

Nanosized Bimetallic Ni-X/SiO₂ Catalysts Prepared by SOMC/M route: Characterization and Catalytic Properties in Styrene Hydrogenation

L. Deghedi,⁽¹⁾ A. de Mallmann,⁽¹⁾ G. Bergeret,⁽²⁾ M. Corral Valero,⁽³⁾ J.A. Dalmon,⁽²⁾ J.-P. Candy,⁽¹⁾ A.-C. Dubreuil,⁽³⁾ L. Fischer,⁽³⁾ J.-M. Basset⁽¹⁾

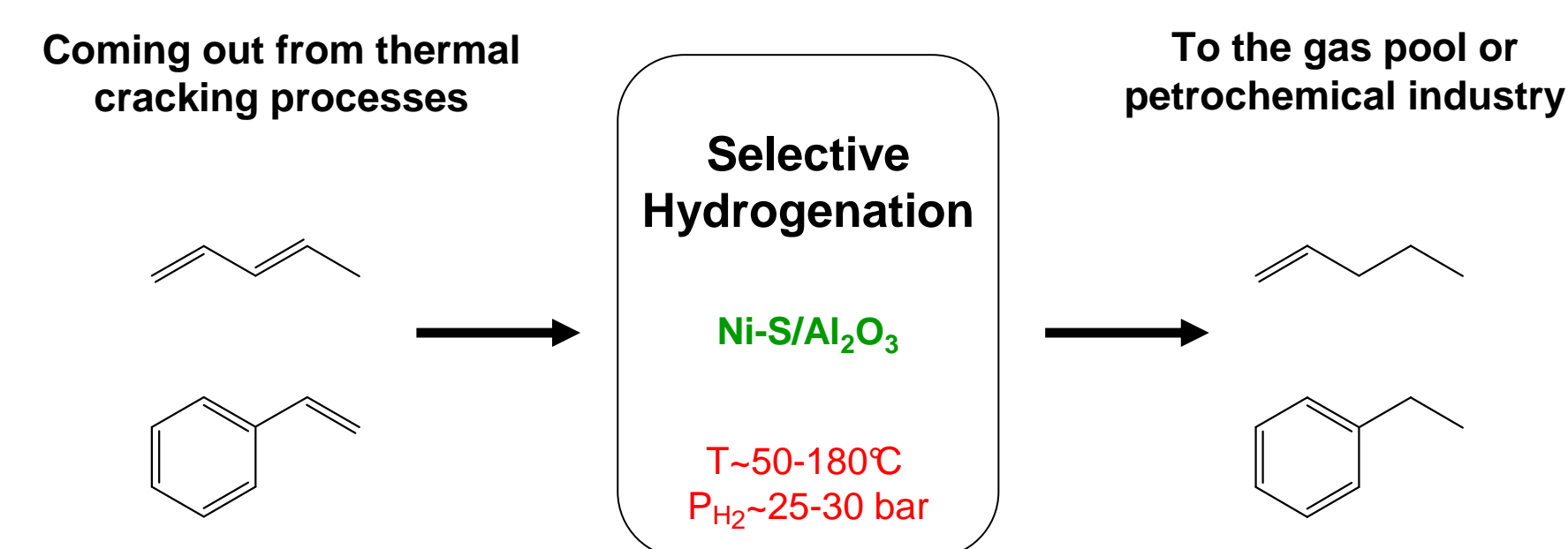
✉ layane.deghedi@cpe.fr

⁽¹⁾ Université de Lyon, Laboratoire C2P2, équipe LCOMS, ESCPE Lyon, 43 bd. du 11 novembre 1918, F-69616 Villeurbanne, France.

⁽²⁾ Université de Lyon, IRCELYon, 2 av. A. Einstein, F-69616 Villeurbanne, France.

⁽³⁾ Institut Français du Pétrole, BP 3, 69390 Vernaison, France.

Industrial Background



Drawbacks of the Ni-S catalyst:

- Insufficient or non-homogeneous passivation: risk of explosion because of the high exothermicity of total hydrogenation reactions of olefins and aromatics.
- Excess passivation: inactive Ni₃S₂ formed.

Aims

- Replace Ni-S by a well defined bimetallic Ni-X catalyst
- Understand the selectivation mechanism in the hydrogenation of styrene

Strategy

- Surface OrganoMetallic Chemistry on Metals (SOMC/M) is an effective route to prepare well defined bimetallic catalysts by the means of a controlled reaction between reduced metal particles and organometallic compounds.
➔ SOMC/M used to prepare well defined bimetallic Ni-X/SiO₂ catalysts.

- Selectivity in the hydrogenation of a C=C double bond against an aromatic ring can be explained by geometric or electronic effects.

According to the electronegativities in the Pauling scale (χ):

$$\chi_{Zr} < \chi_{Ni} \rightarrow \text{Zr is an electro-donor towards Ni}$$

$$\chi_{Sn} \sim \chi_{Ni} \rightarrow \text{Sn is electronically neutral towards Ni}$$

$$\chi_{Au} > \chi_{Ni} \rightarrow \text{Au is an electro-attractor towards Ni}$$

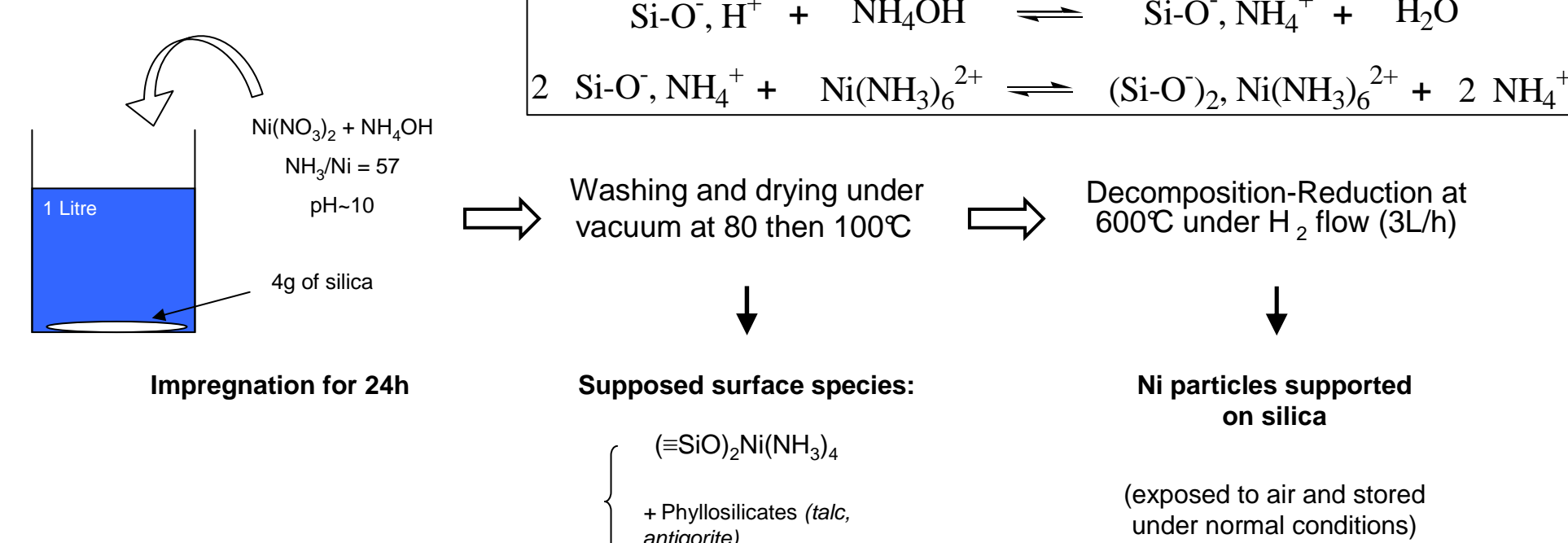
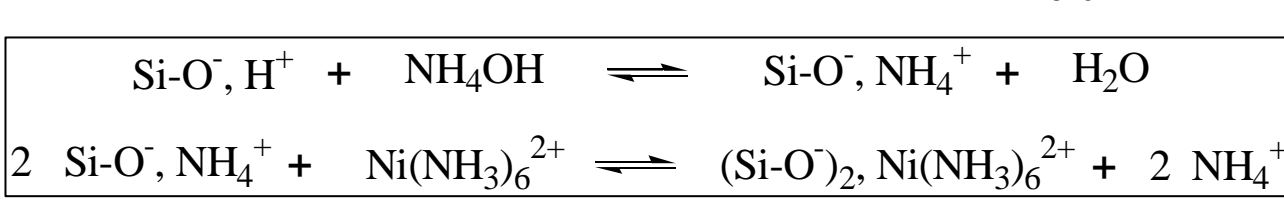
- ➔ Ni-Sn, NiZr and Ni-Au catalysts prepared to study the possible geometric and electronic effects on selectivity in the hydrogenation of styrene.

Preparation and characterization of the catalysts

Ni/SiO₂ parent catalyst

Preparation Method:

Impregnation by cationic exchange of Ni(NH₃)₆²⁺:

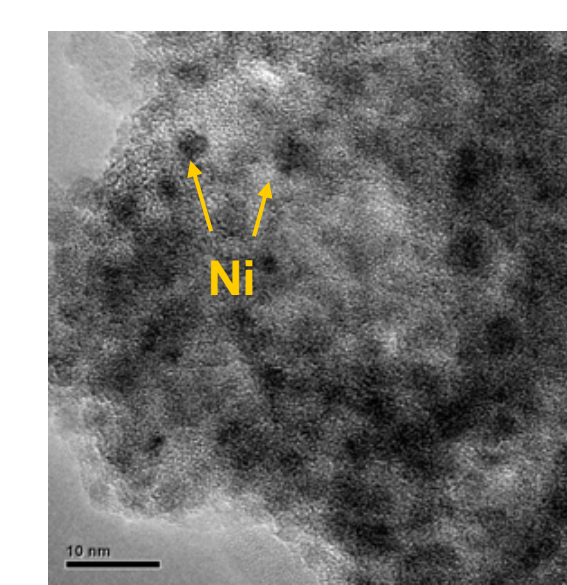


Characterization:

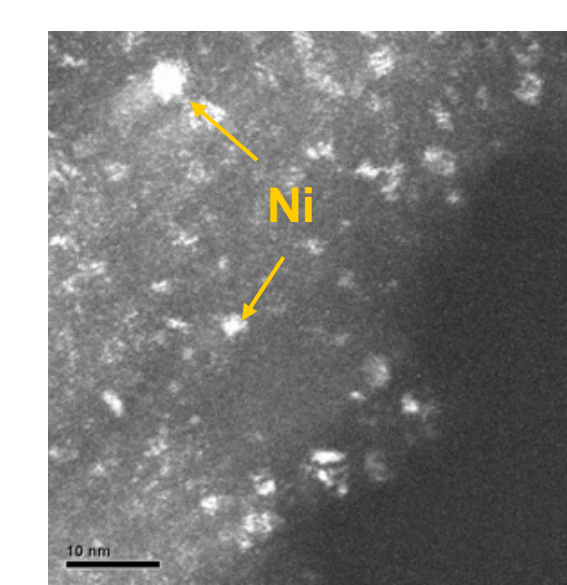
Ni loading: 11%w

Characterization technique	Estimated Ni particle size
Magnetic measurements	3.9 nm (2 - 6 nm)
H ₂ adsorption	3.4 nm
XRD	2 - 3 nm
TEM	3.1 nm (1 - 5.5 nm)

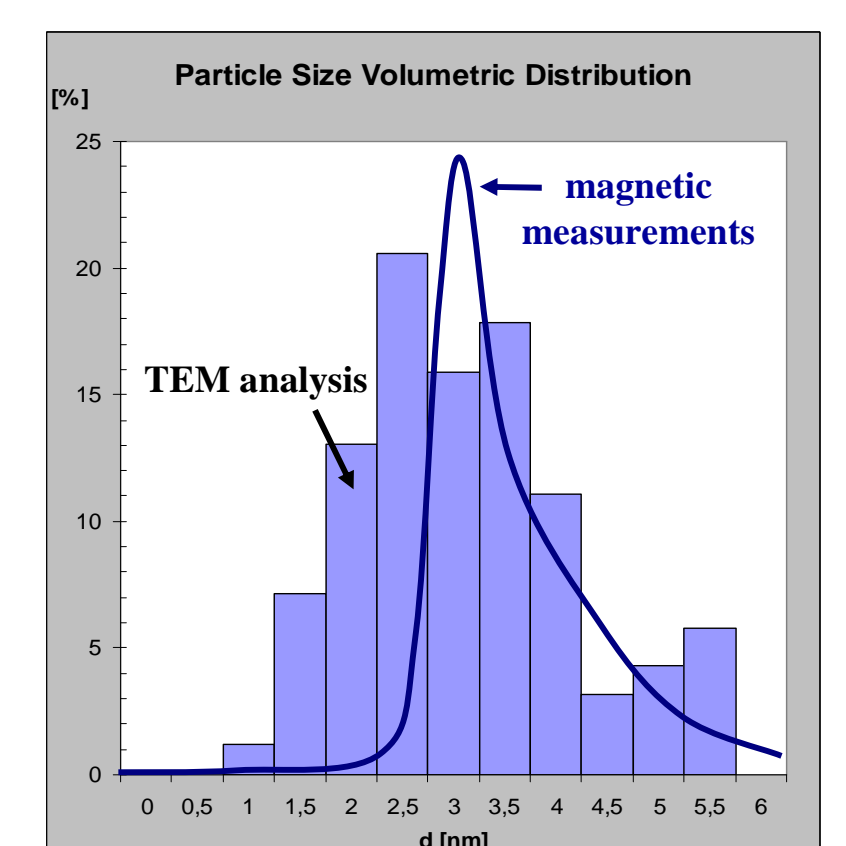
TEM images



Bright Field

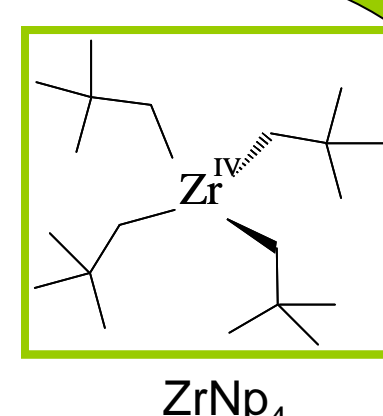


Dark Field



Ni - Zr

The Ni/SiO₂ parent catalyst was first reduced under flowing H₂ at 400°C. ZrNp₄ was then sublimed at 60°C on the Ni catalyst, under ca. 50 mbar H₂. The catalyst was then heated under flowing H₂ at 400°C.



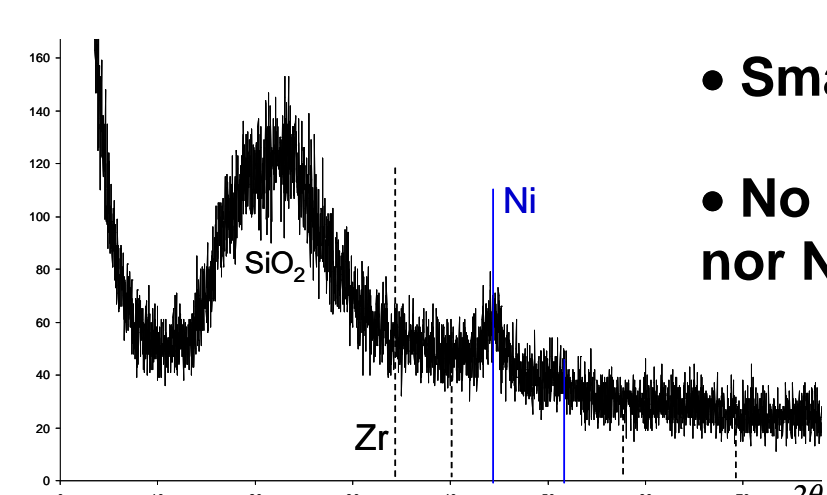
Zr/Ni content: 0.2

H₂ adsorption measurements:

H₂ adsorbed after grafting = 0.69 x (H₂ adsorbed before grafting)

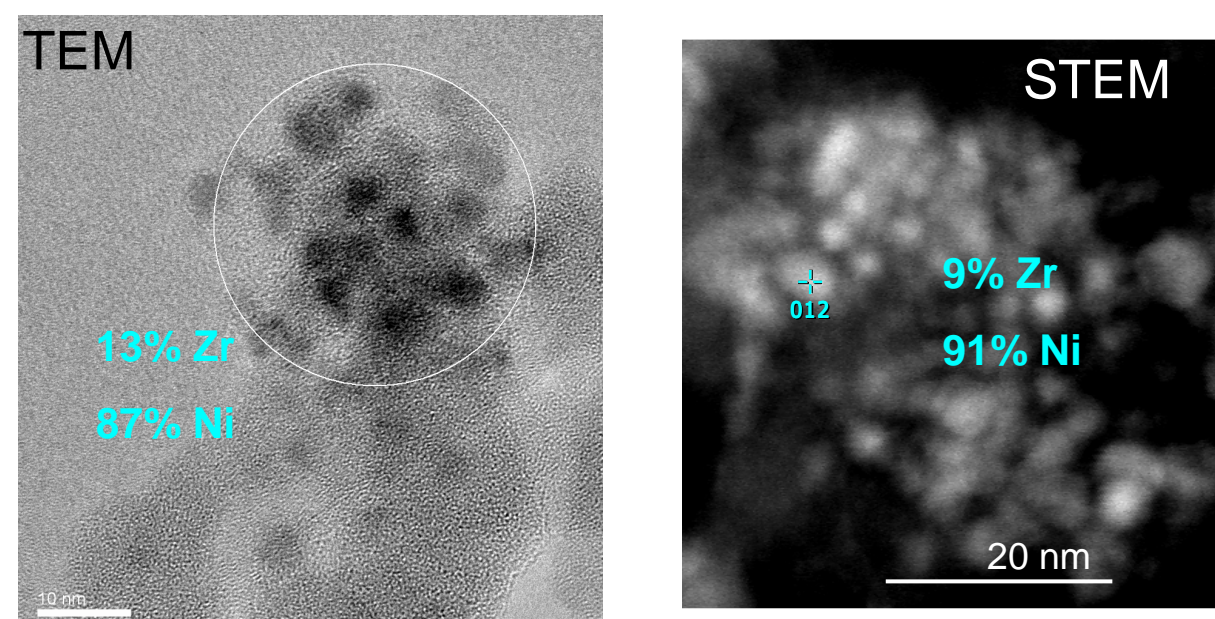
➔ 31% loss of Ni surface sites

XRD experiments performed at RT after exposure to air:



- Small Ni particles of ca. 2 nm
- No proof of existence of Zr, nor Ni-Zr alloy

TEM/EDS/STEM analysis:



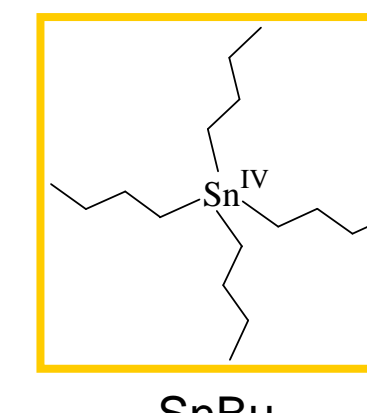
Particles with a blurred aspect, average size of ca. 3-4 nm

- bimetallic Ni-Zr particles with variable compositions in Zr and Ni
- Ni particles

XAFS (Zr and Ni K-edges): No evidence for a Ni-Zr bond. Only light neighbours for Zr (Zr-O)

Ni - Sn

The Ni/SiO₂ parent catalyst was first reduced under flowing H₂ at 400°C. SnBu₄ was then grafted on reduced Ni/SiO₂ under ca. 100 mbar H₂. The catalyst was then heated under flowing H₂ at 400°C.



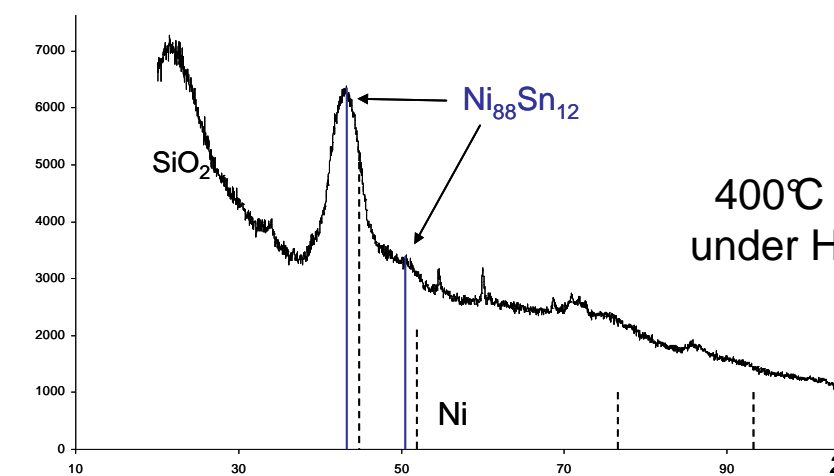
Sn/Ni content: 0.3

H₂ adsorption measurements:

H₂ adsorbed after grafting = 0.33 x (H₂ adsorbed before grafting)

➔ 67% loss of Ni surface sites

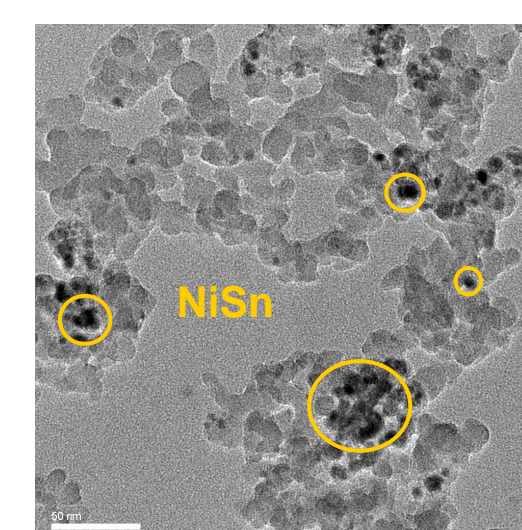
XRD experiments performed in situ, during the heating at 400°C under flowing H₂:



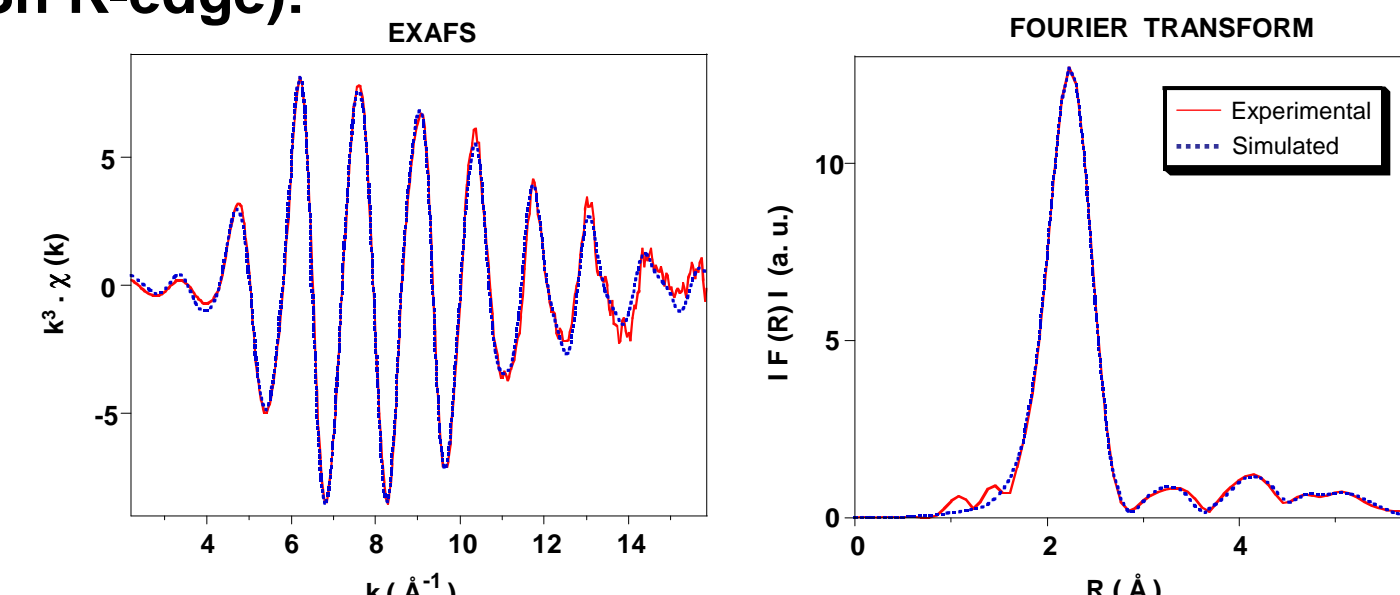
➔ Formation of a Ni-Sn solid solution, which is stable even after exposure to air

TEM/EDS analysis:

➔ Well defined bimetallic Ni-Sn particles with variable compositions in Sn and Ni



XAFS (Sn K-edge):



- Sn-Ni contributions: 8 Ni neighbours at 2.61(1) Å
- Further Ni and Sn layers: 3.60(2) Å: 1Ni; 4.55(2) Å: 9Ni; 5.11(2) Å: 2Sn

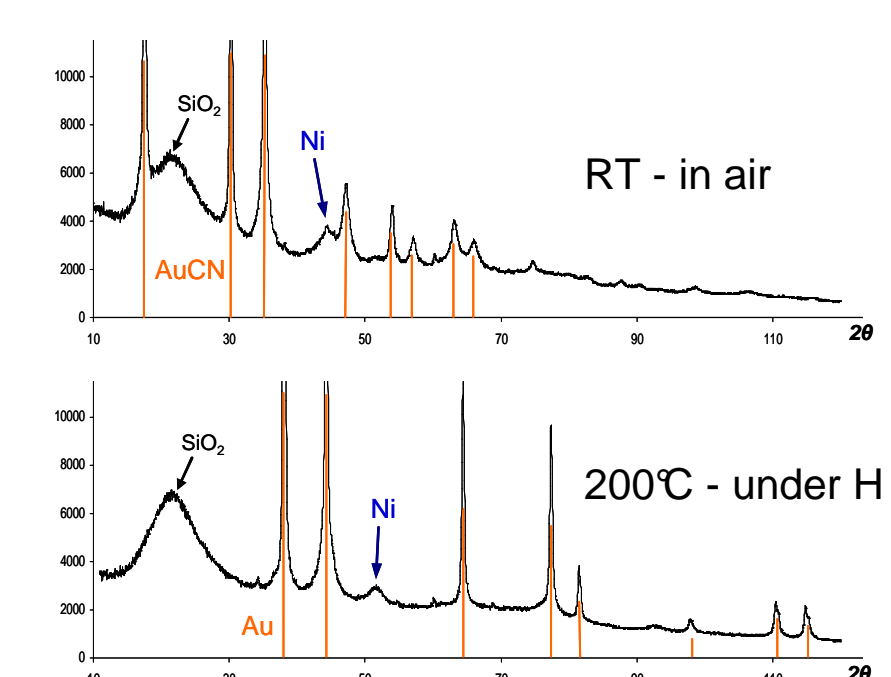
Ni - Au

The Ni/SiO₂ parent catalyst was first reduced under flowing H₂ at 400°C. The catalyst was then transferred in a Schlenk tube, covered with n-heptane under H₂ and AuCN was introduced for grafting at RT. After evacuation of the solvent, the catalyst was heated under flowing H₂ at 400°C.

Au^I - CN

Au/Ni content: 0.25

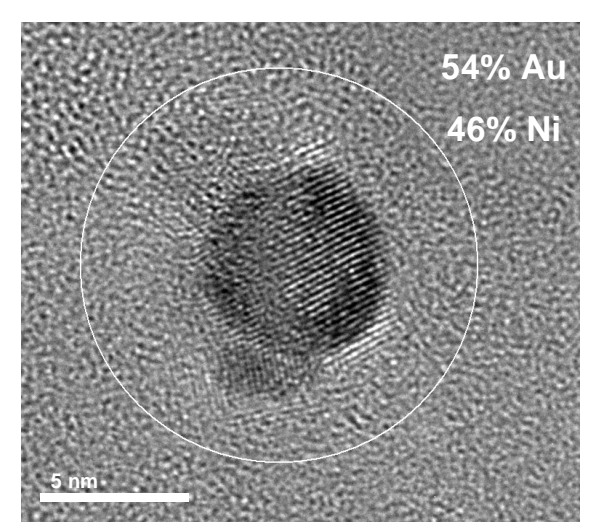
XRD experiments performed in situ, during the heating at 400°C under flowing H₂:



- AuCN decomposes into Au particles at 200°C
- Ni particles of ca. 3 nm
- Au particles of ca. 15 nm

TEM/EDS/STEM analysis:

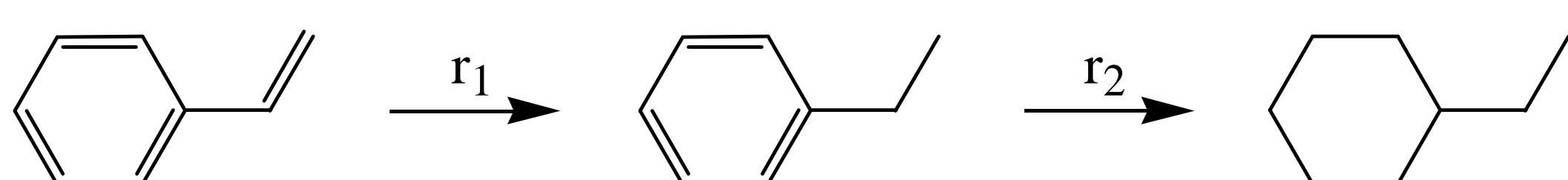
- Well defined bimetallic Ni-Au particles with variable compositions in Au and Ni size varies from 4 to 150 nm
- Ni particles of ca. 3 nm, these particles have a blurred aspect



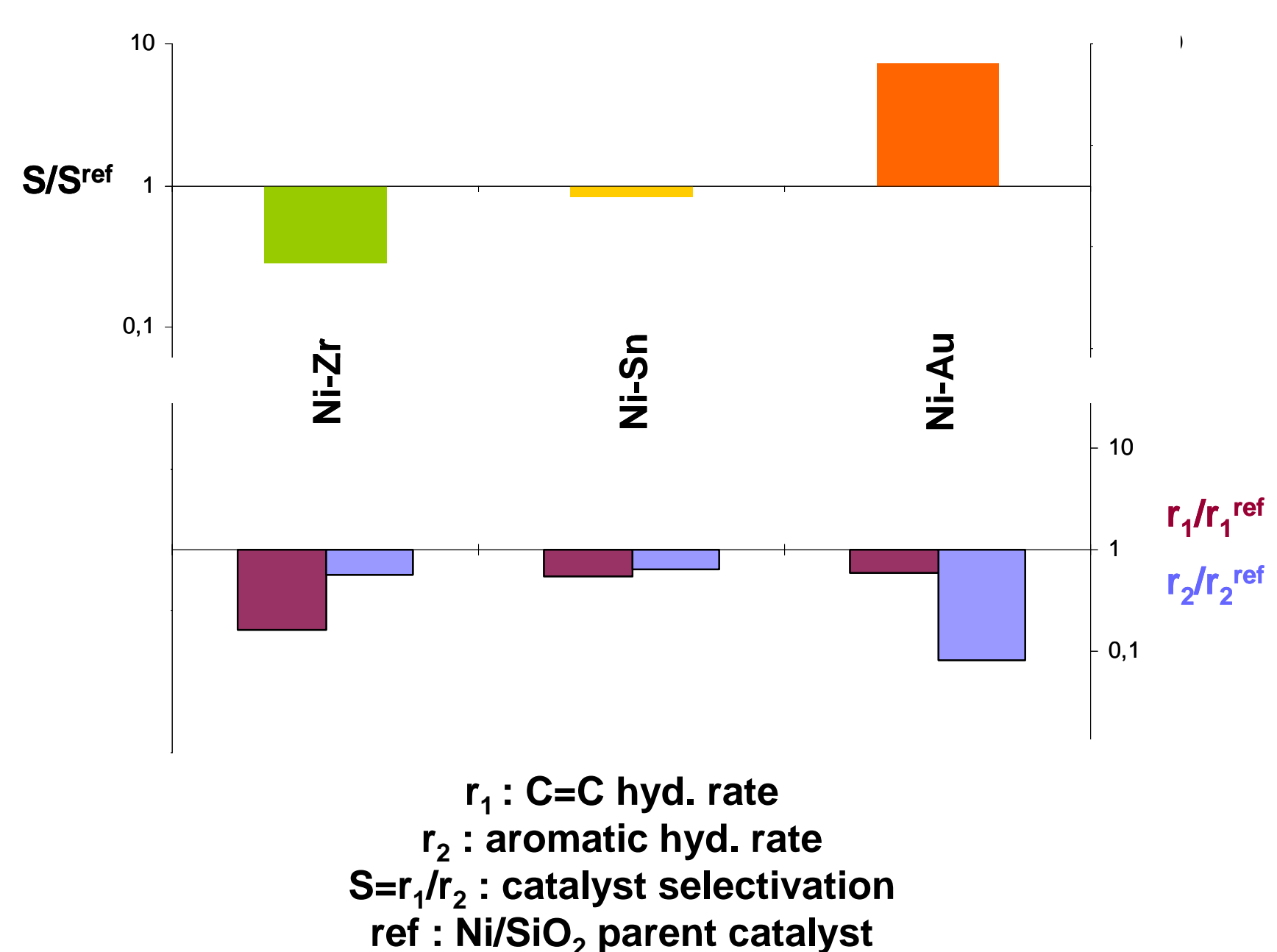
XAFS (Au L_{III} and Ni K-edges):

- Presence of large Au particles
- Simultaneous Au-Ni contributions at 2.59(4) Å, only for low Au content: Au/Ni < 0.05

Styrene hydrogenation



50 mL n-heptane, 20-40 mg of catalyst NiX/SiO₂, Styrene/Ni₂=5000, 700 rpm, at 5°C/15bar then 150°C/60bar



NiZr : decrease of r_1 and r_2 (geometric effect) but r_1 is more affected than r_2
➔ the electro-donor effect of Zr poisons the C=C hyd.
➔ selectivity decrease

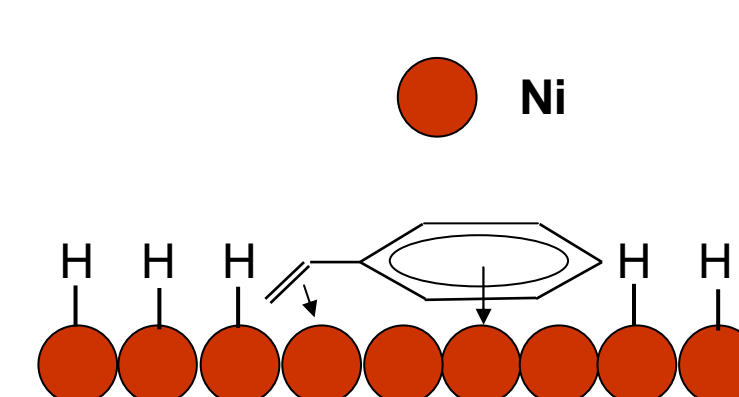
NiSn : decrease of r_1 and r_2
➔ geometric effect affects in the same manner the 2 reaction rates
➔ no effect on selectivity

NiAu : decrease of r_1 and r_2 (geometric effect) but r_2 is more affected than r_1
➔ the electro-attractor effect of Au promotes the C=C hyd.
➔ selectivity increase

Conclusion

Bimetallic Ni-X/SiO₂ catalysts with X: Zr, Sn and Au were prepared and well characterized. Catalysts revealed different catalytic properties in the hydrogenation of styrene:

Ni parent catalyst

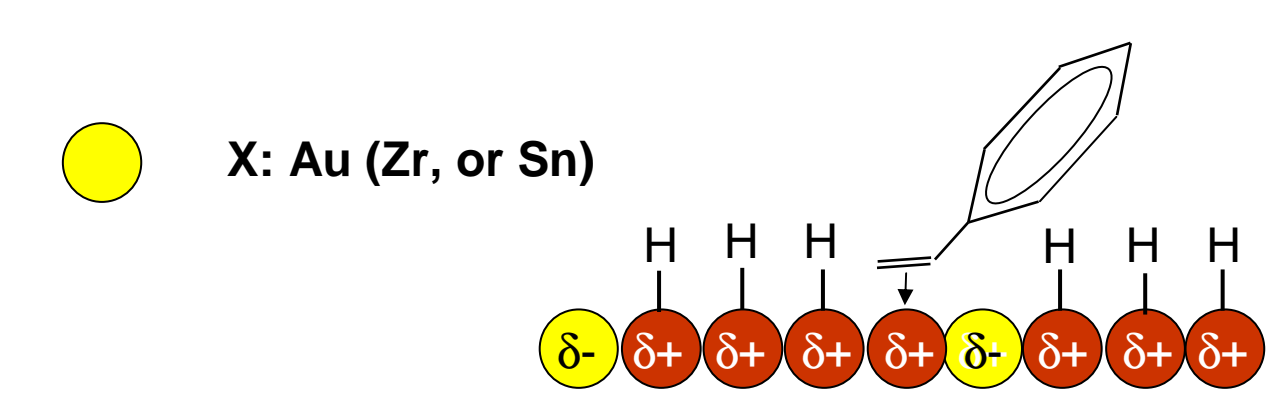


- The aromatic ring can adsorb and react with surface Ni-H

- The C=C double bond can adsorb and react with surface Ni-H

➔ Total hydrogenation is possible

Modified Ni-X catalyst



- There aren't enough adjacent Ni-H sites for the aromatic ring to adsorb and react
➔ Inhibition of the aromatic ring hydrogenation

- The C=C double bond can adsorb and react with less surface Ni-H:
➔ C=C hydrogenation is slowed down (geometric effect)

- with Ni-Sn catalyst, Ni is electronically unaffected,
➔ no change in selectivity

- with Ni-Zr catalyst, Ni is electronically enriched, which poisons C=C hyd.
➔ selectivity decreases

- with Ni-Au, Ni is electro-deficient which favours C=C hyd.
➔ selectivity increases