Experimental/Theoretical Studies Aimed at Development of Carbon-Tolerant Catalysts

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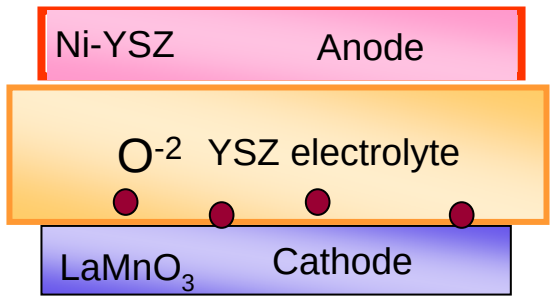
Conclusion

- First principles approach to the development of novel catalysts
- Carbon chemistry on Ni surface
  - Can be modified by alloying
  - Respective rates of C-O and C-C bond formation impact the extent of carbon poisoning
  - Sn/Ni surface alloy is a promising carbon-tolerant catalyst

Fuel Cell Technology

- Development of efficient energy conversion systems
- Low temperature fuel cells (PEMFC)
  - CO poisoning, slow kinetics, over-potential losses
- High temperature fuel cells (SOFC)



- Limitation: Deactivation of Ni/YSZ anode catalysts
  - Carbon poisoning
  - Sulfur poisoning

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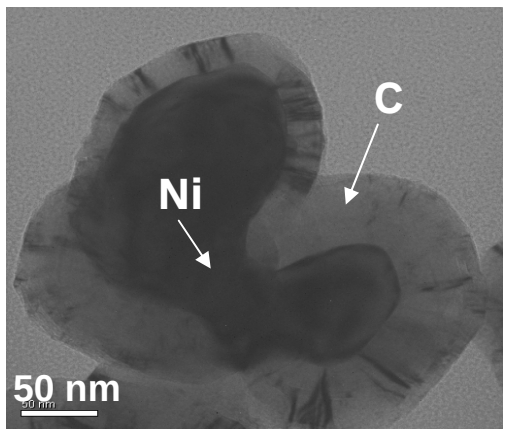
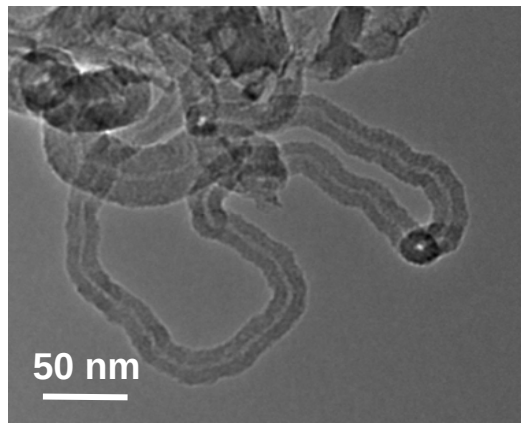
Carbon Poisoning of Ni

- Monometallic Ni catalysts
  - Deactivate severely during steam reforming of hydrocarbons
    - Extended carbon structure formed: graphitic layers, nano-tubes, …





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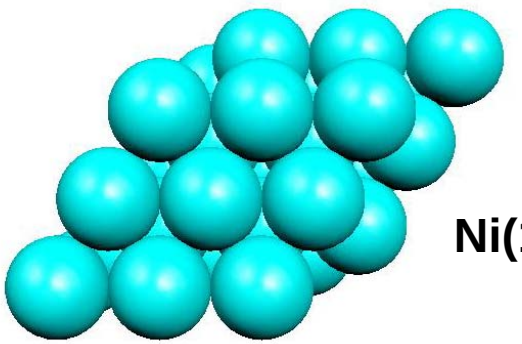
Objectives

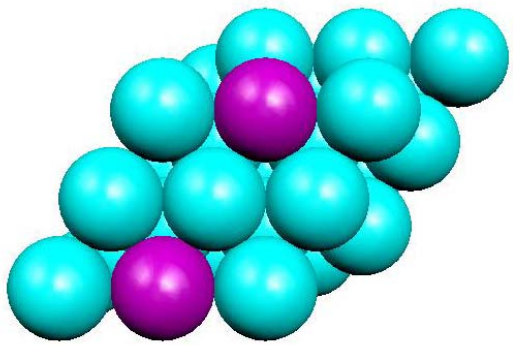
- Utilize first principles calculation (DFT) to study
  - Carbon chemistry over Ni surfaces
  - Can we understand and control carbon chemistry and therefore affect the deactivation?
    - Ni alloying?
- Steam reforming of methane and isooctane using Ni and Ni alloys
- Catalysts characterization

DFT Methodology

- Accurate and efficient first-principles calculations
  - Adsorption energies, activation barriers, vibrational and electronic spectra, …
  - Model systems
  - Ni(111) and Ni(111) alloys



Ni(111)



Ni(111) alloy

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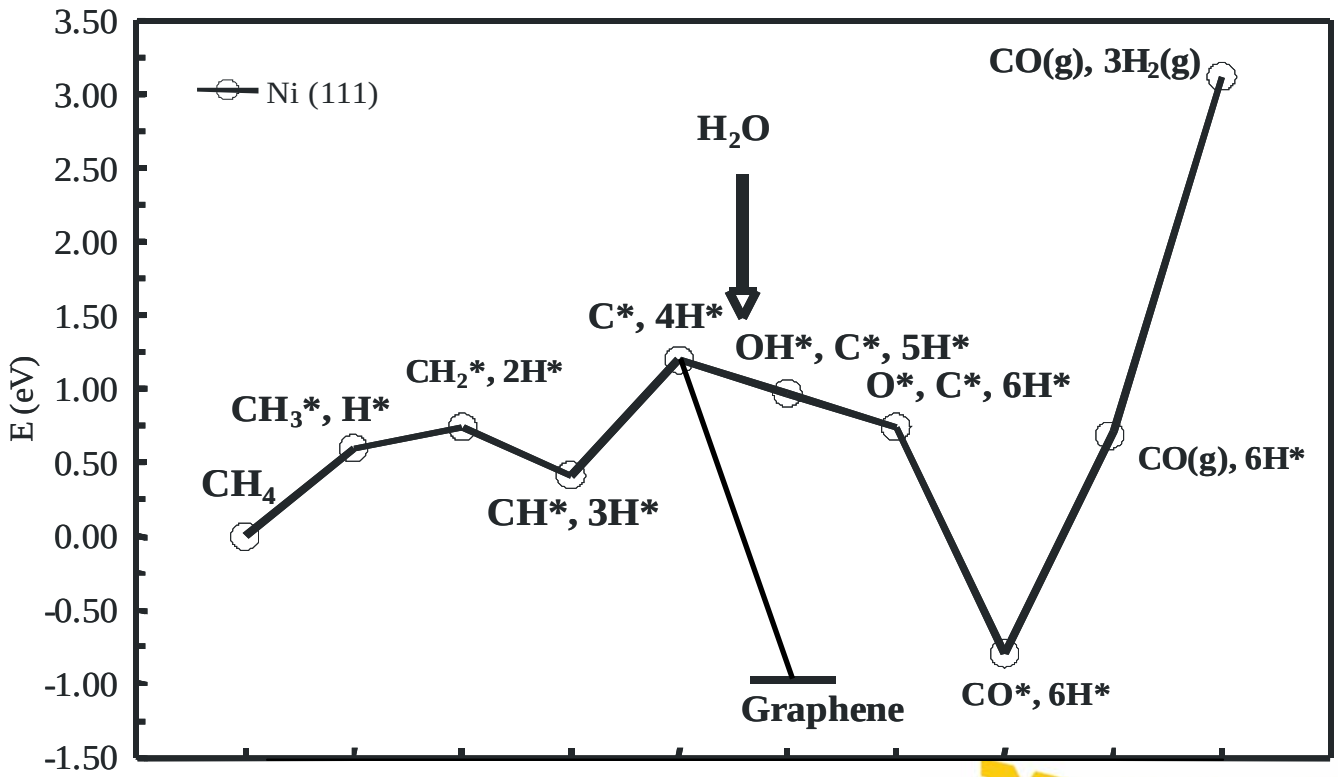
Steam reforming over Ni(111)

- DFT calculated elementary step reaction energies for methane steam reforming on Ni(111)



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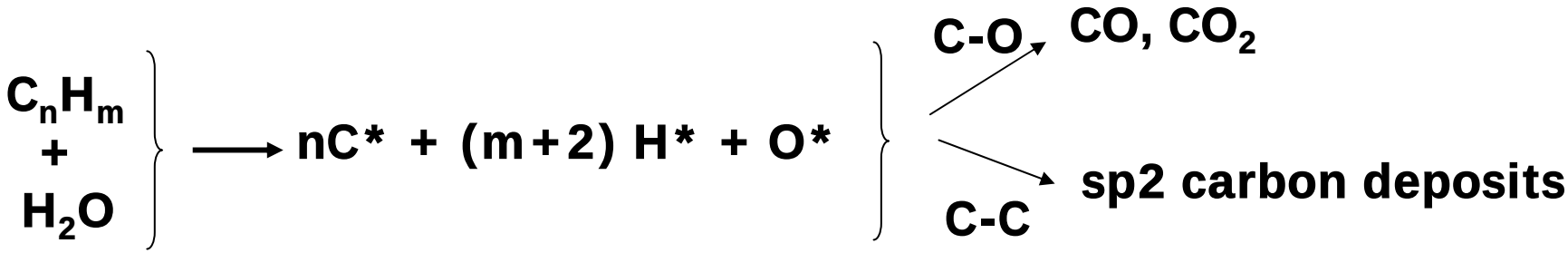
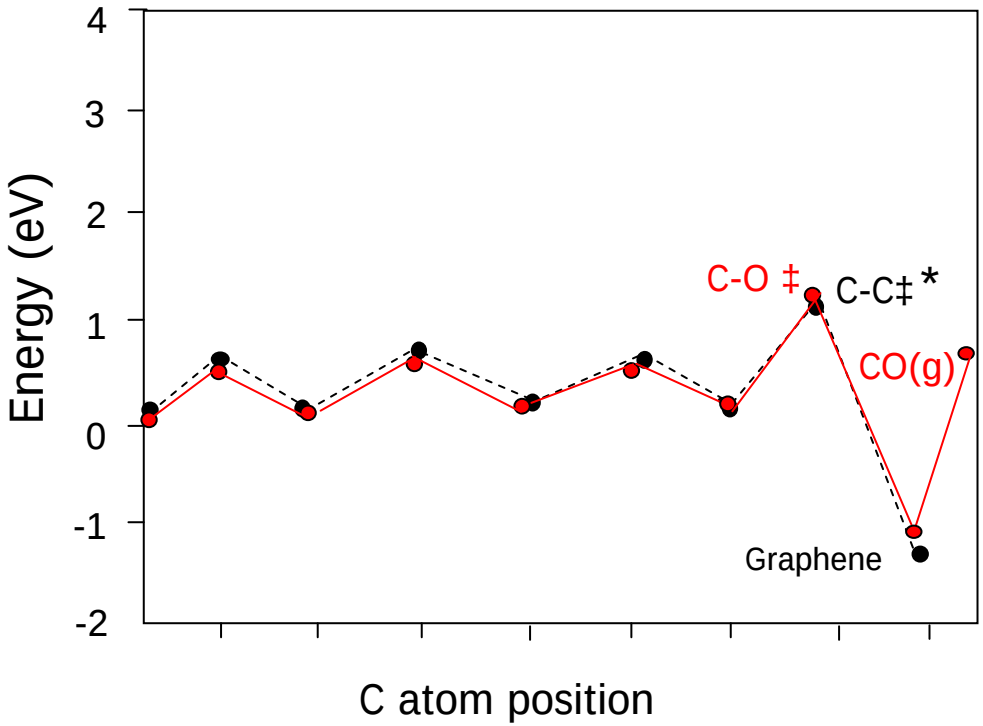
Carbon Chemistry

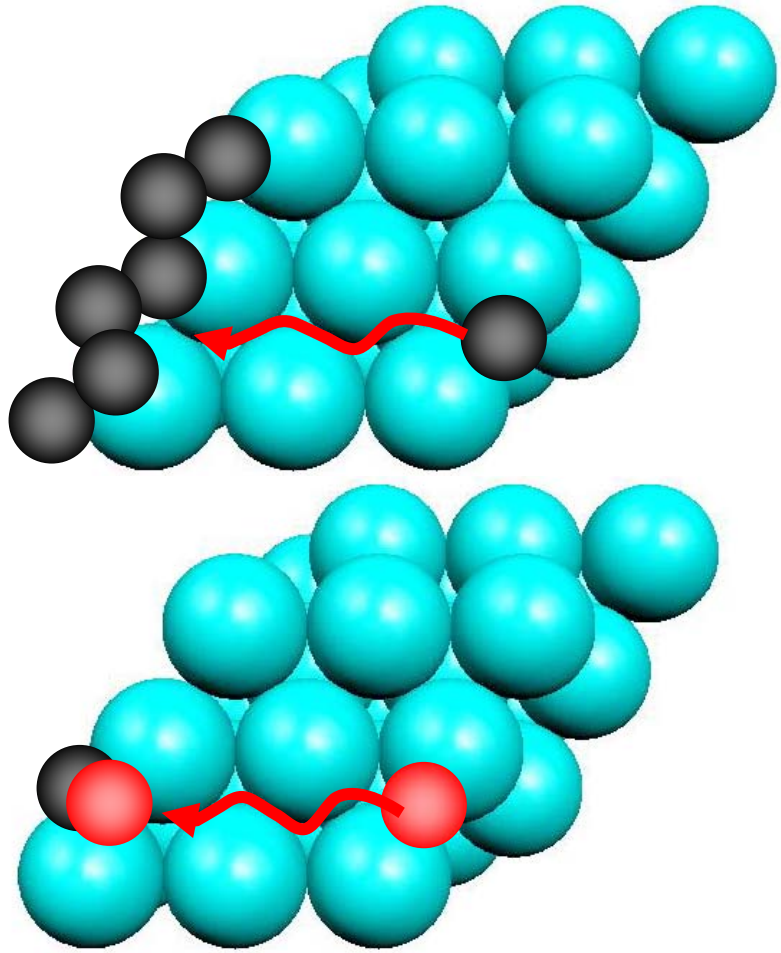
- Can be described by a mechanism of competing pathways



- The C-O and C-C bond formation is important

DFT: C-O and C-C bond formation on Ni(111)





* *Abidil-Petersen, J. Phys. Rev. B, 2006*

Formation of C-C and C-O bonds are kinetically comparable on Ni(111)

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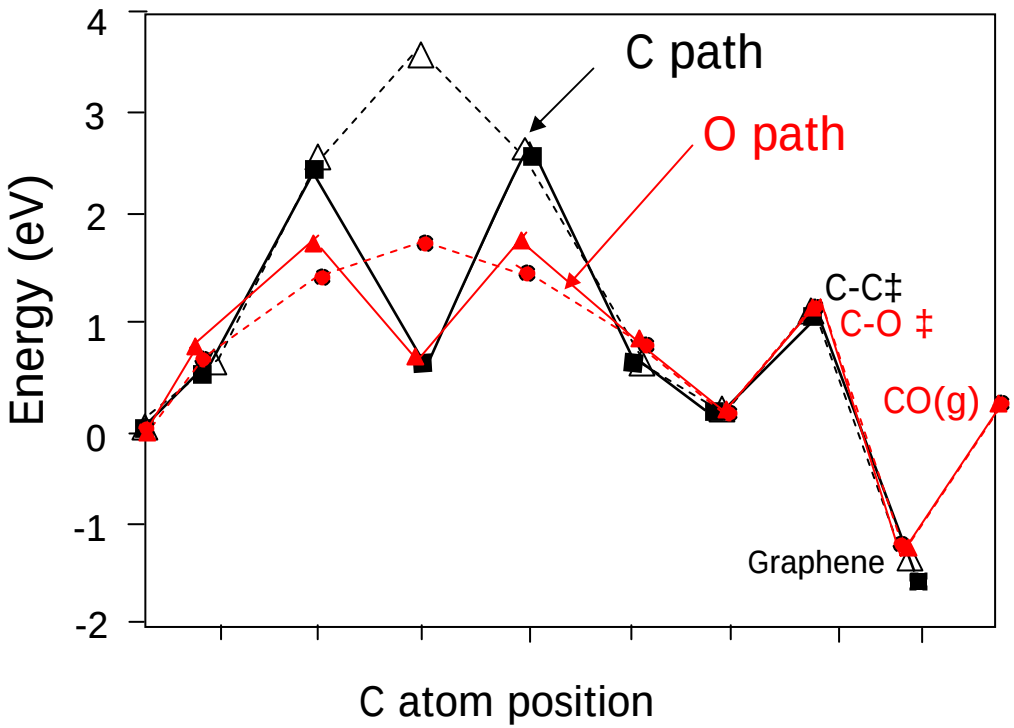
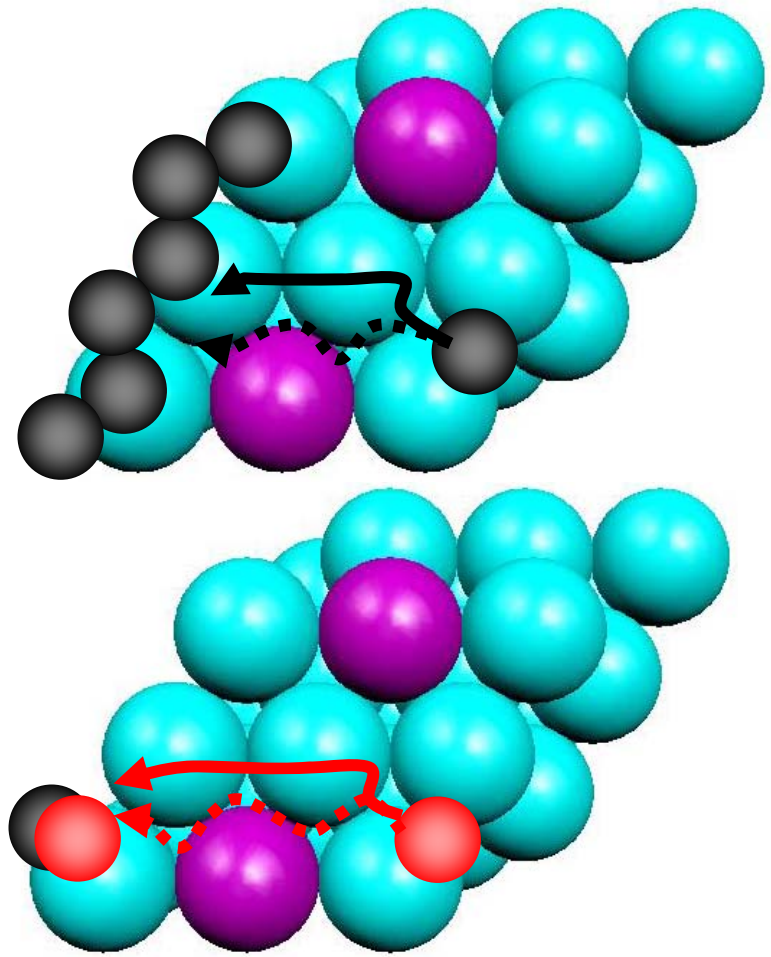
DFT: C-O and C-C formation on Sn/Ni(111) alloy





- C and O diffusion become kinetically important
- The barrier for C-C bond formation is much higher than for C-O bond formation

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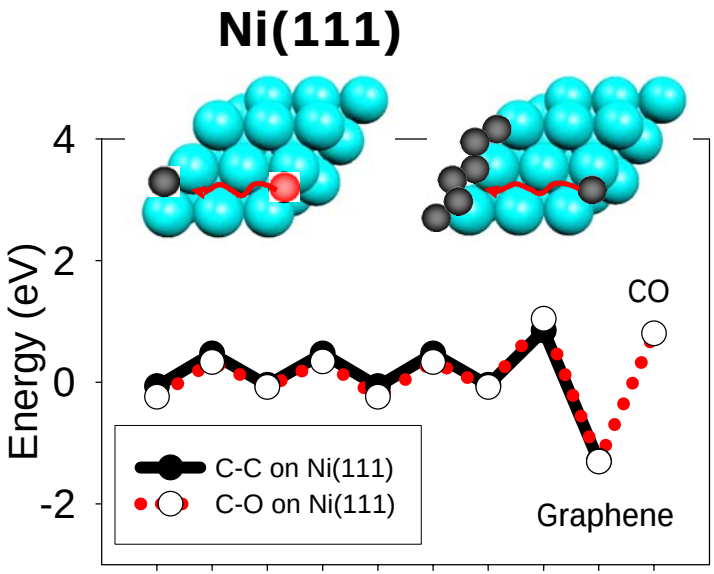
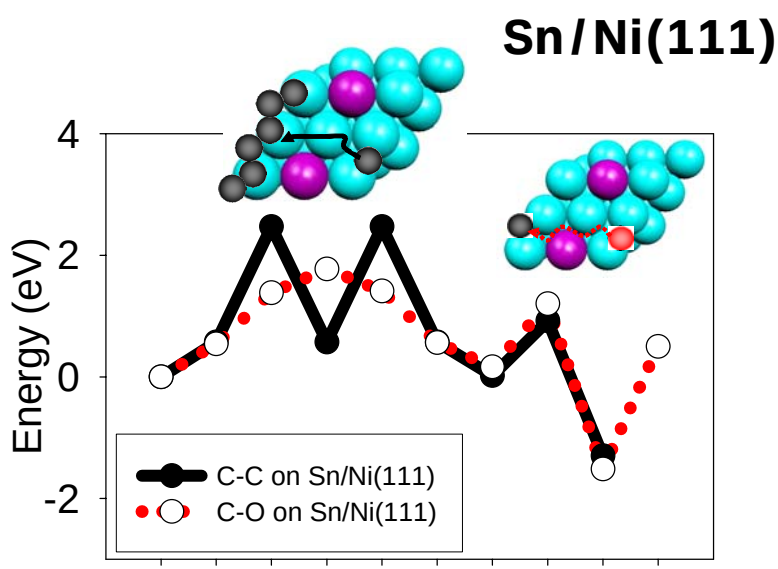
DFT: C-O vs. C-C formation





- C and O compete to react with C on Ni(111)
- Sn alloying increased the barrier for C-C bond formation more than for C-O bond formation

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DFT: Sn/Ni formation energy

- Can we synthesize Sn/Ni surface alloy?
- DFT calculated formation energies

  E = E(Sn/Ni_slab) – E(Ni_slab) – e(Sn) + e(Ni)

  - Sn/Ni surface alloy
    - -2.04eV/A^2
  - Sn/Ni bulk alloy
    - 1.67 eV/A^2
  - Ni surface
    - 0 eV/A^2
- There is a thermodynamic driving force to form Sn/Ni surface alloy!

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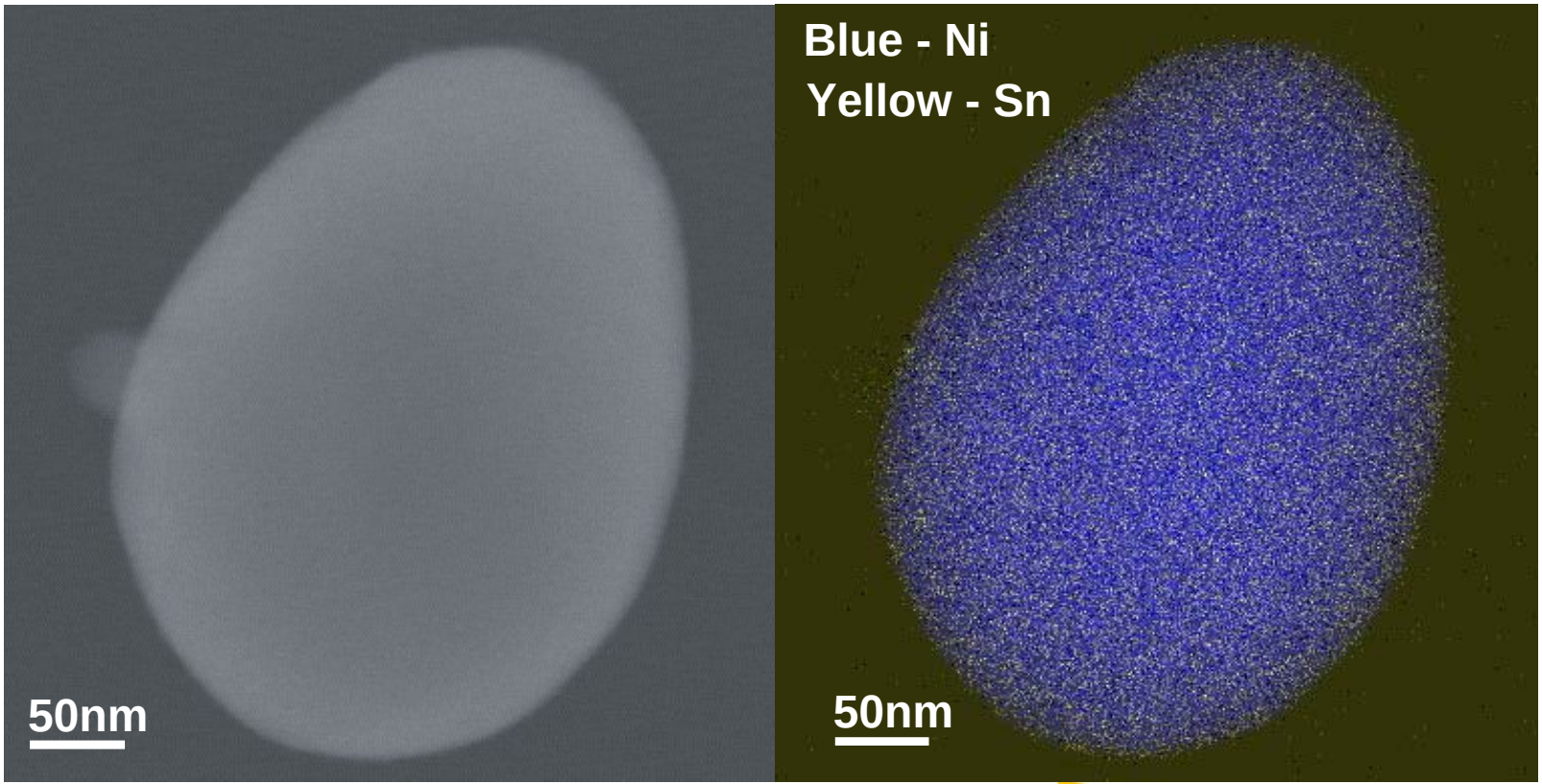
Experiments: Catalyst Synthesis

- Support
  - 8%YSZ synthesis: Co-precipitation method
- Ni-YSZ
  - Ball milling method
  - 30 vol% Ni loading
  - Sintering
  - Reduction: 30% H_2/N_2 at 900°C for 5 hrs
- Sn impregnation
  - Incipient wetness

Sn/Ni Characterization

- STEM/EDS experiments



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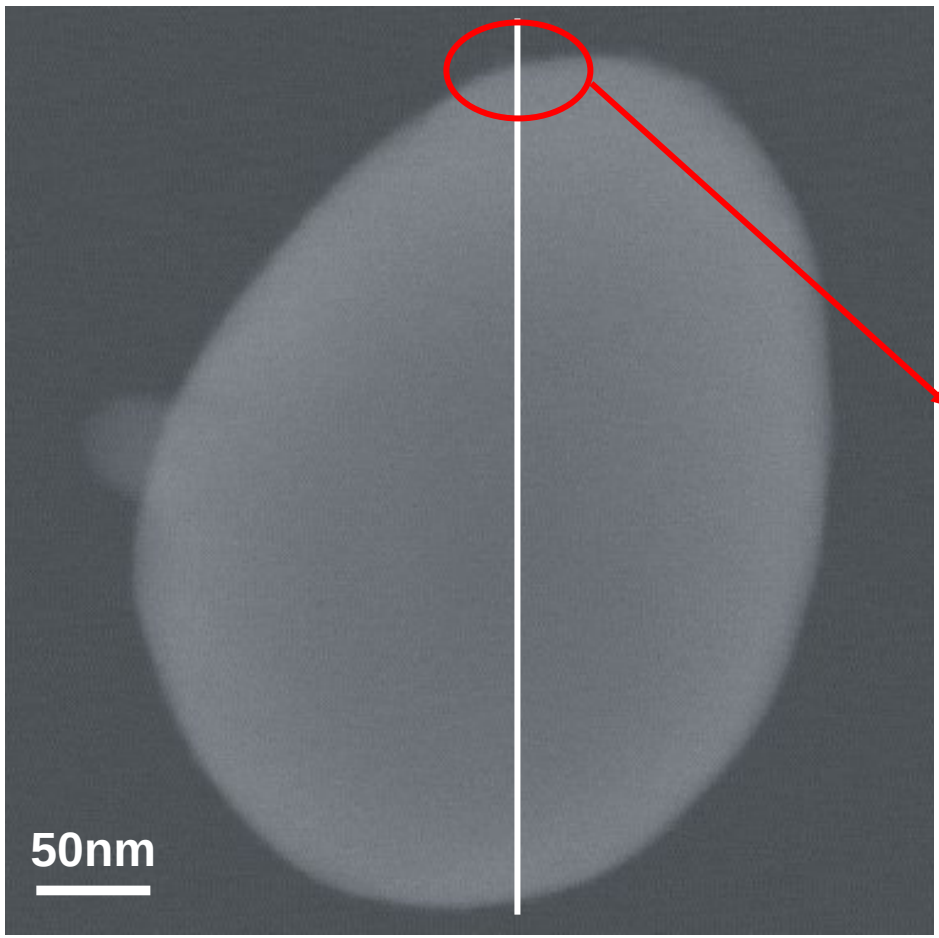
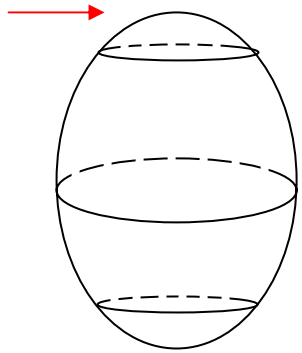
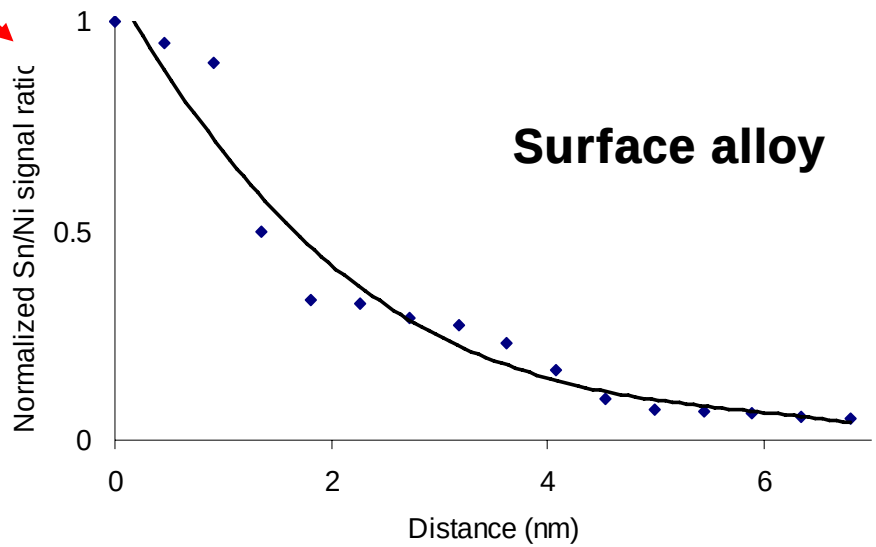
EDS: Line Scan







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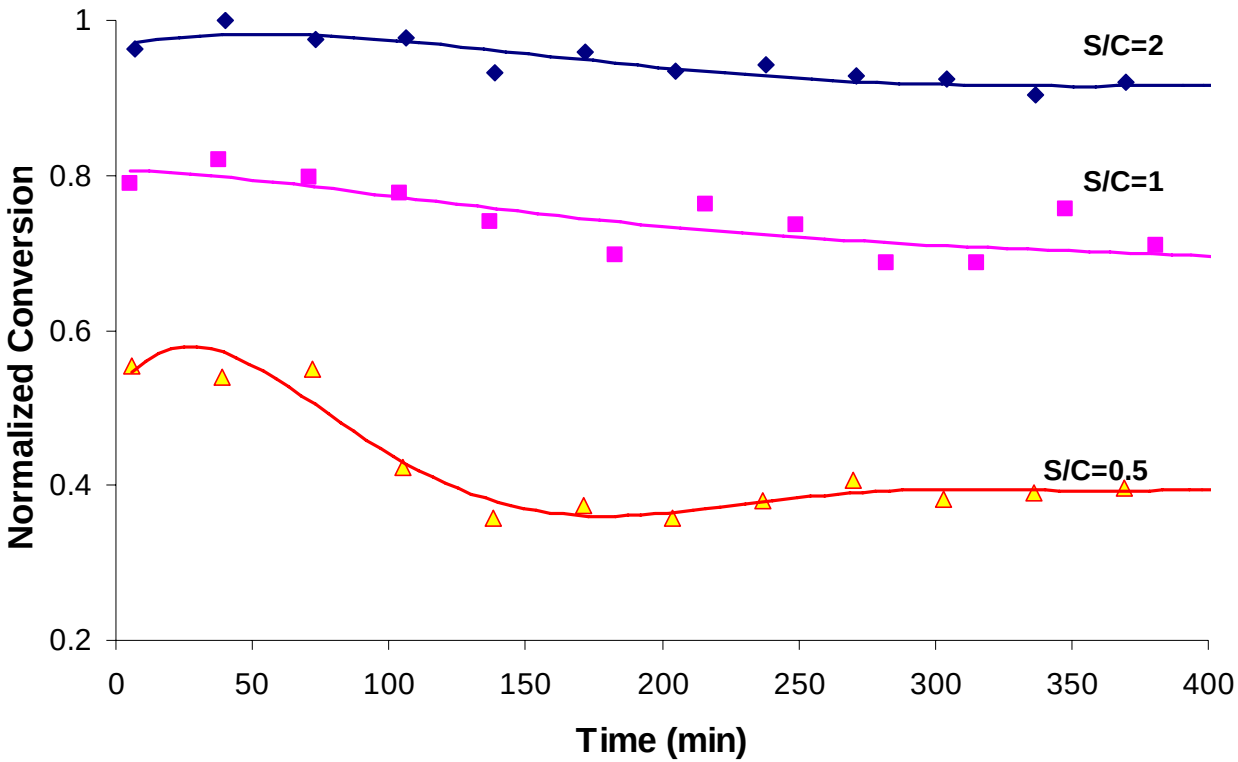
Steam reforming of methane on Ni/YSZ



- Reaction Conditions
  - Temp = 800°C
  - GHSV=50,000 h^{-1}
  - Reduction=5hrs at 900 °C

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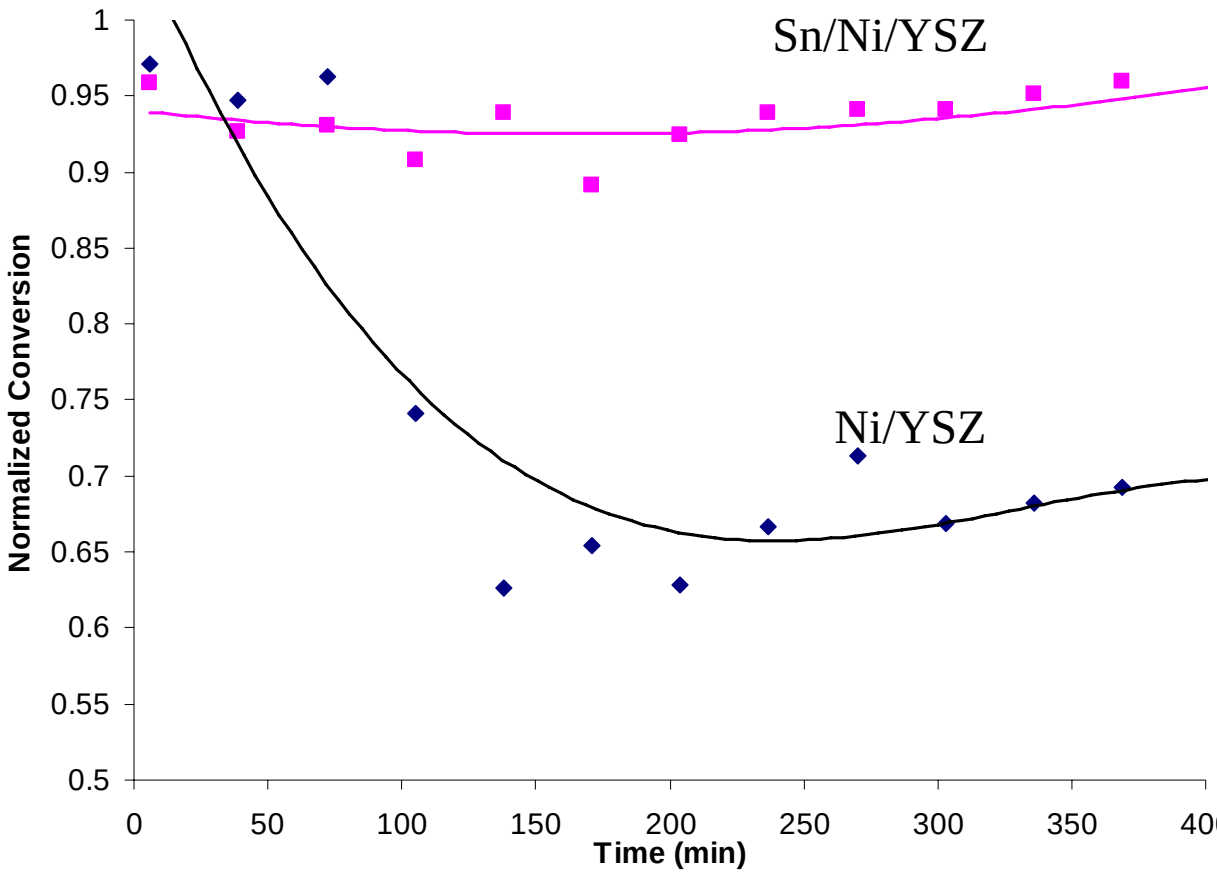
Steam Reforming of Methane



- Reaction Conditions
  - S/C =0.5
  - Operating Temp = 800°C
  - GHSV = 50,000 h^{-1}

Sn/Ni alloying results in improved catalyst stability

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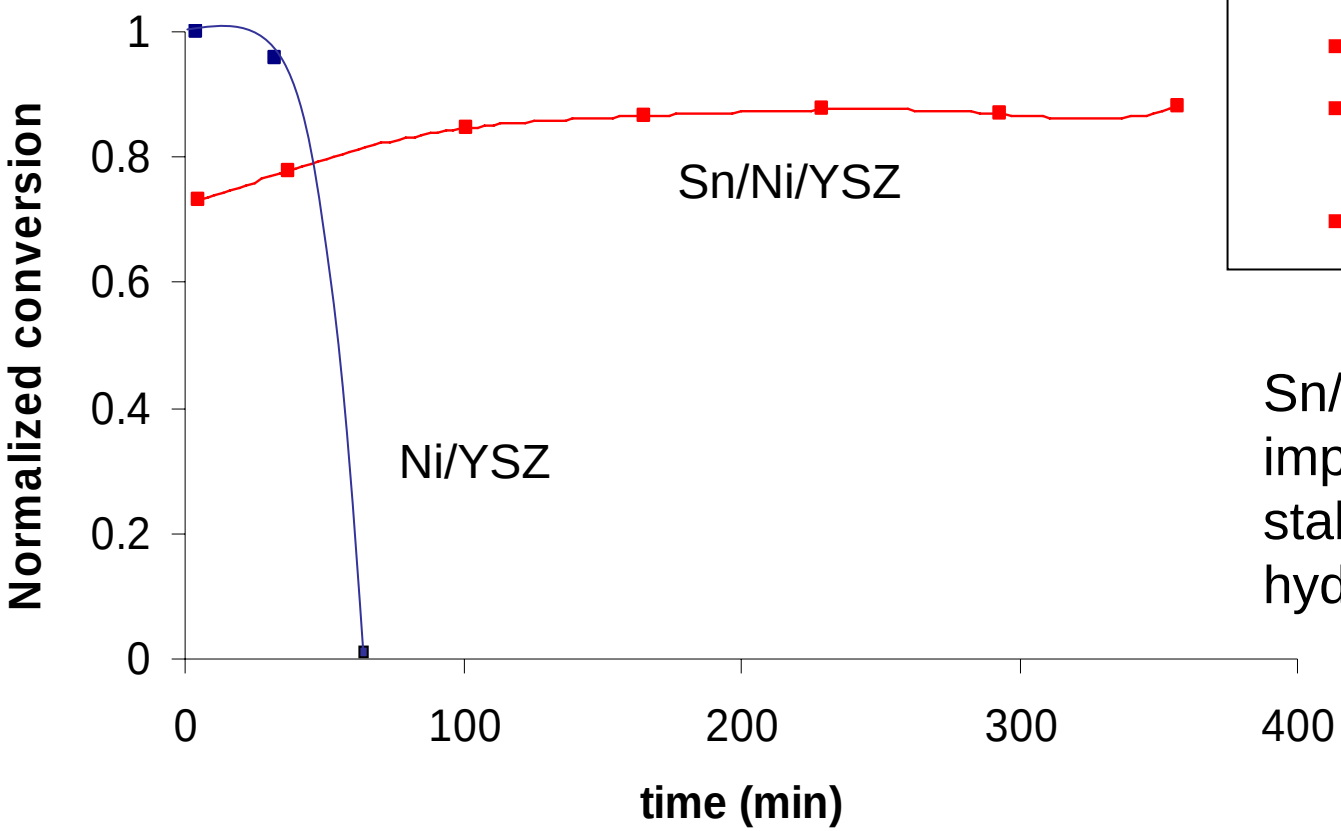
Steam Reforming of Isooctane



- Reaction Conditions
  - S/C =1.5
  - Operating Temp = 800°C
  - GHSV = 50,000 h^{-1}

Sn/Ni alloying results in improved catalyst stability even for heavy hydrocarbon fuels

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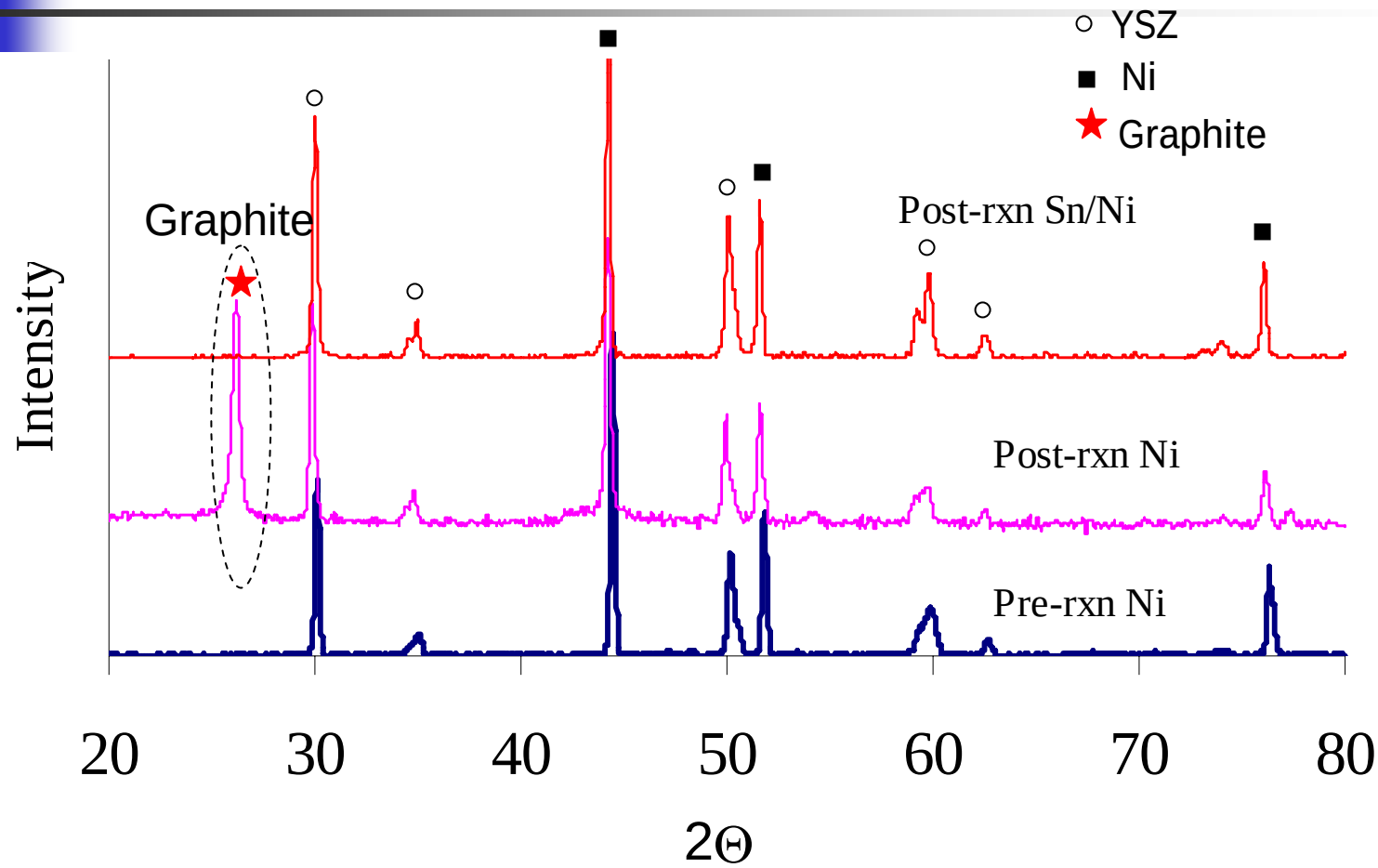
XRD: Post SR of Isooctane



- No graphite was detected in the case of Sn/Ni alloy
  - Similar results were obtained for methane steam reforming

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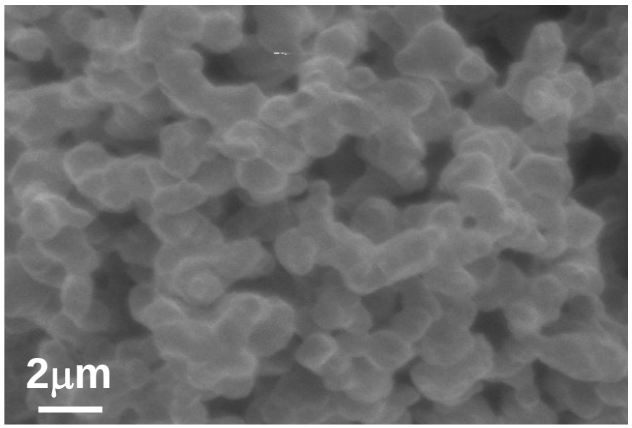
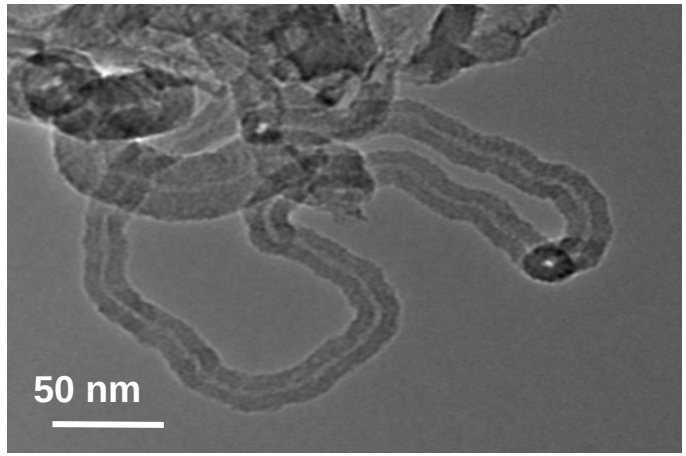
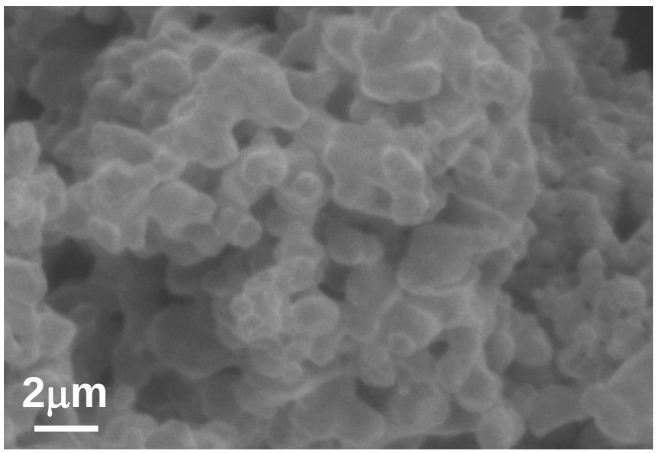
SEM/TEM: Post SR of Isooctane

SEM: Fresh Ni/YSZ

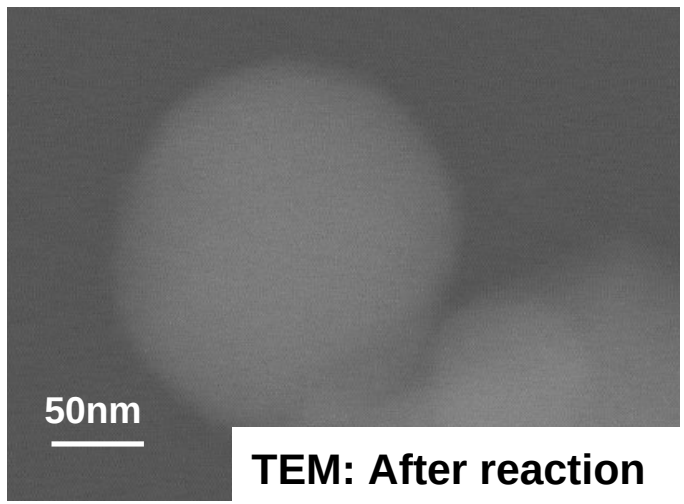


TEM: After reaction



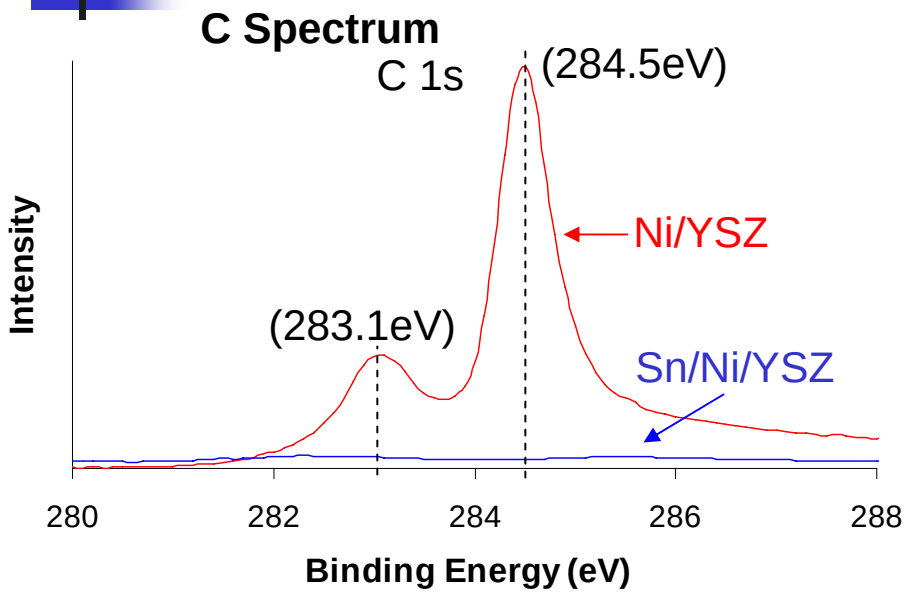


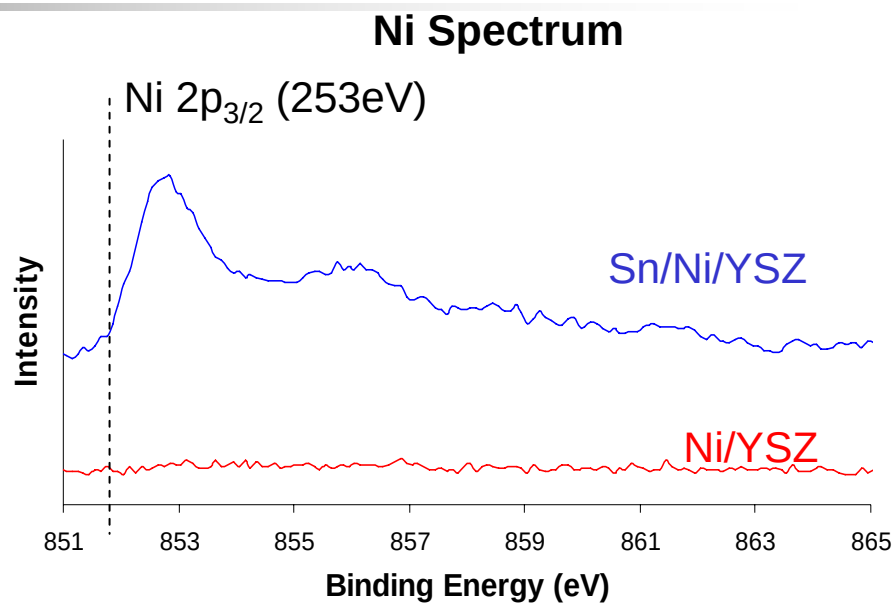
SEM: Fresh Sn/Ni/YSZ



TEM: After reaction

XPS: Post SR of Isooctane





- Ni/YSZ
  - 2 C peaks detected
  - No Ni peak detected
- Sn/Ni/YSZ
  - No carbon peak
  - Strong Ni peak signal

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Conclusion

- First principles approach to the development of novel catalysts
- Carbon chemistry on Ni surface
  - Can be modified by alloying
  - Respective rates of C-O and C-C bond formation impact the extent of carbon poisoning
  - Sn/Ni surface alloy is a promising carbon-tolerant catalyst

Acknowledgments

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