

## Supporting Information

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### **Carbon Nanofibers Modified with Heteroatoms as Metal-Free Catalysts for the Oxidative Dehydrogenation of Propane**

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## SUPPLEMENTARY INFORMATION

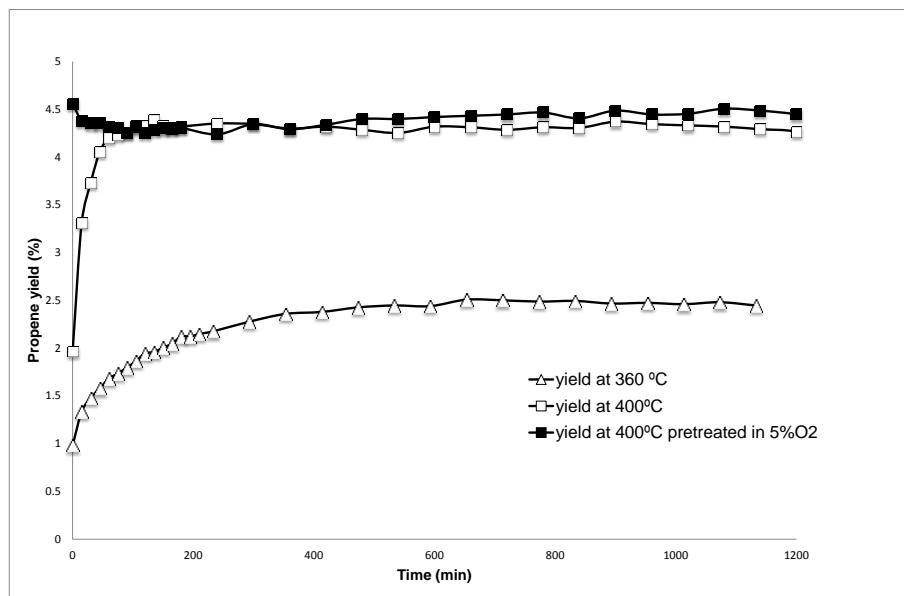


Figure S1. Effect on the induction period of the reaction temperature and of a pretreatment in 5% O<sub>2</sub> at the reaction temperature

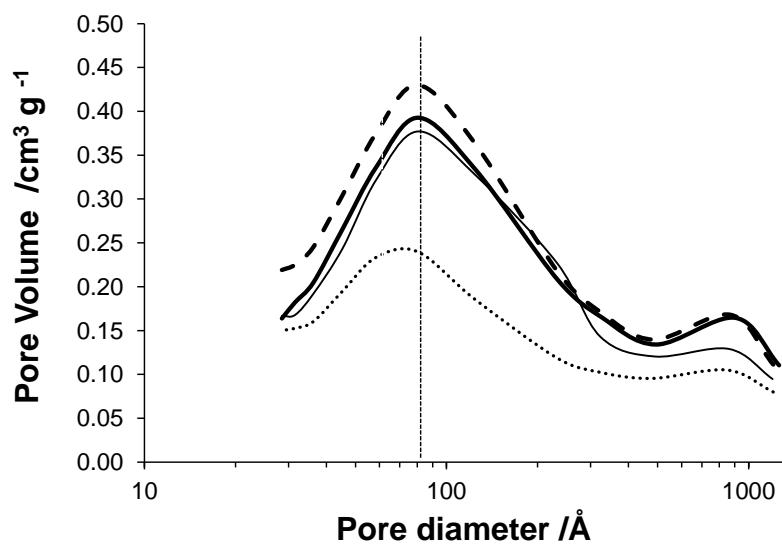


Figure S2. Pore size distribution measured by BJH method of adsorption isotherm for CNF with different boron loadings. (.....) CNF, ( - - - ) 0.5%B-CNF, ( — ) 1%B-CNF, ( —·— ) 2%B-CNF.

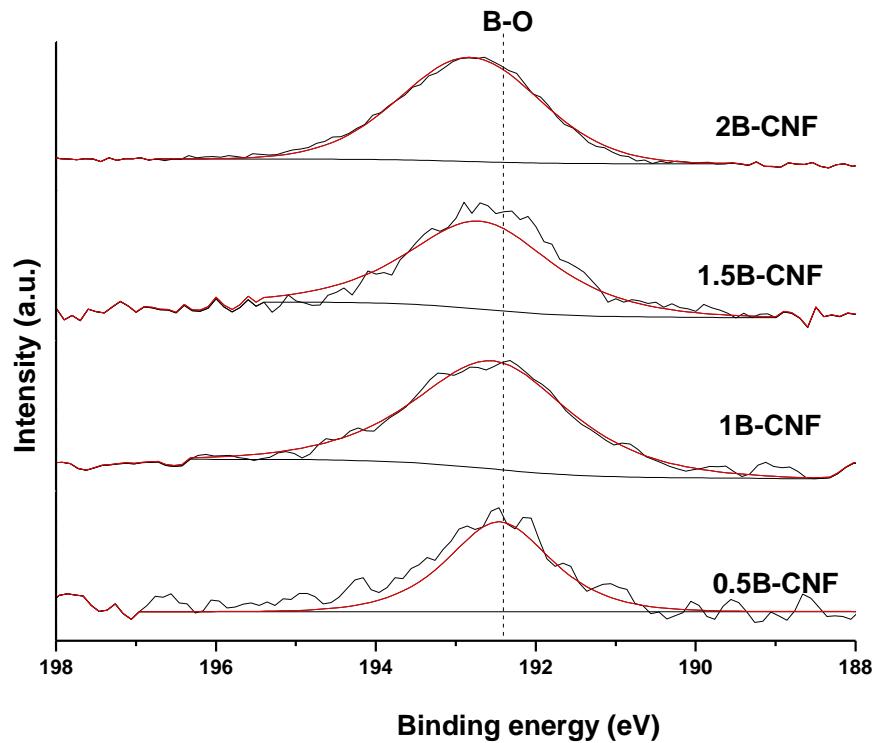


Figure S3. XPS B *1s* peak of CNFs with several percentages of boron

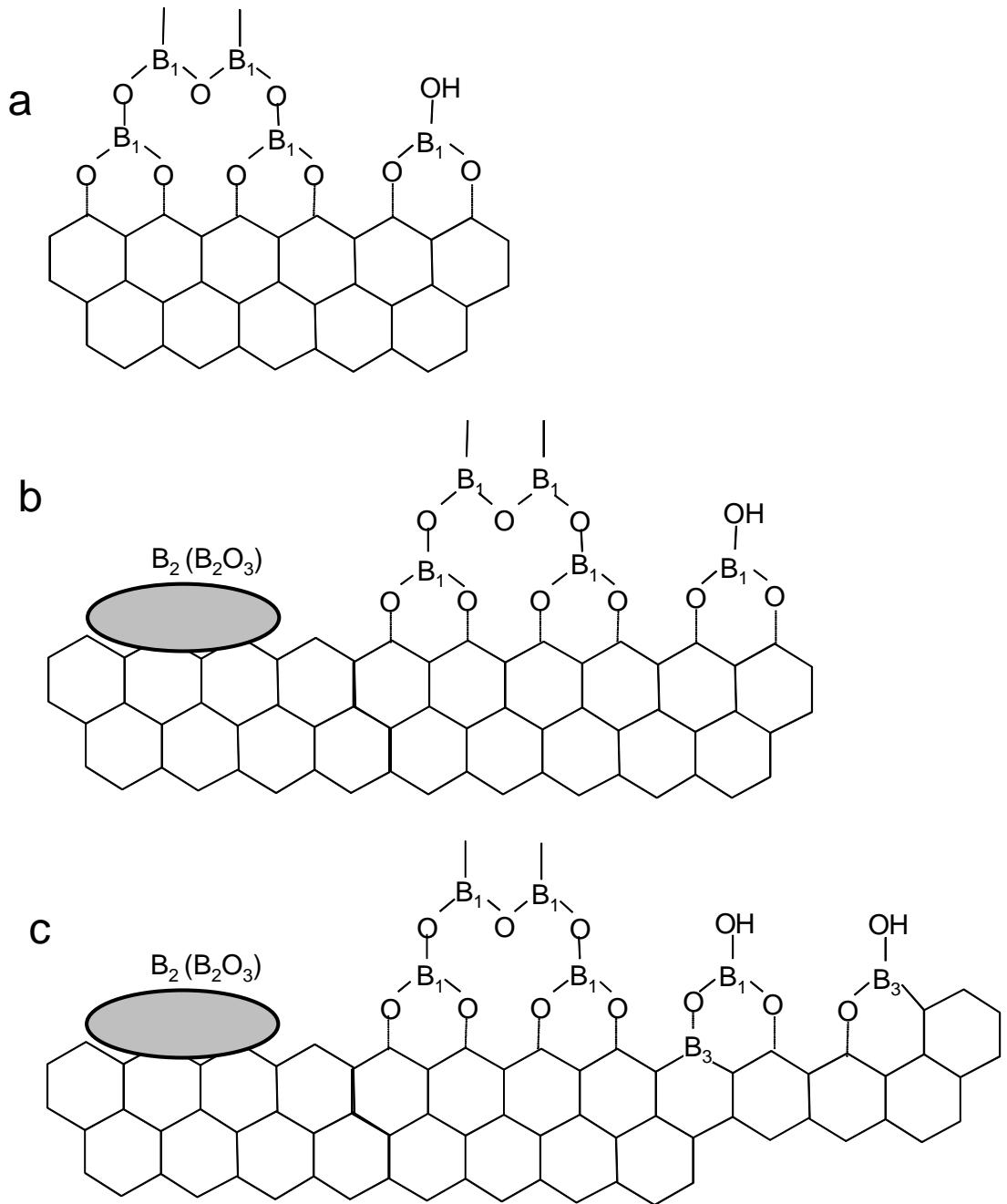


Figure S4. Representation of Boron species determined according the assignments of XPS deconvolution peaks after calcination at different temperatures (a) calcination at 673 K ; (b) calcination at 773 K; (c) calcination at 973 K and above.

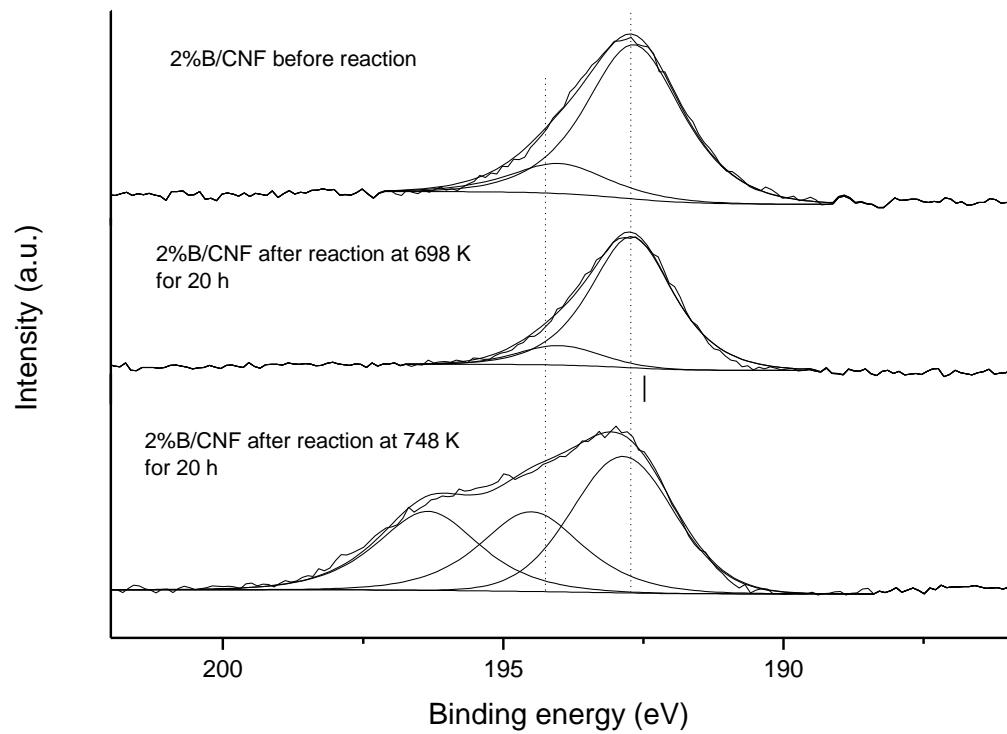
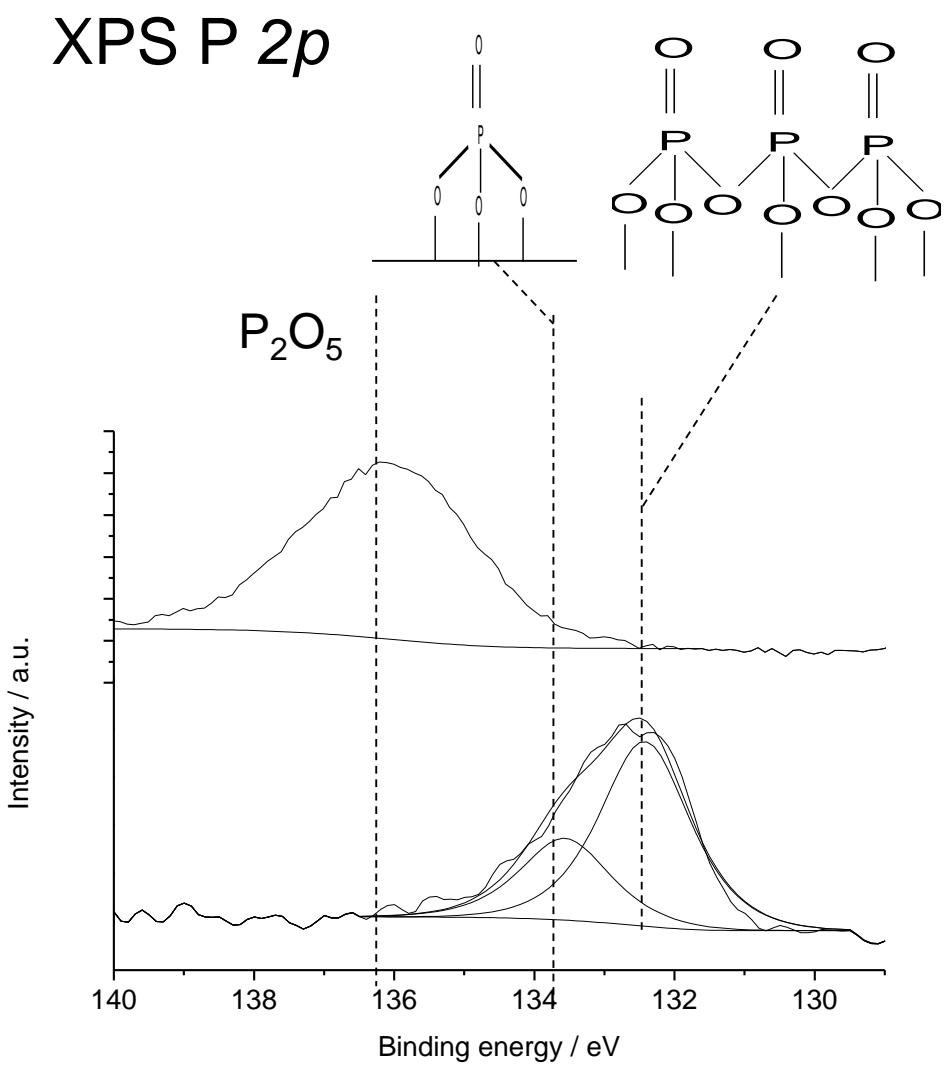


Figure S5. XPS B *1s* peak after long term reaction during 20 h for catalyst tested at two reaction temperatures 698 and 748 K.



Figure

Figure S6. Representation of phosphorous species assigned to each peak of XPS deconvolution of P 2p peak.

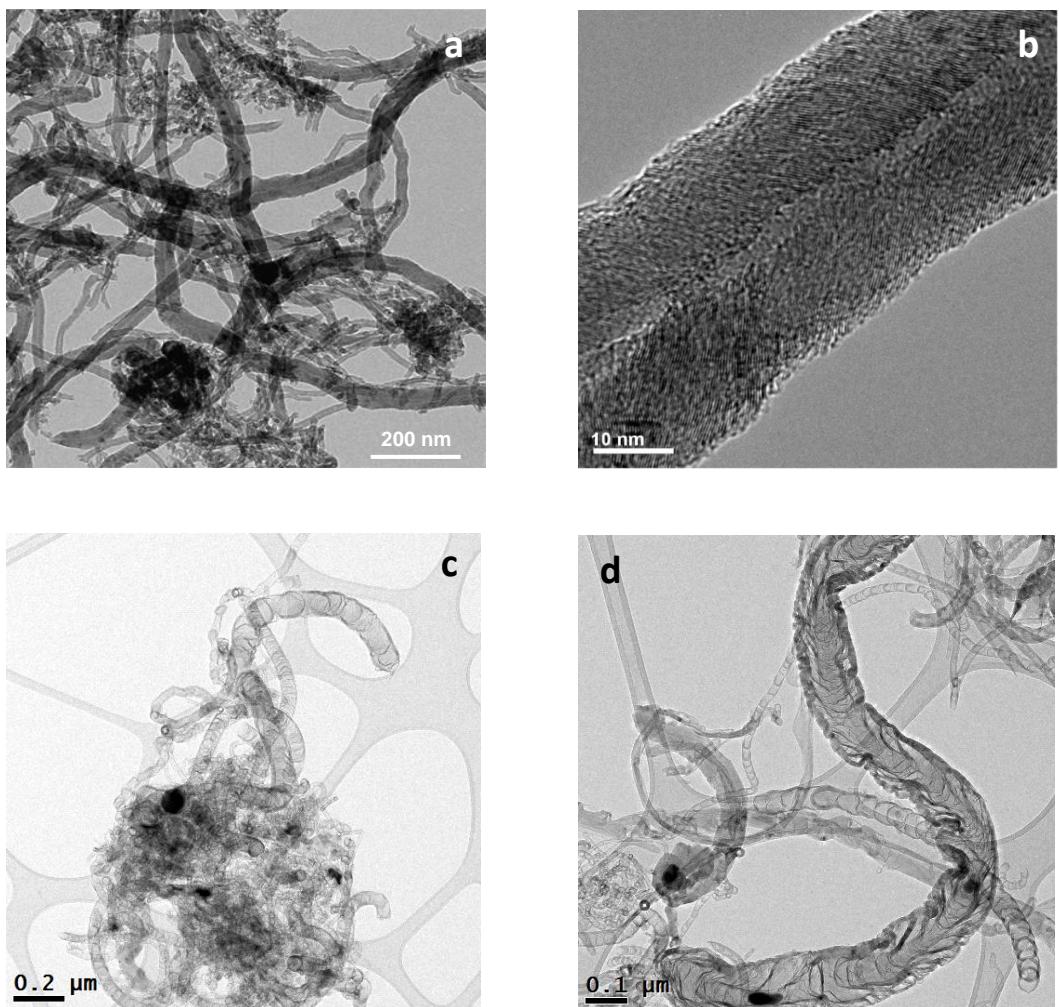


Figure S7. TEM images of pristine CNFs (a,b) and N-doped CNFs (c,d)

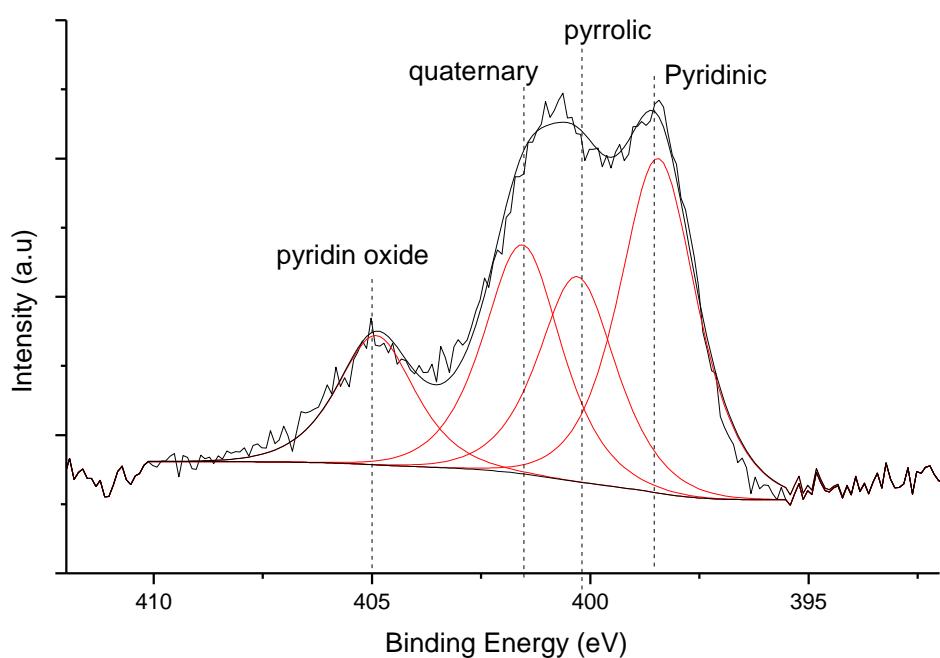


Figure S8. XPS N 1s peak of N-CNF

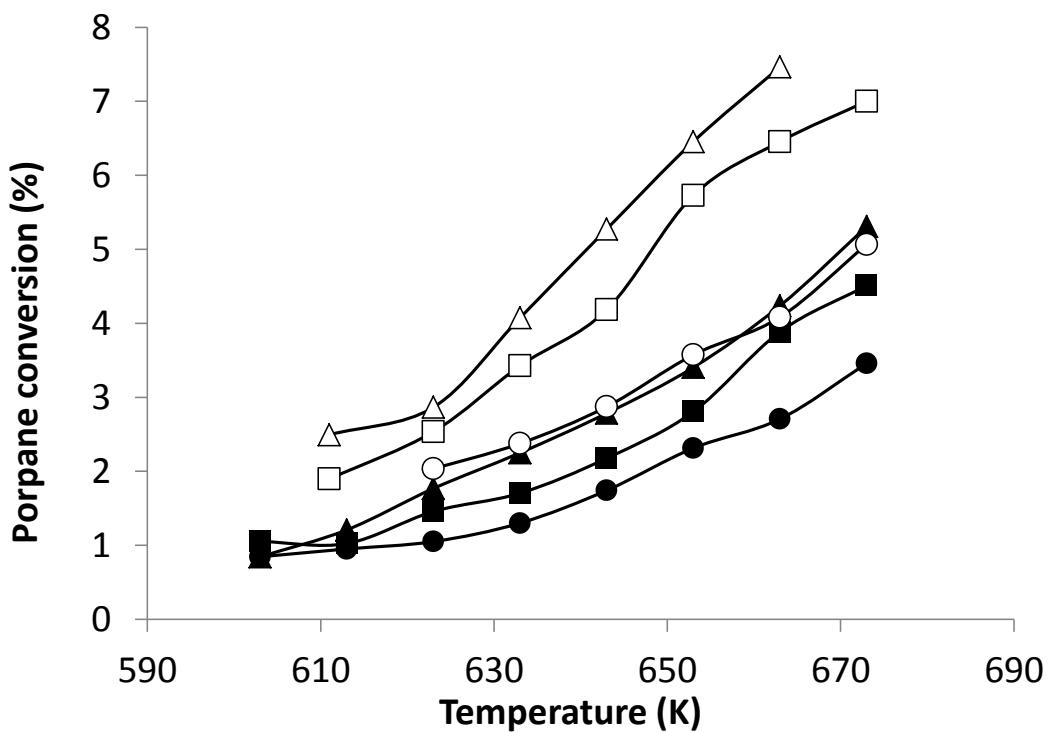
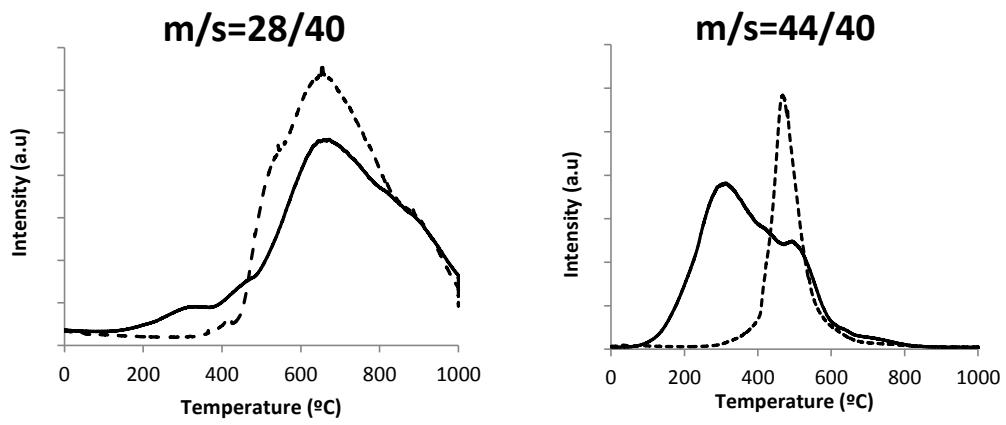
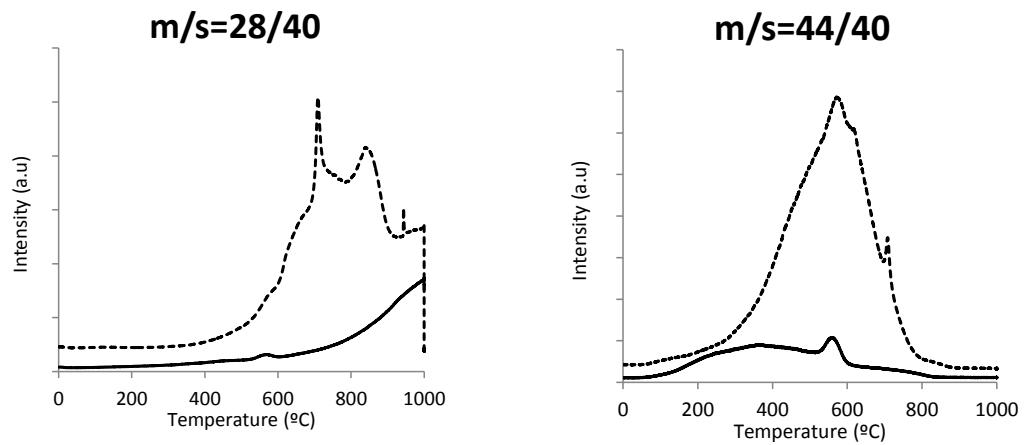


Figure S9. Propane conversion as a function of reaction temperature using CNF (empty symbols) and 1.5%P<sub>TPP</sub>-CNF (filled symbols) as catalysts and different feed flow rates: (triangles) 40 ml/min, (squares) 60 ml/min, (circles) 100 ml/min.

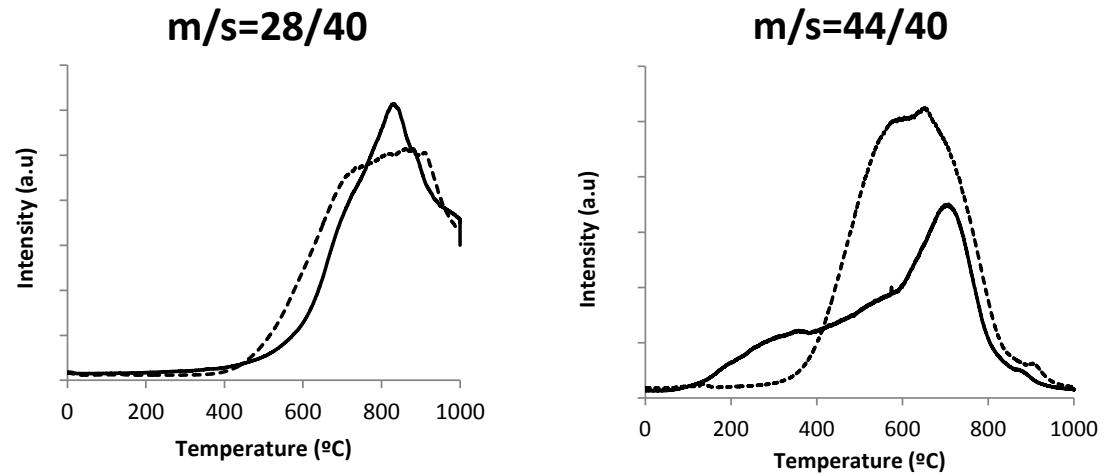
a) CNF



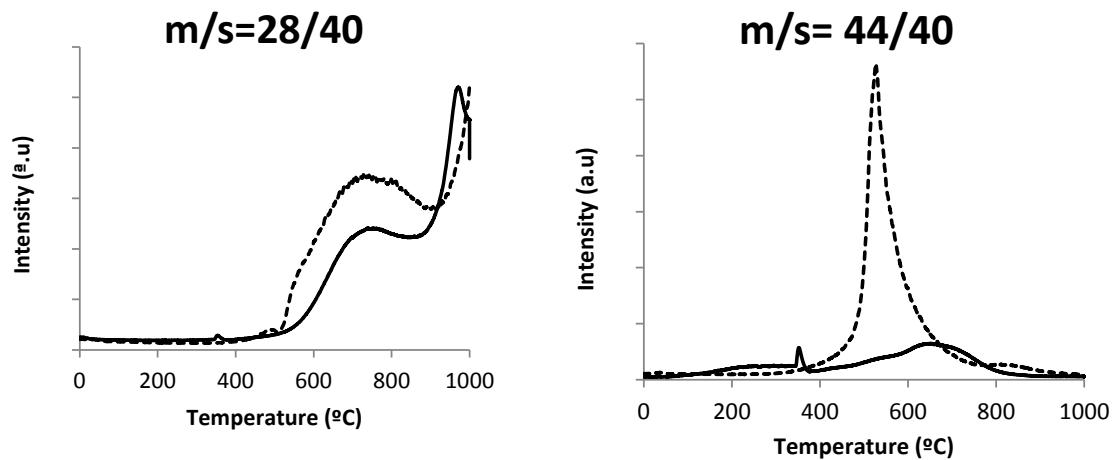
b) N-CNF



c) 1.5% B-CNF



d) 1.5%P<sub>phosphate</sub>-CNF



e) 1.5%P<sub>TPPhosphine</sub>-CNF

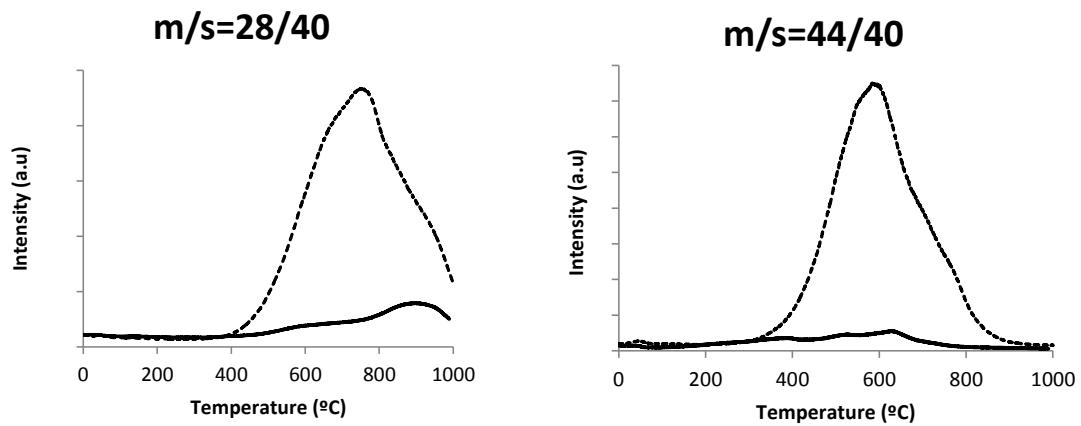
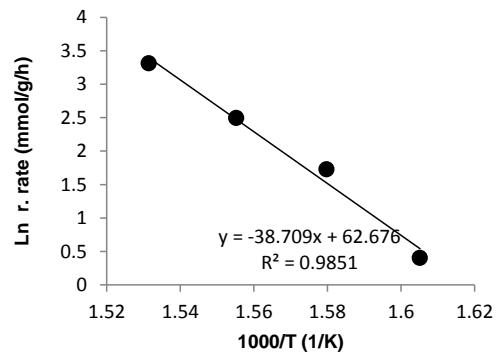
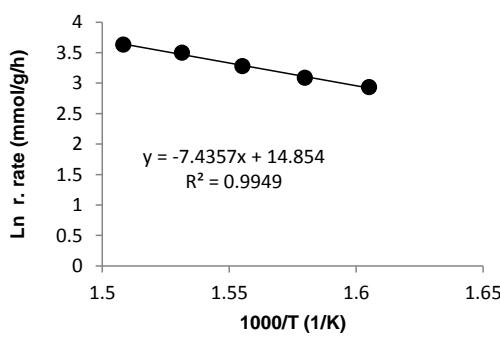
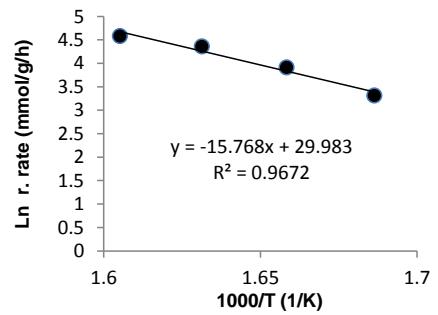
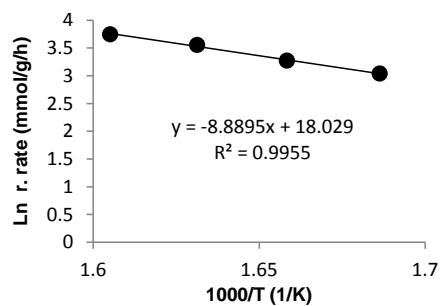


Figure S10. m/s signals 28/40 and 44/40 in Temperature programmed desorption (TPD) before and after ODH reaction for the different catalysts. Before ODH reaction, solid line and after ODH reaction, dashed line.

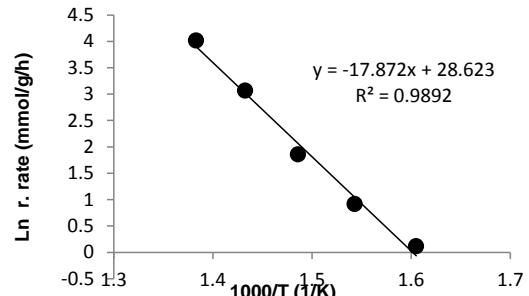
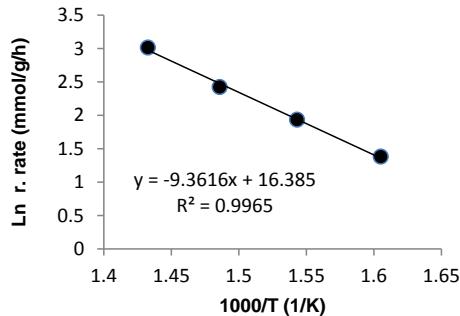
a) CNF 100 ml min



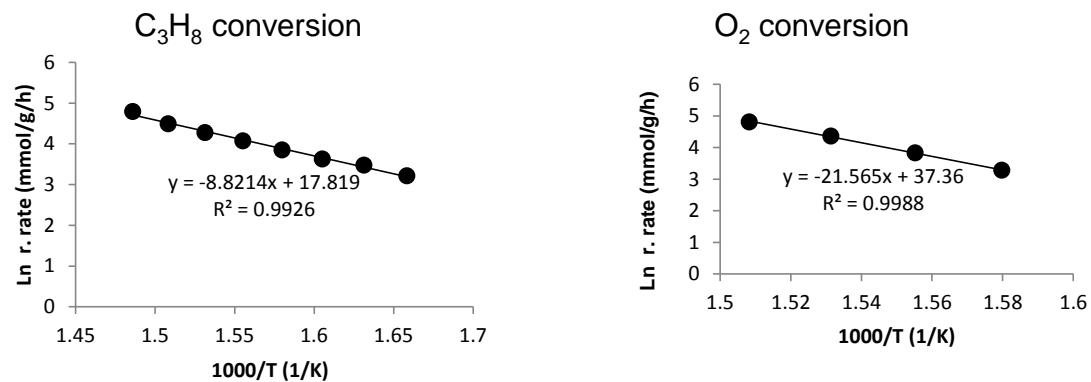
b) N-CNF



c) 1.5B-CNF



d) 1.5%P<sub>phosphate</sub>-CNF



e) 1.5%P<sub>TPP</sub>-CNF

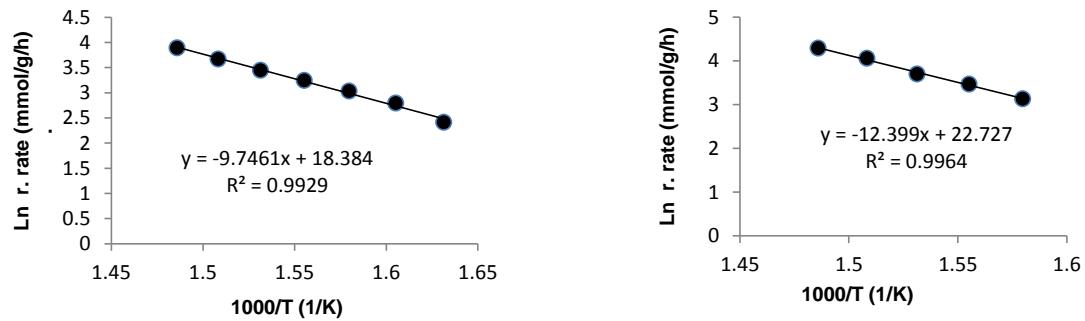


Figure S11. Arrhenius plots for the different catalysts in the kinetic regime

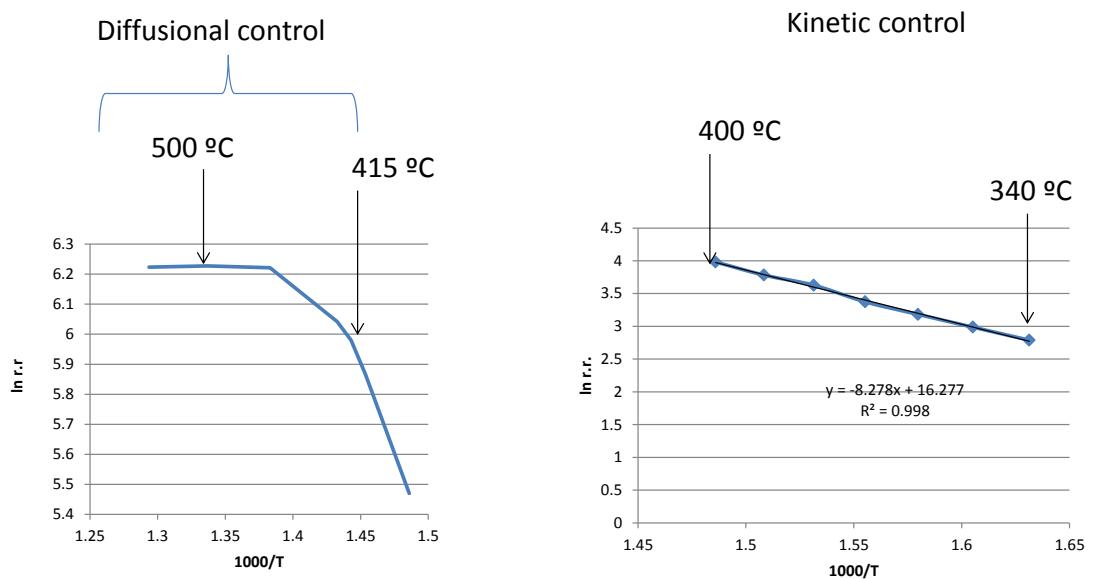


Figure S12. Dependence of Arrhenius plots with respect to the reaction temperature for 1.5% B-CNF.