CO_2-SR Ciclyc Technology: Capture and Conversion of CO_2 with hybrid catalysts for storage and conversion with methane (CO_2-SR)

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ProCAT
Tecnologías de Procesos Catalíticos

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CIENTÍFICO Y TÉCNICO

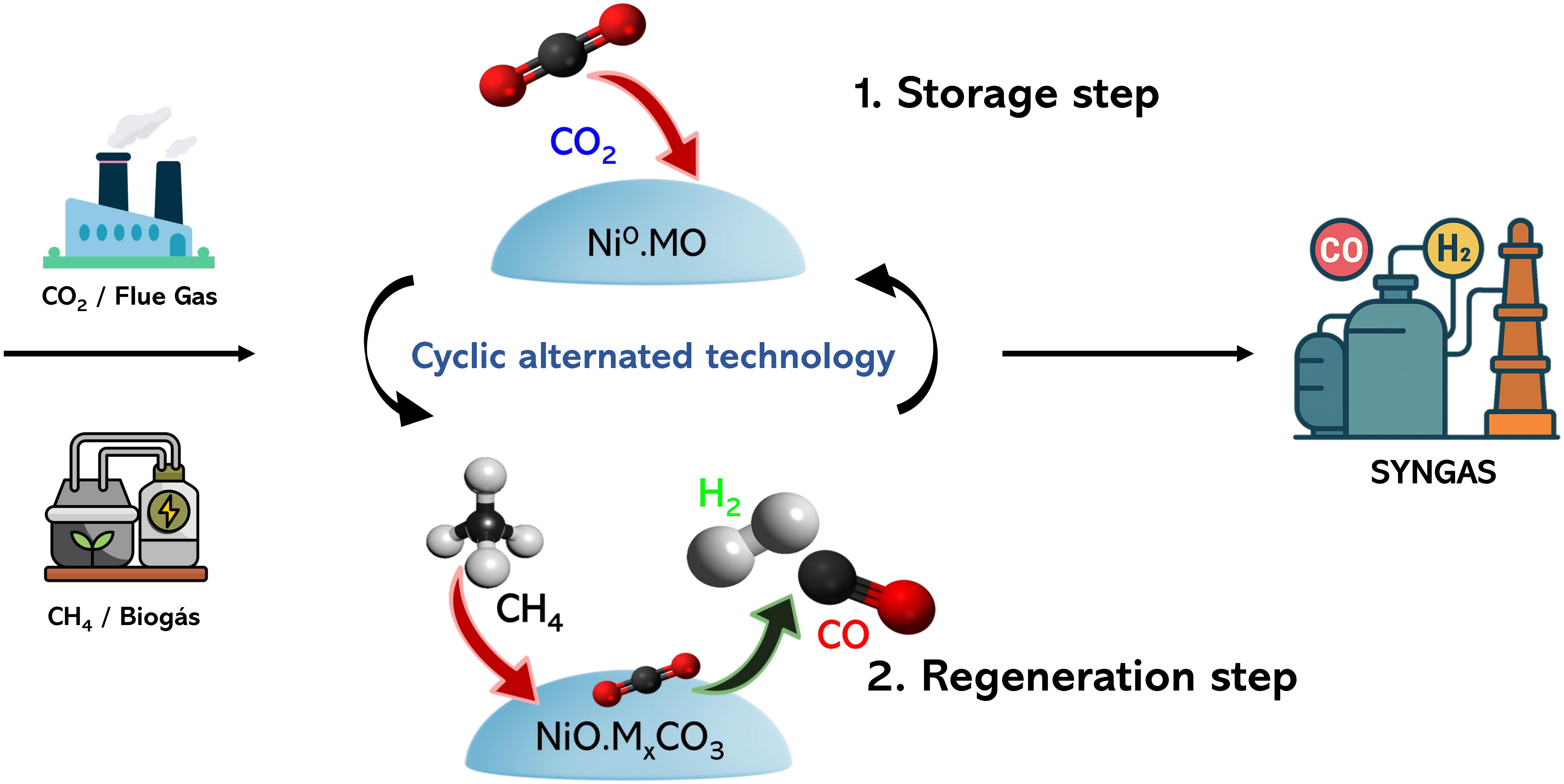
SUBDIVISIÓN DE PROGRAMAS
TEMÁTICOS CIENTÍFICO-TÉCNICOS

Proyecto de I+D+i Retos Investigación

PID-2021-1240198OB-100

C. Herrera-Delgado

CO_2 – *Storage Regeneration Technology*



CO_2 / Flue Gas

CH_4 / Biogás

CO_2

$Ni^0.MO$

1. Storage step

Cyclic alternated technology

CH_4

H_2

CO

$NiO.M_xCO_3$

2. Regeneration step

SYNGAS

Screening of Ni-based catalyst for CO_2 capture and conversion

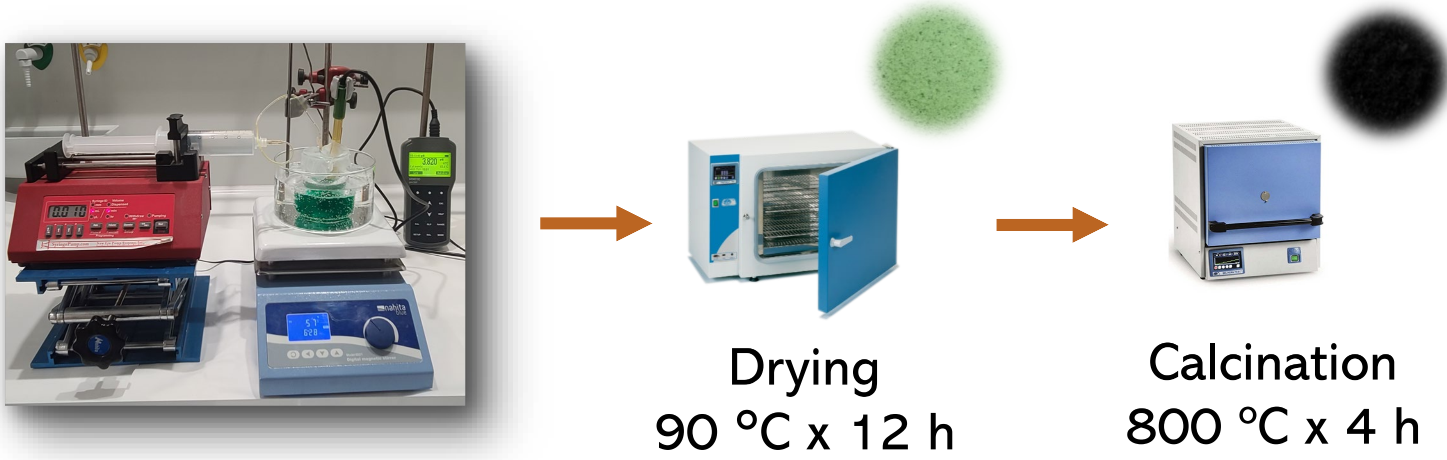
Dual Function Materials

- CO_2 storage → Alkali/Alkaline earth metal-(Ce, La)
- Catalytic conversion and regeneration → Nickel-(Rh)

Model catalyst Ni:Ba 1:1 (at.) **Ni:Me 10:1 (at.)**

- $Ni(NO_3)_2 \cdot 6\ H_2O$
- **Alkaline or alkaline earth metal**
  - $Ba(NO_3)_2$
  - KNO_3
  - $Ca\ (NO_3)_2 \cdot 4H_2O$
  - $Sr(NO_3)_2$
  - $La(NO_3)_2.xH_2O$
  - $Ce(NO_3)_3\text{-}6H_2O$
  - $Rh(NO_3)_3 \cdot xH_2O$
- **3 % wt. colloidal SiO_2 (LUDOX)**

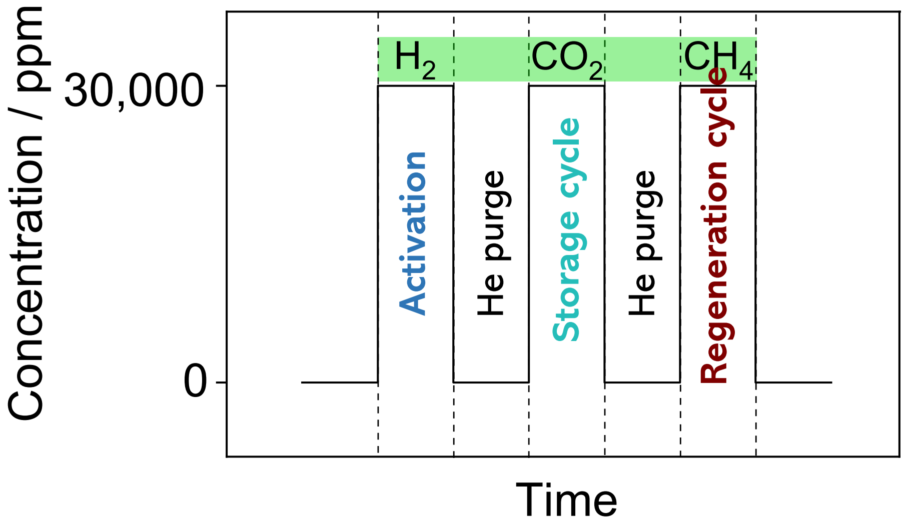
Ammonia induced coprecipitation-Ureolysis-induced coprecipitation



+ H_2O wash

XRD, Raman, FT-IR, ATD-TG, XPS, CO_2-TPD, A_{BET}, H_2-TPR

Study of the Cyclic Process of CO_2 Storage and Regeneration

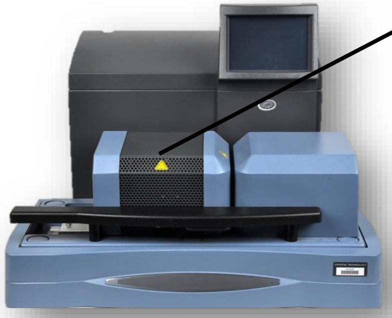


- ✓ **In situ activation**

  @600 °C; 1 h; 3 % H_2/He
- ✓ **Cyclic stages: CO_2 Storage**

  CH_4 Regeneration
- ✓ He purge between stages
- ✓ Total flow of 100 ml·min^{-1}

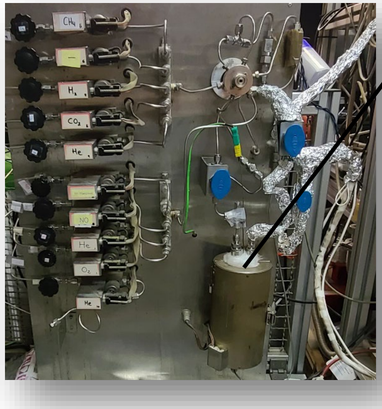
TG-MS



SDT Q600 T.A. Instrument

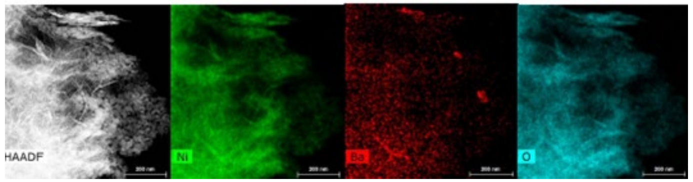
MS-PFEIFFER QMS 200

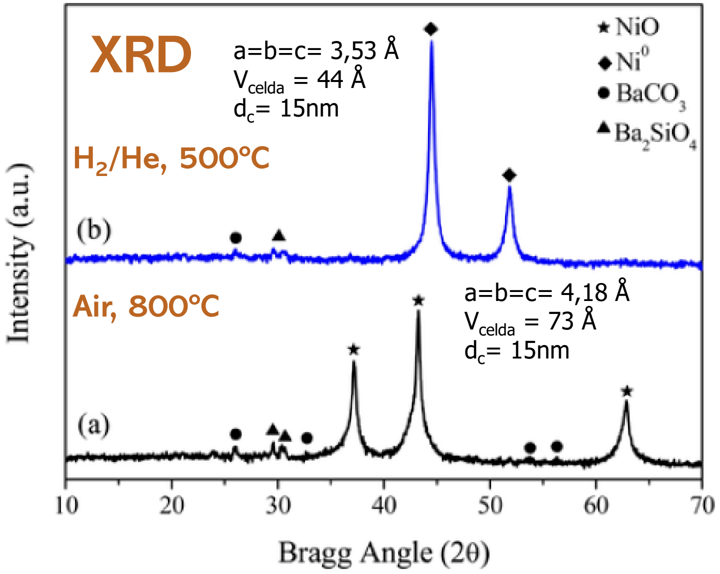
TRM-MS

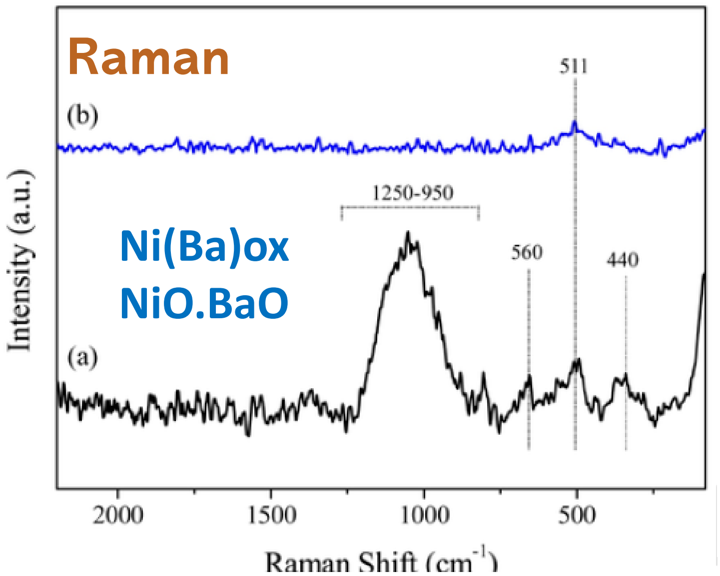


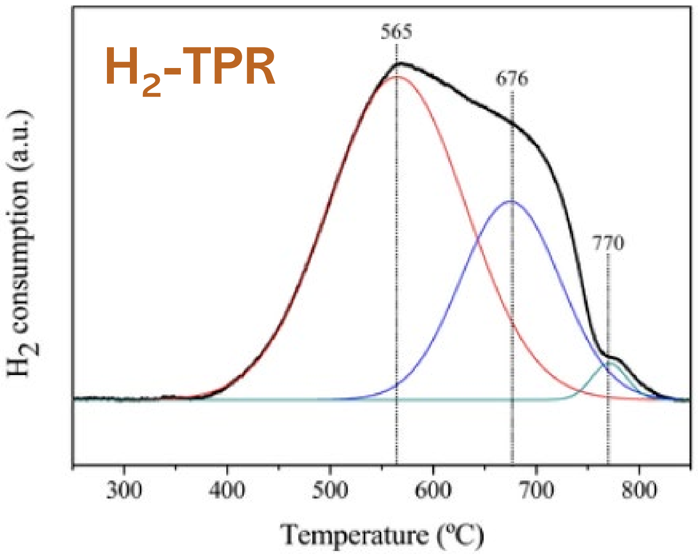
CO_2 storage and in situ regeneration with CH_4 over a model **NiBa (1/1)** catalyst

	A_{BET} (m^2/g)	Vp(cm^3/g)	Dp (Å)
NiBa	112	0,18	64









$Ni^{4+} \rightarrow Ni^{2+}$ **NiO_2.BaO** = $NiBaO_3$

$Ni^{2+} \rightarrow Ni^0$ **NiO.BaO** = $NiBaO_2$

	T(°C)	CO_2 net adsorption capacity (mmol CO_2/g cat)
CO_2-He-Ar	600	0,23
	650	0,37
	700	0,13

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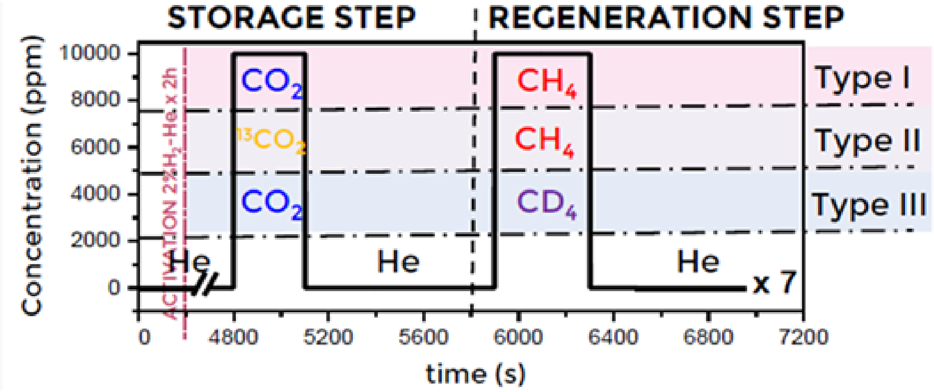
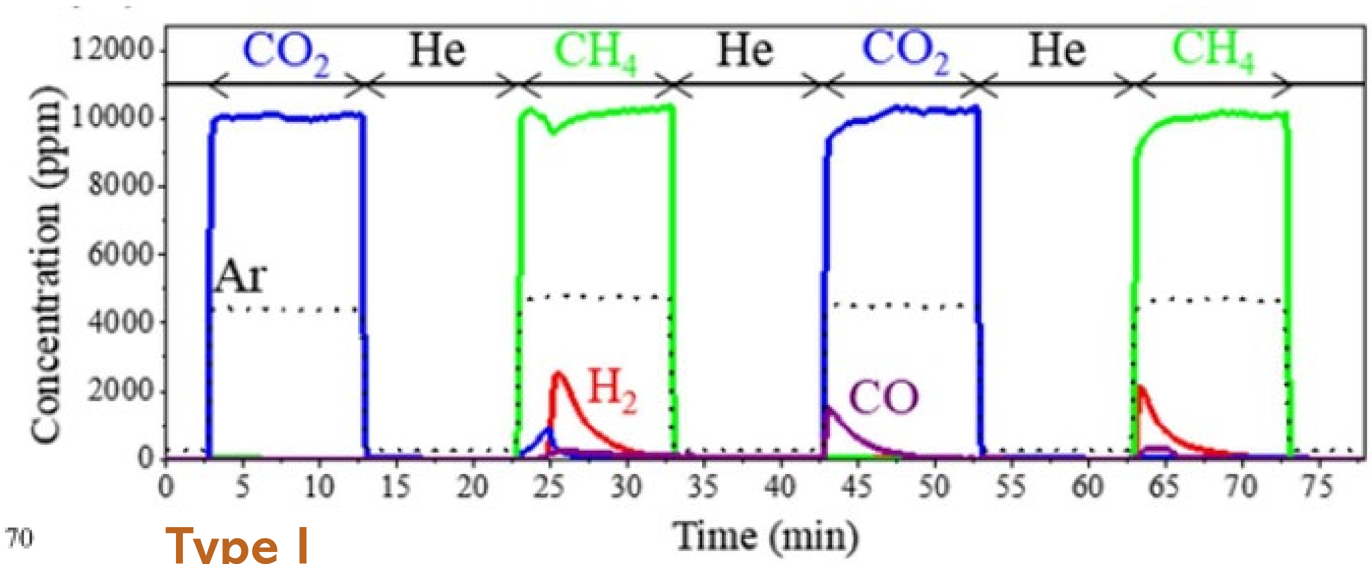
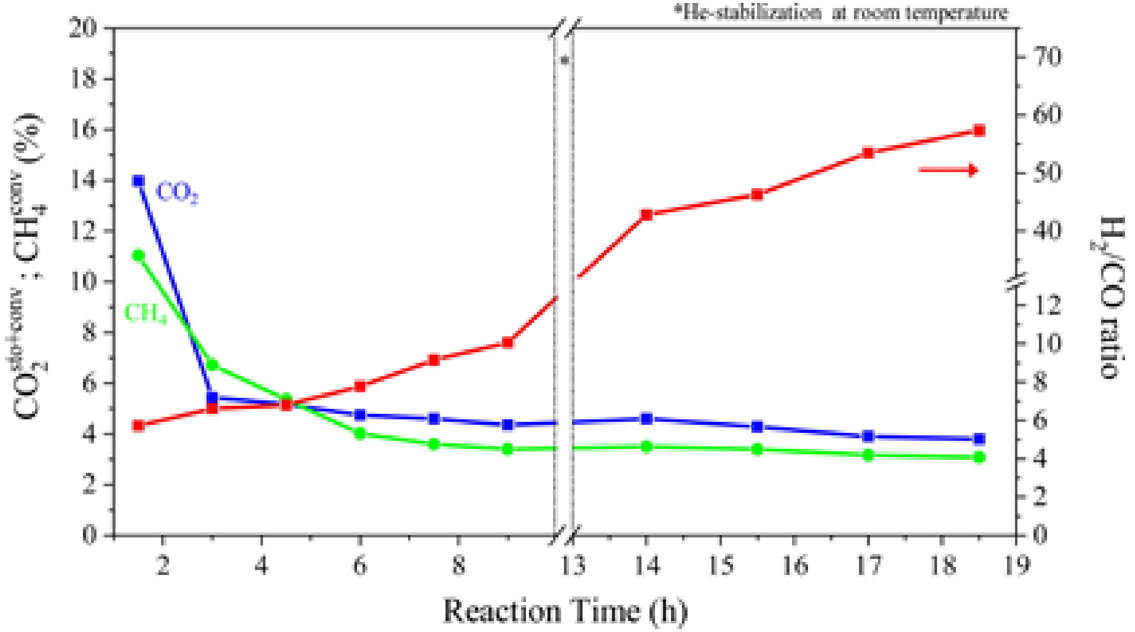
CO_2 storage and in situ regeneration with CH_4 over a model **NiBa (1/1)** catalyst





Type I



CO_2-Storage

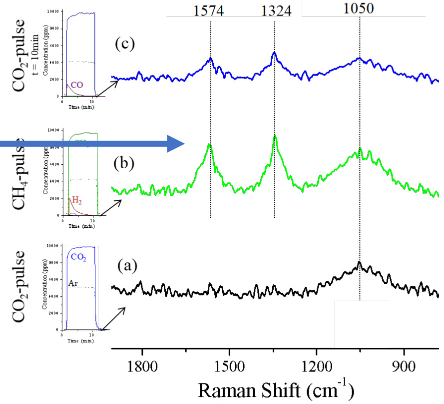
$2CO_{2\,(g)} \rightarrow CO_2^{sto} + (CO_{(g)} + {}^*O)$

$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$

CH_4-Regeneration

$CH_{4(g)} + CO_2^{sto} \rightarrow 2H_{2(g)} + 2CO_{(g)}$

$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)}$



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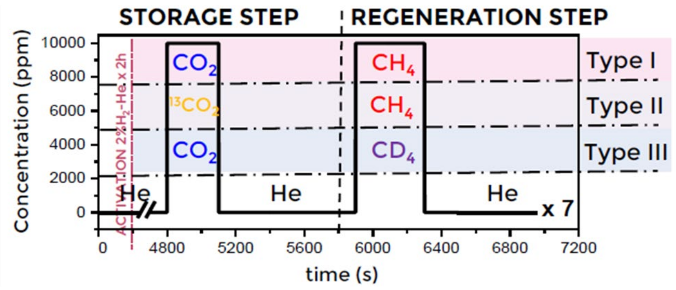
CO_2 storage and in situ regeneration with CH_4 over a model **NiBa (1/1)** catalyst

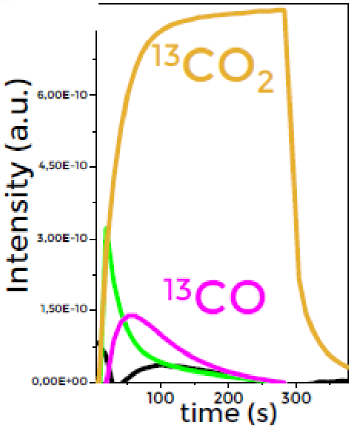


$^{13}CO_2 \rightarrow {}^{13}CO_2^{sto}(+{}^{13}CO+O^*)$

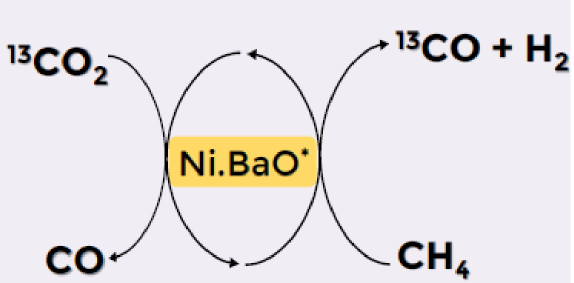
$^{13}CO_2 + C \rightarrow \boxed{CO+{}^{13}CO}$

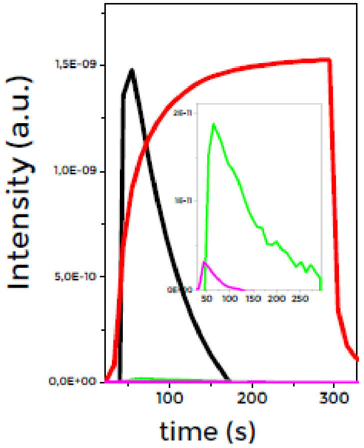
$^{13}CO_2 + H_2 \rightarrow {}^{13}CO + H_2O$

$H_2O + C \rightarrow 2CO + H_2$



TYPE II





$CH_4 + {}^{13}CO_2^{sto} \rightarrow \boxed{CO+13CO} + 2H_2$

$CH_4 \rightarrow C + 2H_2$

$^{13}CO_2^{sto} + H_2 \rightarrow {}^{13}CO + H_2O$

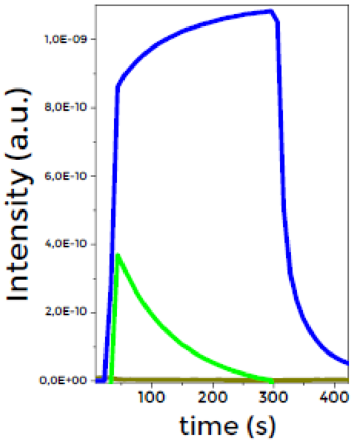
$H_2 + O^* \rightarrow H_2O$

$CO_2 \rightarrow CO_2^{sto}(+CO+O^*)$

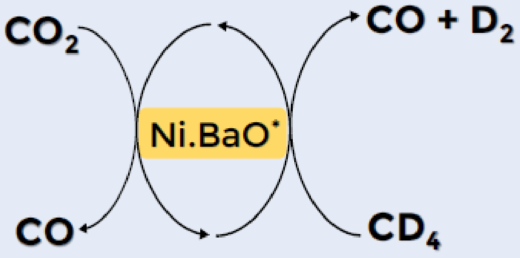
$CO_2 + C \rightarrow 2CO$

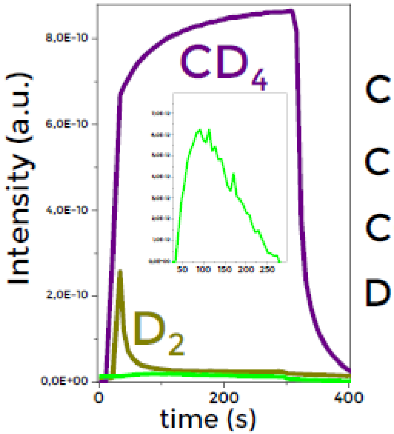
$CO_2 + D_2 \rightarrow CO + D_2O$

$D_2O + C \rightarrow 2CO + D_2$



TYPE III





$CD_4 + CO_2^{sto} \rightarrow 2CO + 2D_2$

$CD_4 \rightarrow C + 2H_2$

$CO_2^{sto} + D_2 \rightarrow CO + D_2O$

$D_2 + O^* \rightarrow D_2O$

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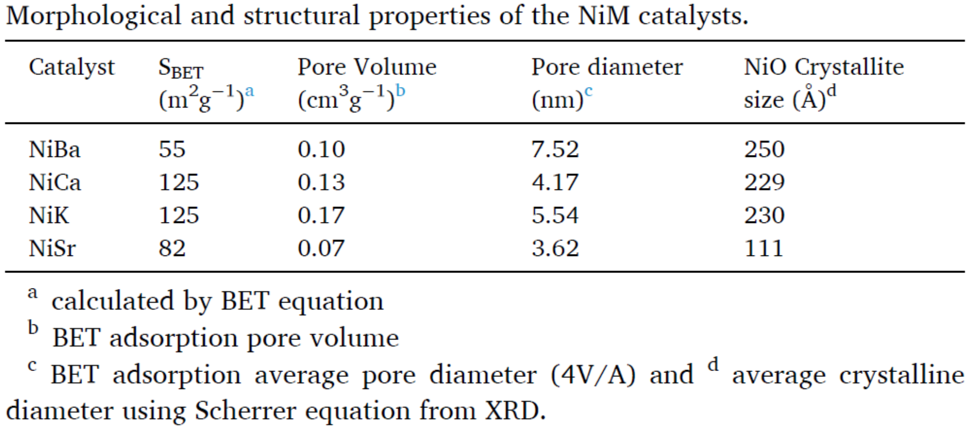
Influence of second metal incorporation Ni-(Ba, K, Ca, Sr), 10/1



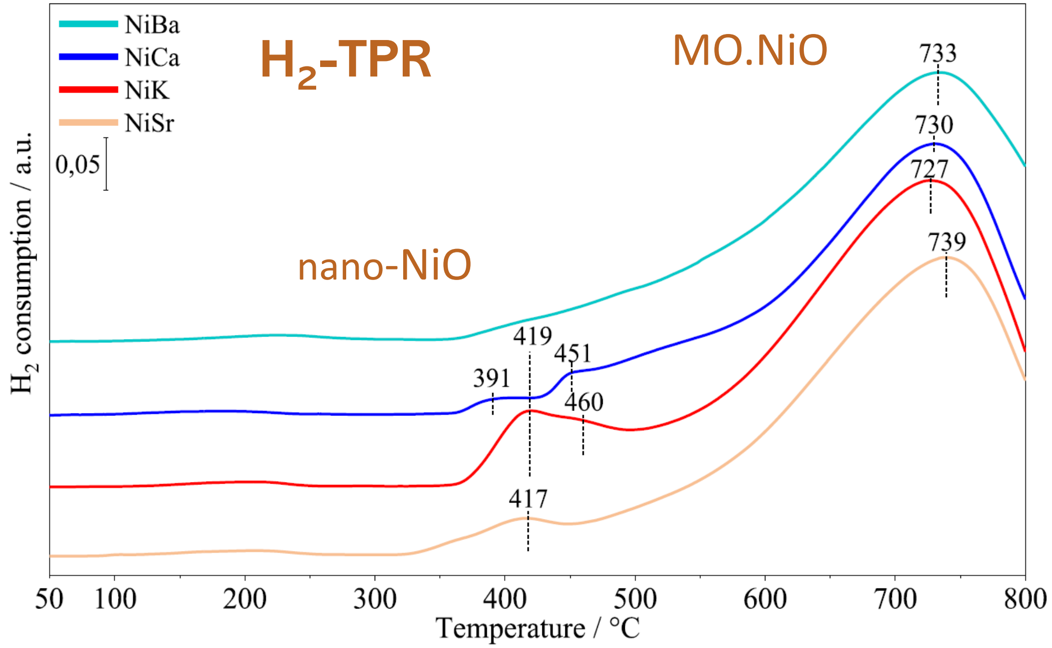
Morphological and structural properties of the NiM catalysts.

Catalyst	S_{BET} (m^2g^{-1})[a]	Pore Volume (cm^3g^{-1})[b]	Pore diameter (nm)[c]	NiO Crystallite size (Å)[d]
NiBa	55	0.10	7.52	250
NiCa	125	0.13	4.17	229
NiK	125	0.17	5.54	230
NiSr	82	0.07	3.62	111

[a] calculated by BET equation

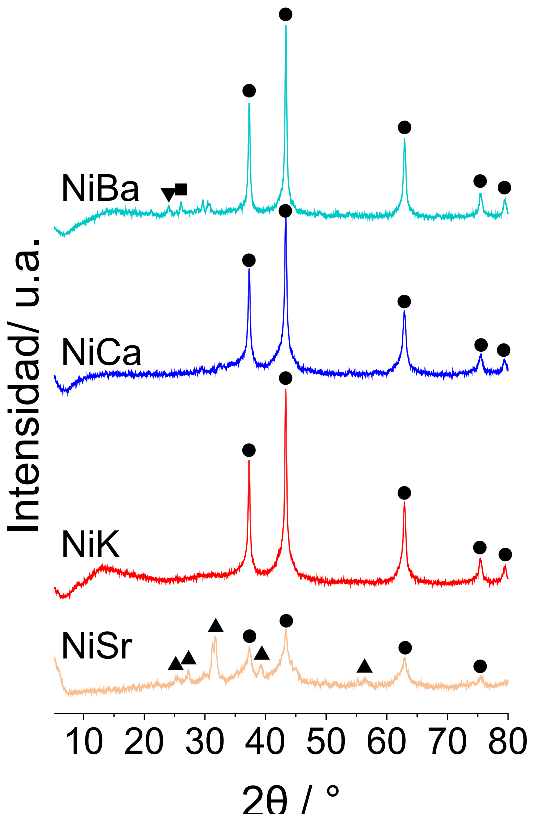
[b] BET adsorption pore volume

[c] BET adsorption average pore diameter (4V/A) and [d] average crystalline diameter using Scherrer equation from XRD.



XRD

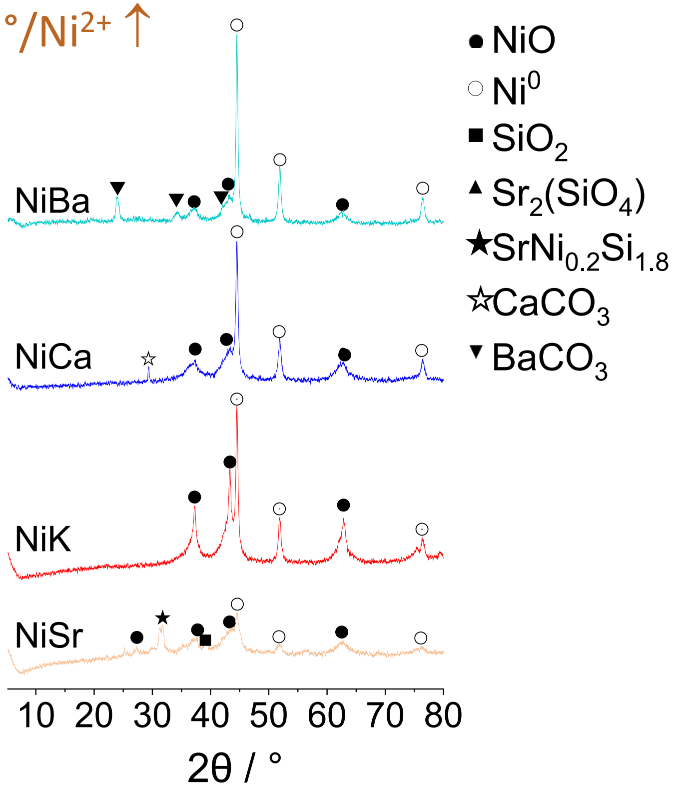
Calcined @800°C, air



Reduced, @500°C, H_2/He

NiBa and NiCa

Ni°/Ni^{2+} ↑



Ni $2p_3/_2$ peak Ni^{2+} (855,1-855,9 eV) Ba<Ca<K<Sr

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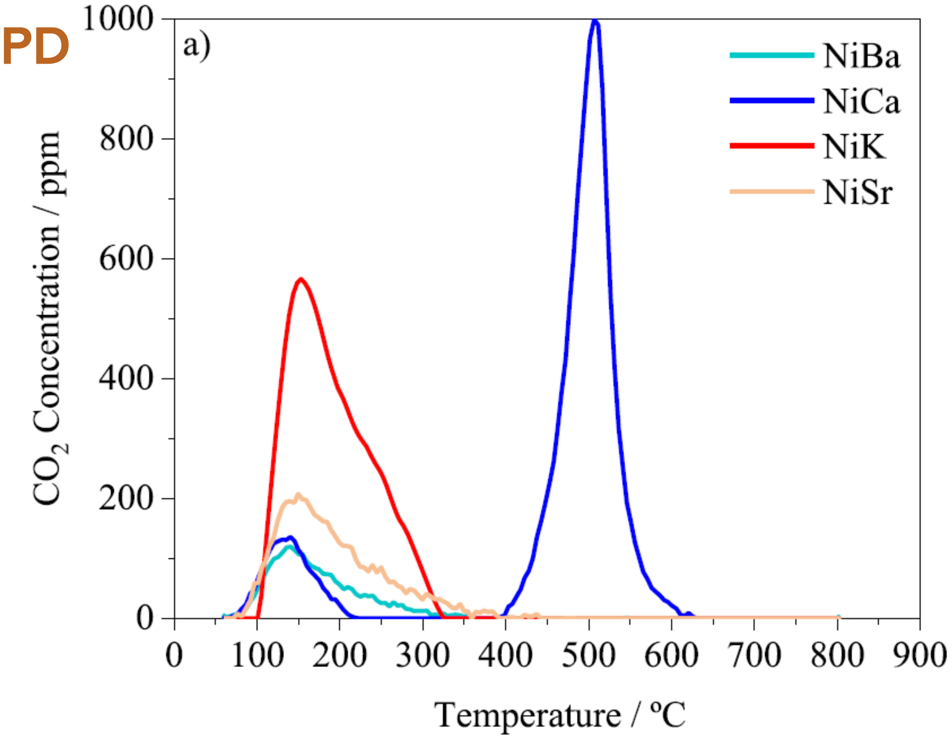
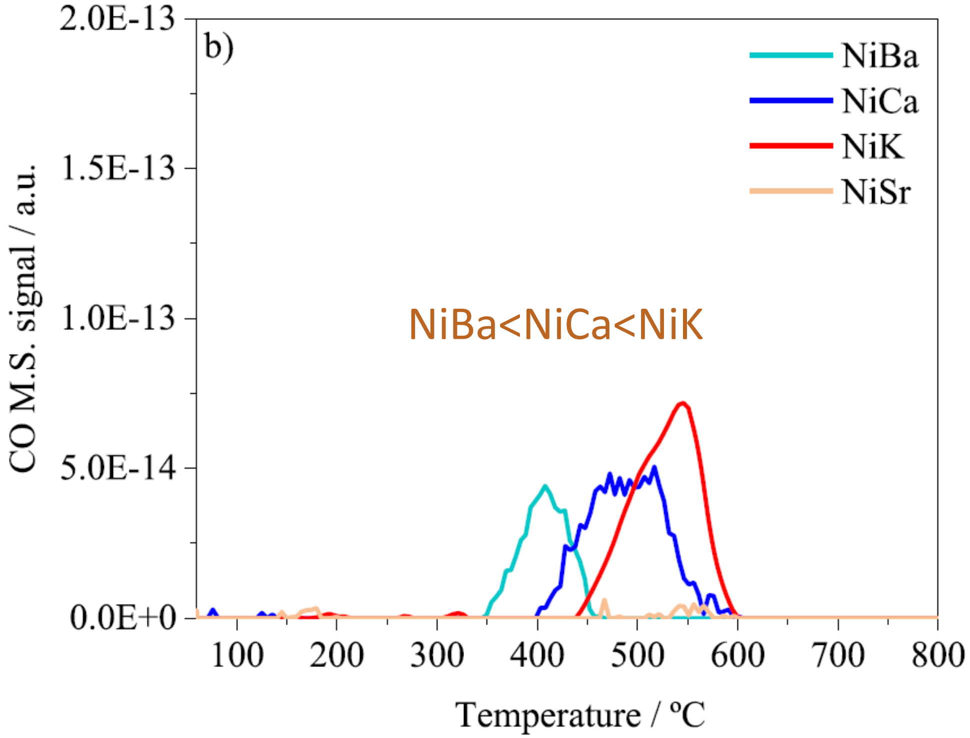
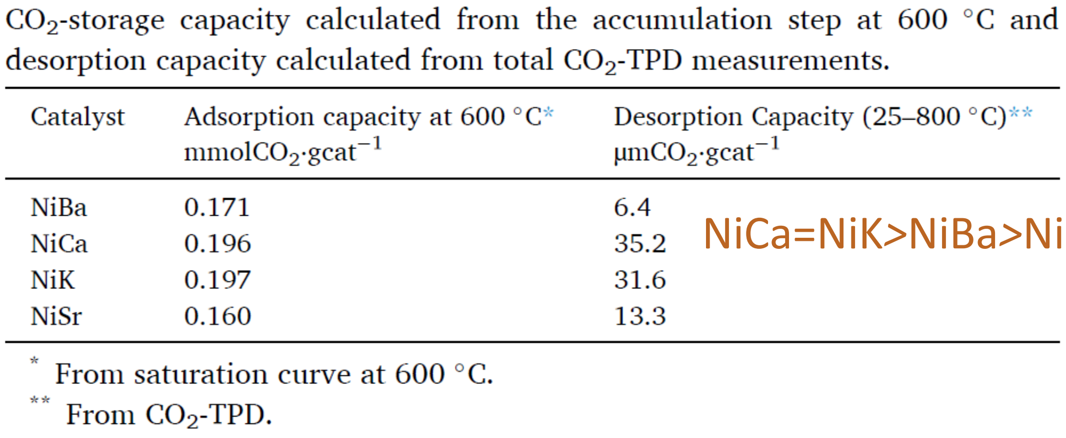
Influence of second metal incorporation Ni-(Ba, K, Ca, Sr), 10/1

CO_2-TPD





NiBa<NiCa<NiK



CO_2-storage capacity calculated from the accumulation step at 600 °C and desorption capacity calculated from total CO_2-TPD measurements.

Catalyst	Adsorption capacity at 600 °C* mmolCO_2·gcat^{-1}	Desorption Capacity (25–800 °C)** μmCO_2·gcat^{-1}
NiBa	0.171	6.4
NiCa	0.196	35.2
NiK	0.197	31.6
NiSr	0.160	13.3

[*] From saturation curve at 600 °C.

[**] From CO_2-TPD.

NiCa=NiK>NiBa>NiSr

Ni $2p_{3/2}$ peak (855,1-855,9 eV) Ba<Ca<K<Sr

The CO_2 removal efficiency and product distribution are influenced not only by the density and strength of surface basic sites, but also by the redox properties of the Ni–M systems

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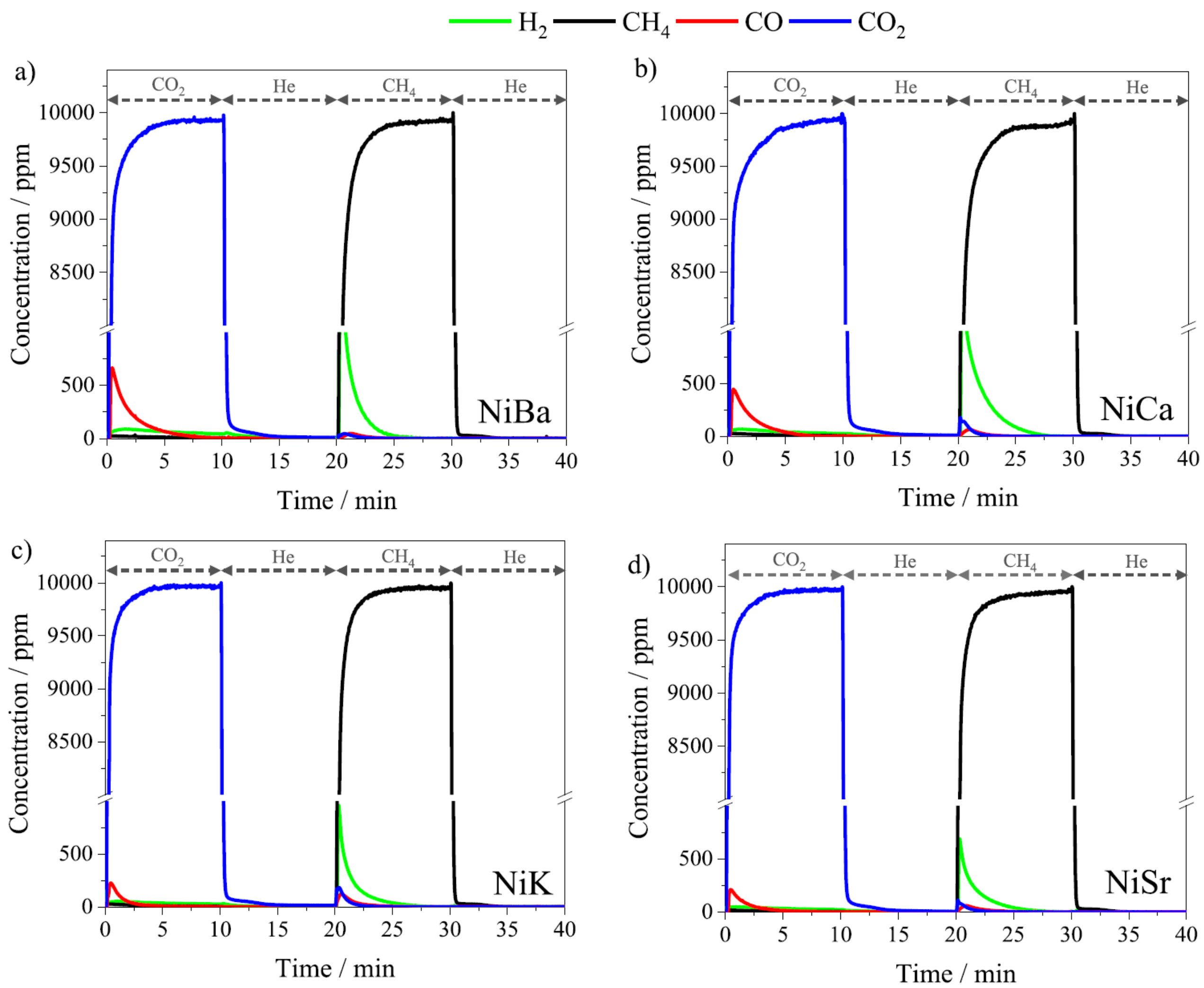
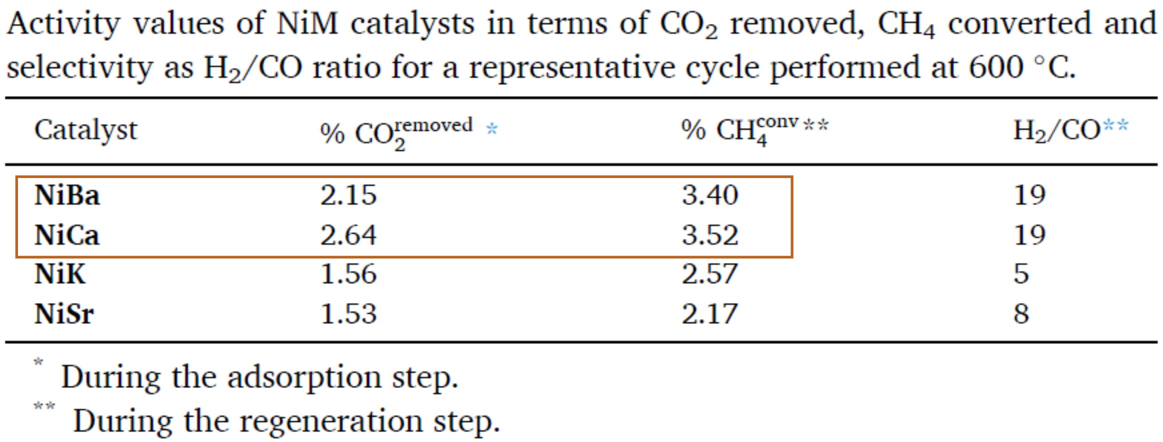
Influence of second metal incorporation Ni-(Ba, K, Ca, Sr), 10/1



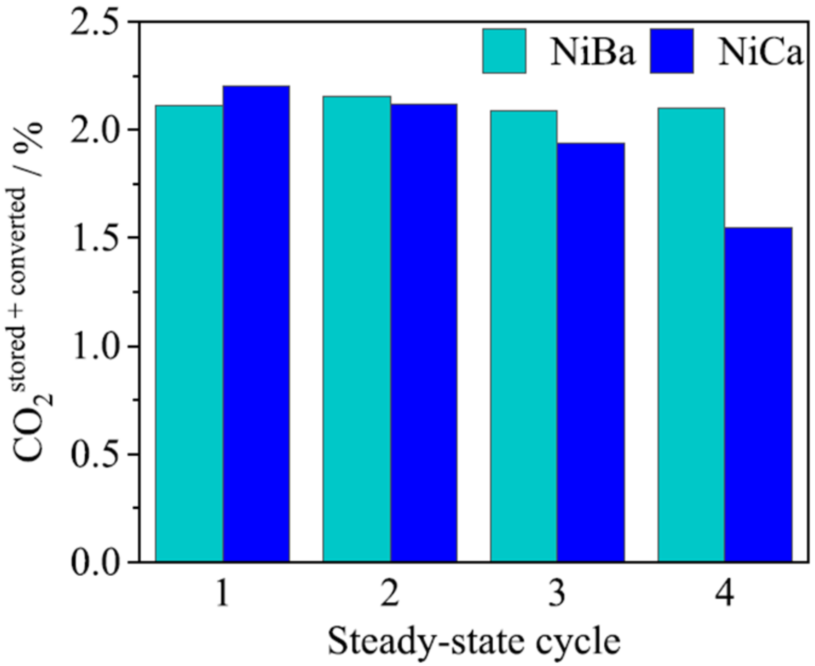


Activity values of NiM catalysts in terms of CO_2 removed, CH_4 converted and selectivity as H_2/CO ratio for a representative cycle performed at 600 °C.

Catalyst	% $CO_2^{removed}$ *	% CH_4^{conv} **	H_2/CO**
NiBa	2.15	3.40	19
NiCa	2.64	3.52	19
NiK	1.56	2.57	5
NiSr	1.53	2.17	8

[*] During the adsorption step.

[**] During the regeneration step.



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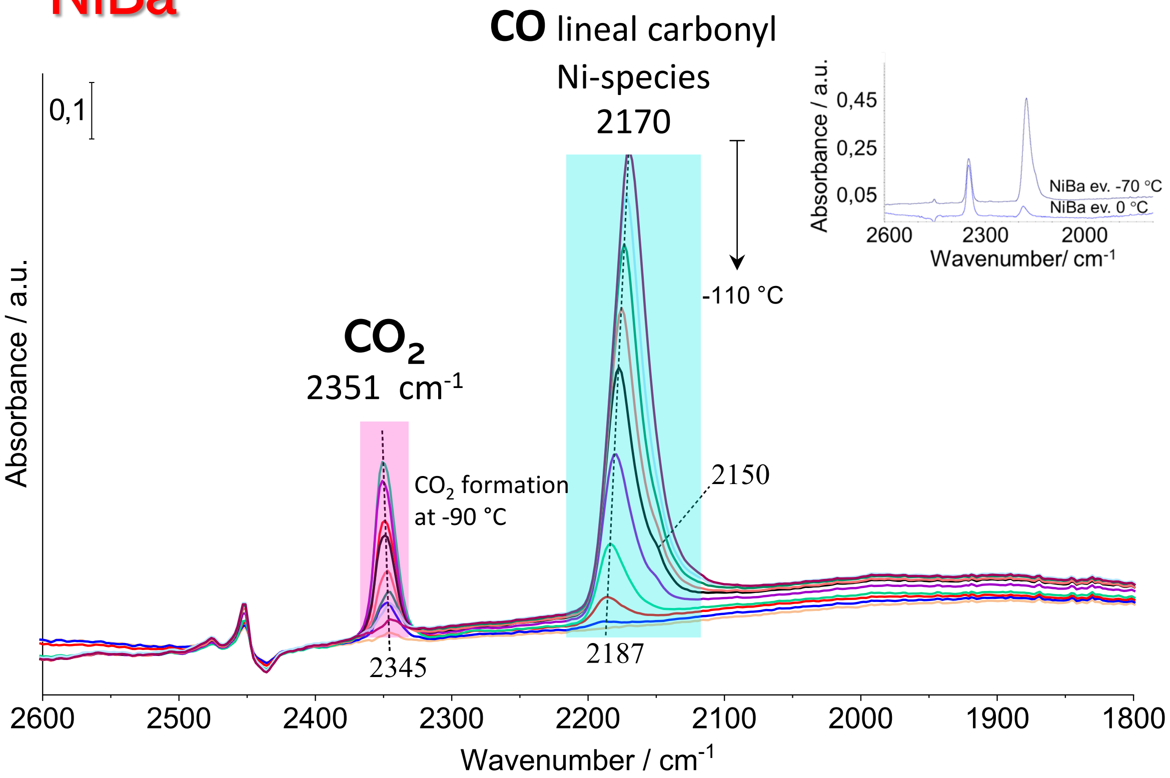
Study of oxygen mobility in bimetallic NiBa and NiK, 10/1

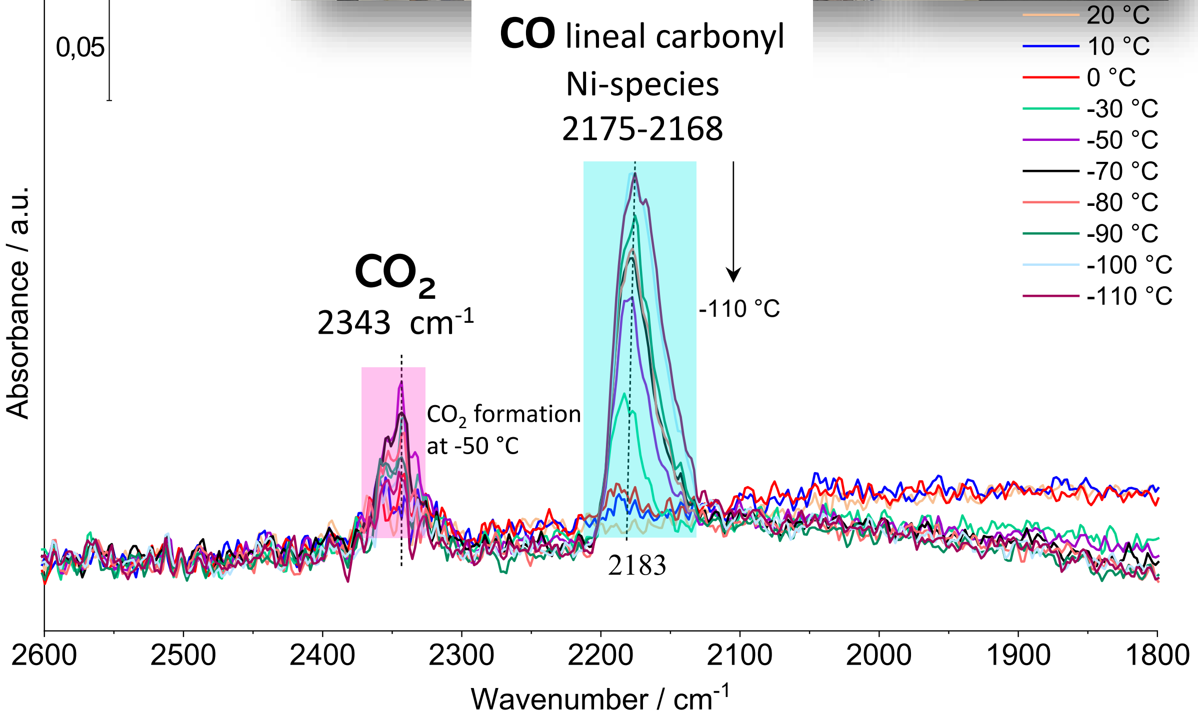
CO adsorption– FTIR *in situ*

5 Torr CO, -110°C to r.t.. ,evacuation 10^{-3}Pa

NiBa



NiK



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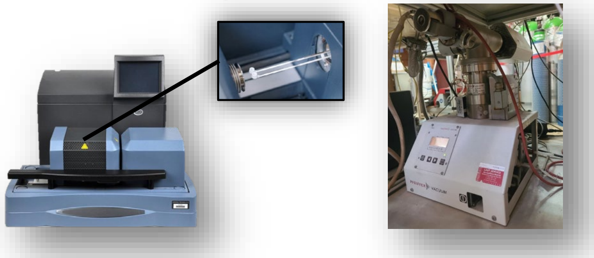
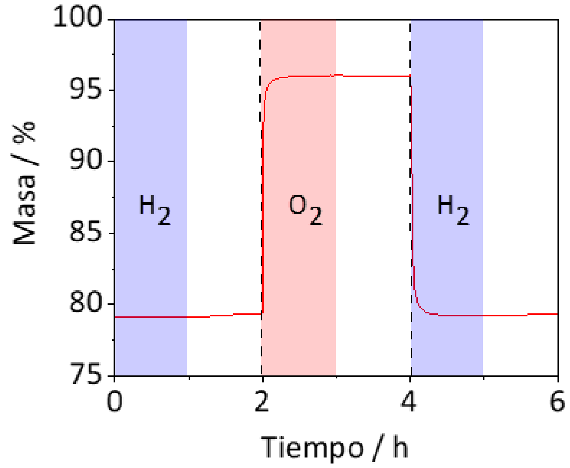
Study of oxygen mobility in bimetallic NiBa and NiK, 10/1

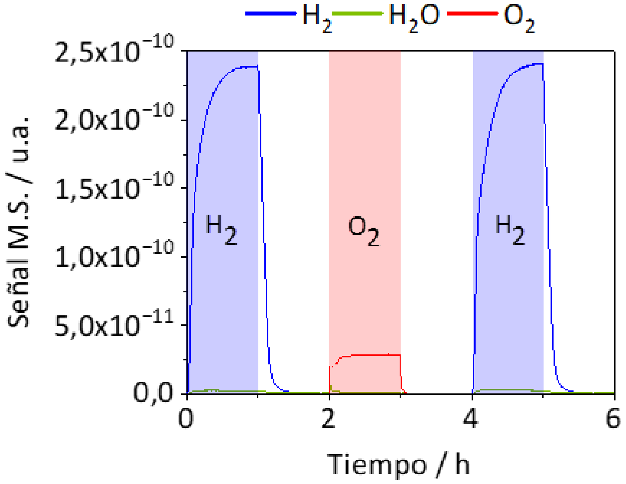
Cycles TG-MS O_2-H_2

Activation *in situ*:
@600 °C; 1 h; 3 % H_2/He
100 ml·min^{-1} (3 ml·min^{-1} He/O_2/H_2)

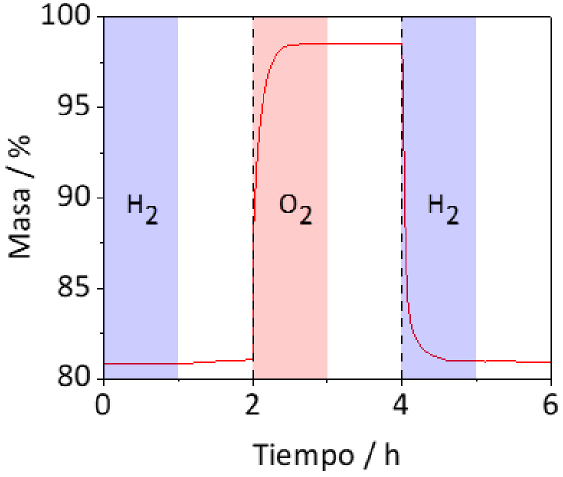


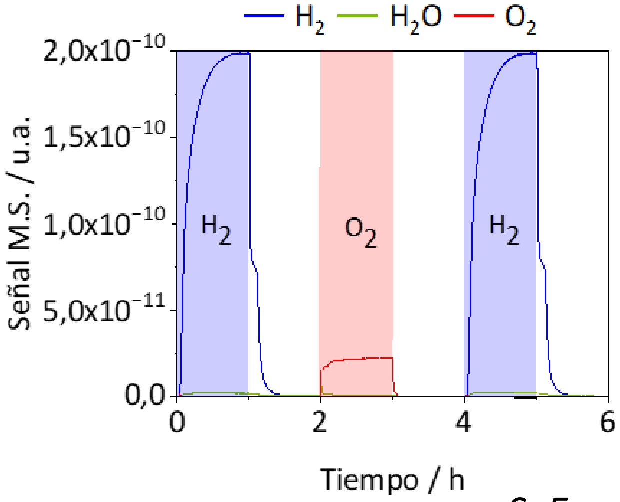
NiBa

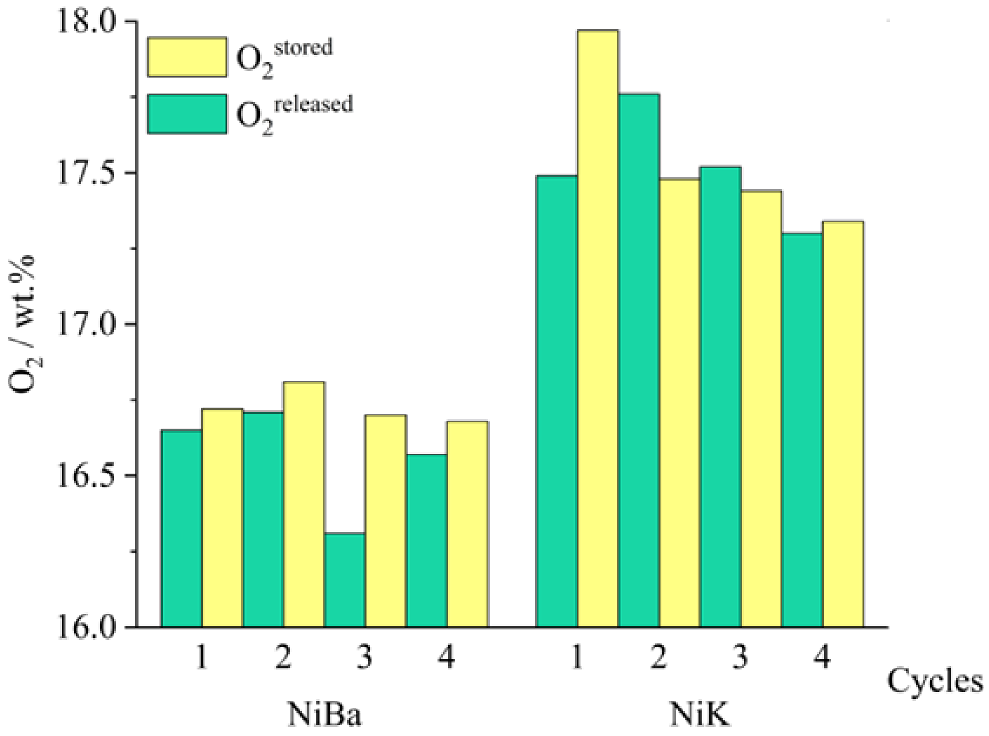




NiK







Reversible oxygen exchange

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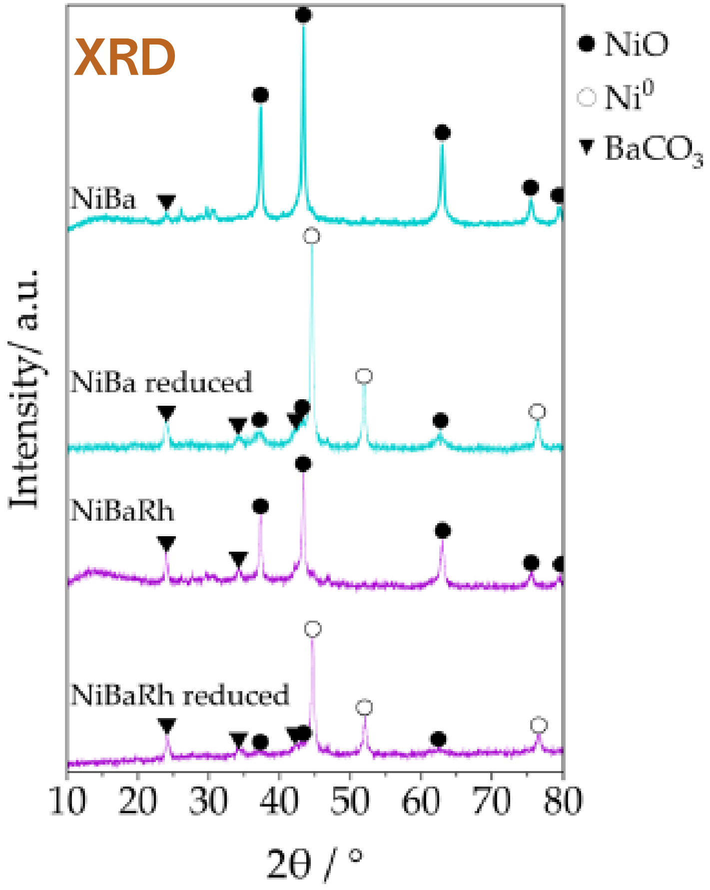
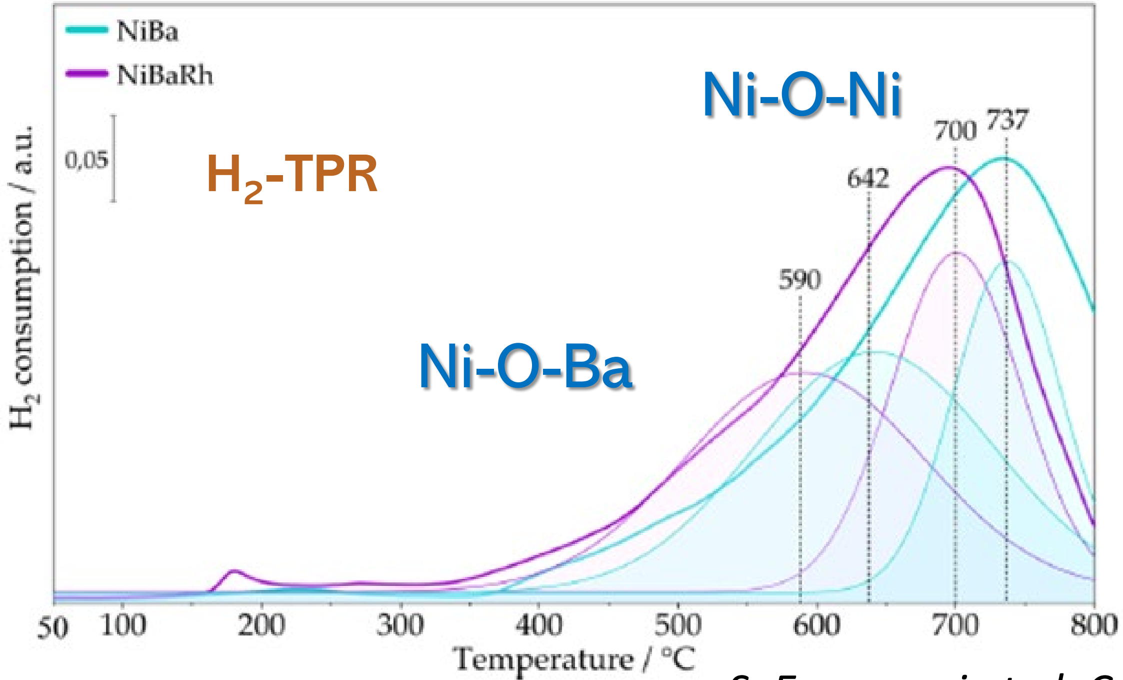
Role of Ni/Ba Surface Domains and Rh Promotion

NiBa 1/1
NiBa 10/1
NiBaRh 10/2/0,1
NiBaRh 10/1/0,1

	A_{BET} [a]	V_p [b]	* d_p [c]	NiO crystal size [d]	Ni/Ba [e]	Ni/Rh [e]
	$m^2 \cdot g^{-1}$	$cm^3 \cdot g^{-1}$	Å	Å	-	-
NiBa 10/1	55	0.10	75.2	250.4	9.5/1	-
NiBaRh 10/2/0.1	64	0.09	57.3	231.5	4.6/1	93.6/1

[a] calculated by BET equation, [b] BET adsorption pore volume, [c] BET adsorption average pore diameter (4V/A) [d] average crystalline diameter using Scherrer equation from XRD and [e] from XPS measurements.





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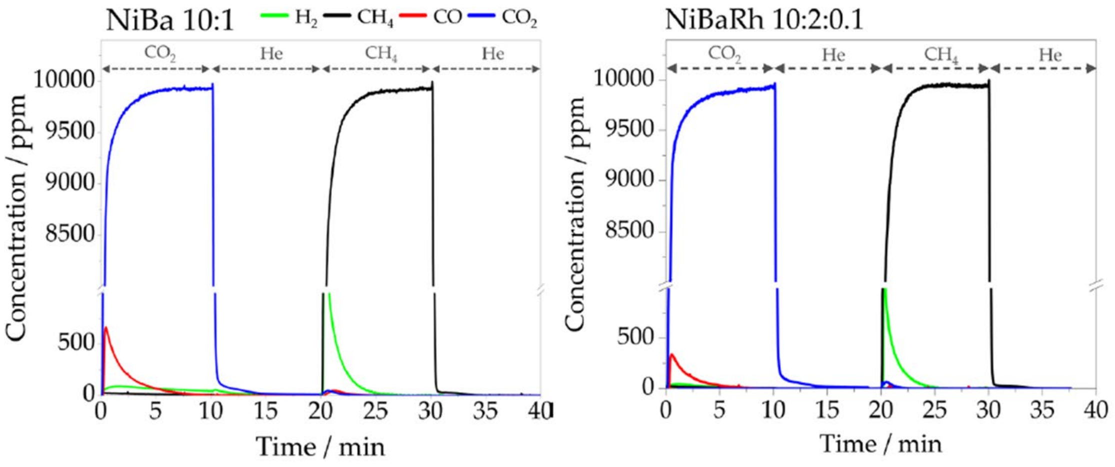
Role of Ni/Ba Surface Domains and Rh Promotion

NiBa 1/1
NiBa 10/1
NiBaRh 10/2/0,1
NiBaRh 10/1/0,1



	Cycle CO_2		Cycle CH_4	
	mmol $CO_2 \cdot g^{-1}_{cat}$	X_{CO2}	H_2/CO	X_{CH4}
NiBa 10/1	0.146	1.84	3.95	3.21
NiBaRh 10/2/0.1	0.159	2.06	15.8	2.86
NiBaRh 10/1/0.1	0.230	2.81	0.81	2.69
NiBa 1/1	0.253	2.87	0.07	2.40

$$BaO + CO_2 \rightarrow BaCO_3$$

$$CO_2 + Ni \rightarrow CO + Ni{-}O$$

$$CH_4 \rightarrow C^* + 2H_2$$

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$

S. Essounani et al. Catalysts, submitted

Conclusions

- The results demonstrate that the catalytic performance of these materials is determined by the structural organization of the Ni–Alkaline interface and the stability of the carbonate species formed during operation.

- These results highlight the importance of controlling the oxygen mobility for the rational design of multifunctional catalysts capable of coupling cyclic CO_2 capture and catalytic conversion in CO_2-SR processes

CO_2-SR Ciclyc Technology: Capture and Conversion of CO_2 with hybrid catalysts for storage and conversion with methane (CO_2-SR)

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