# Impact of $CeO_2$ shell architecture on the catalytic behavior of $Ni/SiO_2$ catalyst for hydrogen production via ethanol steam reforming

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RESUMO - Catalisadores $Ni/SiO_2@CeO_2$ com estrutura *hollow core–shell* foram sintetizados com diferentes espessuras de céria, com o objetivo de investigar a influência da arquitetura da casca de $CeO_2$ durante a reforma a vapor do etanol (ESR). Os materiais foram obtidos com hexametilenotetramina (HTMA), o que possibilitou o recobrimento homogêneo do catalisador $Ni/SiO_2$ sintetizado anteriormente. Quatro amostras foram preparadas com variações da concentração dos precursores e caracterizadas por MEV, MET, EDS, DRX e Fisissorção. A variação sistemática da espessura da camada permitirá uma avaliação abrangente das relações entre estrutura e atividade na reforma a vapor do etanol (ESR), destacando o papel fundamental do controle morfológico na otimização da produção de hidrogênio e da estabilidade catalítica.

ABSTRACT - Hollow core–shell $Ni/SiO_2@CeO_2$ catalysts were synthesized with varying $CeO_2$ shell thicknesses to investigate the influence of shell architecture on catalytic performance during ethanol steam reforming (ESR). The materials were synthesized using hexamethylenetetramine (HTMA), enabling the formation of uniform nanometric $CeO_2$ coatings around the $Ni/SiO_2$ core. Four samples with controlled shell thicknesses were obtained by adjusting synthesis. Characterization techniques including SEM, TEM, XRD, and Physisorption confirmed the formation of $CeO_2$ shells composed of nanoparticles, with average thicknesses ranging from 7 to 60 nm. The systematic variation of shell thickness allowed for a comprehensive evaluation of structure–activity relationships in ESR, highlighting the critical role of morphological control in optimizing hydrogen production and catalyst stability.

## Introduction

The increasing global demand for sustainable energy has driven the development of efficient catalytic systems for hydrogen production. Among them, ethanol steam reforming (ESR) emerges as a promising route due to ethanol's high hydrogen content, ease of storage, and availability from biomass sources [1]. Nickel-based catalysts are employed in ESR due to their cost-effectiveness and high activity. However, a major limitation of this process is the severe coke formation, which leads to catalyst deactivation and reduced operational lifetime [2].

To mitigate this issue, the use of cerium oxide ($CeO_2$) r coating material has gained attention due to its high oxygen mobility and redox capacity, which facilitate the oxidation of surface carbon species and promote catalyst regeneration [3].

In this context, hollow $CeO_2$ shells with controlled thickness were synthesized for influenci studies in nikel catalysts.

## Experimental

Silica was synthesized via the Stöber method, using tetraethyl orthosilicate (TEOS, ≥98%, Sigma-Aldrich) as the silica precursor. In a typical synthesis, TEOS and an aqueous ammonia solution (25–28%, Sigma-Aldrich)—a corrosive and volatile compound requiring proper ventilation and the use of personal protective equipment (PPE)—were mixed and stirred at room temperature for 24 hours to allow for particle nucleation and growth. Subsequently, nickel(II) sulfate hexahydrate ($NiSO_4 \cdot 6H_2O$, ≥98%, Sigma-Aldrich). The temperature was then increased to 80 °C to promote ammonia evaporation, which led to a pH-induced precipitation of nickel phyllosilicates on the silica surface. The process was monitored until the pH naturally decreased to 7. The resulting solid was separated by centrifugation, washed with deionized water and ethanol, and then dried at 80 °C overnight.

A portion of the dried $Ni/SiO_2$ material was subjected to ceria coating. The powder was dispersed in an ethanolic solution containing cerium (III) nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$, ≥99%, Sigma-Aldrich) and hexamethylenetetramine (HMTA, ≥99%, Sigma-Aldrich) and stirred at 80 °C for 8 hours. This procedure yielded the first $CeO_2$ layer. After centrifugation and drying, part of the produced catalyst was subjected to additional identical coating steps three times to obtain materials with different layers. All synthesized catalysts were calcined in air at 500 °C for 7 hours, with a heating rate of 5 °C·min⁻¹. In total, five catalysts were obtained, including four core–shell $Ni/SiO_2@CeO_2$ materials with increasing ceria shell thicknesses as show in table 1.

**Table 1.** Synthesized catalysts.

| Name | Number of shell layers |
|---|---|
| Ni/SiO2 | 0 |
| 1L | 1 |
| 2L | 2 |
| 3L | 3 |
| 4L | 4 |

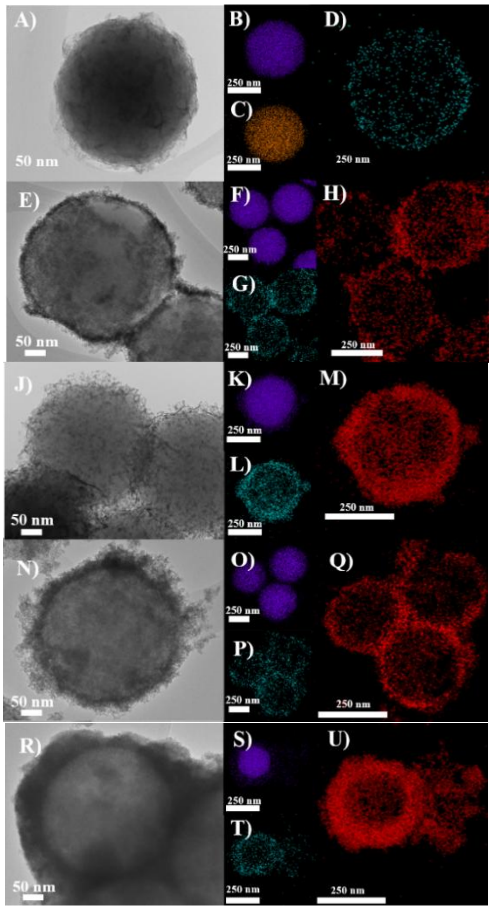


**Figure 1.** TEM and EDS analisys of A), B), C) and D) $Ni/SiO_2$ ; E), F), G) and H) 1L; J), K), L) and M) 2L; N), O), P), and Q) 3L; R), S), T) and U) 4l

## Results e Discusion

The results from SEM, TEM, XRD, and BET analyses confirmed the successful formation of $CeO_2$ layers composed of nanoparticles, with average shell thicknesses varying between 7 and 60 nm.

## Conclusions

TEM confirms the $CeO_2$ shell thickness was successfully controlled, resulting in a range from 7 to 60 nm. Physisorption results indicated an increase in surface area, due the formation of $CeO_2$ nanoparticles on the catalyst surface. Future work will includ detail studies on catalytic conversion and selectivity, as well as morphological and compositional analyses to further elucidate the role of shell thickness in catalytic performance and stability.

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## References

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