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Oxidative Dry Reforming of CH_4 on Ni supported Ca-modified ZrO_2 catalysts with different crystalline phases

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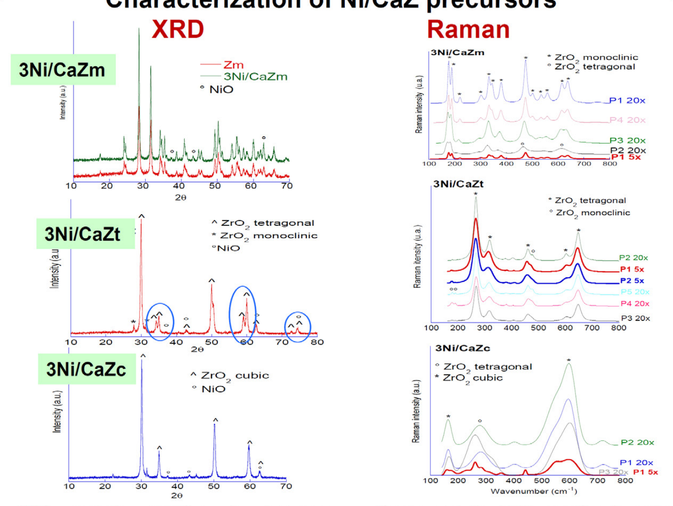
Introduction

Hydrogen industrial production as syngas via CH_4-steam reforming is energy-intensive process and often limited to large-scale plants. Methane Oxidative Dry Reforming (CH_4-ODR) offers a synergistic alternative by combining exothermic catalytic partial oxidation (CPO) with endothermic dry reforming (DR), thereby reducing energy consumption and mitigating catalyst deactivation through the oxidation of coke deposits. Meanwhile it contributes to CO_2 utilization, with ensuing emission reduction into the atmosphere.

Nickel is widely recognized as the preferred active phase for these reactions, although it is prone to sintering and carbon deposition. The aim of this work, part of a fundamental study involving Ni/ZrO_2 catalysts resistant to sintering and carbon deposition in the CH_4-CPO reaction[1], is to clarify both the influence of the ZrO_2 support crystalline phase (monoclinic, tetragonal, or cubic) and the contribution of the addition of Ca^{2+} species as a basic and structural promoter on the reactivity of the supported Ni species both for syngas production and CO_2 valorization via CH_4-ODR.

Characterization of Ni/CaZ precursors



XRD analysis, sensitive to long-range periodicity, indicated successful preparation of catalysts with the desired phase

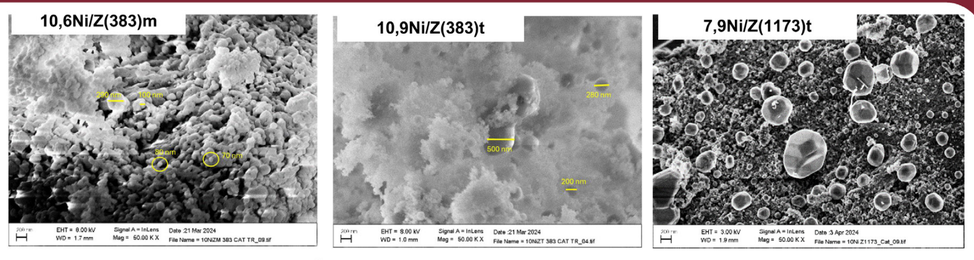
- Ca^{2+} acted as structural promoter stabilizing the cubic phase (solid solution formation)

Raman analysis, highly sensitive to probe short-range order without long-range periodicity, revealed the coexistence of different ZrO_2 phases in the various samples.

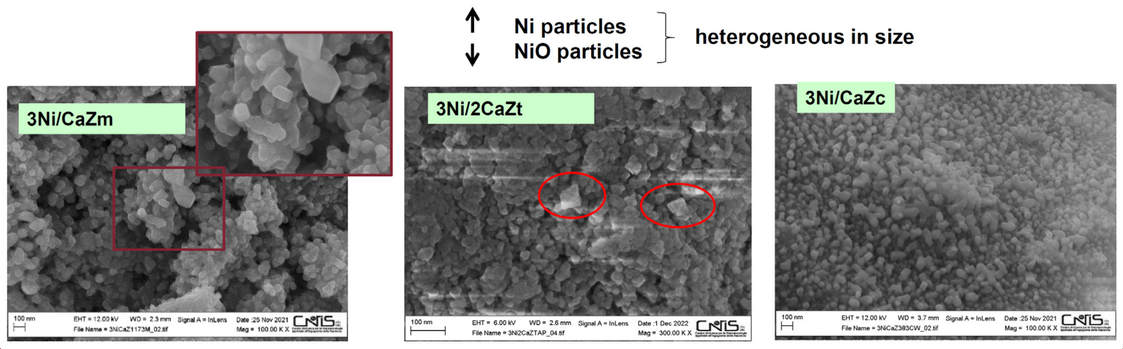
FE-SEM

$d_{Ni} \leq d_{NiO}$: No sintering of Ni particles under catalytic tests

$d_{XRD} < d_{SEM}$: Ni particles are crystallites aggregates



↑ Ni particles
↓ NiO particles
} heterogeneous in size



Catalysts features

Catalysts	S.A. ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Crystallites mean diameter, d_{XRD} (nm)		Ni particle diameter range, d_{SEM} (nm)	
			NiO	Ni	NiO	Ni (post cat.)
Z_{hy}	360					
Zm	5.6	0.041				
10.6NiO/Z(383)m	4.5	0.039	36	45	50÷300	40÷300
10.9NiO/Z(383)t			34	38	60÷150	30÷500
7.9NiO/Z(1173)t			41	47	100÷300	10÷700
3Ni/CaZm	4.8	0,035	45	n.d.	30-150	
3Ni/CaZt	16.1	0,073	28	26	20-40	
3Ni/2CaZt	17.5	0,071	30	n.d.	20-40	
3Ni/CaZc	12.6	0,074	32	n.d.	20-40	

in situ FTIR characterization of Ni/CaZ precursors — CO adsorption at RT

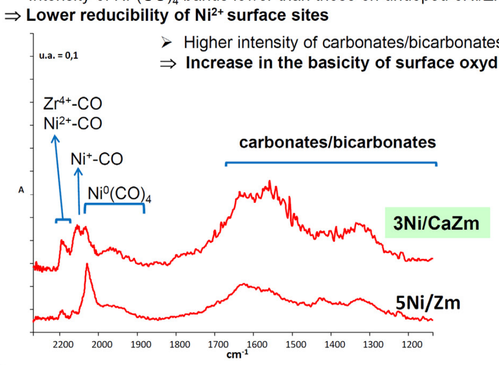
(p_{CO} ~ 100 Torr)

Monoclinic samples

- Intensity of $Ni^0(CO)_4$ bands lower than those on undoped 5Ni/Zm

⇒ **Lower reducibility of Ni^{2+} surface sites**

- ➢ Higher intensity of carbonates/bicarbonates bands
- ⇒ **Increase in the basicity of surface oxydic sites**



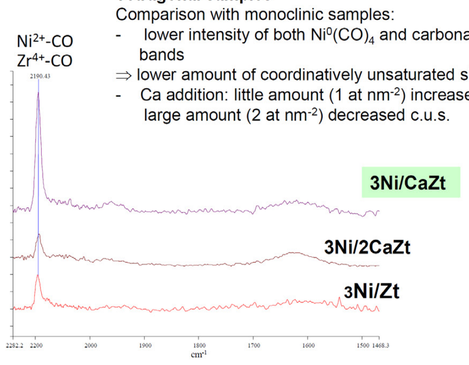
Tetragonal samples

Comparison with monoclinic samples:

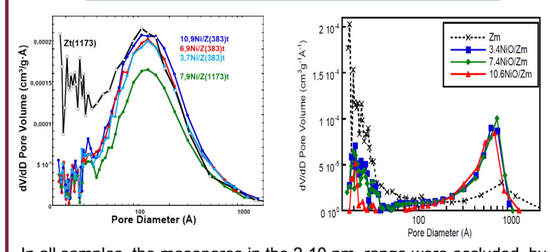
- lower intensity of both $Ni^0(CO)_4$ and carbonates/bicarbonates bands

⇒ lower amount of coordinatively unsaturated sites adsorbing CO

- Ca addition: little amount (1 at nm^{-2}) increased c.u.s. amount, large amount (2 at nm^{-2}) decreased c.u.s.



Pore size distribution



In all samples, the mesopores in the 2-10 nm range were occluded by NiO particles.

Tetragonal Ni/Z samples
- pores >10 nm unchanged

Monoclinic samples
- Ni addition opened pores >10 nm

Ni/Z catalysts with different crystalline phase

H_2-TPR characterisation

Ca-modified catalysts - Ni ~ 3 wt%

- **TPR(1) : $NiO + H_2 \rightarrow Ni^0 + H_2O$**

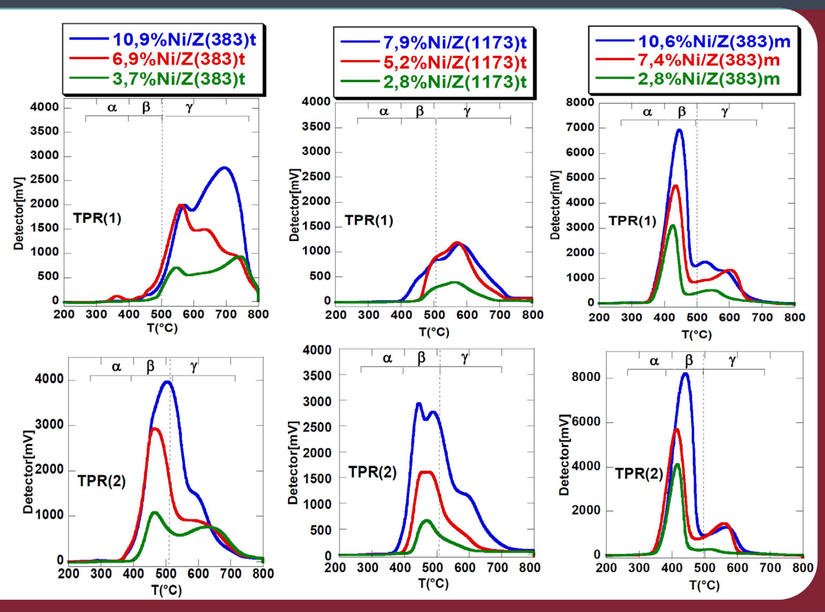
NiO reducibility in Ni/Z:

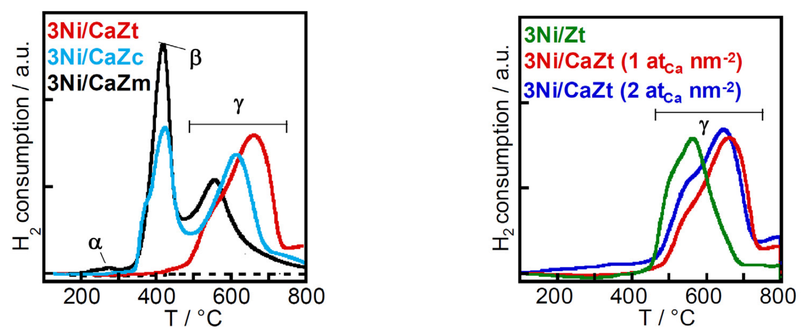
- ✓ The crystalline phase affected the fraction of NiO reduced at high temperature, strongly interacting with the support (γ-species): the γ fraction was larger in the order: **Ni/Z(383)t > Ni/Z(1173)t > Ni/Zm**
- ✓ Different support phase showed different NiO-support interaction
- ✓ Little dependence on Ni content: samples with different NiO loading showed similar heterogeneity (β and γ species)

- **TPO + TPR(2)**

Redox behaviour of stabilized Ni metal particles:

- ✓ On all samples, the fraction of γ species decreased becoming β species.





- The fraction of hardly reducible NiO species (γ species), with strong NiO-support interaction, was larger in the order: **Ni/CaZt > Ni/CaZc > Ni/CaZm**
- In the tetragonal Ni/CaZt catalyst, the fraction of strongly interacting γ-species was larger in the sample containing 1 Ca^{2+} atom nm^{-2}.

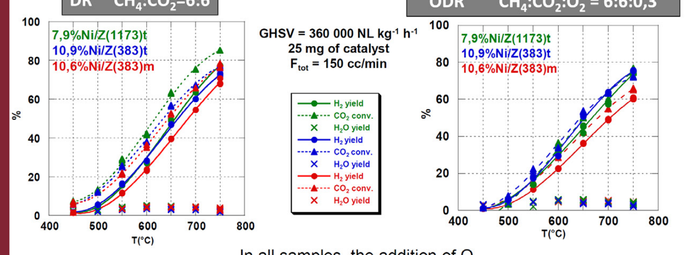
Catalytic activity of Ni/Z for CH_4-ODR

Catalysts with different crystalline phase: ODR *vs* DR on concentrated samples

…as a function of temperature

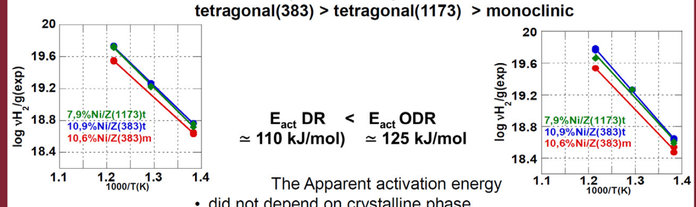
DR $CH_4:CO_2$=6:6 — ODR $CH_4:CO_2:O_2$ = 6:6:0,3

GHSV = 360 000 NL kg^{-1} h^{-1}
25 mg of catalyst
F_{tot} = 150 cc/min



In all samples, the addition of O_2
- ➢ little decreased the activity for H_2 production
  - CPO and combustion competed with DR
- ➢ limited the activity for the undesired Reverse Water Gas Shift

ODR activity of Ni/Z catalysts followed the order:
tetragonal(383) > tetragonal(1173) > monoclinic



E_{act} DR < E_{act} ODR
≃ 110 kJ/mol) ≃ 125 kJ/mol

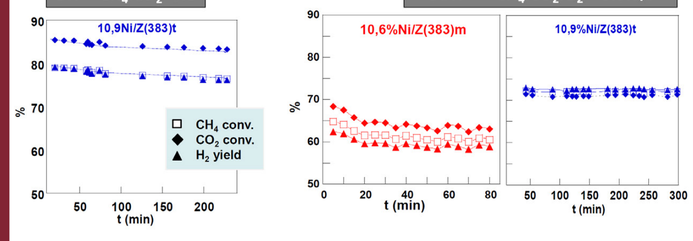
The Apparent activation energy
- did not depend on crystalline phase
  ⇒ active sites of the same types;
- higher in ODR than in DR
  ⇒ active Ni sites affected by O_2 coverage

H_2 yield on	10,9Ni/Z(383)t_{AA}		10,6Ni/Z(383)m		7,9Ni/Z(1173)t_{AA}	
DR $CH_4:CO_2$	73→79	☺	65→69	☺	77→79	☺
ODR $CH_4:O_2:CO_2$	73→76	☺	62→80	☺	69→74	☺

- **H_2 yield increased in consecutive runs for both DR and ODR:**
  ⇒ Useful particles' rearrangement

…as a function of time

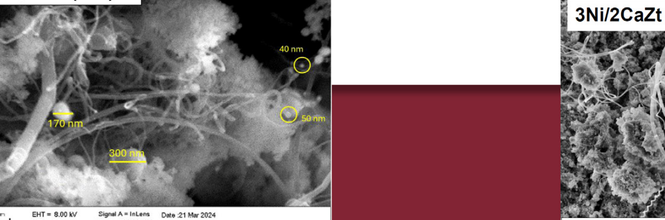
DR $CH_4:CO_2$=6:6 — ODR $CH_4:CO_2:O_2$ = 6:6:0,3



- ➢ poor stability of tetragonal catalyst for DR
- ➢ good stability of tetragonal catalyst for ODR

Catalysts with different Ni loading

Monoclinic Ni/Z(383)m — **Tetragonal Ni/Z(383)t**

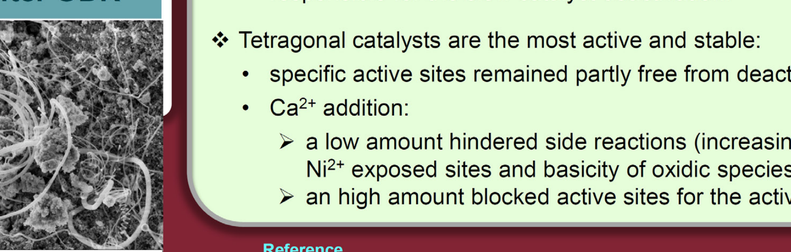


- the amount of Ni active sites increased with Ni content
- active Ni sites was already present at low loading

⇒ **Crystalline phase is crucial for determining Ni sites reactivity!**

Ca-modified catalysts - Ni ~ 3 wt%

$CH_4 : CO_2 : O_2$ = 2 : 1.5 : 0.25 (%v/V) ,
GHSV = 360 000 NL kg^{-1} h^{-1}

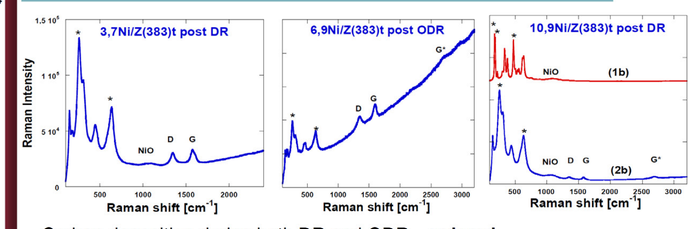


ODR activity of Ca-modified catalysts followed the order:
tetragonal > cubic > monoclinic

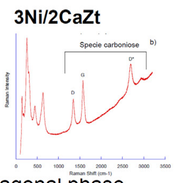
Larger amount of Ca (2 Ca^{2+} atom/nm^2) blocked CH_4 and CO_2 activation, especially below 550 °C

A low amount of Ca^{2+} (1 Ca^{2+} atom/nm^2) on the tetragonal surface increased CO_2 conversion, and H_2 yield and selectivity.

Raman characterization on used catalyst



- ➢ Presence of NiO nanoparticles, identified by the band at about 1080 cm^{-1} (2LO mode).



Carbon deposition during both DR and ODR - **ordered** (G, 1580 cm^{-1}, G*- II° order, 2690 cm^{-1}) **and disordered** (D, 1350 cm^{-1}) **graphitic species**

Favored
- on particles of tetragonal phase
- at higher Ca content

FE-SEM after DR

FE-SEM after ODR

Concluding remarks

- ❖ Ni^0 particle heterogeneity → dependence on the ZrO_2 crystalline phase both as size and interaction strength with the support
- ❖ CH_4-ODR activity in tetragonal and monoclinic catalysts:
  - different dependence on Ni loading
  - similar apparent activation energy
  - ⇒ active Ni^0 sites are only a small fraction of the exposed ones
  - ⇒ active Ni^0 sites are already formed at low loading in tetragonal samples.
- ❖ Carbon deposition - Raman and FESEM evidences
  - ordered carbon nanotubes formed on catalysts in the tetragonal phase
  - disordered carbon structures for cubic and monoclinic phases responsible for the slow catalyst deactivation.
- ❖ Tetragonal catalysts are the most active and stable:
  - specific active sites remained partly free from deactivating species.
  - Ca^{2+} addition:
    - ➢ a low amount hindered side reactions (increasing Lewis acidity of Ni^{2+} exposed sites and basicity of oxidic species)
    - ➢ an high amount blocked active sites for the activation of reactants.

Reference

1. Campa, M.C., Pettiti, I., Tuti, S., Luccisano, G., Ardemani, L., Luisetto, I., Gazzoli, D., Pietrogiacomi, D. *Materials* 2021, 14, 2495.