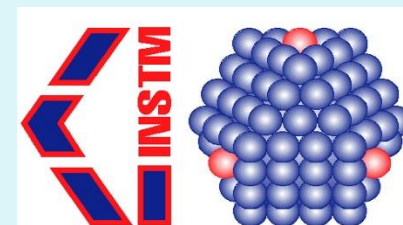


LAYERED NI-AL-HYDROTALCITE-DERIVED CATALYSTS AS HIGHLY ACTIVE MATERIALS FOR POWER-TO-GAS PROCESS

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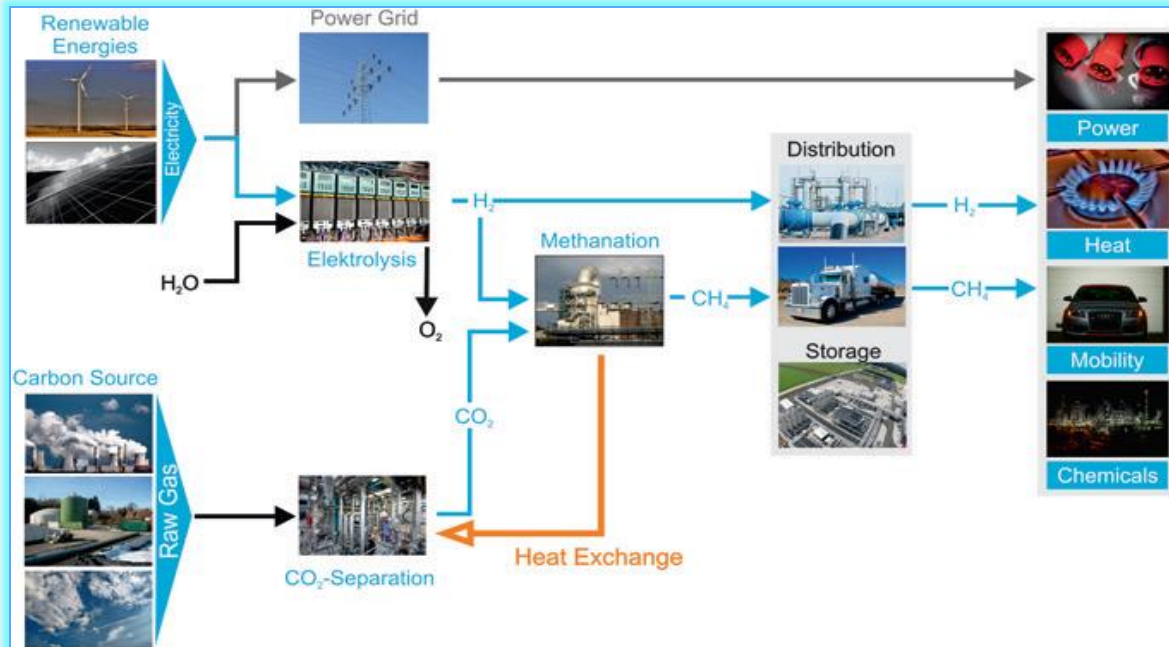
Introduction



An overview of the power-to-gas process



3-step (Electricity \longrightarrow H₂ \longrightarrow Synthetic Gas)

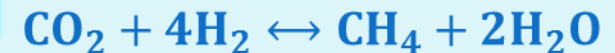


Challenges: electrical power supply from renewable energies :

- long term storage
- transportation from remote areas.

The Power-to-Gas (PtG) is a promising technology to reduce the energy loss using the hydrogenation of CO₂

Sabatier Reaction



Although is thermodynamically favorable, catalyst is necessary to obtain an appropriate rate.

Methanation Catalysts

- Several metal-based catalytic system (Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt) supported on (SiO_2 , TiO_2 , Al_2O_3 , ZrO_2 , CeO_2 and mixed oxides).
- Ni based catalysts are commonly used for the methanation process
 - Deactivation at low T, due to the interaction of the metal particles with CO and the formation of mobile Nickel carbonyls that lead to the metal sintering
- Activity and selectivity are strongly influenced by the amount of Ni, the size of dispersed Ni particles, MSI (metal-support-interaction) composition of the support (Al_2O_3 , ZrO_2 , CeO_2 , TiO_2)*
- The amount of Ni is critical to enhance the reaction rates at low temperature

*Abate et al. *Ind. Eng. Chem. Res.* 2016, 55, 4451–446

Ni-Al hydrotalcite (HT) preparation

❖ Synthesis method:
Co-precipitation

Na(OH) (1.2 M)
Na₂CO₃ (0.8 M)

Precursor solution

Ni(NO₃)·6H₂O (0.75M)

Al(NO₃)·9H₂O (0.25M)

Atomic ratio Al/Ni → 1/3

Crystal growth condition :

❖ aging 20-24h

❖ pH=12 and 8.7

❖ T=65°C

❖ **vigorous stirring**

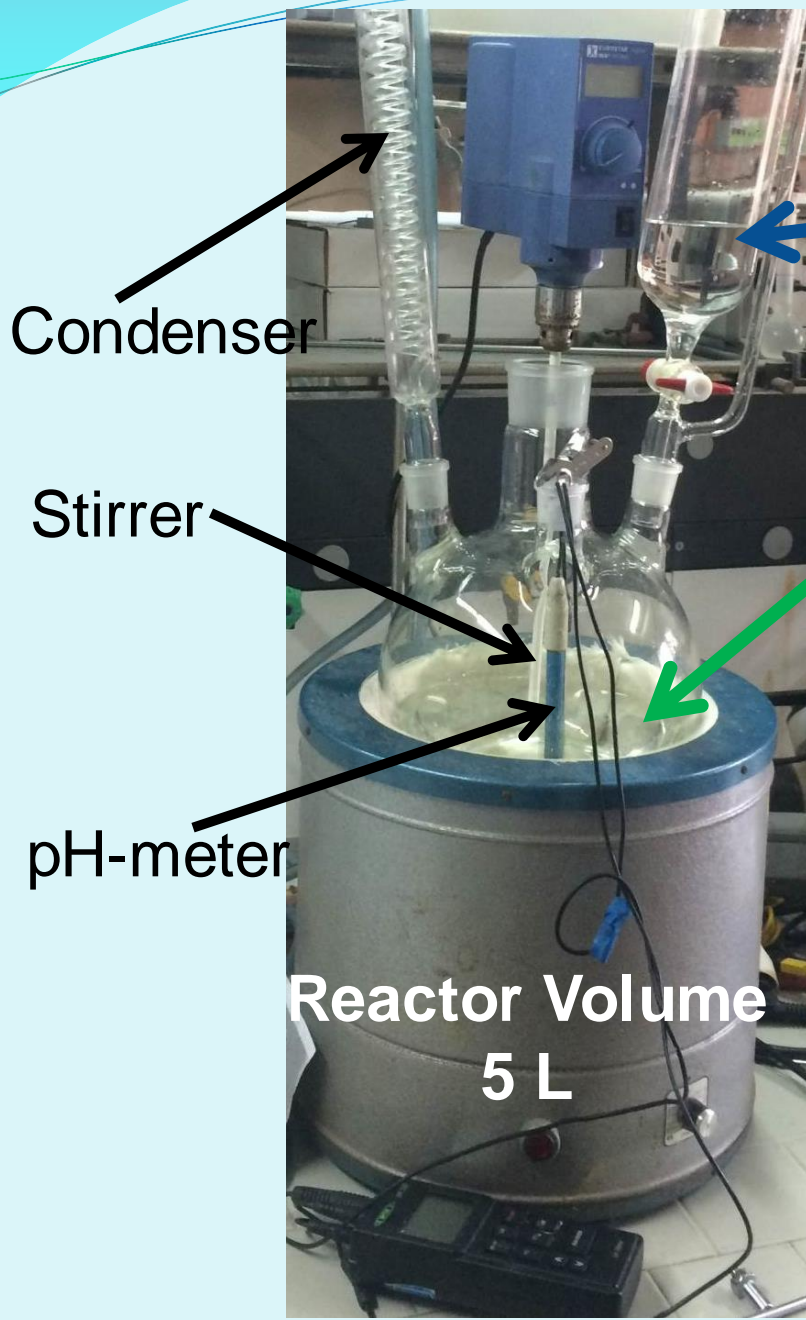
Final steps

○ *filtration*

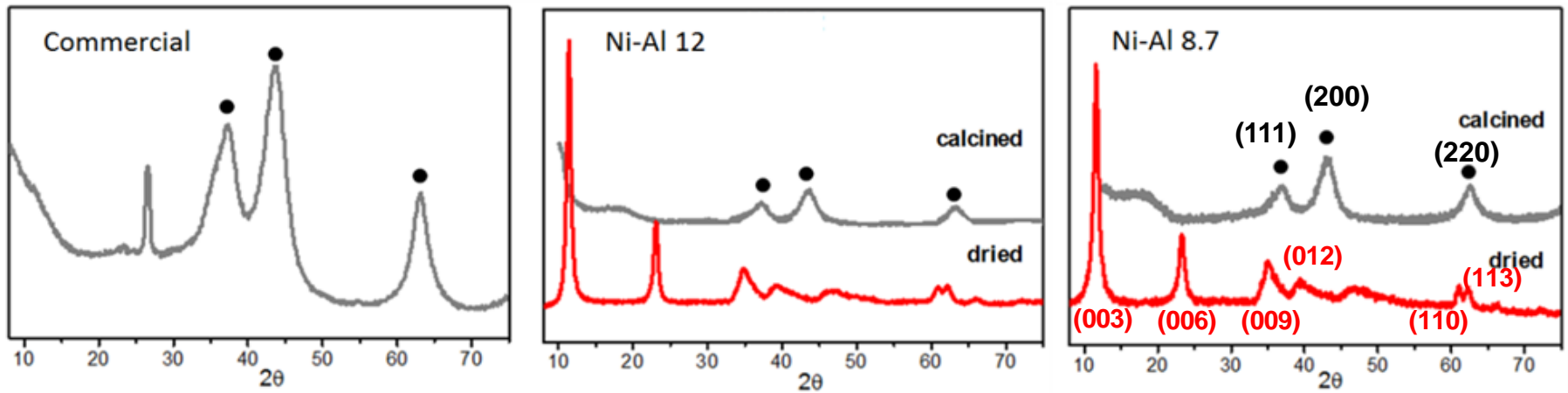
○ *washed with distilled water*

○ *dried at 110°C for 4 h*

○ *annealed at 450°C for 6h*



XRD



c value corresponds to three times the interlayer distance

$$c/3 = \frac{d(003) + 2 * d(006)}{2}$$

Sample	d (Å)	a(Å)	c(Å) dried
<u>Ni-Al 8.7</u>	35.7	4.17	29.07
<u>Ni-Al 12</u>	35.5	4.17	28.77
<u>Commercial</u>	41.6	4.18	-

a parameter indicates the average cation-cation distance

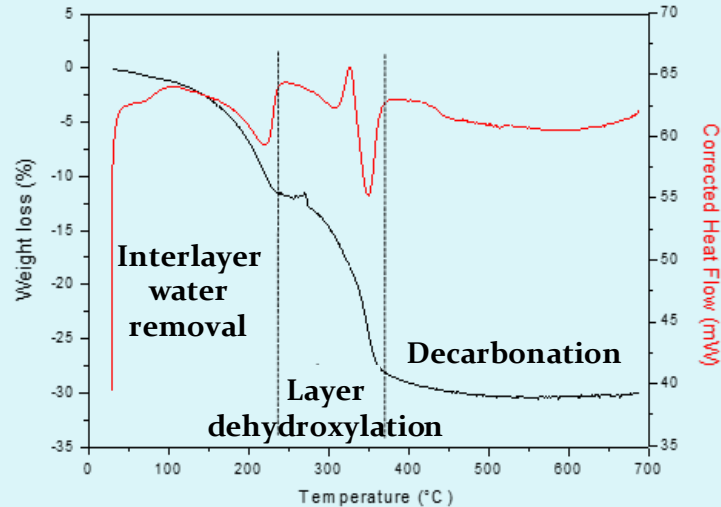
$$a_0 = (d_{111}) \cdot \sqrt{3}$$

d Scherrer formula (111) plane

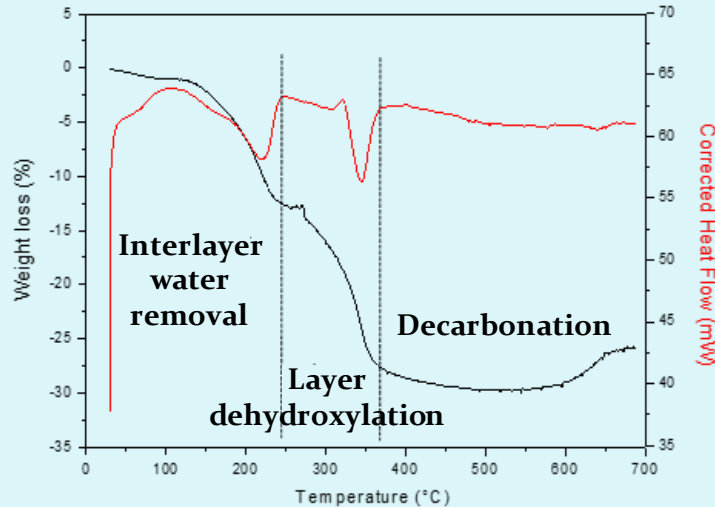
$$d = \frac{k\lambda}{B \cos \theta}$$

Termogravimetric analysis

NiAl-8.7 dried

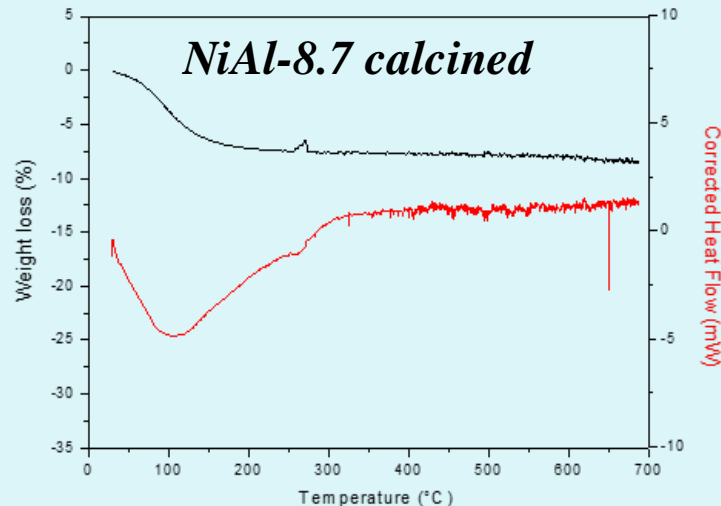


NiAl-12 dried

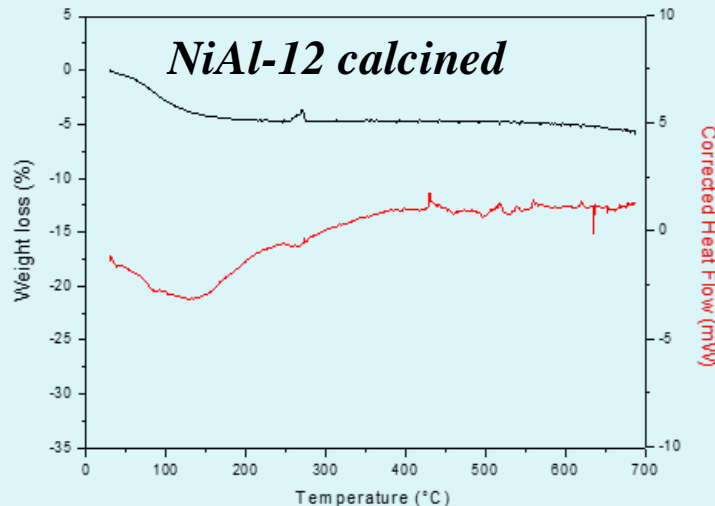


Physically adsorbed water started to be removed below 100 °C. The finalization of this process (100-200°C) led to an intermediate metastable mixture of phases, where the dehydrated hydrotalcite coexisted with the solid solution of spinels.

NiAl-8.7 calcined



NiAl-12 calcined

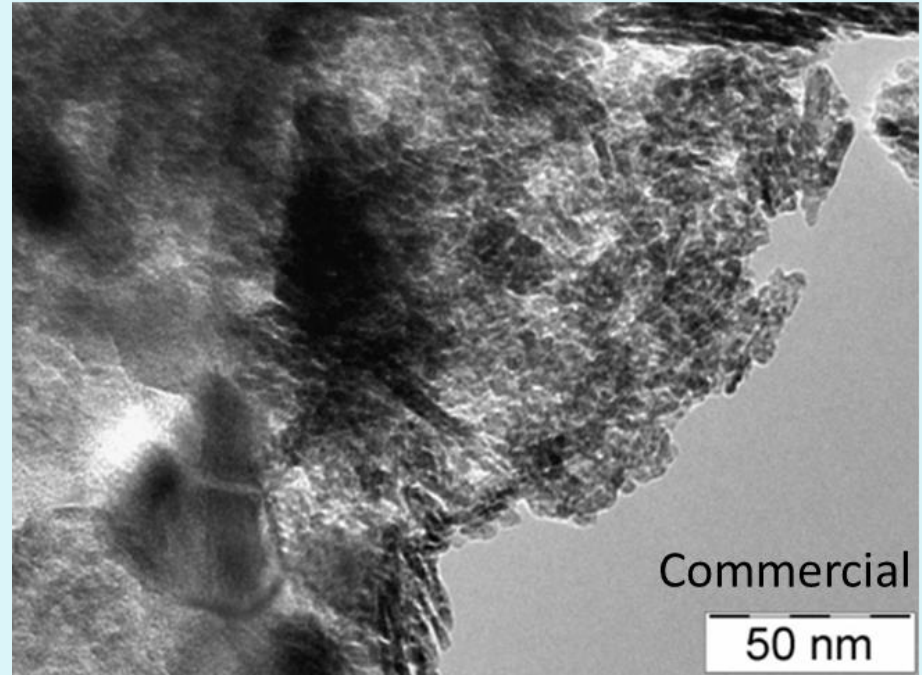
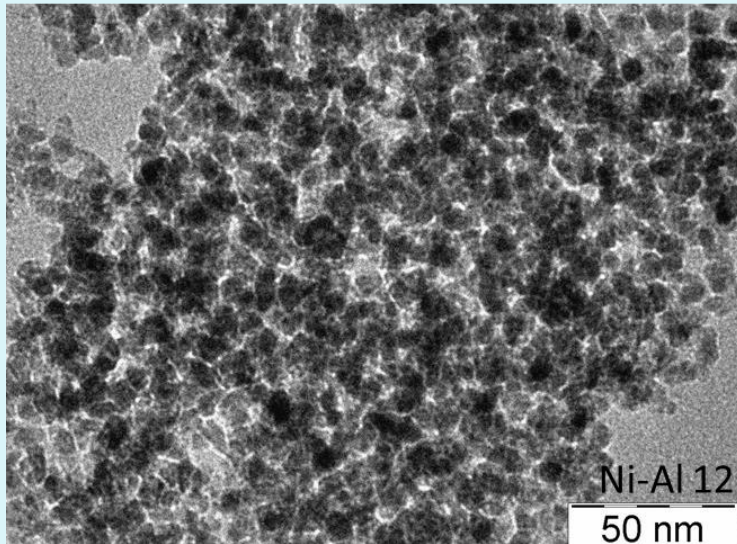
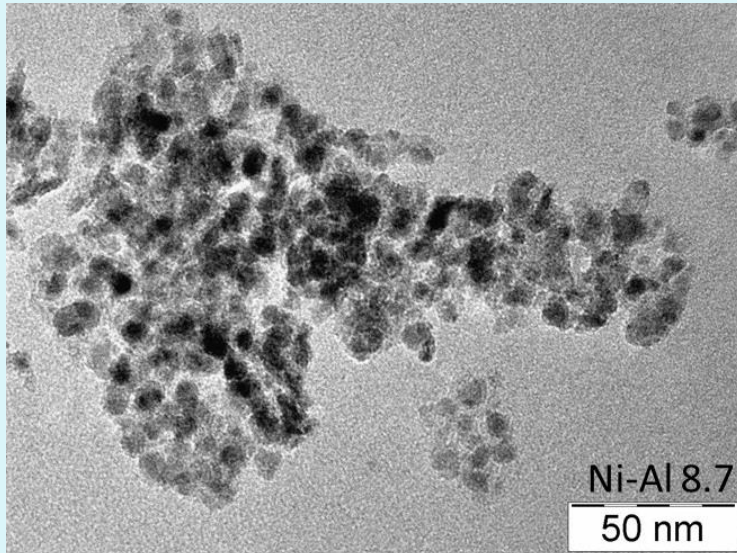


The formation of an intermediate metastable phase, suggests that at 200 °C, the hydrotalcite structure collapsed completely.

The final decarbonation step at high temperature led to a stable mixed oxidic structure.

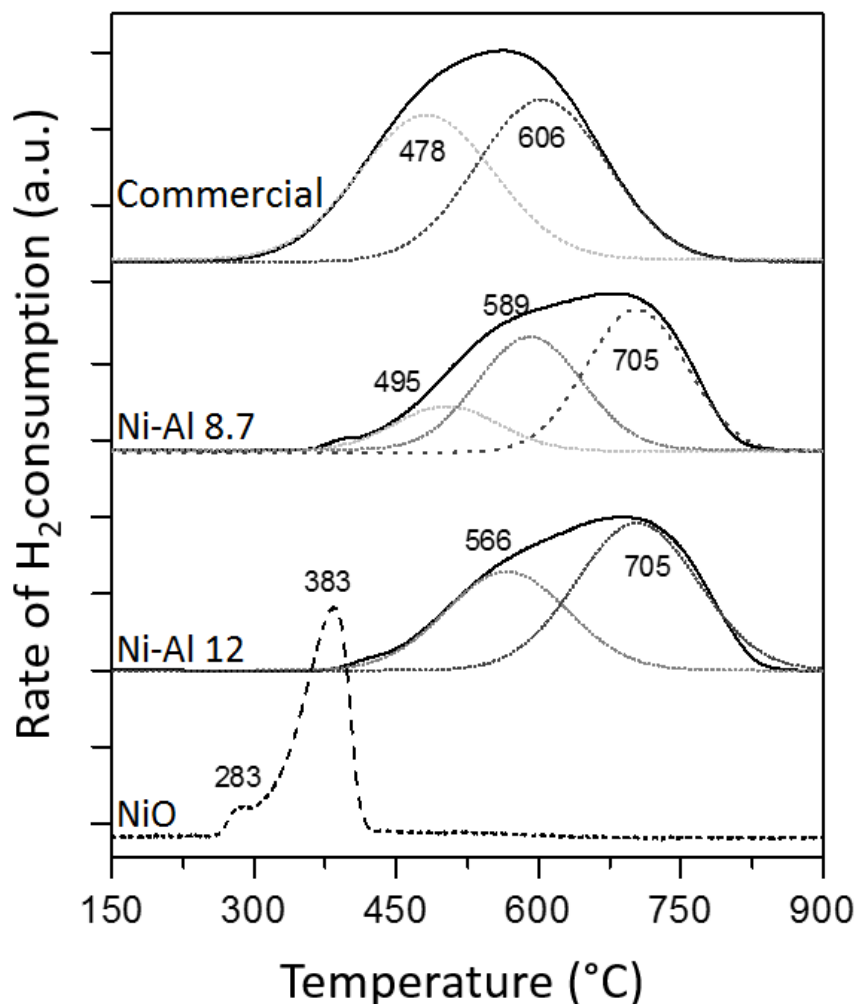
TEM

highly dispersed Ni round-shaped nanoparticles



more
inhomogeneous distribution
and shape of Ni particles

TPR

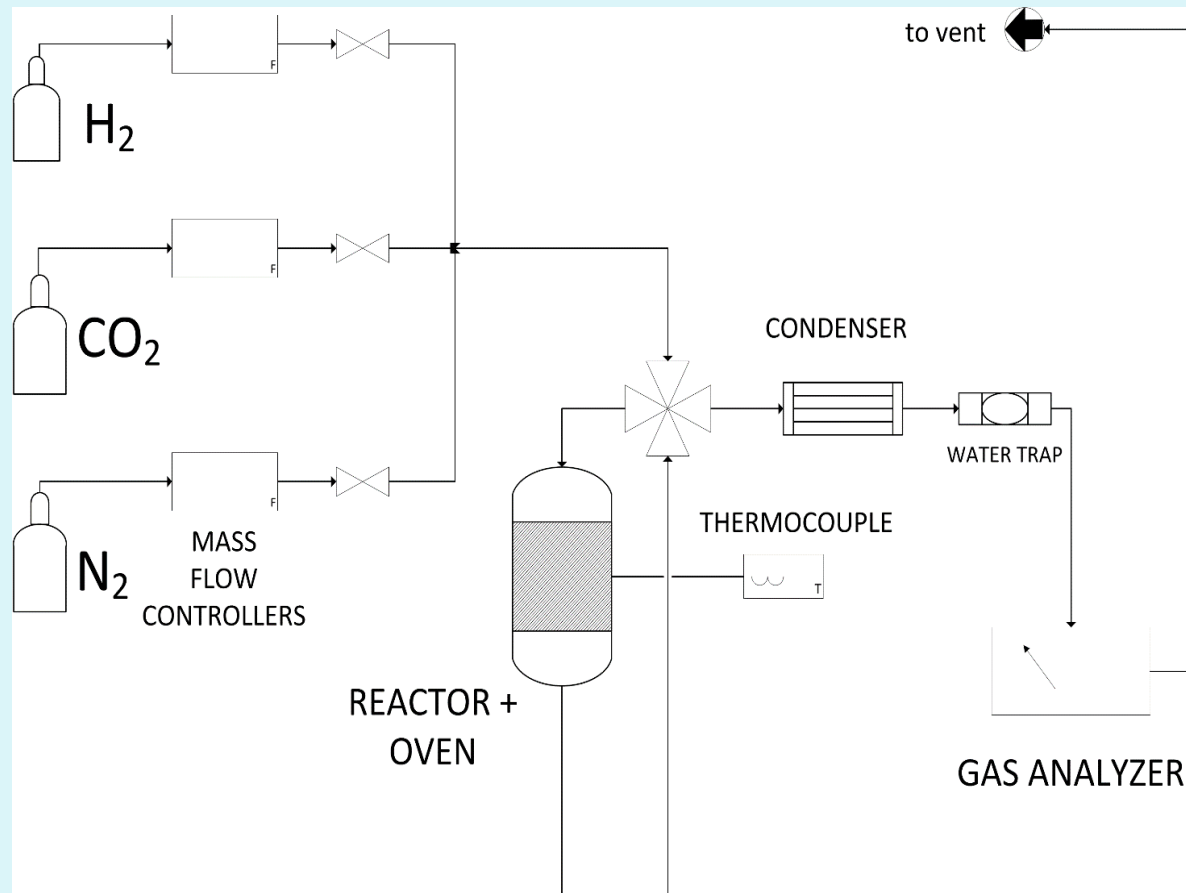


Sample	NiO ^a (wt%)	H ₂ /NiO ^b (%)	MSA ^c (m ² _{Ni} /g _{cat})
<u>Ni-Al 8.7</u>	75	84.3	42.2
<u>Ni-Al 12</u>	76	86.0	51.8
<u>Commercial</u>	76	69.4	28.4

- a. Calculated by AAS
- b. Calculated by H₂-TPR measurements
- c. Calculated by CO-Chemisorption in the T-range 100-400 °C.

- superficial oxide nanoparticles, weakly interacting with alumina support (478-495)
- strongly interacted with Al₂O₃ or Ni-Al mixed oxide (566-705°C)[1]

Experimental apparatus



Pellets 500-900 μm
Catalyst amount 600 mg
Catalytic bed $d=4$ mm
 $h=50$ mm
Reduction $10\text{H}_2-90\text{N}_2$ at
 500°C per 3 h

Reaction T $250\div 400^\circ\text{C}$
Increasing step 25°C

Feeding mixture:
Stoichiometric $\text{H}_2/\text{CO}_2 = 4$
 10H_2 2.5CO_2 87.5N_2
GHSV $20000\div 30000\text{ h}^{-1}$

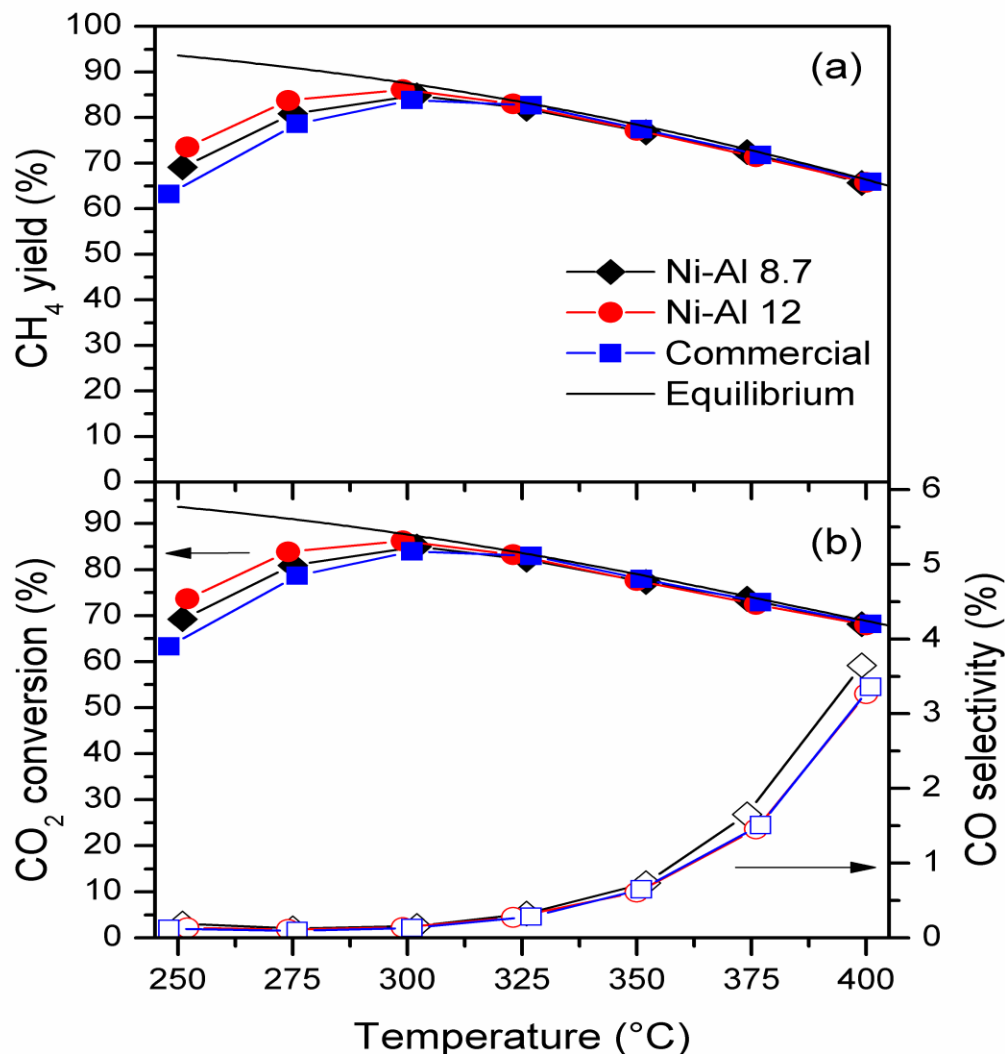
Catalysts Activity Performance

Three Ni-based catalysts with high nickel content (75%) have been tested at atmospheric pressure with high N_2 dilution and $GHSV=20,000\text{ h}^{-1}$

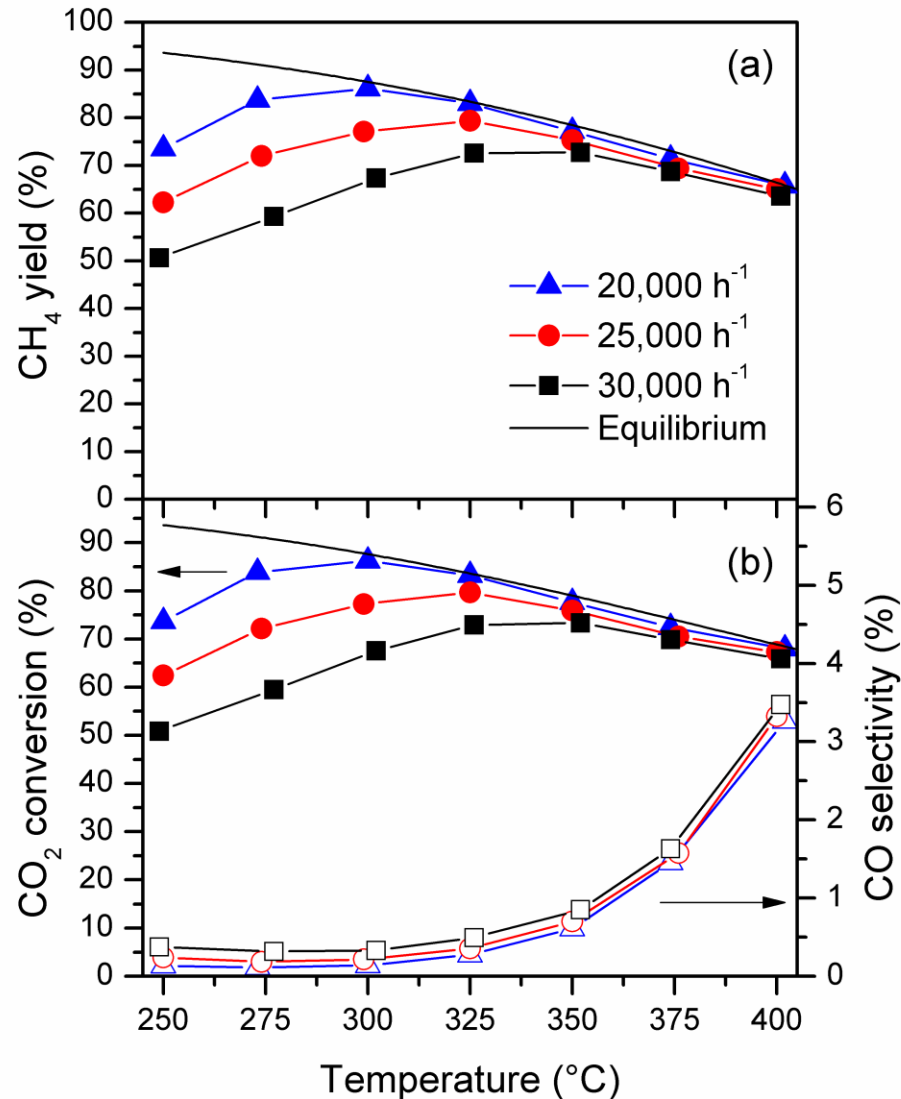
*High conversion
still at low
temperature*

A low amount of CO was detected even at high temperature, when CO production via reverse water gas shift reaction (RWGSR) is thermodynamically favored

*All the samples
presented the yield
peak at $\approx 300\text{ }^\circ\text{C}$.*

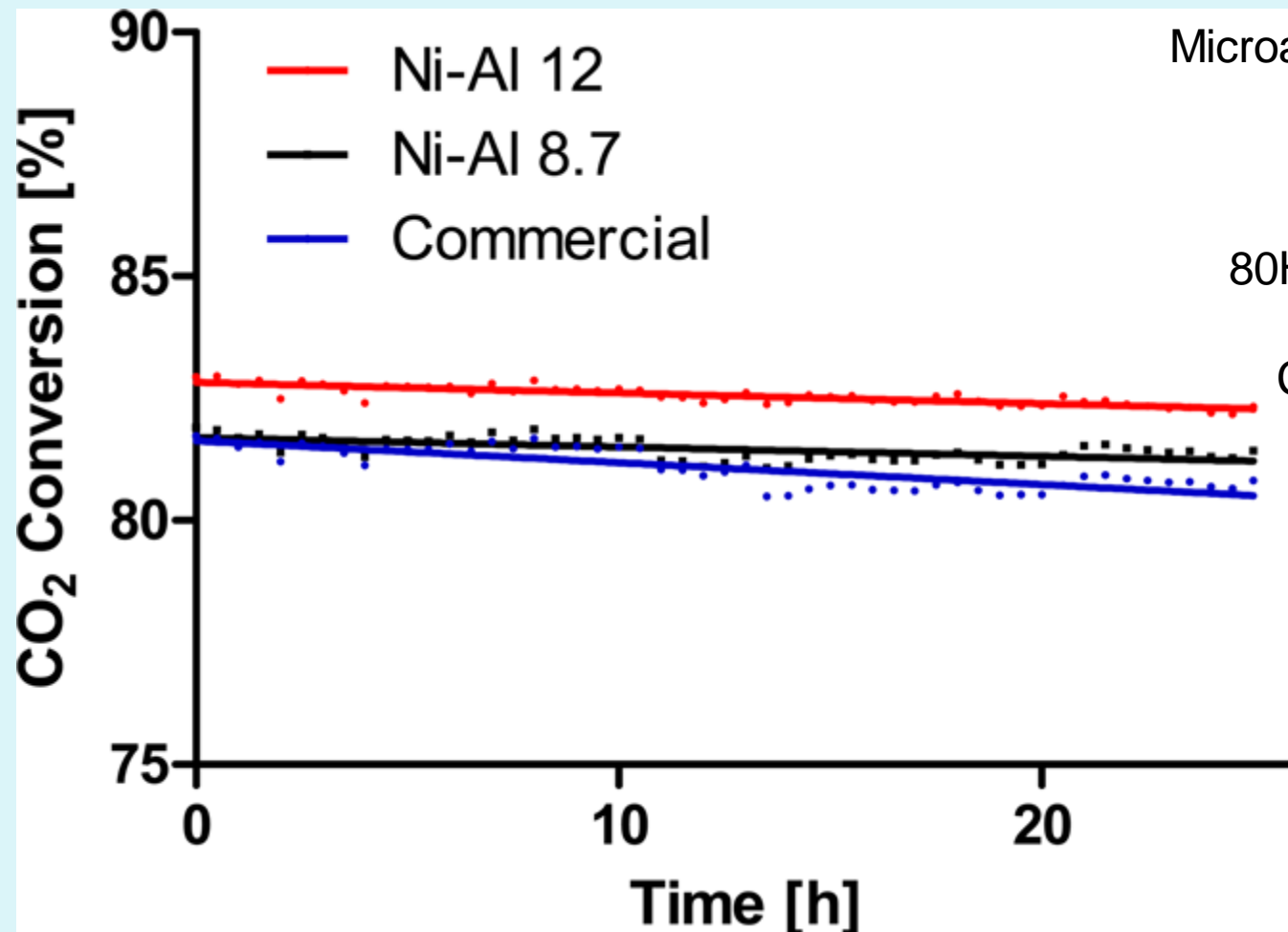


Catalyst Activity Performance: impact of GHSV on the Ni-Al 12



The conversion dropped with increasing the GHSV, while the curve peak (conversion maximum) seems to shift toward a higher temperature value.

Stability testing



Microactivity Efficient equipment
(micromeritics)

$T=300^{\circ}\text{C}$

$\text{GHSV}=20000\text{h}^{-1}$

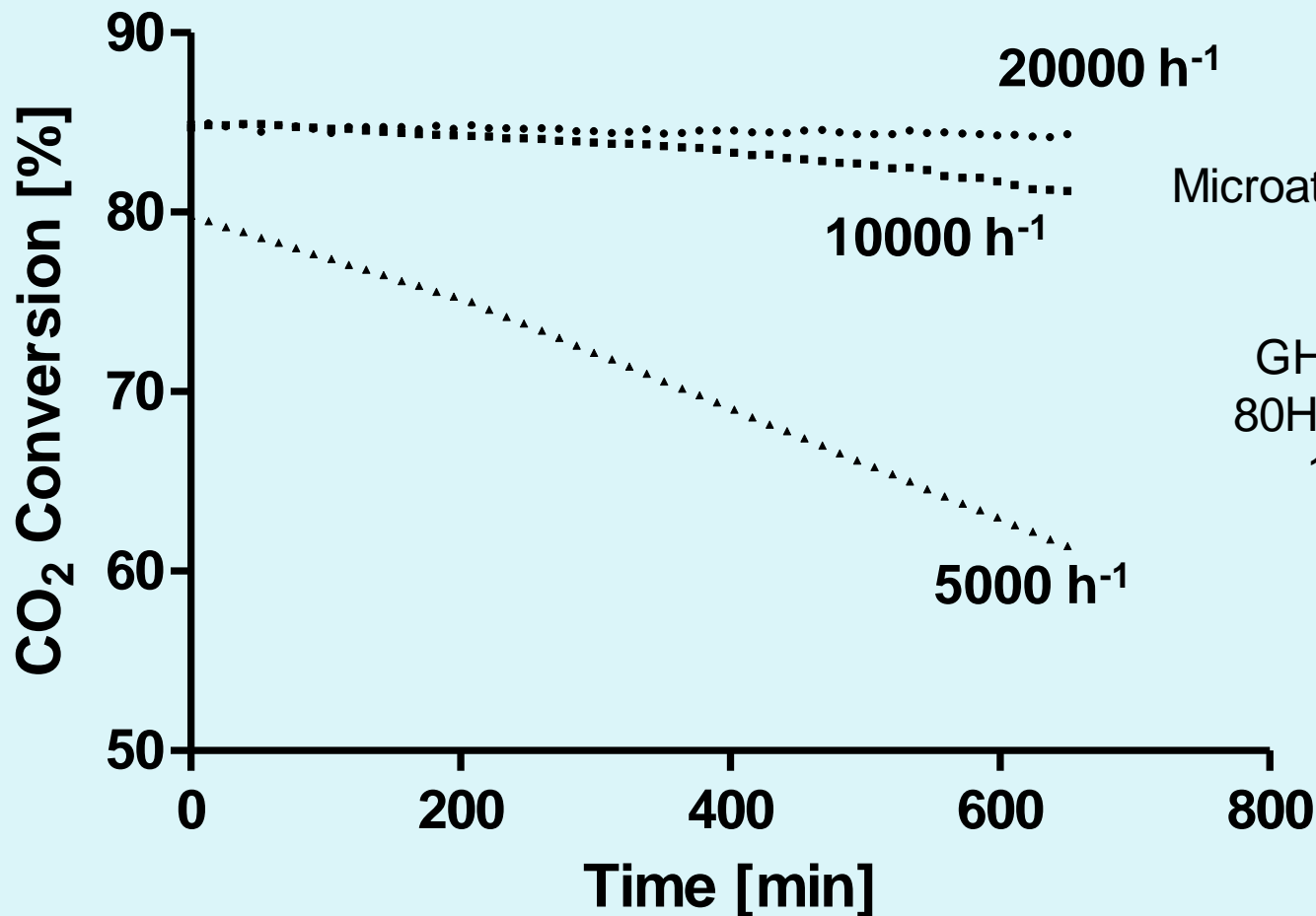
$80\text{H}_2\text{-}20\text{CO}_2$ feed mixture

50 mg of catalyst

Catalytic bed= 3 cm^3

Effect of GHSV on stability

Ni-Al₁₂



Microactivity Efficient equipment
(micromeritics)

T=300°C

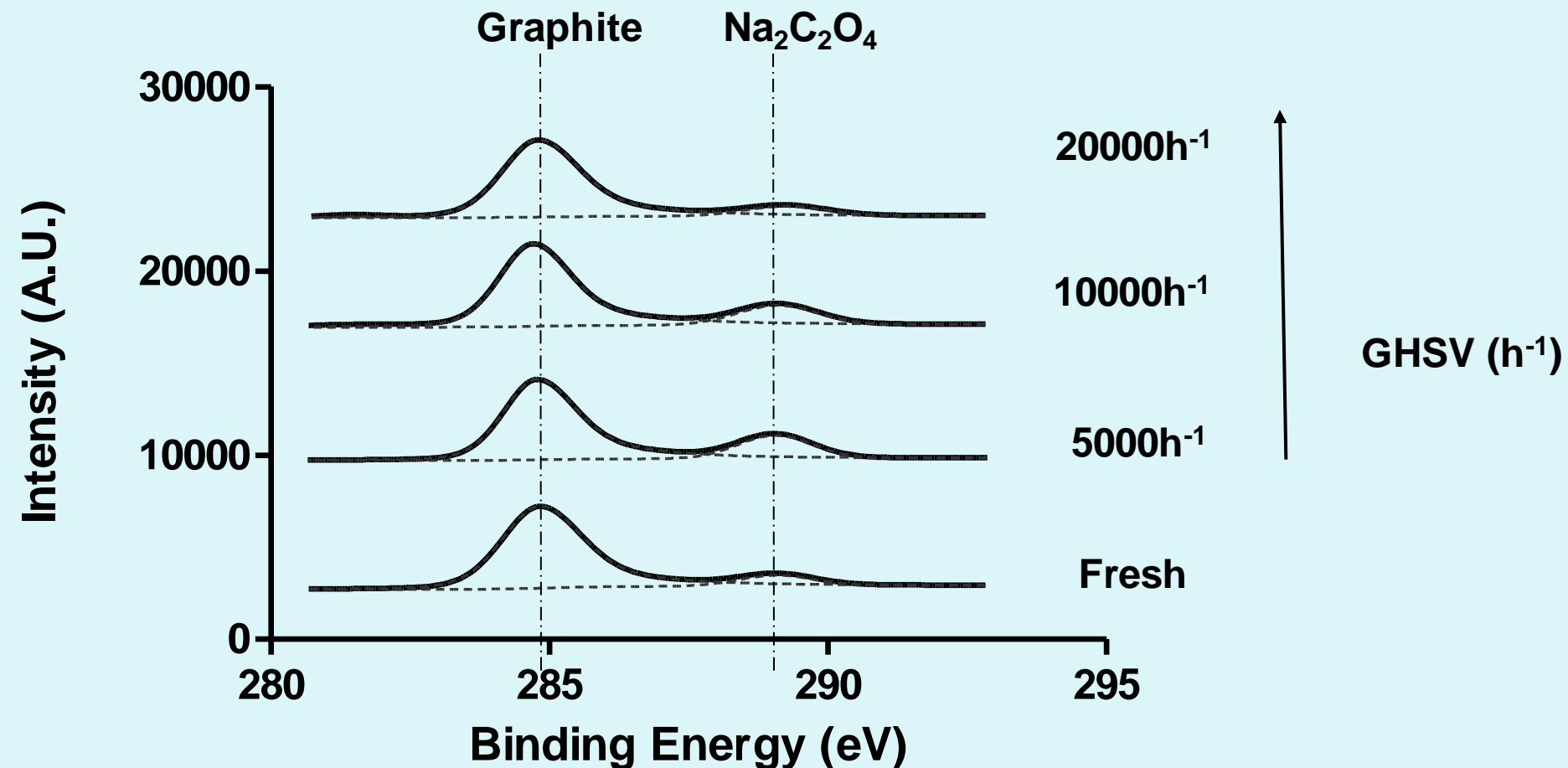
GHSV=10000-20000h⁻¹

80H₂-20CO₂ feed mixture

130 mg of catalyst

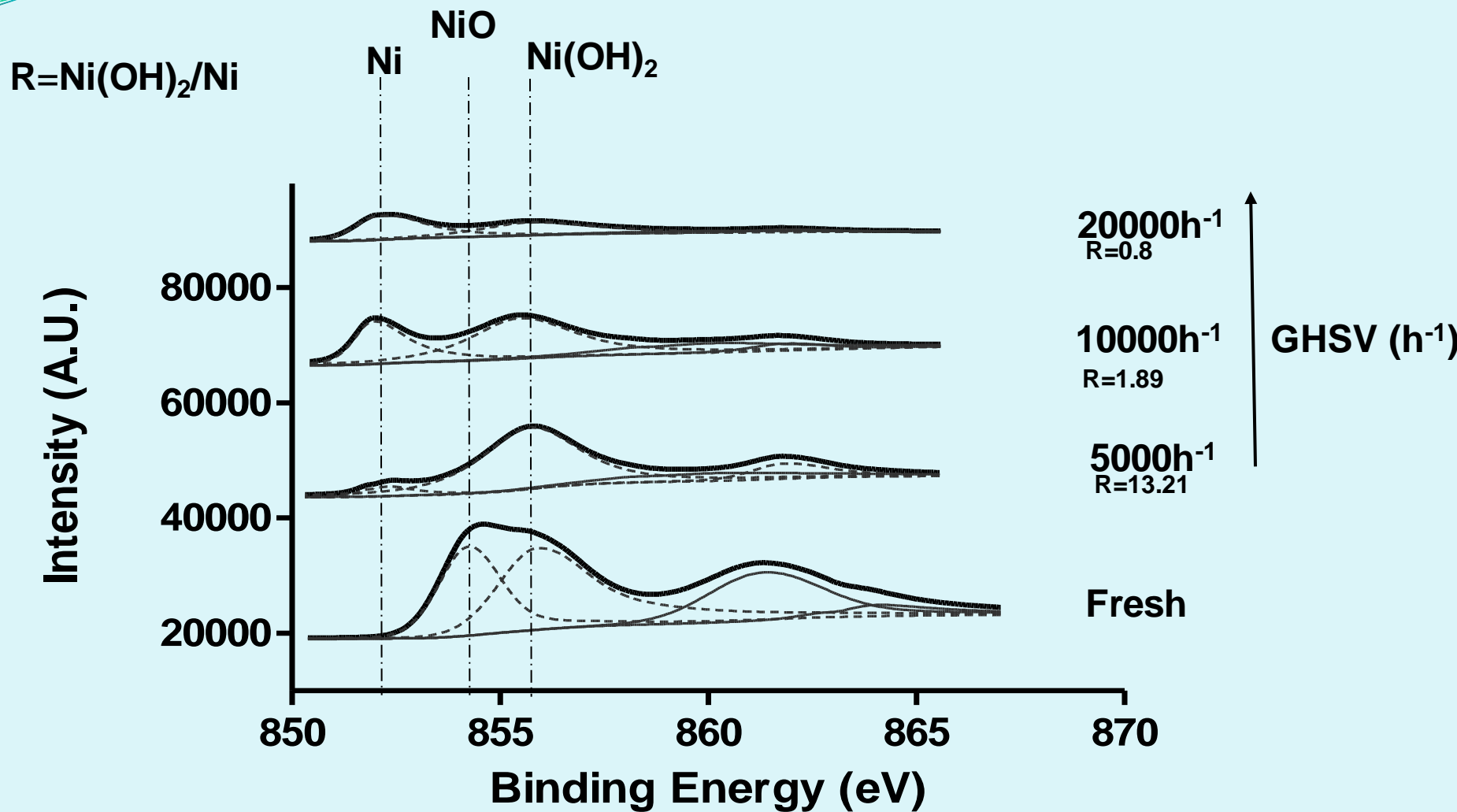
XPS profile :C1s

PHI VersaProbe II analyzer. Ni 2p, C1s, binding energies (BE) were recorded using AlK α (1486.6eV) as the excitation source and a pass energy of 23.5 eV. The X-ray setting was 100 μ 100W20kv_HP. A Shirley background was applied and all the XPS peaks were fitted with asymmetric function by using Multipak (Matlab) software. Position of XPS peaks of the corresponding elements is referred to the C1s peak of carbonaceous contamination, whose energy is taken equal to 284.80 eV.



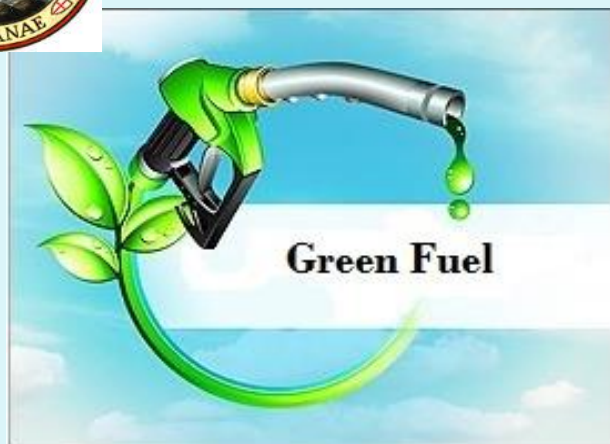
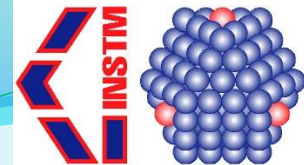
The TGA profiles didn't show any weight loss, typically in the temperature range 450-700

XPS profile : Ni 2p_{3/2}



Conclusions

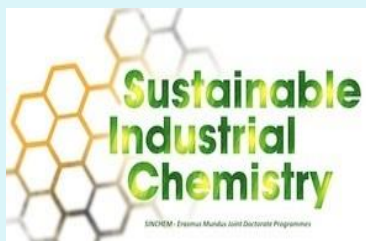
- Two Ni-Al hydrotalcite samples for carbon dioxide methanation have been synthesized via co-precipitation of nitrates salts in alkaline solution at different pH (Ni-Al 8.7 and Ni-Al 12). They have been studied and compared with a reference commercial catalyst consisting in Ni (75 wt%) on $\gamma\text{-Al}_2\text{O}_3$. All the samples have been characterized from a physico-chemical standpoint
- The experimental campaign was carried out by testing. Methane yield values resulted (in the region far from chemical equilibrium) with the following order: Ni-Al 12 > Ni-Al 8.7 > commercial catalyst. The higher conversion can be put in relation with the NiO reducibility, metal surface area (MSA) and nickel dispersion.
- the good stability was observed for hydrotalcite system at high GHSV (20000 h^{-1})
 - lower GHSV and consequently the low contact time, favor the oxidation of the Ni metal and the formation of NiO and $\text{Ni}(\text{OH})_2$ species, probably due to the presence of H_2O formed
 - Stability may be further promoted by introducing other elements increasing Ni reducibility (CeO_2)



Thank you for your kind attention



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