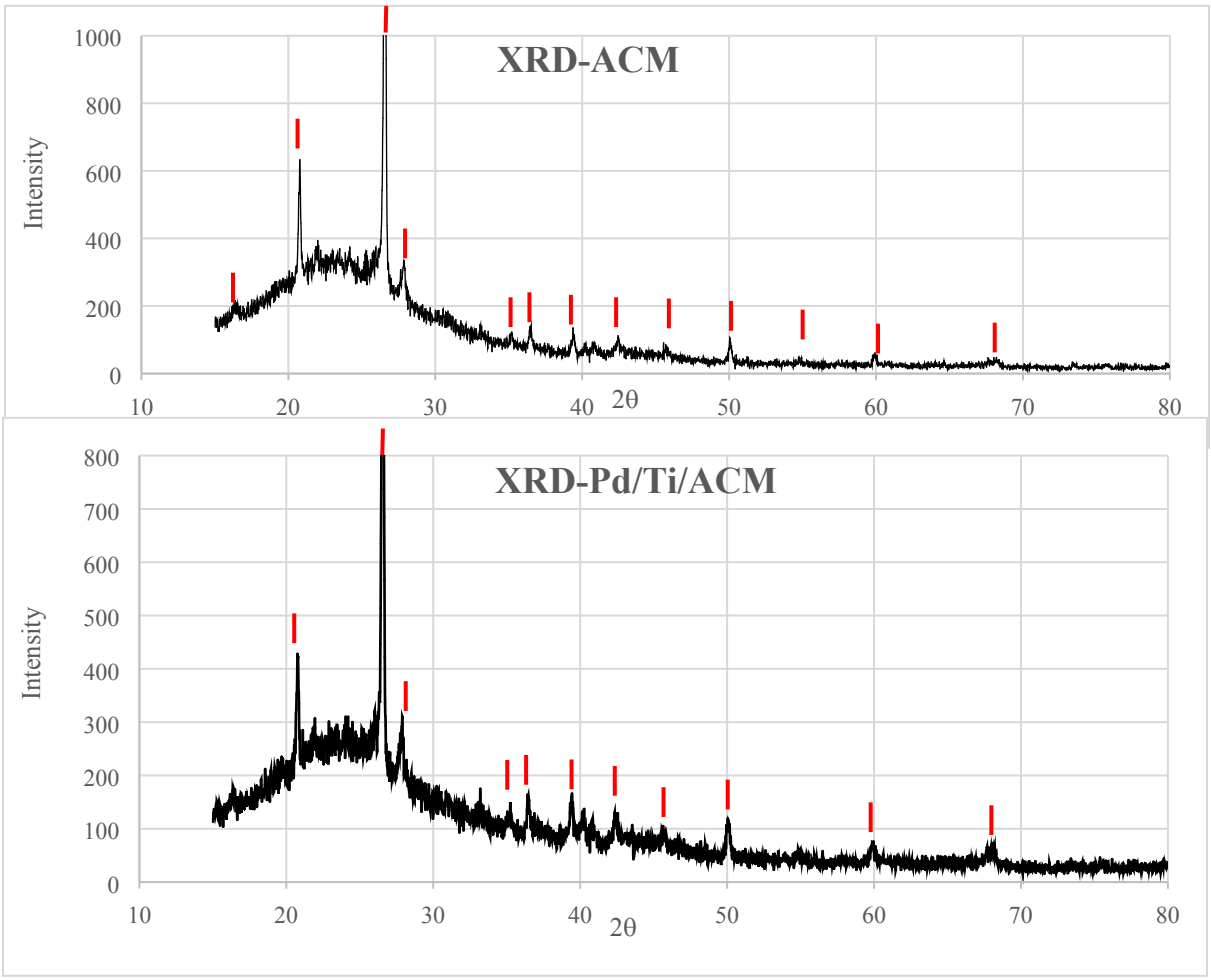
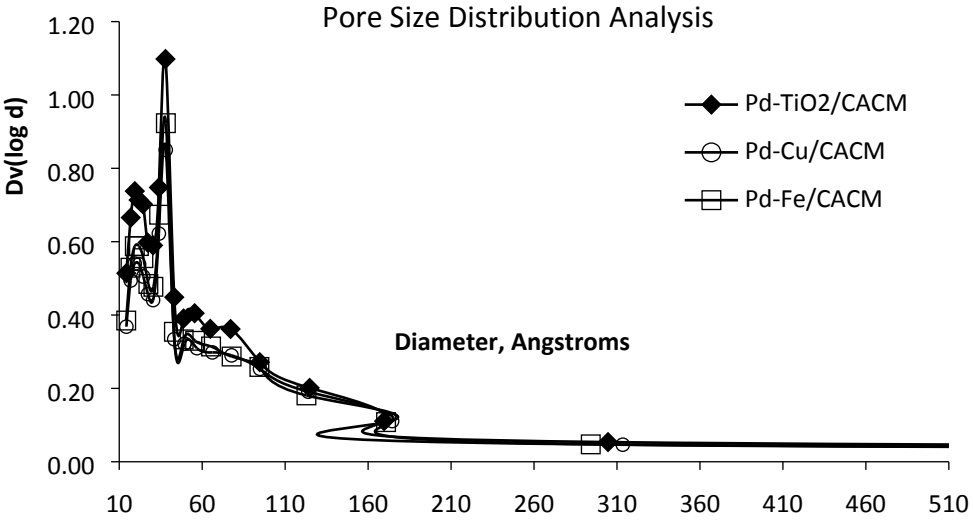
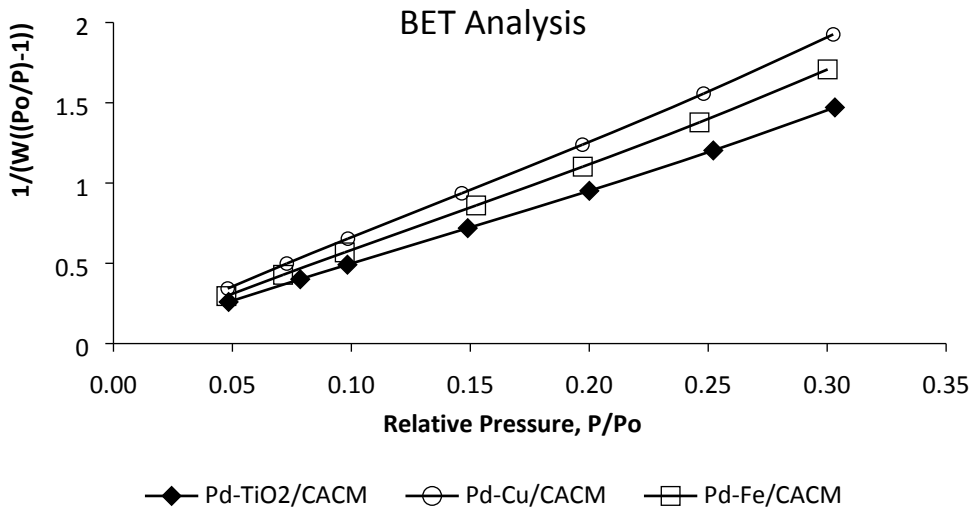


Figure SI-2: XRD analysis of ACM and Pd/ACM, Pd-Cu, Pd-Fe, and Pd-Ti/CACM catalysts [X-ray diffraction (XRD) was performed on a PANalytical X'Pert PRO using a Cu-Ka radiation source (l = 1.5418 Å) with step size of 0.02° and 2θ range of 15° to 80°].





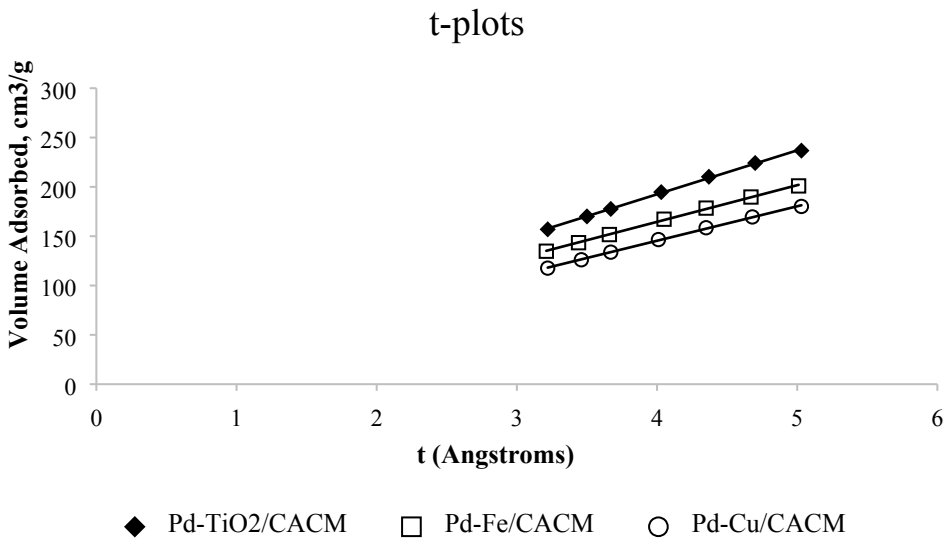


Figure SI-3. BJH, t-plot and BET analysis of fresh catalysts.

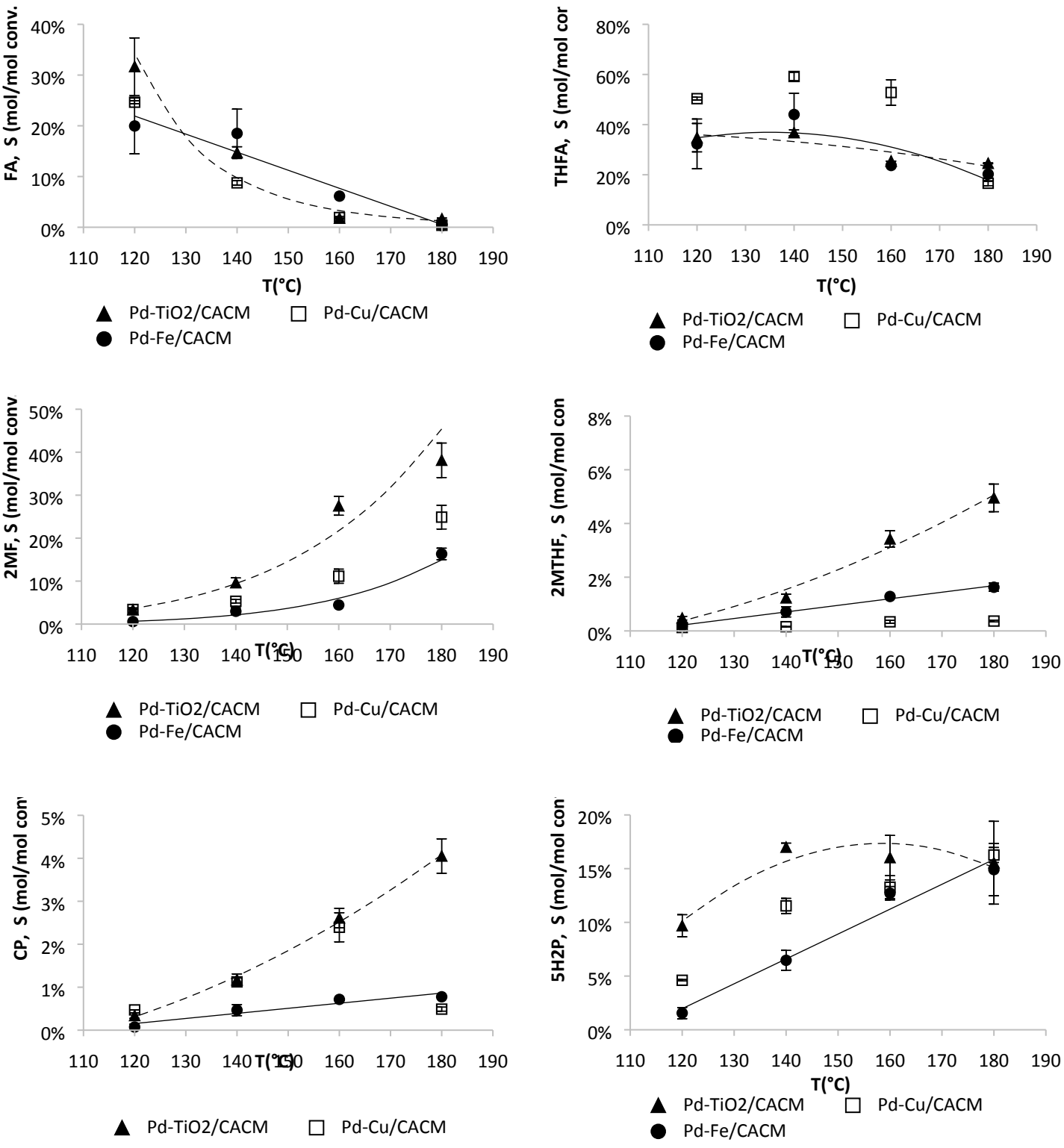


Figure SI-4: Effect of reaction temperature on product selectivity (FA, furfuryl alcohol; THFA, tetrahydrofurfuryl alcohol; 2MF, 2-methyl furan; 2MTHF, 2-methyl tetrahydrofuran; 5H2P, 5-hydroxy-2-pentanone; CP, cyclopentanone). Reaction Condition: P=300 psig , LHSV =1.32 1/h, 5 g of catalyst.

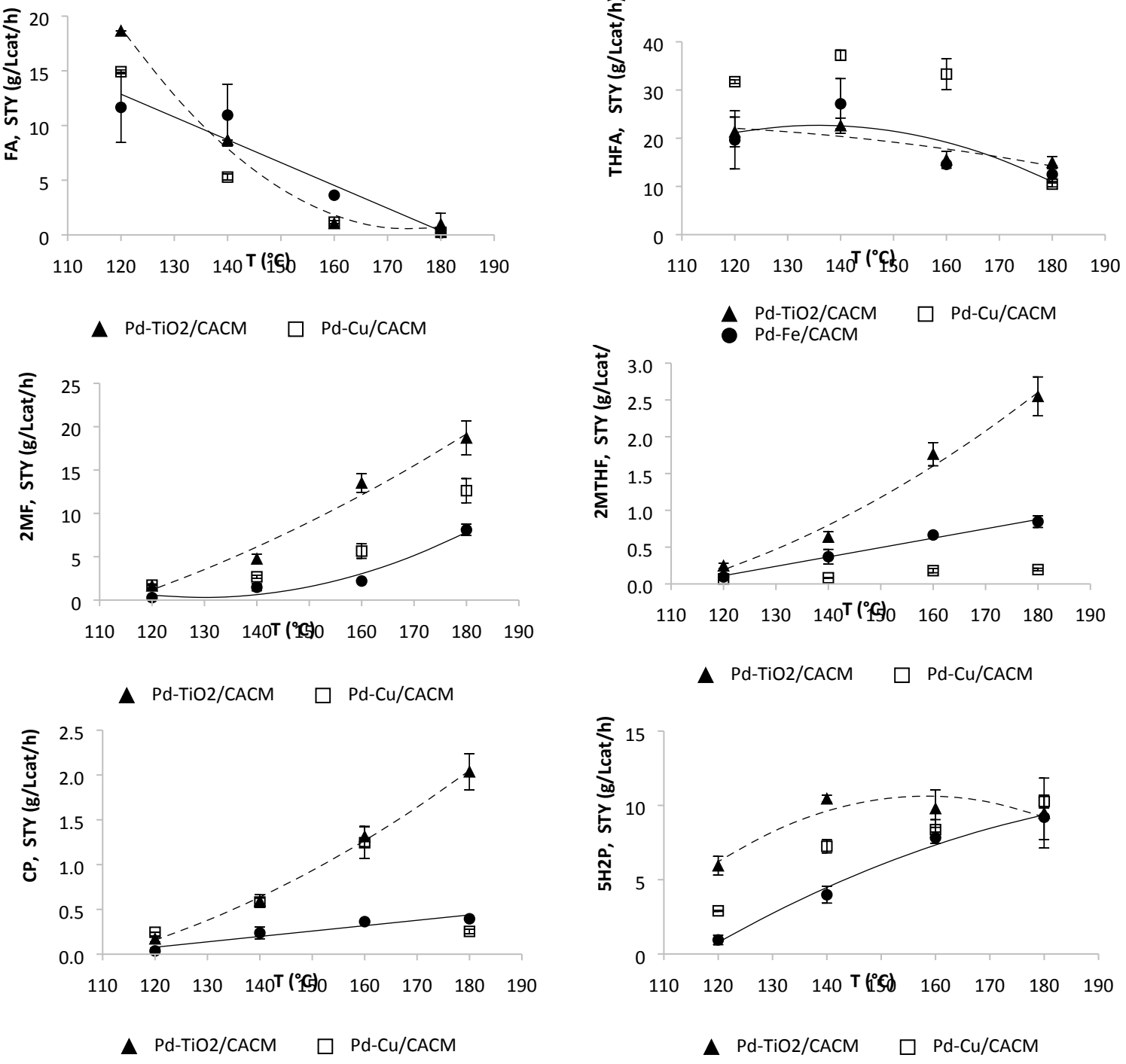
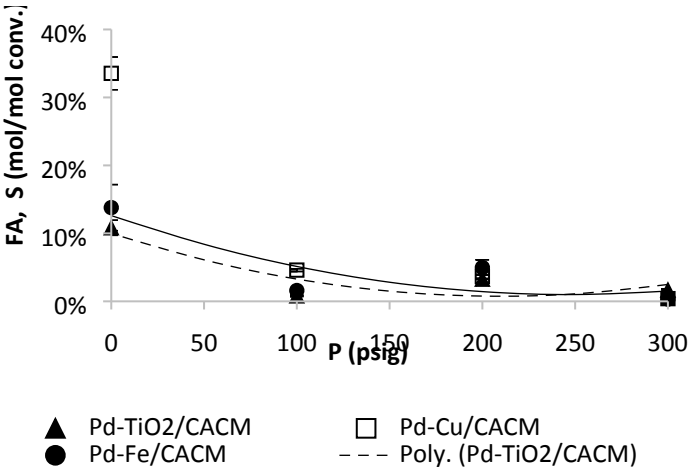
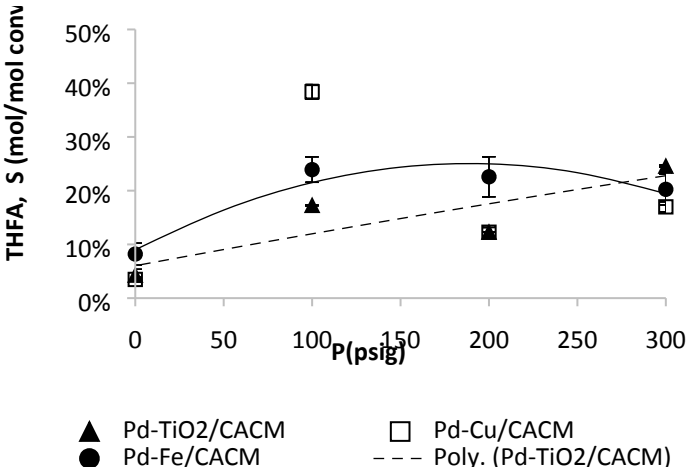
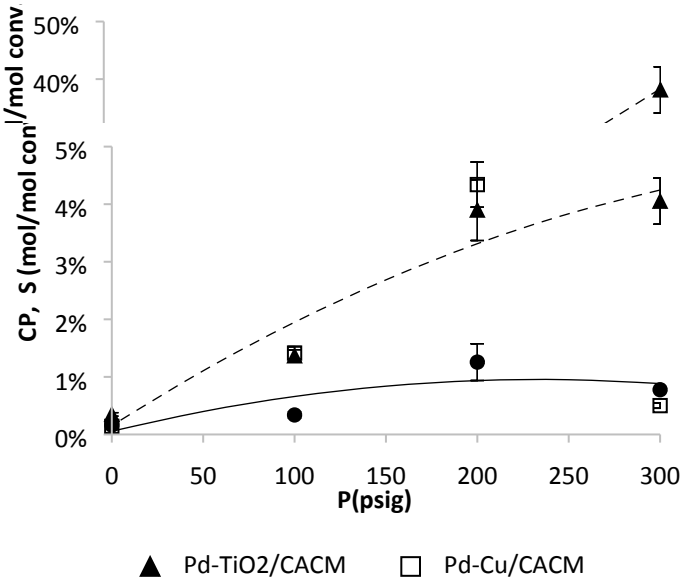


Figure SI-5: Effect of temperature on product space time yield







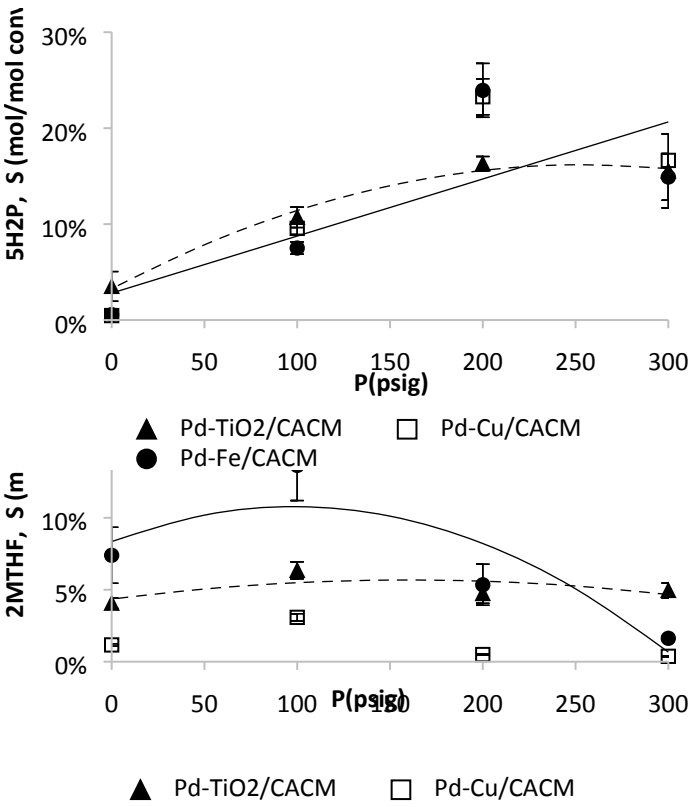


Figure SI-6: Effect of hydrogen pressure on product selectivity. Reaction Condition: T=180 °C, LHSV =1.32 1/h, 5 g of catalyst.

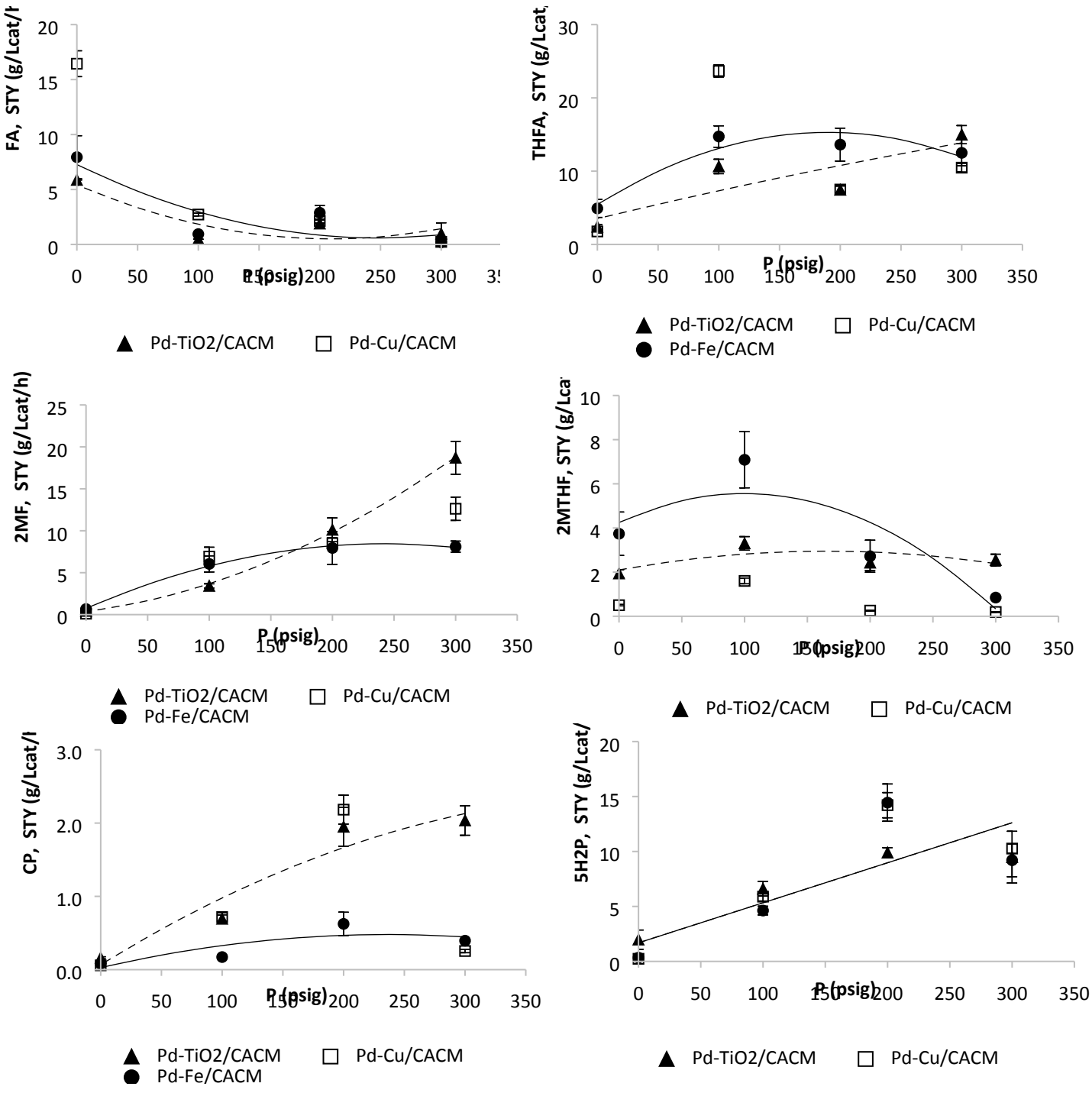
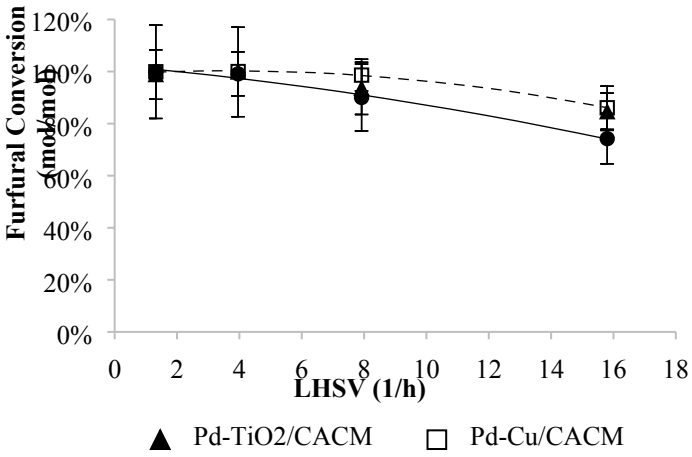


Figure SI-7: Effect of pressure on product space time yield.



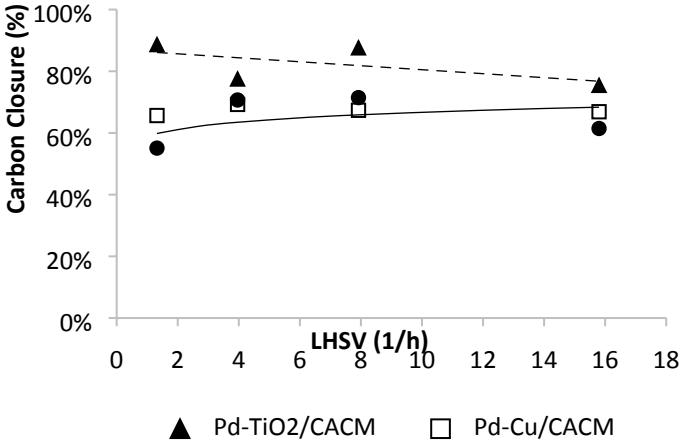
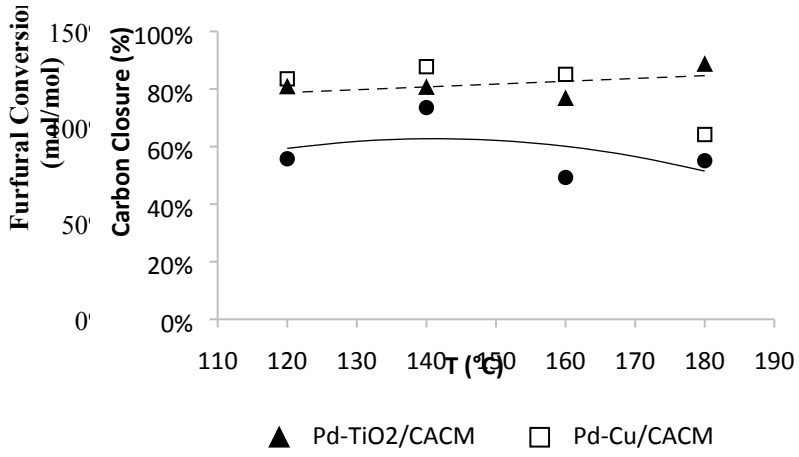
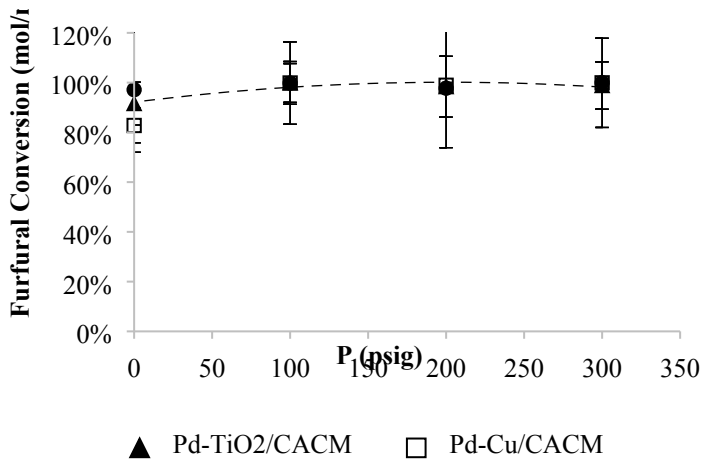
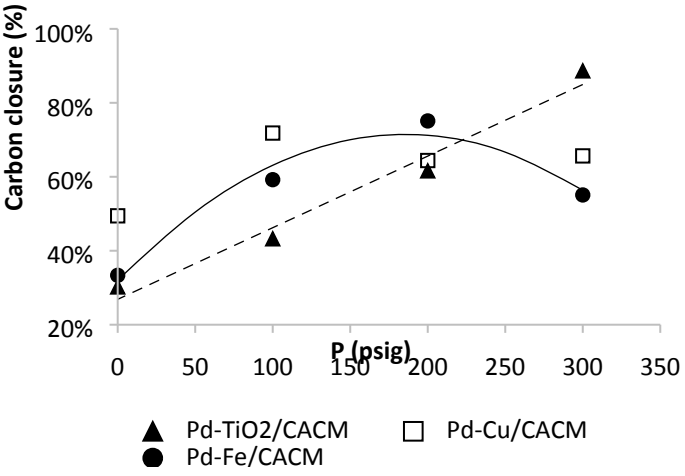
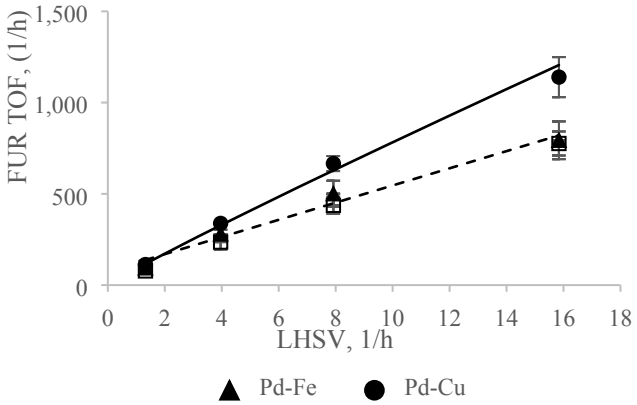


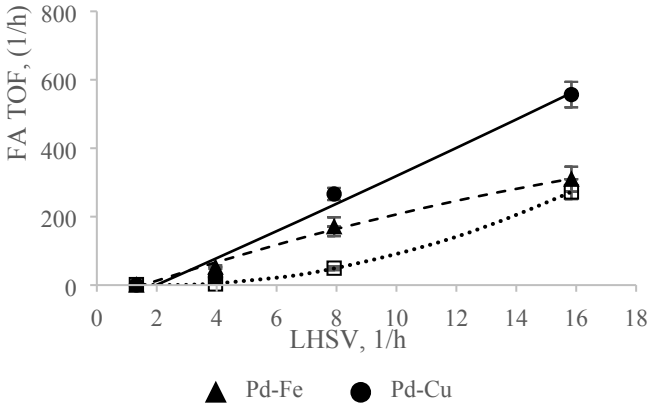
Figure SI-8: Effect of temperature (LHSV 1.32 h^{-1}, 300 psig), pressure (LHSV 1.32 h^{-1}) and LHSV (180°C, 300 psig) on furfural conversion and carbon closure

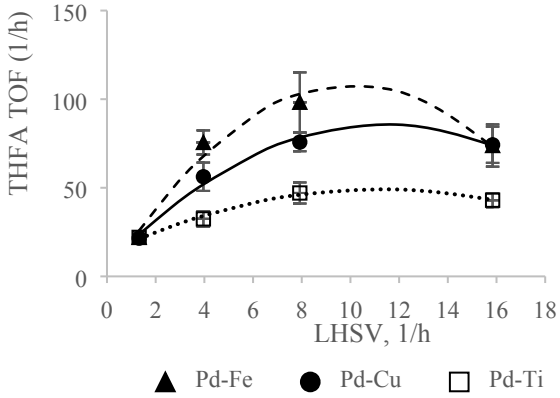


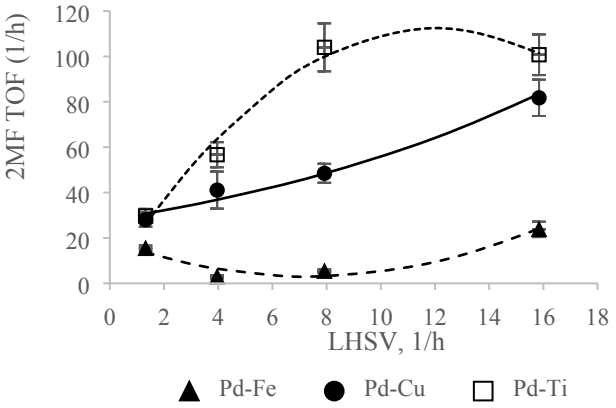


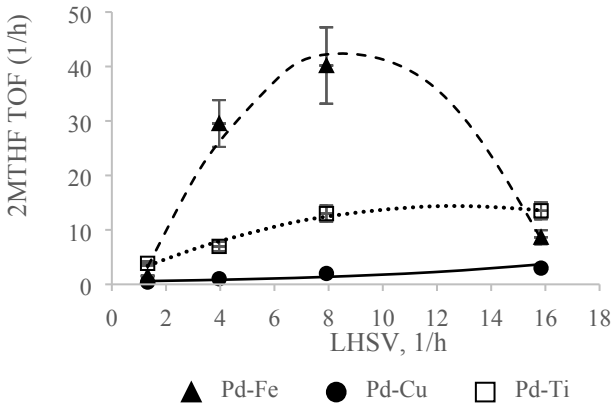


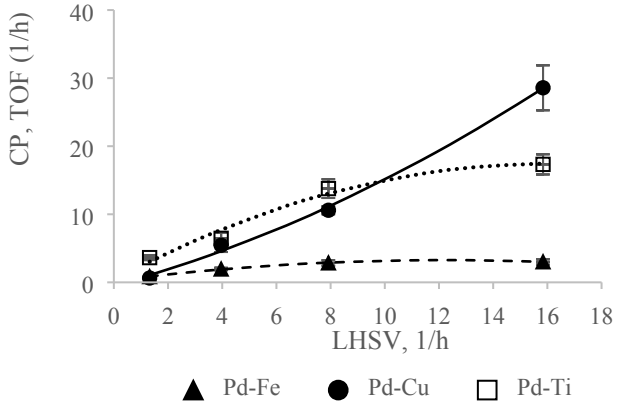

FUR TOF, (1/h)
1,500
1,000
500
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu


FA TOF, (1/h)
800
600
400
200
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu


THFA TOF (1/h)
150
100
50
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu
Pd-Ti


2MF TOF (1/h)
120
100
80
60
40
20
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu
Pd-Ti


2MTHF TOF (1/h)
50
40
30
20
10
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu
Pd-Ti


CP, TOF (1/h)
40
30
20
10
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu
Pd-Ti

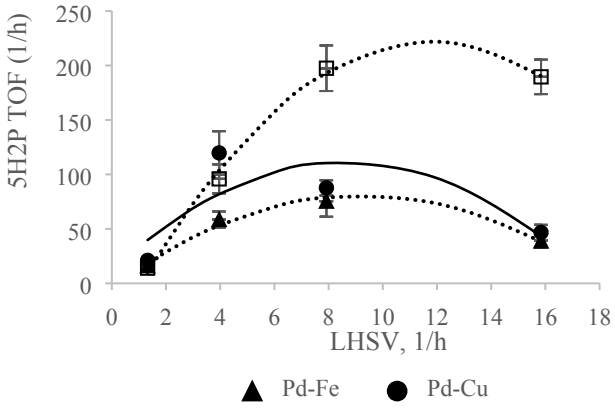

5H2P TOF (1/h)
250
200
150
100
50
0
0 2 4 6 8 10 12 14 16 18
LHSV, 1/h
Pd-Fe
Pd-Cu

Figure SI-9: Effect of LHSV on furfural and product TOF (mol consumed or produced/mole of active Pd/h). P = 300 psig, T = 180 °C, 5 g of catalyst.

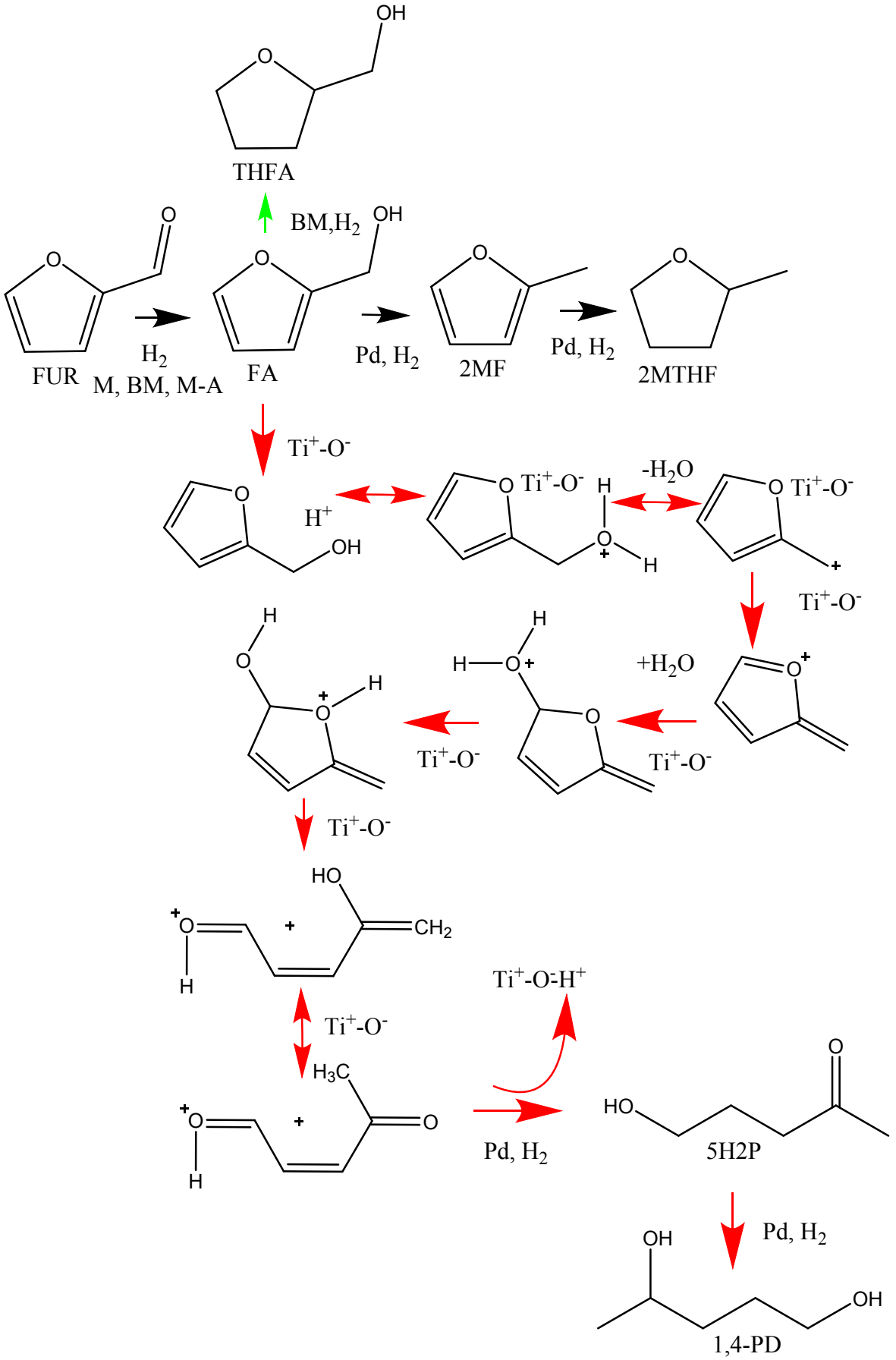


Figure SI-10: Speculative reaction pathway for 5H2P formation from furfural hydrogenation using Pd/TiO_2/CACM. M is metal site, BM is a bi-metal (e.g., Pd-Fe), M-A is metal/acid.