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CO_2 methanation over Ni nanoparticles dispersed on CeO_2 supports: the effect of support synthesis method and the resulting nano-configurations

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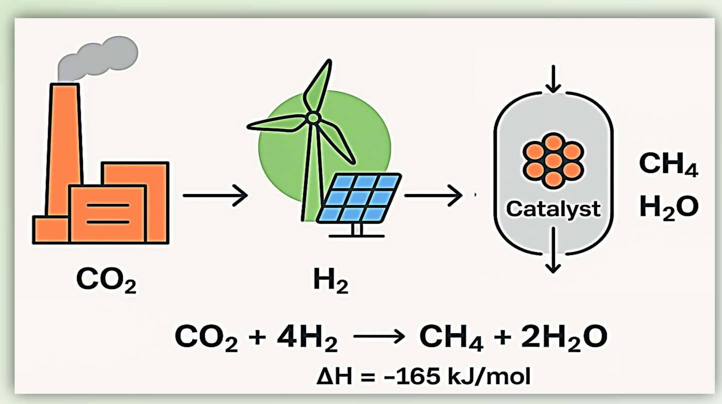
Motivation

CO_2 methanation reaction (Sabatier reaction), is an exothermic process that converts CO_2 into methane using H_2 as a reducing agent.



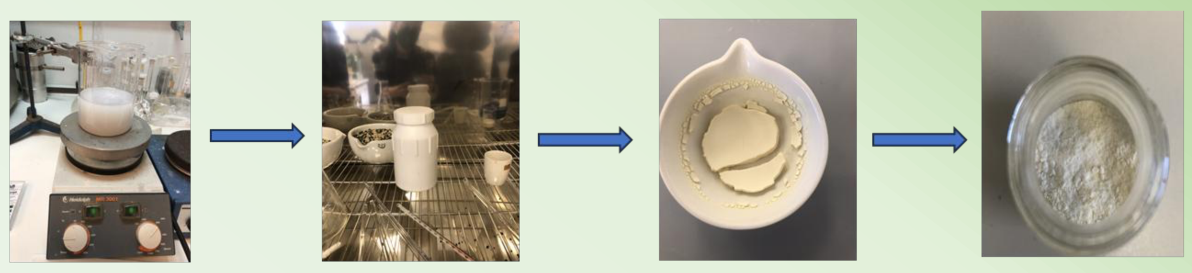
Sabatier reaction can be considered as an alternative strategy for capturing and recycling emitted CO_2, offering significant potential for reducing fossil fuel dependence and consequently lowering atmospheric CO_2 concentration levels. Additionally, it can serve as a safe and efficient method for storing and transporting H_2, as part of the Power-to-Gas (PtG) process. This approach helps overcome the safety challenges and high costs associated with transporting H_2 produced from renewable energy sources. In present study, the effect of the CeO_2 support synthesis method and the resulting CeO_2/Ni nanostructures were investigated. The catalytic performance and stability of the above materials were examined over CO_2 methanation reaction through kinetic experiments conducted over a temperature range of 150-600° C, as well as 12-hour stability tests at 380° C.

Synthesis

1) Synthesis of CeO_2 supports

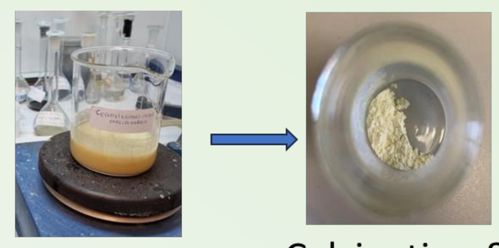
- **CeO_2-NR** (Hydrothermal method)

$Ce(NO_3)_3\cdot 6H_2O$
NaOH, H_2O



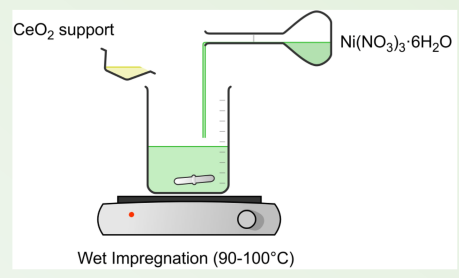
- **CeO_2-PR** (Co-precipitation method)

$Ce(NO_3)_3\cdot 6H_2O$
NH_3, H_2O



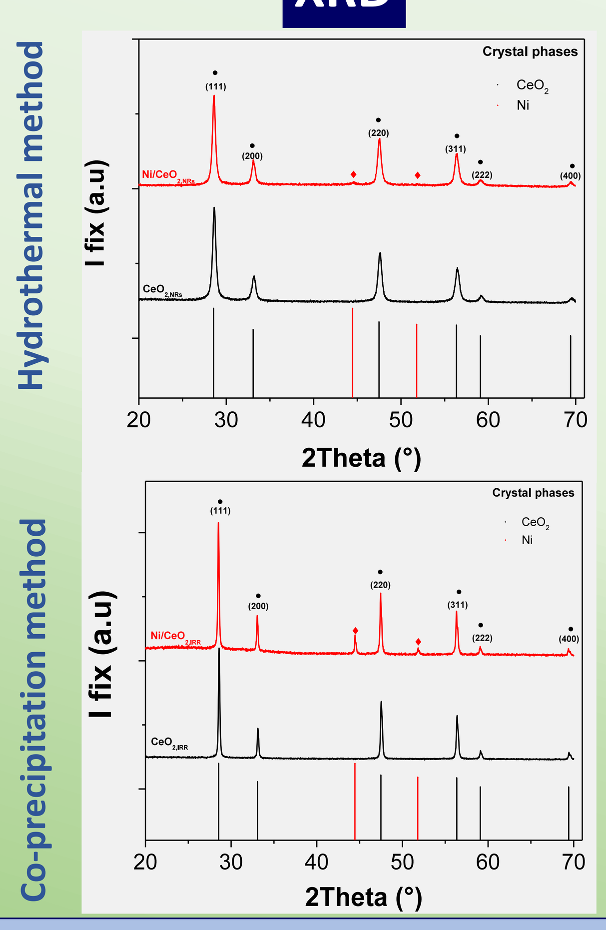
2) Synthesis of 10% Ni/CeO_2 catalysts (Wet impregnation)

The CeO_2 supports were impregnated with an aqueous $Ni(NO_3)_2\cdot 6H_2O$ solution to achieve a 10 wt.% Ni loading. After pH adjustment with ammonia, the mixture was dried and reduced in a 25% H_2/Ar flow at elevated temperatures to obtain the final Ni/CeO_2 catalysts.

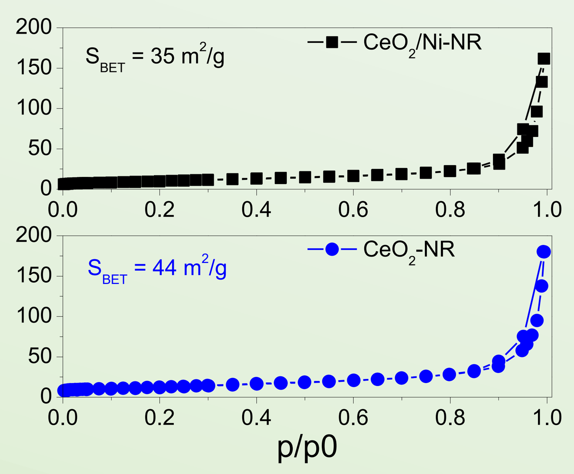


Materials Characterization

XRD

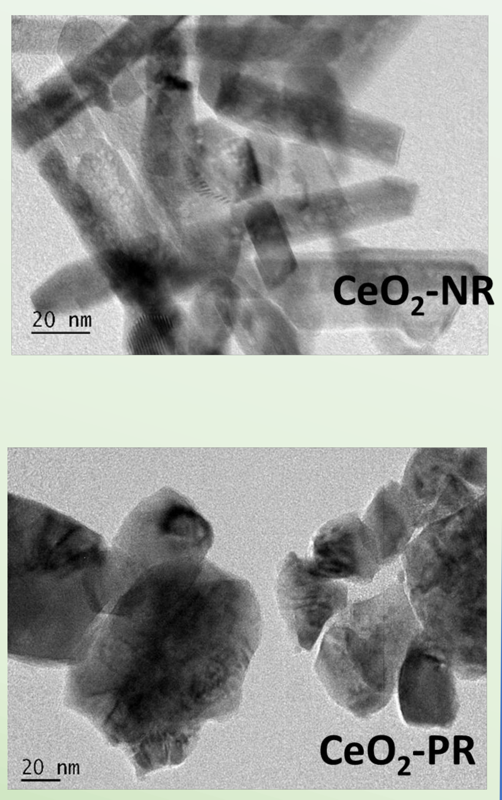


N_2 Porosimetry

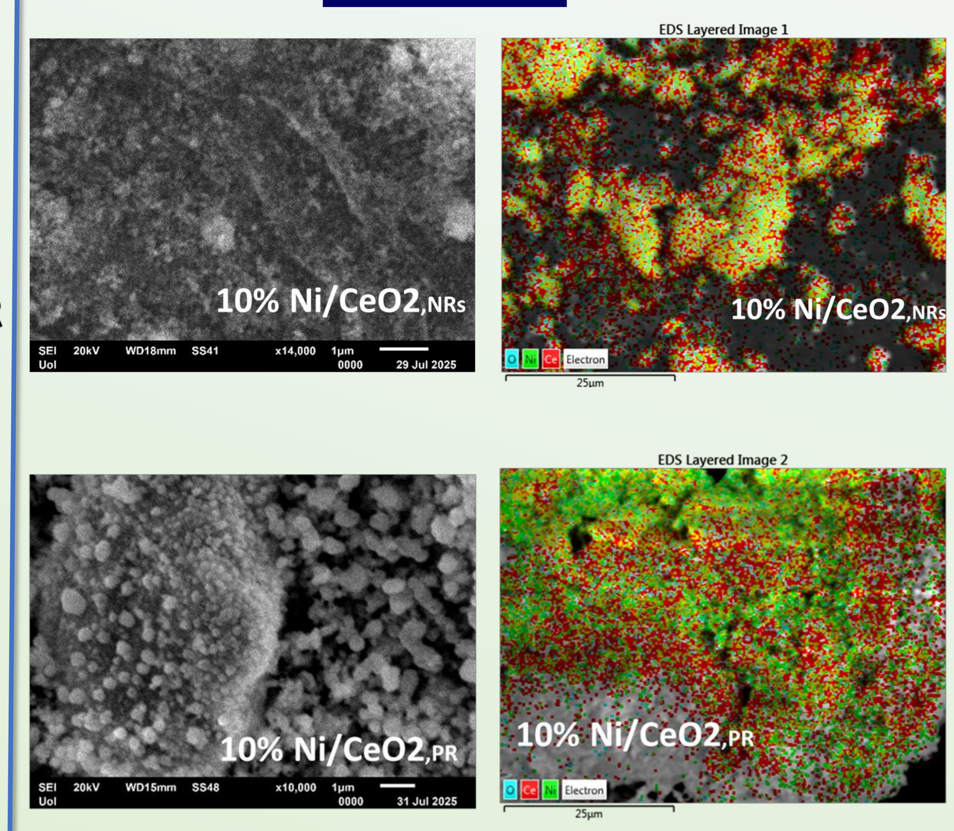


Supports & Catalysts	Ni Content (wt %)	S_{BET} (m^2/g)
$CeO_{2,NRs}$	-	44
$CeO_{2,PR}$	-	6.1
Ni/$CeO_{2,NRs}$	10	35
Ni/$CeO_{2,PR}$	10	10.05

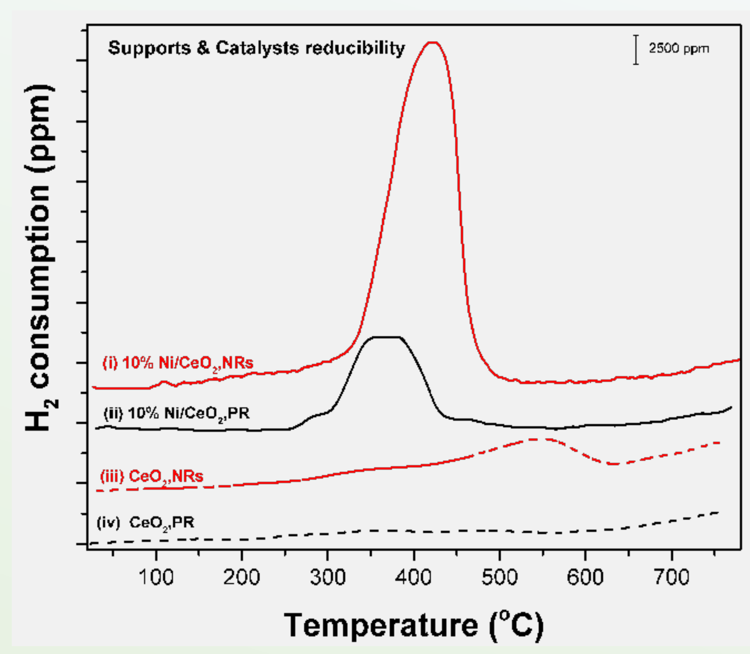
TEM



SEM/EDS



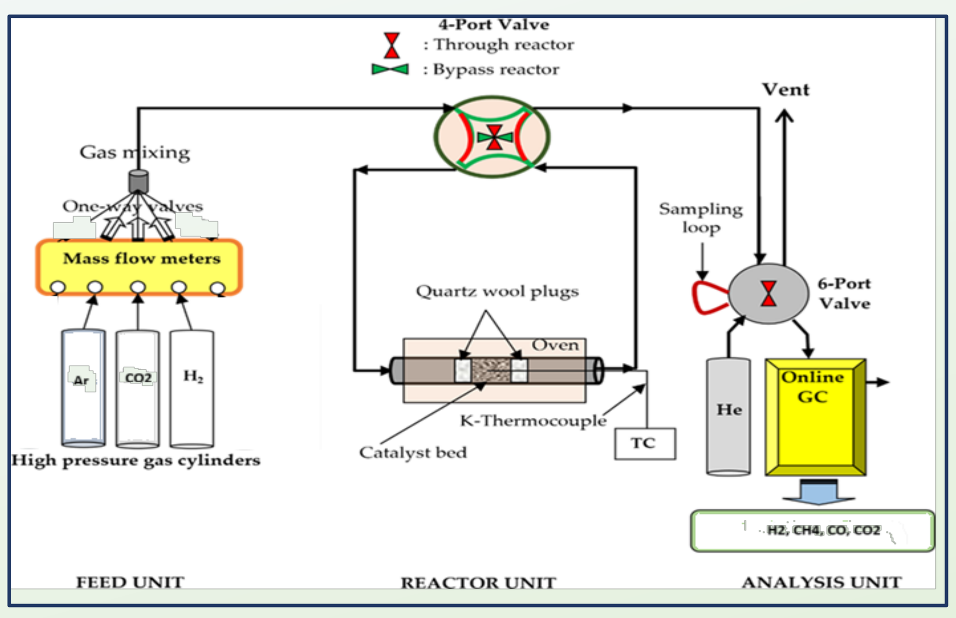
H_2-TPR



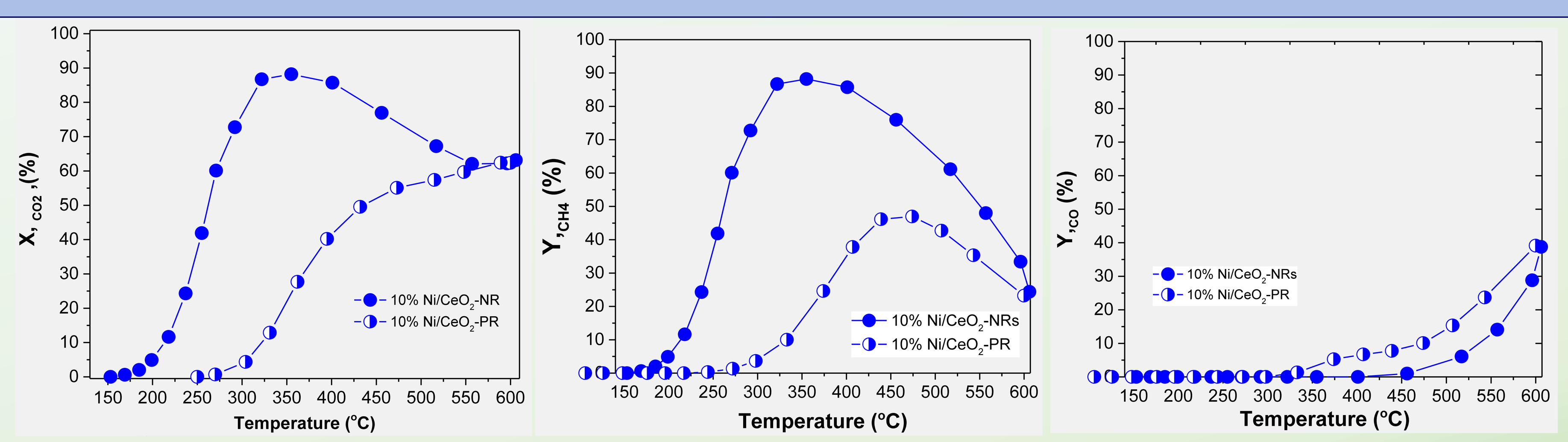
H_2-TPR profiles of the (i) 10% Ni/$CeO_{2,NRs}$, (ii) 10% Ni/$CeO_{2,PR}$ (iii), $CeO_{2,NRs}$ (iv) and $CeO_{2,PR}$

Sabatier reactions

- A tubular (I.D. = 3 mm), quartz, fixed-bed type reactor, m_{cat}=50 mg, temperature range of 150–600 °C. Feed conditions: 20% H_2/5% CO_2/75% Ar at 1 bar F_t = 50 mL/min (i.e. Weight basis Gas Hourly Space Velocity = 60,000 mL/g·h



- The "light-off" behavior of the catalysts was expressed in terms of % CO_2 conversion (X_{CO2}), % yield of CH_4 and CO (Y_{CH4} and Y_{CO}) and % selectivity of CH_4 and CO (S_{CH4} and S_{CO})



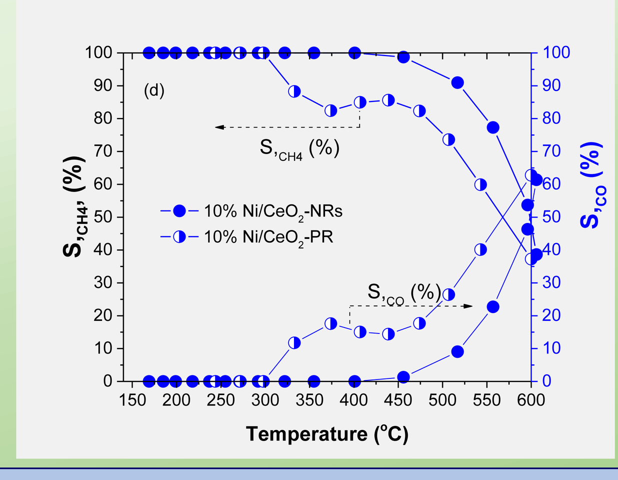
$$X_{CO_2}\,(\%) = 100 * \frac{[CH_{4,out}]+[CO_{out}]}{[CH_{4,out}]+[CO_{out}]+[CO_{2,out}]} \quad (1)$$

$$Y_{CH_4}\,(\%) = 100 * \frac{[CH_{4,out}]}{[CH_{4,out}]+[CO_{out}]+[CO_{2,out}]} \quad (2)$$

$$Y_{CO}\,(\%) = 100 * \frac{[CO_{out}]}{[CH_{4,out}]+[CO_{out}]+[CO_{2,out}]} \quad (3)$$

$$S_{CH_4}\,(\%) = 100 * \frac{[CH_{4,out}]}{[CH_{4,out}]+[CO_{out}]} \quad (4)$$

$$S_{CO}\,(\%) = 100 * \frac{[CO_{out}]}{[CH_{4,out}]+[CO_{out}]} \quad (5)$$



Conclusions

The supports synthesis method plays a crucial role in the performance of catalytic materials, as it affects the degree of nickel (Ni) dispersion and metal-support interactions. Notably, nanostructured supports like nanorods enhance nickel (Ni) catalysts, achieving up to 90% methane yield, at 355° C. These innovative materials, with specialized nanoconfigurations, offer both exceptional catalytic performance and improved stability, positioning them as promising materials in catalytic technology and methane production processes.

Acknowledgments

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