Hydrogenation of model compounds with nickel carbide and phosphide in mild conditions

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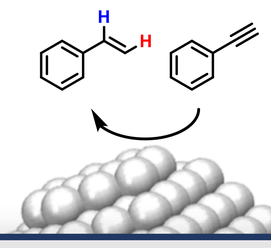
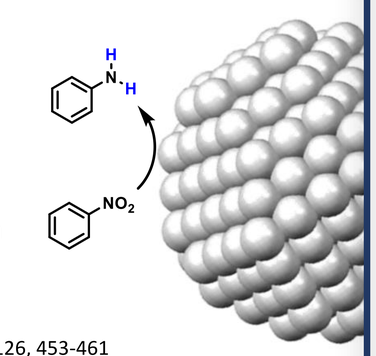
Why nickel-containing nanoparticles for hydrogenation catalysis?

- Ni(0) are excellent catalysts for alkene/carbonyl/nitro/nitrile moieties
  BUT poorly selective, air-sensitive and poisoned by nitrogen/phosphorus/sulfur/CO
- Needs for modified nickel catalysts: carbides and phosphides!
- Colloidal syntheses *via* thermal decomposition of $Ni(acac)_2$ and C/P insertion

[1] Godard *et al.*, *Dalton Transactions,* **2017**, *46*, 12381
[2] Tracy *et al.*, *Chem. Mater.*, **2014**, *26*, 3057-3064



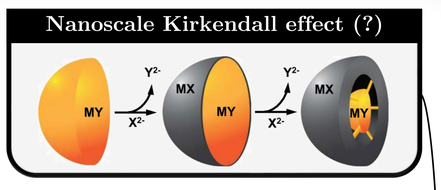


Literature on hydrogenation with Ni_2P and $Ni_{12}P_5$ but not Ni_3C

[3] Carenco *et al.*, *Nano Today,* **2012**, 7, 21-28
[4] Liu *et al.*, *React. Kinet. Mech. Catal.*, **2019**, 126, 453-461

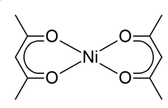
Carbidization and subsequent phosphidization of Ni(0) nanoparticles

- One-pot two steps synthesis of Ni_3C, Ni_2P and $Ni_{12}P_5$ unsupported nanoparticles

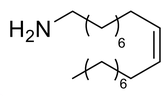


[5] Tracy *et al.*, *Nanoscale,* **2014**, *6*, 12195-12216

Nickel reduction | **Carbidization** | **Phosphidization**

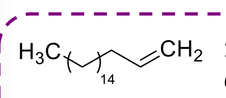


Nickel acetylacetonate $Ni(acac)_2$
Ni source

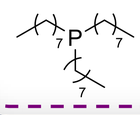


Oleylamine (OAm)
Solvent/surfactant/reducing agent

$Ni(acac)_2$ + 8. OAm + 9.15 ODE —(250 °C, 30 min, N_2)→ [Ni(0)] → Ni_3C



1-octadecene (ODE)
C source/solvent

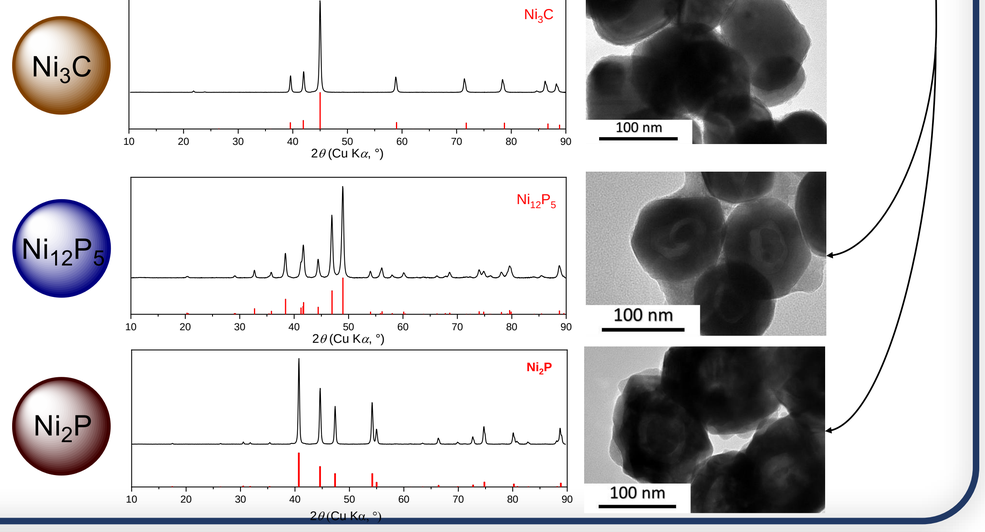


Trioctylphosphine (TOP)
P source/surfactant

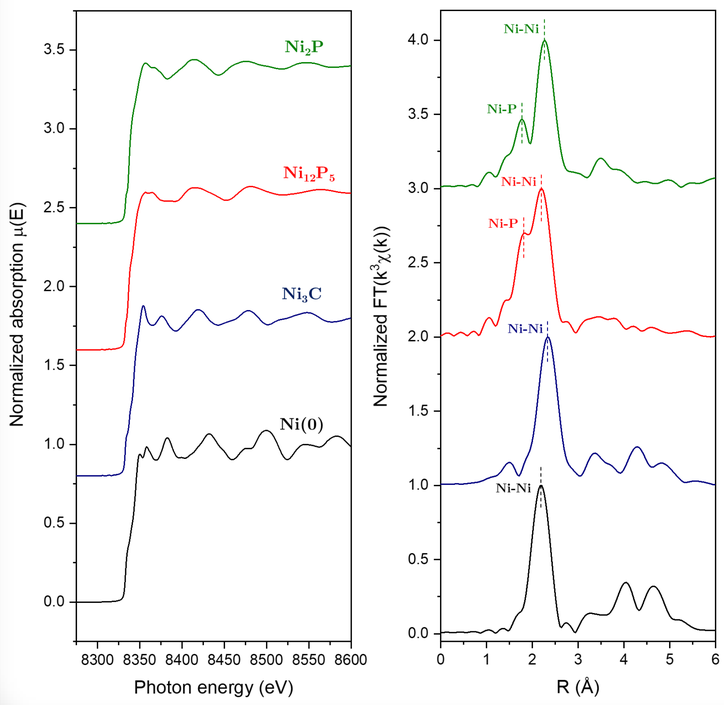
Boiling points
OAm – 364 °C
ODE – 315 °C
TOP – 287 °C

1) 0.4 equiv. TOP injection at 285 °C
2) 300 °C, 30 min, N_2

1) 0.8 equiv. TOP injection at 250 °C
2) 300 °C, 30 min, N_2



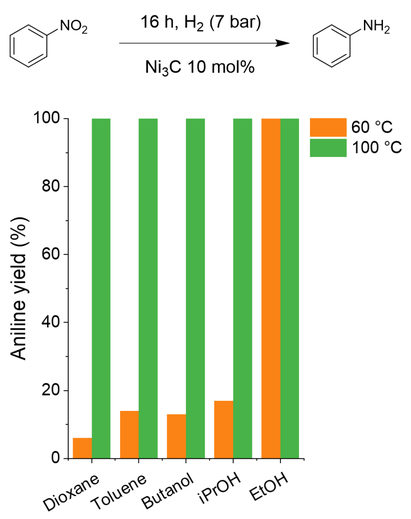
X – ray absorption spectroscopy (XAS)

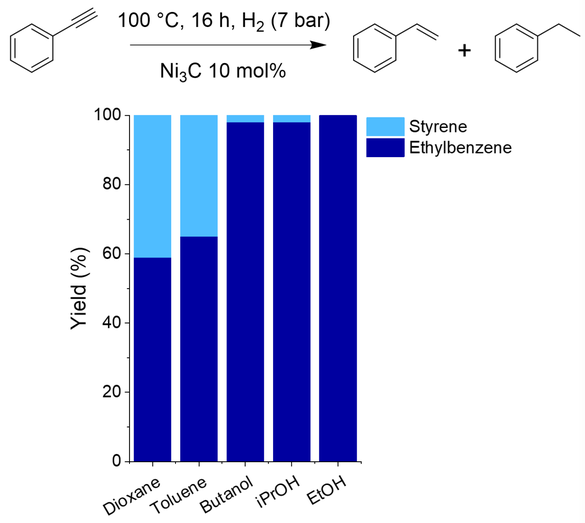


- Spectra identical to the reported ones in literature
- Covalent character of the nickel carbides and phosphides
- Extension of the Ni – Ni bond upon insertion of C and P atoms

Hydrogenation with Ni_3C

- Nitrobenzene and phenylacetylene hydrogenation in mild conditions (7 bar H_2, 60 °C)
- Higher yields in protic and polar solvents (alcohols)





Conclusions

- Succesful synthesis *via* a solvothermal reaction of a family of unsupported nanoparticles (carbide Ni_3C and phosphides Ni_2P / $Ni_{12}P_5$) presenting similar morphologies
- Characterization of the catalysts by XAS: in agreement with literature
- First catalytic results on nitrobenzene and phenylacetylene hydrogenation

Perspectives

1. COMPARATIVE STUDY WITH Ni_2P AND $Ni_{12}P_5$
2. EXTENSION TO OTHER FUNCTIONAL GROUPS (carbonyl, nitrile, furfural)
3. ADDITION OF A CO-CATALYST (amines, phosphines)

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