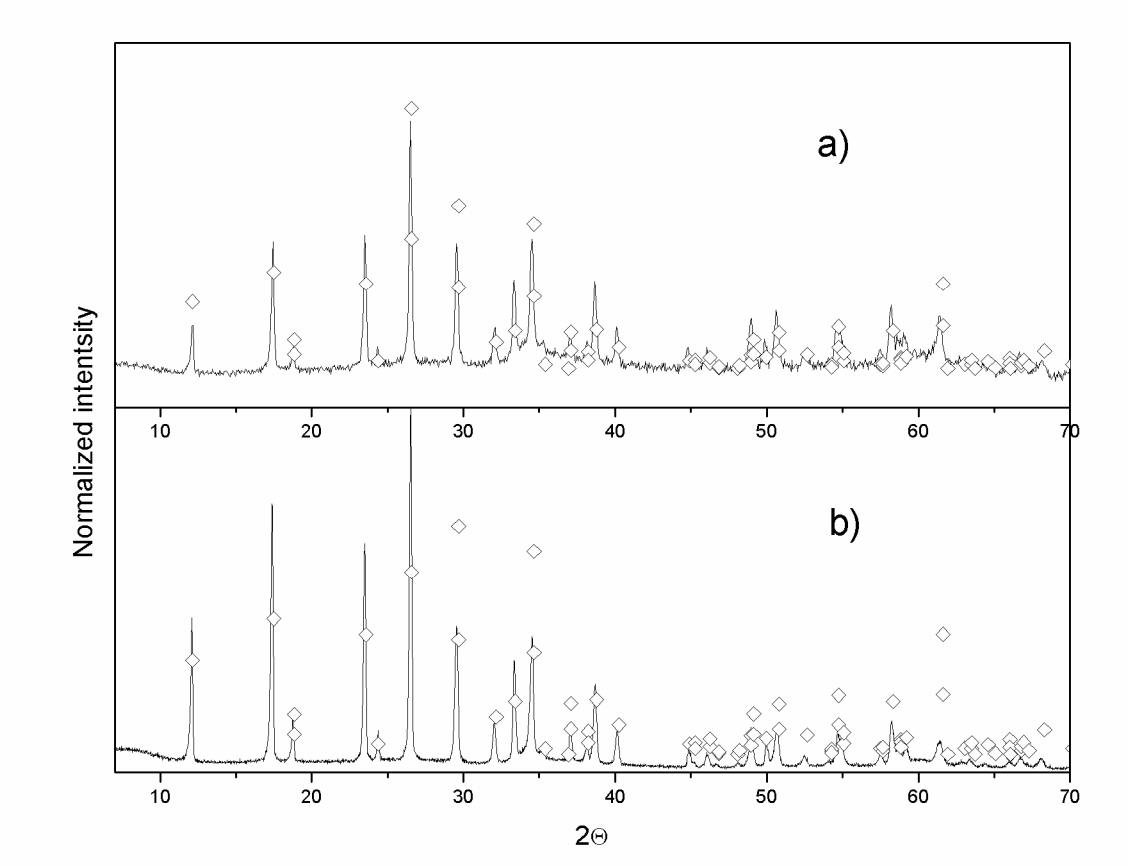

Fig. S1. XRD patterns of layered precursor a) NH_4-NiMo-a ; b) NH_4-NiMo-b. The ◊ symbol refers to the simulated peaks from the ICSD-165342 pattern.

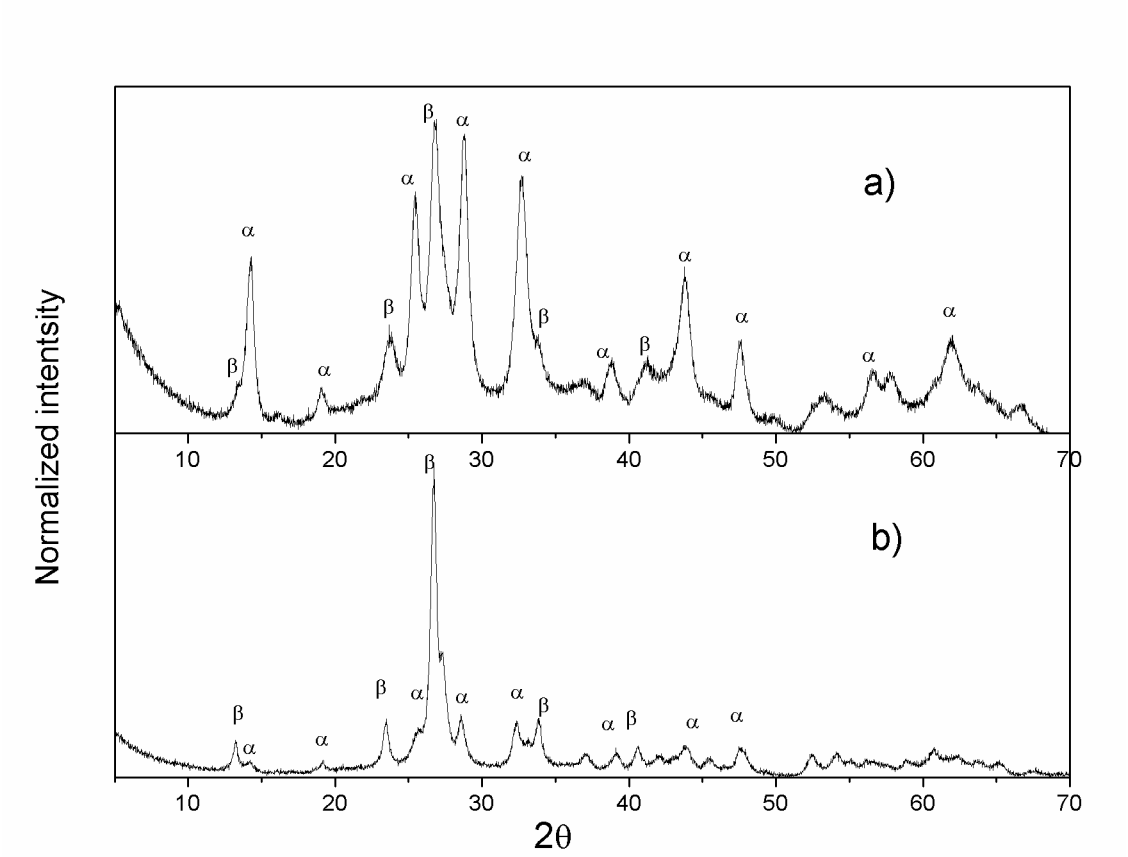

Fig. S2. XRD patterns for mixed oxides a) NiMo-a-ca; b) NiMo-b-ca.
The α and β symbols are for α-$NiMoO_4$ (ICSD-81059) and β-$NiMoO_4$ [38] phases patterns, respectively.

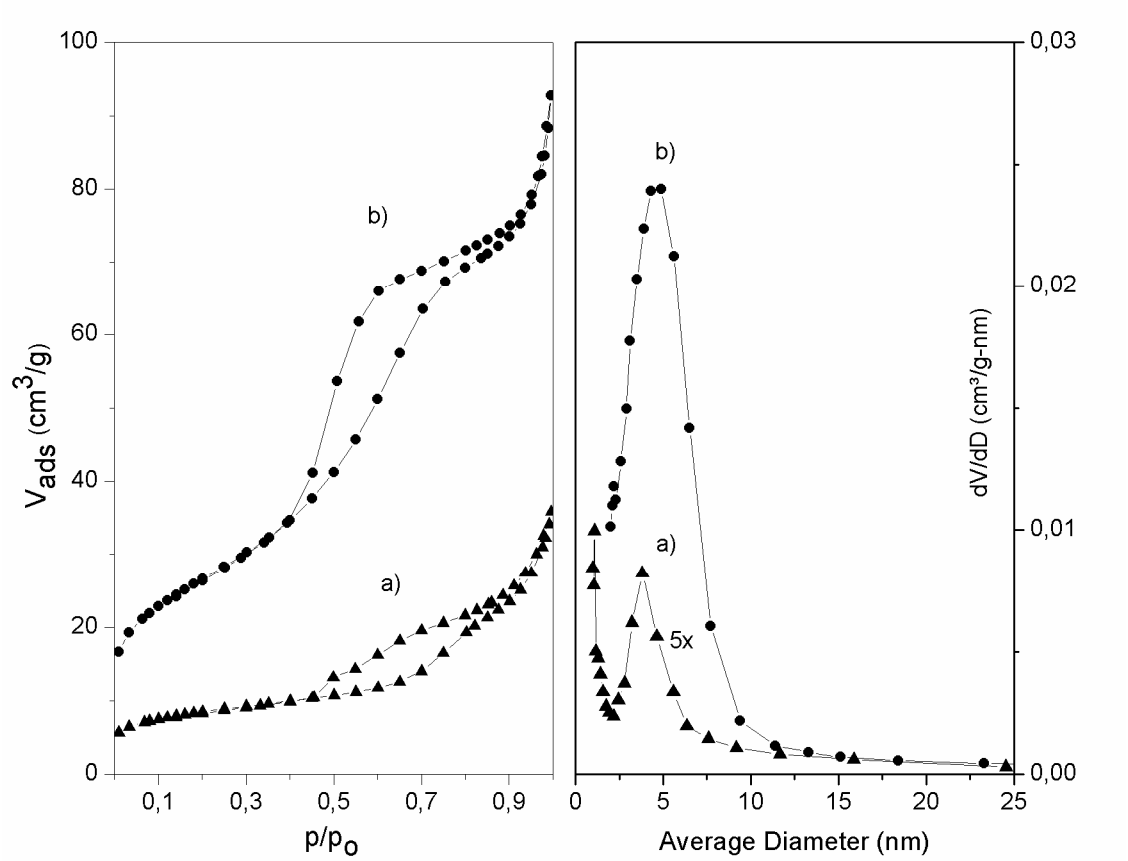

Fig. S3. N_2 adsorption isotherms (left) and pore size distribution (right) for both mixed-oxides a) NiMo-a-ca; b) NiMo-b-ca

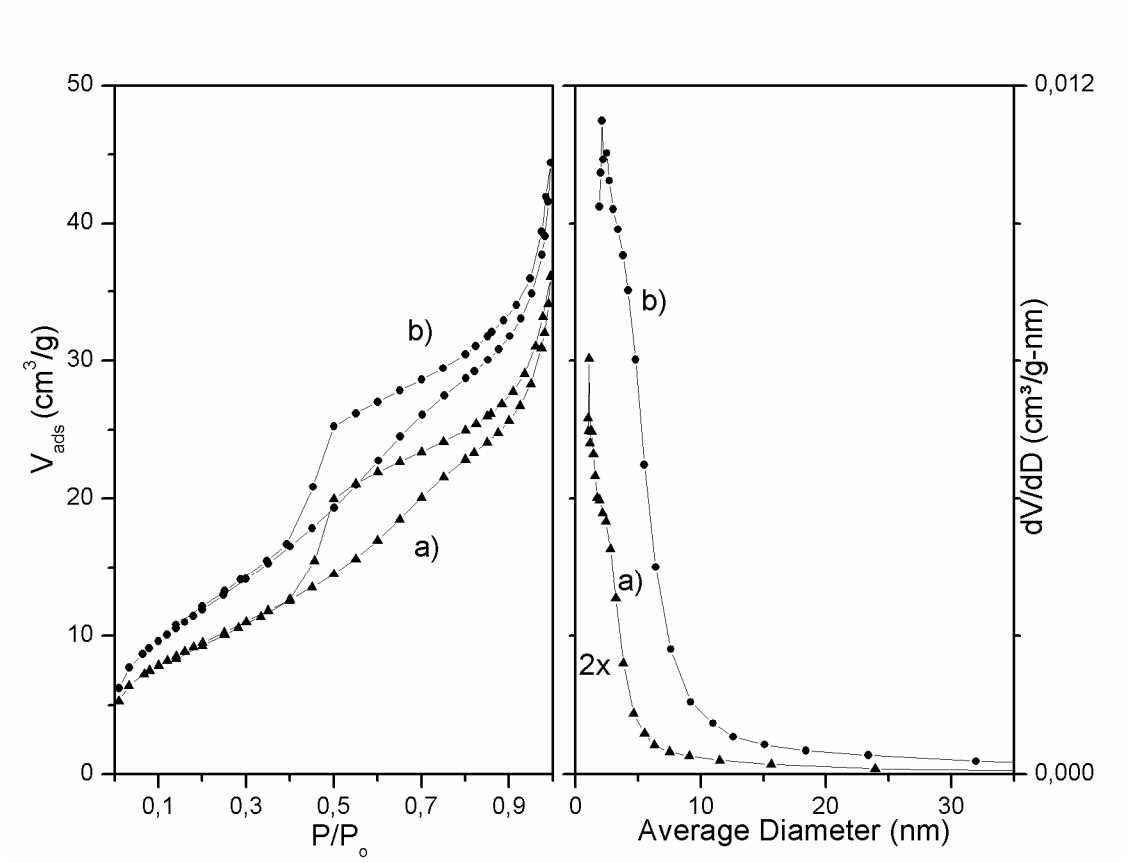

Fig. S4 N_2 adsorption isotherms (left) and pore size distributions (right) for both unsupported sulfides a) NiMo-as; b) NiMo-bs

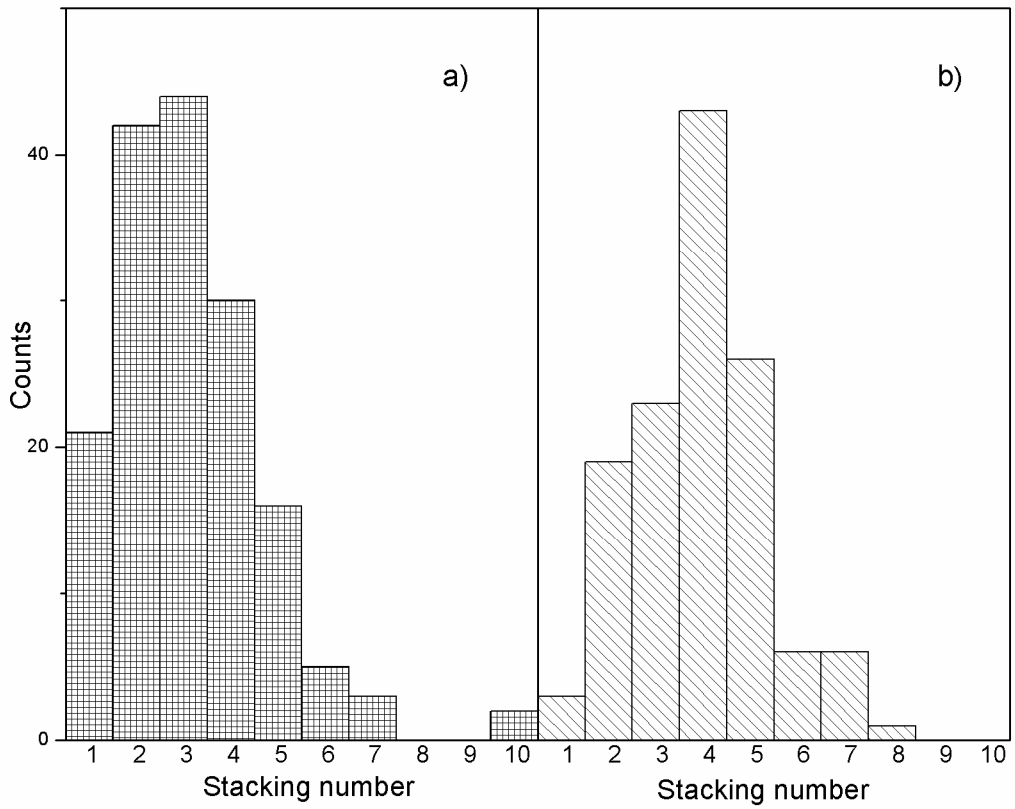

Fig. S5. (A) The distribution for slab stacking degree of sulfides a) NiMo/Al_2O_3 and b) NiMo-as

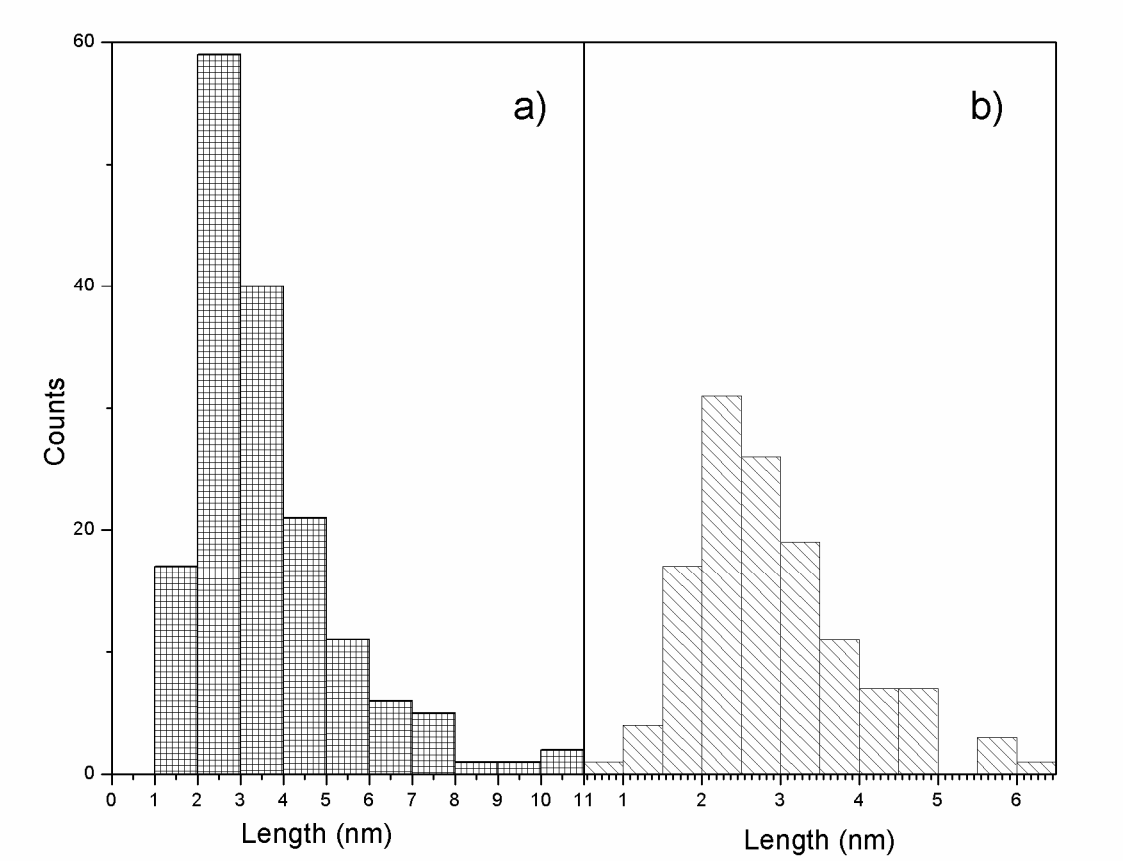

Fig. S5. (B) The distribution for slab length of sulfides
a) NiMo/Al_2O_3 and b) NiMo-as

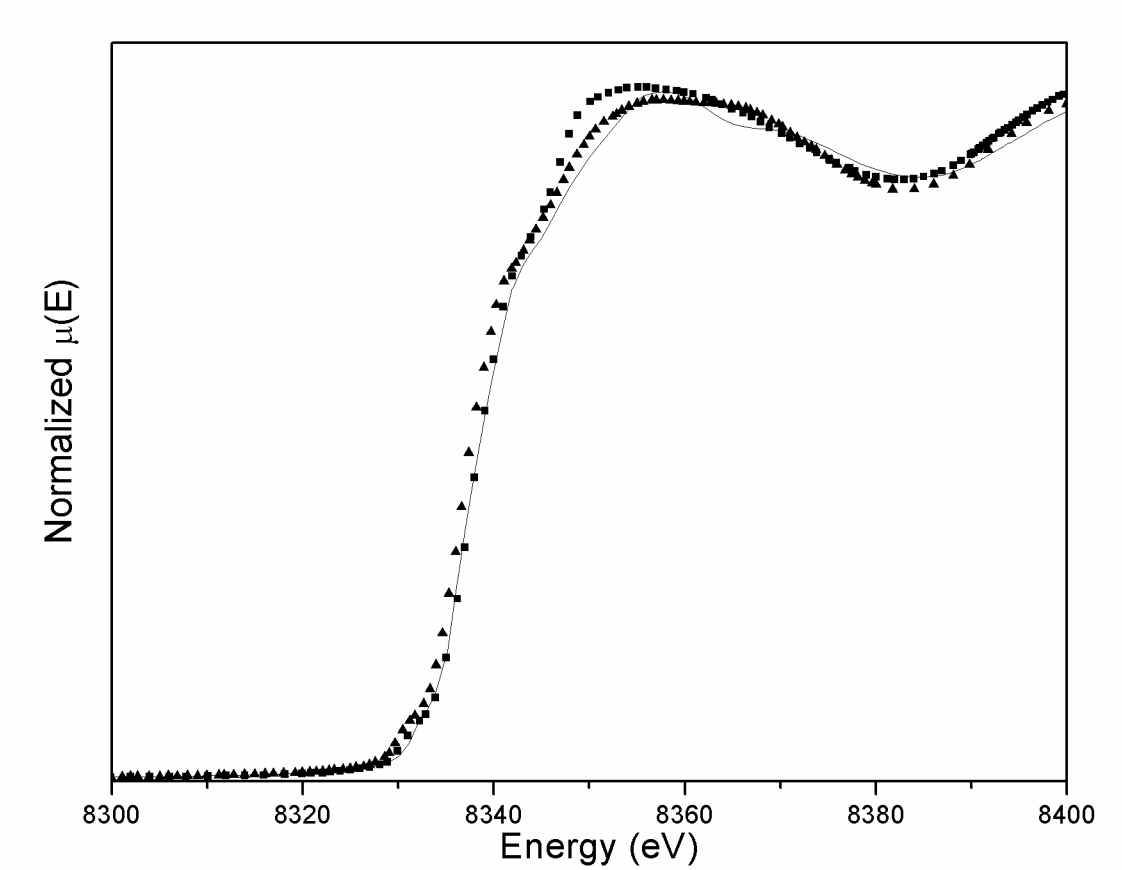

Figure S6. XANES spectra in the Ni K-edge for unsupported catalysts, ■ NiMo-as and ▲ NiMo-bs, and a Ni_3S_2 (solid line) commercial pattern

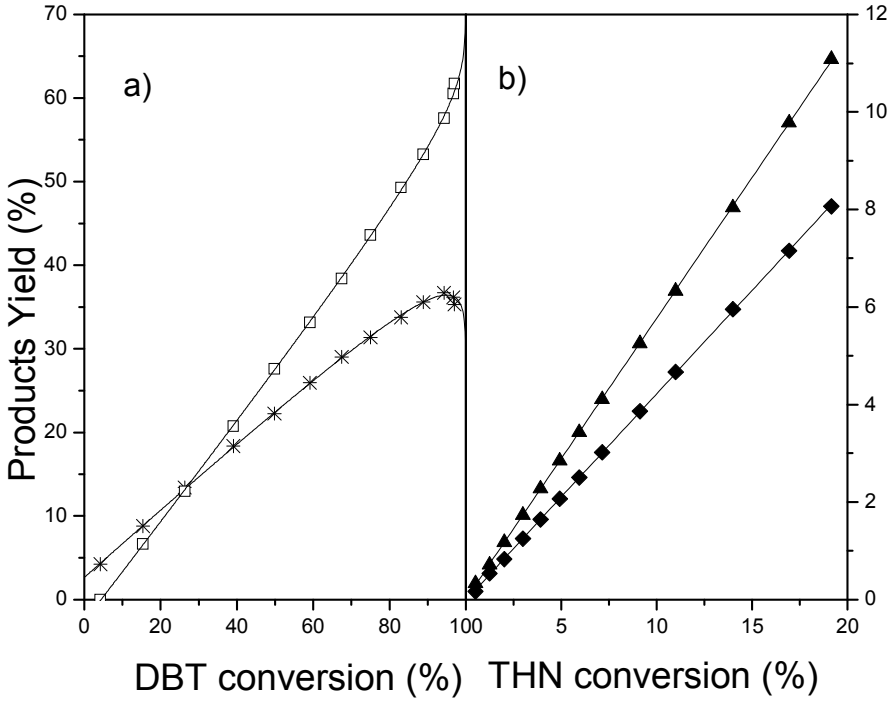

Figure S7. Products yield *vs* reactant conversion for NiMo-bs bulk sulfide catalyst. a) □ CHB and * BPH and first order fit (solid lines). b) ♦ cis-decalin and ▲trans-decalin and zero order fit (solid lines).

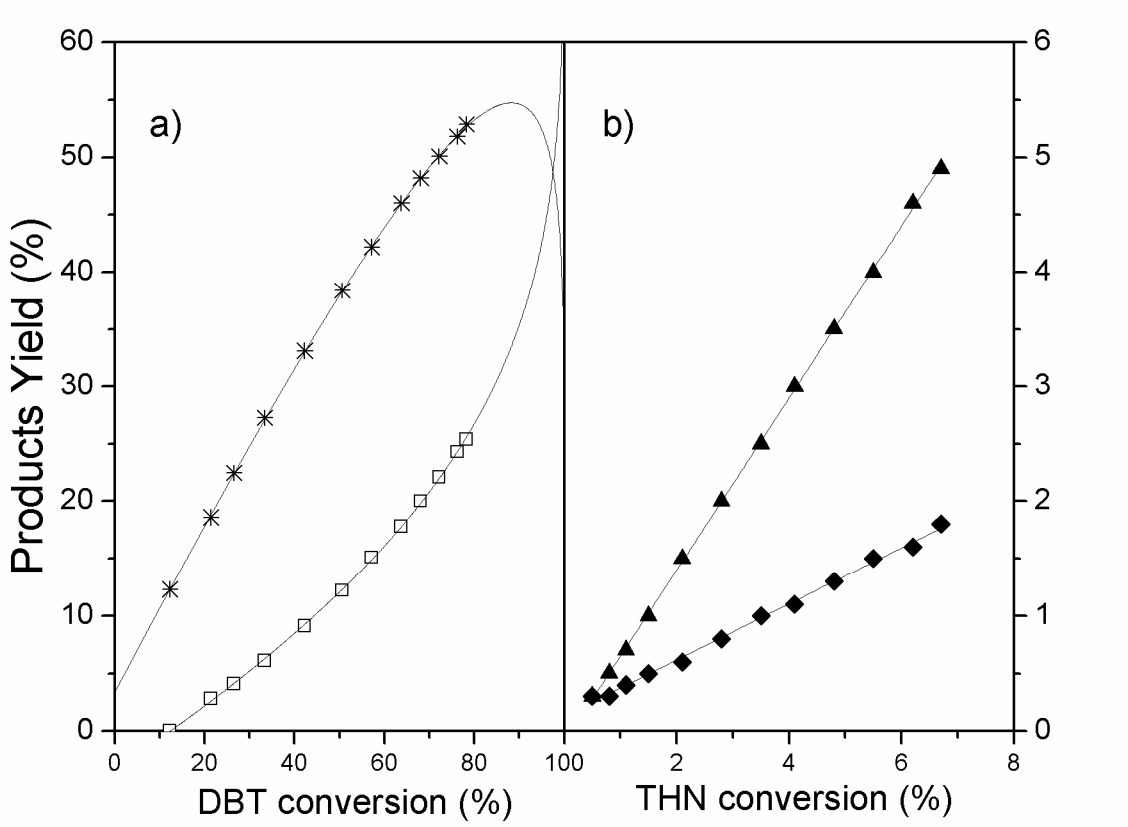

Figure S8. Products yield *vs* reactant conversion for $NiMo/Al_2O_3$ sulfide catalyst. a) □ CHB and * BPH and first order fit (solid lines). b) ♦ cis-decalin and ▲trans-decalin and zero order fit (solid lines).

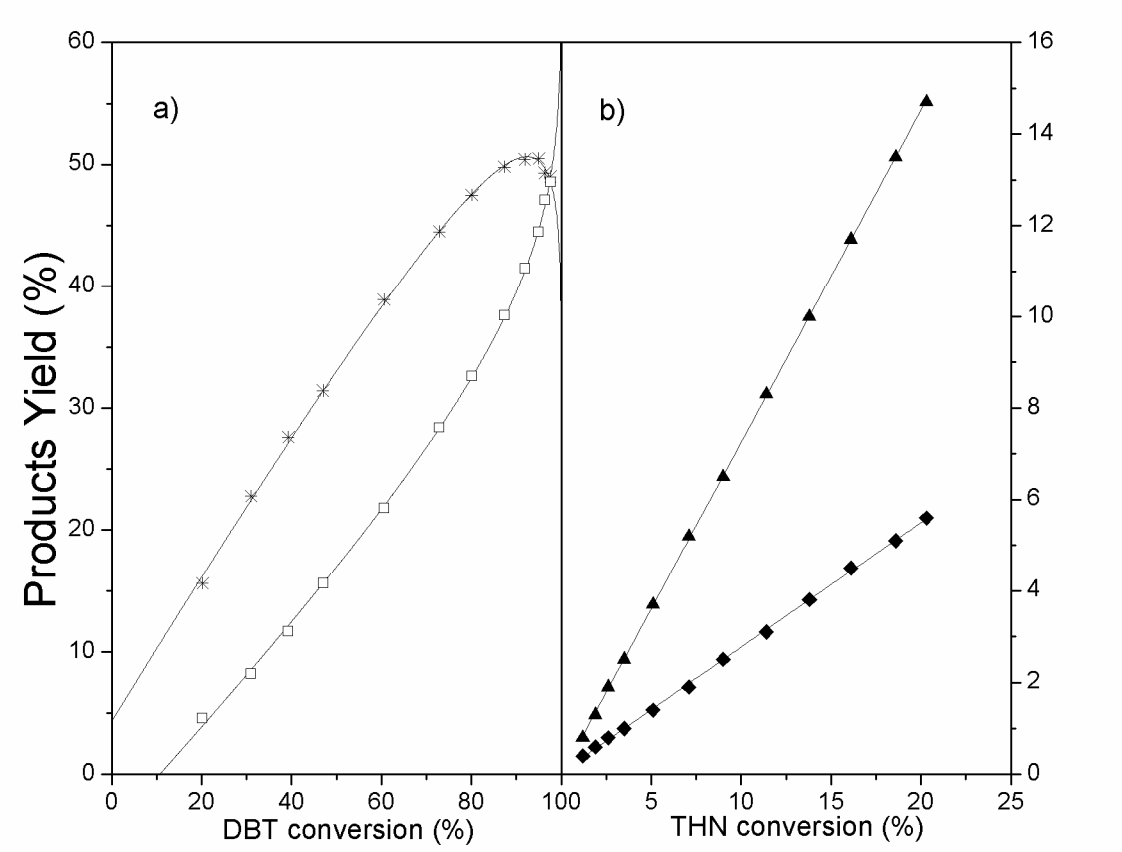

Figure S9. Products yield *vs* reactant conversion for $NiMoP/Al_2O_3$ sulfide catalyst.

a) □ CHB and * BPH and first order fit (solid lines). b) ♦ cis-decalin and ▲trans-decalin and zero order fit (solid lines).