

Microstructural Design of Ni–Fe Catalysts for Ethanol Steam Reforming: From SiO₂–Supported to CeO₂ Core–Shell Architecture

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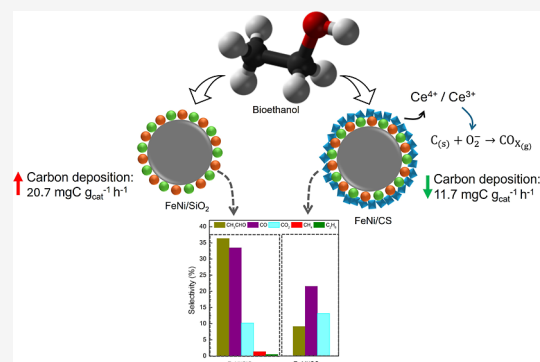
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ABSTRACT: Efficient and stable catalysts for ethanol steam reforming (ESR) are strategic for sustainable hydrogen production. In this study, a rational microstructural architecture of catalysts is investigated by combining nickel and iron active metals, supported on shape-controlled SiO₂ (FeNi/SiO₂), and adding a protective CeO₂ shell layer (FeNi/CS). This designed microstructure exhibits direct impact on the catalytic properties for ESR, as confirmed by detailed characterization. Temperature-programmed reduction (H₂-TPR) and X-ray Photoelectron Spectroscopy (XPS) results indicated strong metal–support interactions and oxygen vacancies in the CeO₂ shell, which enhanced redox properties. Under ESR conditions at 600 °C, the addition of the ceria shell layer resulted in increased catalytic stability, maintaining 100% ethanol conversion and ~70% H₂ production over 80 h, with minimal carbon deposition (11.7 mgC g_{cat}^{−1} h^{−1}) as compared to FeNi/SiO₂ (20.7 mgC g_{cat}^{−1} h^{−1}). The enhanced properties achieved for the FeNi/CS sample are attributed to the design of the support and the CeO₂ layer, which mitigates metal sintering and maximizes the synergistic effect of the Ni–Fe interaction to effectively hinder coke formation by promoting the gasification of carbon species. These results confirm that the bimetallic active species, engineered with a core–shell design having an active layer over a stable support is a promising strategy to enhance the durability and activity of non-noble metal catalysts for ESR applications.



1. INTRODUCTION

Fossil fuel dependence has precipitated an environmental crisis characterized by unsustainable greenhouse gas emissions causing progressively hazardous climate instability globally. The Intergovernmental Panel on Climate Change (IPCC) emphasizes that limiting global warming to 1.5 °C requires urgent substitution of fossil fuels and adoption of sustainable energy systems.^{1–3} Biofuels, particularly low-carbon alternatives like bioethanol, have gained prominence as available solutions. They reduce reliance on petroleum, mitigate emissions, and align with sustainability frameworks as the UN Sustainable Development Goals (SDGs), which prioritize affordable clean energy and inclusive economic growth.^{4–7}

Hydrogen produced from ethanol steam reforming (ESR) represents a promising pathway for sustainable H₂ generation.^{8,9} ESR efficiency, however, strongly depends on the development of robust catalysts able to promote C–C bond cleavage, suppress coke formation, and maintain stability under redox conditions. Although noble metals such as Rh exhibit excellent activity, their prohibitively high cost motivates the use of Ni-based catalysts.^{10–13} Nickel is highly effective for ethanol activation but suffers from sintering and carbon deposition during prolonged operation.

To address these challenges, strategies involving promoters, bimetallic systems, and advanced support architectures are under investigation.^{10,11,14} Among these strategies, Fe–Ni bimetallic catalysts have demonstrated significant benefits. The introduction of Fe enhances oxygen mobility and promotes CO oxidation through the water–gas shift reaction, mitigates carbon accumulation, and facilitates acetate-mediated reaction pathways that suppress coke precursors.^{15–18} In addition, Fe can promote the formation of Ni–Fe alloy phases and modifies the electronic properties of Ni sites, inhibiting undesired side reactions such as methanation.¹⁹ Recent studies have further demonstrated that Ni–Fe catalysts exhibit improved dispersion of active sites, enhanced hydrogen production, and superior resistance to carbon deposition during ethanol steam reforming.^{19,20}

The support material also plays a key role in determining catalyst performance. Amorphous SiO₂ provides high thermal

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stability and disperses active metals effectively.^{21,22} In contrast, reducible oxides such as CeO₂ exhibit unique redox properties that are particularly advantageous for reforming reactions. CeO₂ possesses a high oxygen storage capacity associated with the reversible Ce⁴⁺/Ce³⁺ redox cycle, which promotes the formation of oxygen vacancies and facilitates oxygen mobility at the catalyst surface. These features enhance the activation of oxygenated intermediates and contribute to the gasification of carbon deposits during reforming reactions. Furthermore, CeO₂ has been widely reported to interact strongly with Ni-based catalysts, improving metal dispersion, stabilizing metallic nanoparticles, and enhancing resistance to sintering and coke formation. When combined with Fe-containing systems, CeO₂ can further promote oxygen transfer processes and improve the redox properties of the catalyst, which are beneficial for ethanol steam reforming.^{23–25}

Recent studies on Ni/CeO₂ systems for ESR have clarified the role of CeO₂ in activating water, stabilizing acetate intermediates and promoting carbon gasification, leading to improved hydrogen yields and slower deactivation.^{21,26,27} In a similar way, Ni/CeO₂ based catalysts doped with Sm³⁺ demonstrated that tuning the oxygen-vacancy concentration and oxygen mobility has a direct impact on ESR activity and stability.²⁸ These works reinforce the central role of CeO₂ redox properties and oxygen vacancies in achieving coke-resistant ESR catalysts.

Beyond conventional supported catalysts, core–shell architectures have emerged as an attractive approach to enhance durability. In these systems, a shell phase (often CeO₂-rich) provides physical confinement for metal nanoparticles, limits sintering, and creates an outer redox-active layer that facilitates water activation and carbon oxidation.^{29–31} Das et al. designed a silica-ceria sandwiched Ni core–shell catalyst for dry reforming of biogas, showing improved resistance to coke formation and long-term stability.²⁹ Tang et al. and Han et al. showed that Ni@CeO₂ and Ni@SiO₂@CeO₂ structures effectively prevent carbon deposition and metal aggregation in methane dry reforming.^{25,31} More recently, Ni-based core–shell catalysts, comprising a ceria shell and supported on silica nanospheres have been successfully applied to ESR, exhibiting improved activity and resistance to deactivation at intermediate temperatures.³² Mesoporous silica-encapsulated core–shell NiRh@NiO catalysts have also delivered enhanced performance in ESR, highlighting the potential of confinement effects and engineering interfaces between metallic phases and oxide shells.³³

Despite recent advances in catalyst design, Fe–Ni core–shell systems remain largely unexplored for ESR, despite its potential to balance catalytic activity, durability, and cost. Therefore, this study investigates the catalytic performance and stability of a tailored FeNi/SiO₂–CeO₂ core–shell catalyst for ethanol steam reforming. The influence of the CeO₂ shell in redox properties, coke suppression, and hydrogen production is systematically evaluated to elucidate the advantages of this architecture for sustainable hydrogen generation.

2. EXPERIMENTAL SECTION

2.1. Catalyst Synthesis

2.1.1. Synthesis of SiO₂ Support. The SiO₂ support was prepared via the Stöber method,²² using tetraethyl orthosilicate (TEOS, Sigma-Aldrich, ≥99%) as the silica precursor, absolute ethanol (Sigma-Aldrich, ≥99.5%) as the solvent, ammonium hydroxide (NH₄OH, Sigma-Aldrich, ≥25%) as the condensation

catalyst, and distilled water for hydrolysis. Initially, 2 mL of TEOS was added to 70 mL of ethanol under magnetic stirring for 5 min. Subsequently, 2.1 mL of NH₄OH and 14 mL of distilled water were introduced into the mixture, which was then stirred continuously for 24 h to form SiO₂ spheres. Then, the material underwent oven-drying at 100 °C for 12 h.

2.1.2. Metal Impregnation on SiO₂ Support (Core). Bimetallic catalysts were obtained by the simultaneous incipient wetness impregnation of metals using a solution of nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, Sigma-Aldrich, 99.9%) and iron nitrate nonahydrate (Fe(NO₃)₃·9H₂O, Sigma-Aldrich, ≥98%) over the SiO₂ previously prepared. The nominal metal loading was set to 10 wt % Ni and 5 wt % Fe, based on prior catalytic performance tests carried out with similar materials, which indicated optimal activity at this composition. Preliminary catalytic tests with different Ni and Fe loadings (5–10 wt %) indicated that catalysts with lower Ni content exhibited lower ethanol conversion and H₂ production, while increasing the Fe content did not significantly improve catalytic performance.

The mixture was heated at 70 °C under magnetic stirring until the solvent evaporated completely. The resulting material was dried at 100 °C for 12 h, followed by calcination in air at 700 °C for 4 h with a heating rate of 10 °C min^{−1}. The sample with the metals supported on SiO₂ is referred to as FeNi/SiO₂.

2.1.3. CeO₂-Shell Preparation. The shell phase was prepared using cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, Sigma-Aldrich, 99.999%) and hexamethylenetetramine (C₆H₁₂N₄, Sigma-Aldrich, ≥99%), which acts as a structuring agent for the shell layer. First, 500 mg of the core phase (FeNi/SiO₂), prepared by adjusting the mass of the metal precursors to achieve the same amounts of Fe and Ni as in the FeNi/SiO₂ sample, was dispersed in 60 mL of ethanol and sonicated for 1 h. Next, 1 g of Ce(NO₃)₃·6H₂O and 4 g of C₆H₁₂N₄ (predissolved in hot water) were added to the suspension. The mixture was stirred at 70 °C for 6 h and the precipitate was then dried at 100 °C for 12 h and calcined in air at 700 °C for 4 h, with a heating ramp of 10 °C min^{−1} to form the FeNi–SiO₂–CeO₂ core–shell catalyst, referred to as FeNi/CS. Control experiment, denoted as FeNi/SiO₂ + CeO₂, was performed using a commercial CeO₂ (Sigma-Aldrich, 99.9%).

2.2. Characterization of the Catalysts

The semiquantitative chemical composition of the catalysts was analyzed using wavelength dispersive X-ray fluorescence spectroscopy (WDXRF). Measurements were performed on a Rigaku Supermini200 spectrometer equipped with an X-ray source of Pd with Ka (λ = 0.988 Å) and Kb (λ = 0.876 Å) radiation. Approximately 70 mg of powdered sample was used, and the measurements were performed in vacuum and analyzed in the SQX software.

The crystalline structure of the synthesized catalysts was evaluated by X-ray diffraction (XRD). Data were collected using a Rigaku SmartLab diffractometer equipped with Cu Kα radiation (λ = 1.5406 Å), scanning the 2θ range of 20°–80° at a rate of 0.050° s^{−1} and a counting time of 1 s per step.

The morphology and particle size of the catalysts were analyzed using field-emission gun scanning electron microscopy (FEG–SEM) on a JEOL JSM-IT700HR microscope operated at accelerating voltages of 3–6 kV. Particle size distributions were determined by measuring diameters from FEG–SEM images using ImageJ software. For a more detailed analysis, high-resolution transmission electron microscopy (HRTEM) was performed on a Thermo Fisher Talos F200X-G2 microscope equipped with an X-FEG field-emission gun, operating at an accelerating voltage of 200 kV. The analyses were performed from a suspension of the powdered samples in isopropyl alcohol, dispersed in ultrasound for 15 min.

Temperature-programmed reduction (TPR) analyses were conducted to assess the reducibility of metallic species, metal–support interactions, and reduction temperature ranges. Experiments were carried out on a Quantachrome ChemBET Pulsar TPR/TPD system. Approximately 100 mg of sample was heated from room temperature to 1000 °C under a 10% H₂/N₂ flow (30 mL min^{−1}) at 5 °C min^{−1}.

Hydrogen consumption was monitored via a thermal conductivity detector (TCD) and estimated using a CuO reference sample.

The Brunauer–Emmett–Teller (BET) method³⁴ was applied to determine the specific surface area of the samples. Measurements were performed on a Micromeritics ASAP 2020 system, utilizing nitrogen adsorption–desorption isotherms.

X-ray Photoelectron Spectroscopy (XPS) measurements were conducted at the Brazilian Nanotechnology National Laboratory (LNNano/CNPEM) in Campinas, Brazil. Spectra were acquired using a Thermo Scientific K-Alpha spectrometer with a monochromatic Al K α X-ray source (1486.6 eV). Data were collected in the binding energy range of 100–1500 eV. All spectra were energy-referenced to the C 1s peak at 284.6 eV and processed using CASA XPS software. The deconvolution of the overlapping peaks was performed using Gaussian–Lorentzian line shapes. The fitting procedures for the core level spectra were constrained by keeping the area ratios of their respective spin–orbit doublets fixed at their theoretical quantum mechanical values.

Structural and vibrational properties were characterized using Raman spectroscopy. A Horiba Jobin Yvon XploRA-PLUS spectrometer with a 532 nm excitation laser and a 50 $\times$ magnification objective lens was employed to collect spectra across the 200–1200 cm^{−1} range. Data processing and spectral analysis were conducted using LabSpec6 software.

For the XRD and TEM analyses of the reduced catalysts, the calcined samples were previously reduced in a tubular furnace under a controlled H₂ atmosphere (30 mL min^{−1}). The temperature was increased to 800 °C at a heating rate of 10 °C min^{−1} and maintained for 1 h, followed by cooling to room temperature under the same H₂ flow. To minimize bulk reoxidation of the active metal species prior to the measurements, the reduced samples were immediately sealed in glass vials with minimal exposure to ambient air.

Thermogravimetric and differential thermal analysis (TG–DTA) was carried out to assess thermal stability and decomposition behavior. A Setaram-LabSys instrument was operated under synthetic air flow (50 mL min^{−1}) from 100 to 1000 °C, with a heating rate of 10 °C min^{−1}.

2.3. Ethanol Steam Reforming (ESR) Reaction

ESR reactions were conducted in a gas-phase fixed-bed reactor system. The setup consisted of a U-shaped quartz tubular reactor (6 mm internal diameter) housed within a resistively heated furnace, with temperature regulation achieved via thermocouples. Outlet gases were analyzed using an Agilent 7890A gas chromatograph (GC) equipped with flame ionization (FID) and thermal conductivity (TCD) detectors.

For each experiment, 20 mg of catalyst was loaded into the reactor, sandwiched between quartz wool plugs to ensure uniform gas flow. Prior to testing, the catalyst was reduced *in situ* under pure H₂ flow (30 mL min^{−1}) at 800 °C for 1 h to activate metallic sites, followed by a 15 min N₂ purge at the same temperature to remove residual hydrogen.

The reactant mixture consisted of ethanol and water with an H₂O/ethanol molar ratio of 3:1, using N₂ as the carrier gas. The feed was generated by passing two separate N₂ streams (30 mL min^{−1} each) through water and ethanol saturators, whose temperatures were independently controlled to ensure the desired composition. This procedure resulted in a total gas flow rate of 60 mL min^{−1}.

All reactions were carried out isothermally at 600 °C under atmospheric pressure. The catalytic tests were performed for 80 h using 20 mg of catalyst. These conditions correspond to a Gas Hourly Space Velocity (GHSV) of 180,000 mL gcat^{−1} h^{−1}.

All catalytic experiments were performed at least in duplicate using independently synthesized catalyst batches. Blank experiments were carried out in the absence of catalyst, with ethanol and water vapor concentrations measured in three consecutive runs under identical inlet flow conditions. The averaged blank values were employed in the calculation of conversions and product yields, and no gaseous reaction products were detected under blank conditions.

The ethanol conversion (χ_{ethanol}) and the product distribution (P_x) were determined according to eqs 1 and 2

$$\chi_{\text{ethanol}} = \frac{(n_{\text{ethanolin}} - n_{\text{ethanolout}})}{n_{\text{ethanolin}}} \times 100 \quad (1)$$

$$P_x = \frac{n_x}{n_{\text{total}}} \times 100 \quad (2)$$

where n_x corresponds to the molar quantity of product x , and n_{total} represents the cumulative moles of all reaction products, excluding water.

The selectivity (s_i) of the catalysts for the respective products and the H₂ yield (y_{H_2}) were determined by eqs 3 and 4

$$s_i(\%) = \frac{n_i \times C_i}{2 \times n_{\text{ethanolconverted}}} \times 100 \quad (3)$$

$$y_{\text{H}_2} = \frac{n_{\text{H}_2}}{6 \times n_{\text{ethanolin}}} \quad (4)$$

where n_i corresponds to the molar quantity of product i , C_i represents the number of carbon atoms in the product i , $n_{\text{ethanol converted}}$ represents the molar quantity of converted ethanol and n_{H_2} is the molar amount of H₂ produced, considering the stoichiometry of the ESR reaction.

3. RESULTS AND DISCUSSION

The chemical composition of the synthesized materials was determined by WDXRF analysis, as listed in Table 1.

Table 1. Chemical Composition Determined by WDXRF and Specific Surface Area (S_{BET}) of Samples. Standard Deviations are <0.5 wt % for Elemental Composition and <5 m² g^{−1} for Surface Area. The Standard Deviation of the Surface Area Measurements is Estimated to be ± 5 m² g^{−1}

samples	elements (wt %)				S_{BET} (m ² g ^{−1})
	Fe	Ni	SiO ₂	CeO ₂	
SiO ₂	-	-	100	-	42
FeNi/SiO ₂	7	13	81	-	84
FeNi/CS	5	10	34	51	45

The synthesized materials exhibited no detectable impurities. As shown in Table 1, the FeNi/SiO₂ and FeNi/CS catalysts displayed metal composition close to the nominal values (5 wt % Fe and 10 wt % Ni), confirming the effectiveness of the synthesis method. The metal loading strategy adopted in this study was based on previously published studies,^{25,35} which reported satisfactory catalytic performance for ethanol steam reforming using catalysts with similar metal loadings. The FeNi/CS sample successfully achieved the targeted CeO₂ shell phase content (~ 50 wt %).

Table 1 also displays the specific surface area (S_{BET}) values with significant variations due to the assembly of the components of the catalyst samples. The SiO₂ support exhibits $S_{\text{BET}} = 42$ m² g^{−1} and the impregnation with Fe and Ni metal salts, this value increases to 84 m² g^{−1}. This significant S_{BET} increase suggests that the finely dispersed metal oxides change the SiO₂ support surface, modifying the surface texture and increasing the area accessible to N₂ adsorption. The impregnation and calcination steps of metal oxides promote the formation of additional interfacial regions between the metal oxide and the silica support, leading to increased surface roughness, which can contribute to the observed increase in S_{BET} .

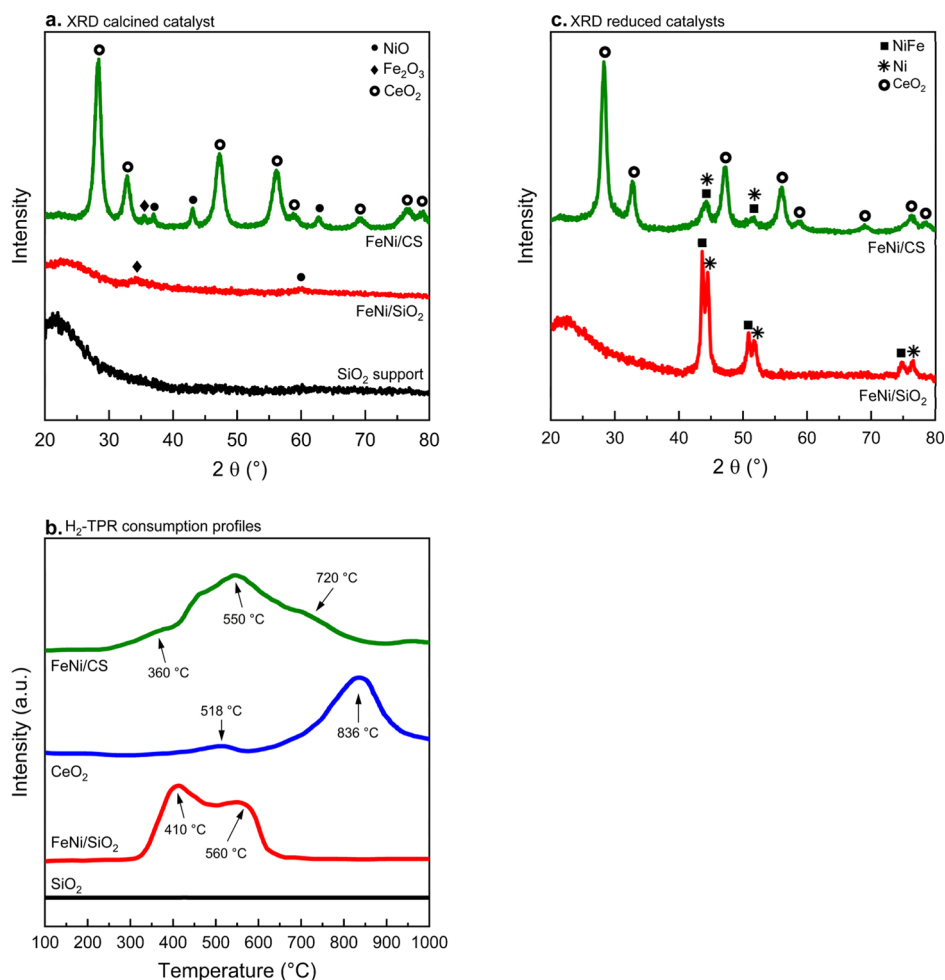


Figure 1. X-ray diffractogram (XRD) patterns of (a) SiO₂ support and calcined catalyst. (b) Normalized H₂-TPR consumption profiles of studied samples. (c) XRD patterns of reduced catalysts.

After deposition of the ceria layer to form the core–shell structure, the specific surface area decreases to 45 m² g^{−1}, a value comparable to that of the SiO₂ support. This behavior suggests that the CeO₂ layer partially covers or blocks surface regions of the FeNi/SiO₂ sample, reducing the surface area accessible to N₂ adsorption while preserving the overall textural framework of the support.

The textural properties derived from N₂ adsorption–desorption isotherms and BJH pore size distribution analyses corroborate these findings and are shown in Figure S2. All samples exhibit type IV isotherms with hysteresis loops, characteristic of mesoporous materials.³⁶ The SiO₂ displays a relatively narrow pore size distribution centered ~15–20 nm, indicative of uniform mesoporous structure. After FeNi incorporation (FeNi/SiO₂), an increase in adsorbed volume and broader pore size distribution are observed, suggesting the development of additional porosity and increased structural heterogeneity due to the deposited metal oxide. In contrast, after deposition of the CeO₂ layer to form the core–shell structure, a decrease in pore volume and a less defined pore size distribution are observed, indicating partial pore blockage or coverage by the ceria layer. This effect reduces the accessibility of N₂ molecules while preserving the mesoporous framework of the support. These results are consistent with the observed decrease in *S*_{BET} and suggest that the CeO₂ shell partially blocks pore access, reducing the available surface area

without significantly altering the mesoporous nature of the support.

The X-ray diffraction (XRD) pattern of the SiO₂ support (Figure 1a) displays a halo at 2θ ~20°, characteristic of amorphous silica.²² No additional diffraction peaks corresponding to crystalline phases are observed. After calcination at 700 °C, no new crystalline phases or structural changes detectable by XRD were identified, indicating that the thermal treatment did not induce crystallization within the resolution of the technique. The FeNi/SiO₂ sample exhibits two small peaks at 2θ ~35° and 60°, consistent with the presence of Fe₂O₃ and NiO phases. The broad reflections suggest small crystallite size and high dispersion of the oxide species. However, due to their low intensity and peak broadening, precise phase identification was limited.

In contrast, the FeNi/CS sample displays well-defined reflections corresponding to the fluorite phase of CeO₂ (ICSD 28709), NiO (ICSD 9866), and Fe₂O₃ (ICSD 15840). The higher intensity of the NiO and Fe₂O₃ reflections in this sample is likely related to a higher crystallinity induced by the ceria shell layer processing, particularly the calcining step at 700 °C.

The incorporation of crystalline CeO₂ increases the overall crystalline fraction of the material, enhancing the visibility of crystalline phases relative to the predominantly amorphous SiO₂ support. Consequently, the amorphous halo attributed to

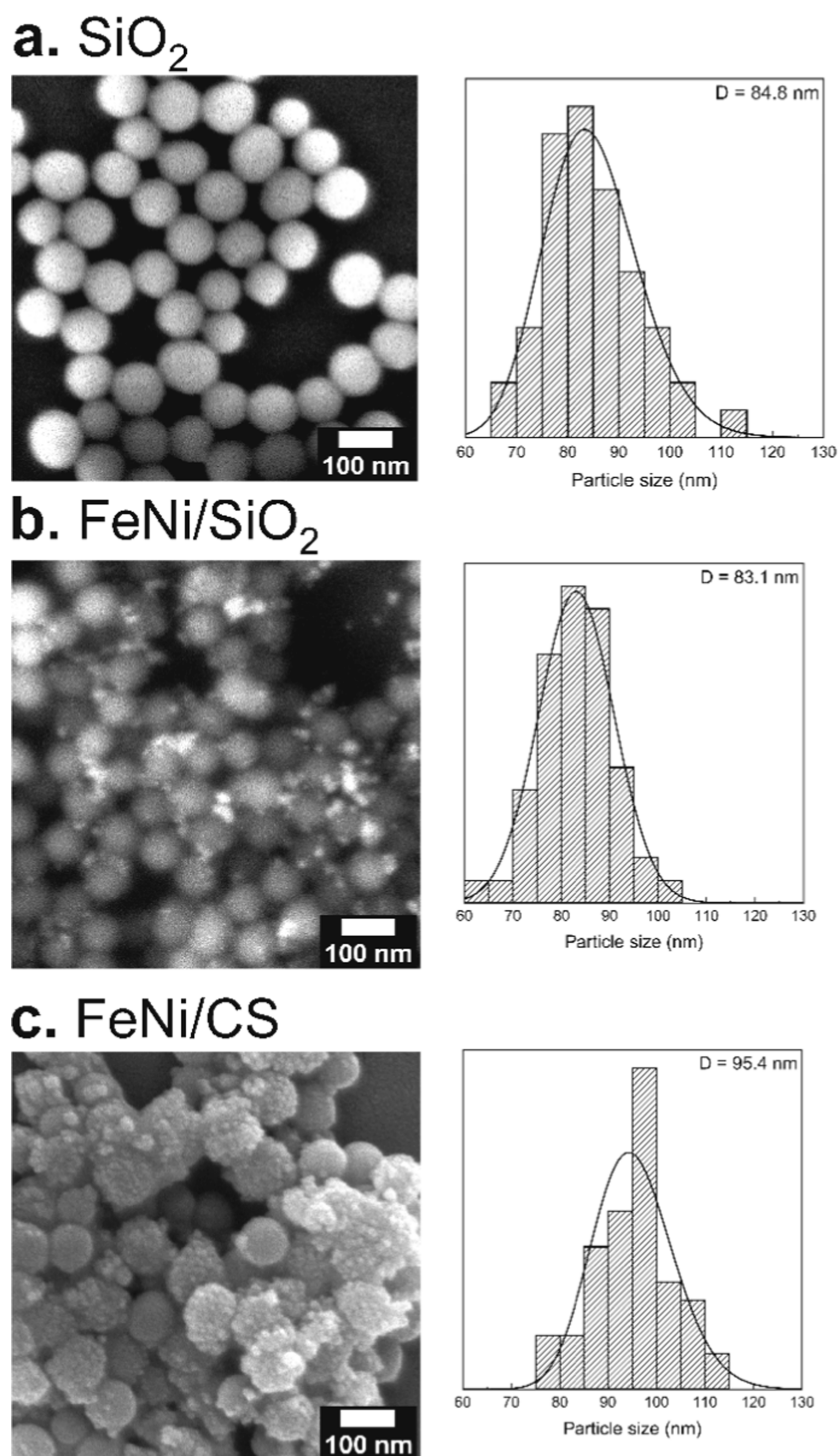


Figure 2. FE–SEM micrographs (left panels) and corresponding particle size histograms (right panels) for (a) SiO₂ support, (b) FeNi/SiO₂, and (c) FeNi/CS catalysts.

SiO₂ becomes small due to the contribution of the crystalline CeO₂ phase.

The H₂-TPR reduction profiles are shown in Figure 1b. SiO₂ exhibits negligible hydrogen consumption under the experimental conditions. For the FeNi/SiO₂ sample, two reduction peaks are observed at ~410 and 560 °C. The lower temperature peak corresponds to the reduction of Ni²⁺ species to Ni⁰, while the maximum at 560 °C is attributed to the reduction of both Fe³⁺ and Fe²⁺ to Fe⁰.^{37,38}

Compared to data reported for monometallic Ni systems, the reduction temperature of Ni species in the FeNi/SiO₂ sample appears slightly lower. However, it should be noted that reduction is strongly dependent on support composition and preparation method. The observed shift is therefore discussed qualitatively and may be associated with the presence of Fe, which can facilitate Ni reduction in bimetallic systems, as reported for Fe–Ni catalysts such as FeNi/MgAl₂O₄.²⁰

To further investigate the reduction of the FeNi/CS sample, a reference CeO₂ material synthesized following the same

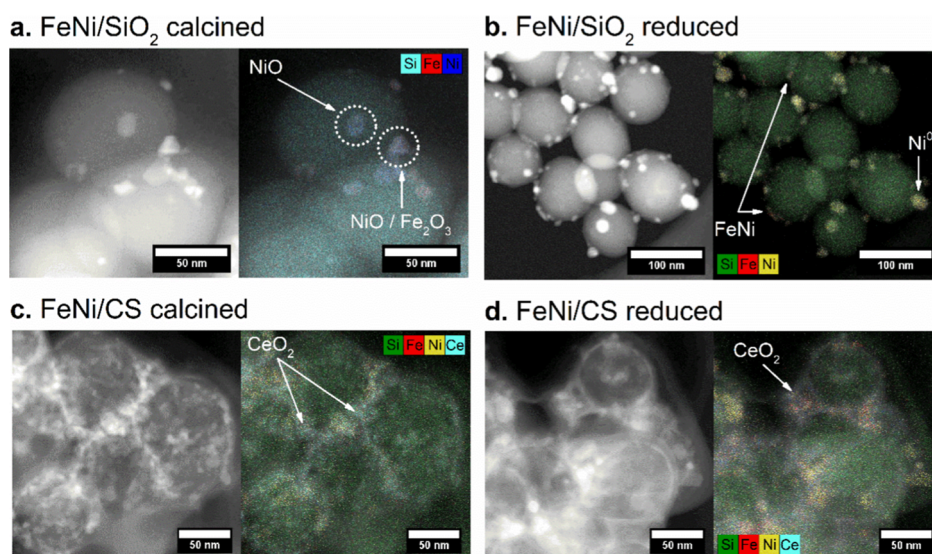


Figure 3. TEM micrographs and corresponding EDS elemental maps of FeNi/SiO₂: (a) calcined and (b) reduced; and of FeNi/CS: (c) calcined, and (d) reduced.

precipitation and calcination procedure used for the CeO₂ shell was analyzed for comparison. The CeO₂ sample exhibits two main reduction maxima at 518 and 836 °C, typically attributed to the reduction of surface Ce⁴⁺ species and bulk Ce⁴⁺ reduction.^{39,40} Differently, the FeNi/CS sample exhibits overlapping reduction regions. The first peak, at ~360 °C, is assigned to the reduction of Ni²⁺ to Ni⁰, while the second peak, near 550 °C, is attributed to the reduction of Fe³⁺/Fe²⁺ to Fe⁰, based on the FeNi/SiO₂ sample profile. Remarkably, the bulk Ce⁴⁺ reduction typically occurring above 800 °C is shifted to lower temperatures in the FeNi/CS sample, as evidenced by a shoulder peak at ~720 °C. The differences observed in the TPR profiles suggest changes in the reducibility of the species present in the FeNi/CS catalyst.⁴¹

The H₂ consumption values calculated for each sample, based on H₂-TPR data integrated between 200 and 1000 °C, were 268 mm³ g⁻¹ for, 61 mm³ g⁻¹, and 42 mm³ g⁻¹ for the FeNi/SiO₂, FeNi/CS, and CeO₂, respectively. These results indicate that the metallic phase in the FeNi/SiO₂ sample is easily reduced. In contrast, the core-shell FeNi/CS sample, with its CeO₂ outer layer, restricts H₂ access and partially shields metal oxide nanoparticles from reduction, explaining the lower H₂ consumption, which is close to that of the CeO₂ reference.

Based on TPR data, all samples were prereduced at 800 °C for 1 h prior to catalytic testing. Figure 1c shows the diffraction patterns after the reduction treatment at 800 °C. For the FeNi/SiO₂ sample, peaks at 2θ ~44°, 51°, and 75° can be associated with the metallic NiFe alloy phase (ICSD 103555), while peaks at ~44.5°, 51.6°, and 76.5° correspond to metallic Ni. The reflections in this region were indexed to both Ni and NiFe alloy. However, due to peak overlap and broadening, a clear distinction between these phases is difficult, suggesting that the reduced catalyst may contain partially alloyed Ni-Fe domains. The FeNi/CS sample exhibits similarly broadened reflections in the metallic region, although distinguishing Ni from NiFe alloy domains is hindered by peak overlap and CeO₂ interference. The diffraction peaks indexed to CeO₂ in the reduced core-shell sample remain at the same positions as those observed in the calcined sample.

The microstructure of the synthesized catalysts was investigated by FE-SEM, and the results are displayed in Figure 2. The particle size histograms for these samples, determined by measuring the diameters of individual particles, are presented alongside their respective micrographs.

SEM images of the SiO₂ support, FeNi/SiO₂, and FeNi/CS catalysts are presented in Figure 2. The SiO₂ support shown in Figure 2a, exhibits dispersed spherical particles with a smooth surface and a size distribution centered at ~85 nm, confirming the effectiveness of the Stöber synthesis in obtaining silica nanospheres.

After metal impregnation, Figure 2b, FeNi/SiO₂ largely preserves the spherical morphology of the support. Localized surface contrast variations indicate that presence of dispersed Fe and Ni oxide domains. The impregnation of metal on the surface promotes some agglomeration of the silica spherical particles. The particle size distribution reveals an average diameter of 83 nm, indicating a small variation compared to the SiO₂ support.

For the FeNi/CS catalyst (Figure 2c), spherical support particles are evident, with surface particulates attributed to NiO and Fe₂O₃ species formed during calcination of the impregnated metal precursors. Regions of aggregated clusters with contrast variations are observed, imparting a rough surface of the core-shell samples, as compared to the other samples. This texture suggests the effective formation of a CeO₂ coating, further supported by a significant increase in the average particle size to 95 nm. Notably, the preservation of the spherical morphology confirms that the core-shell synthesis steps do not substantially alter the structural integrity of the SiO₂ support.

Quantitative particle size distributions were obtained by measuring >200 particles per sample using ImageJ software, applying the circle-equivalent diameter method. The observed morphological changes indicate the presence of a ceria layer on the particle surface, while preserving the overall spherical morphology of the samples.

TEM images were acquired before and after the reduction step to investigate its effect on surface morphology. This step, performed prior to the ESR reaction, converts the oxides into

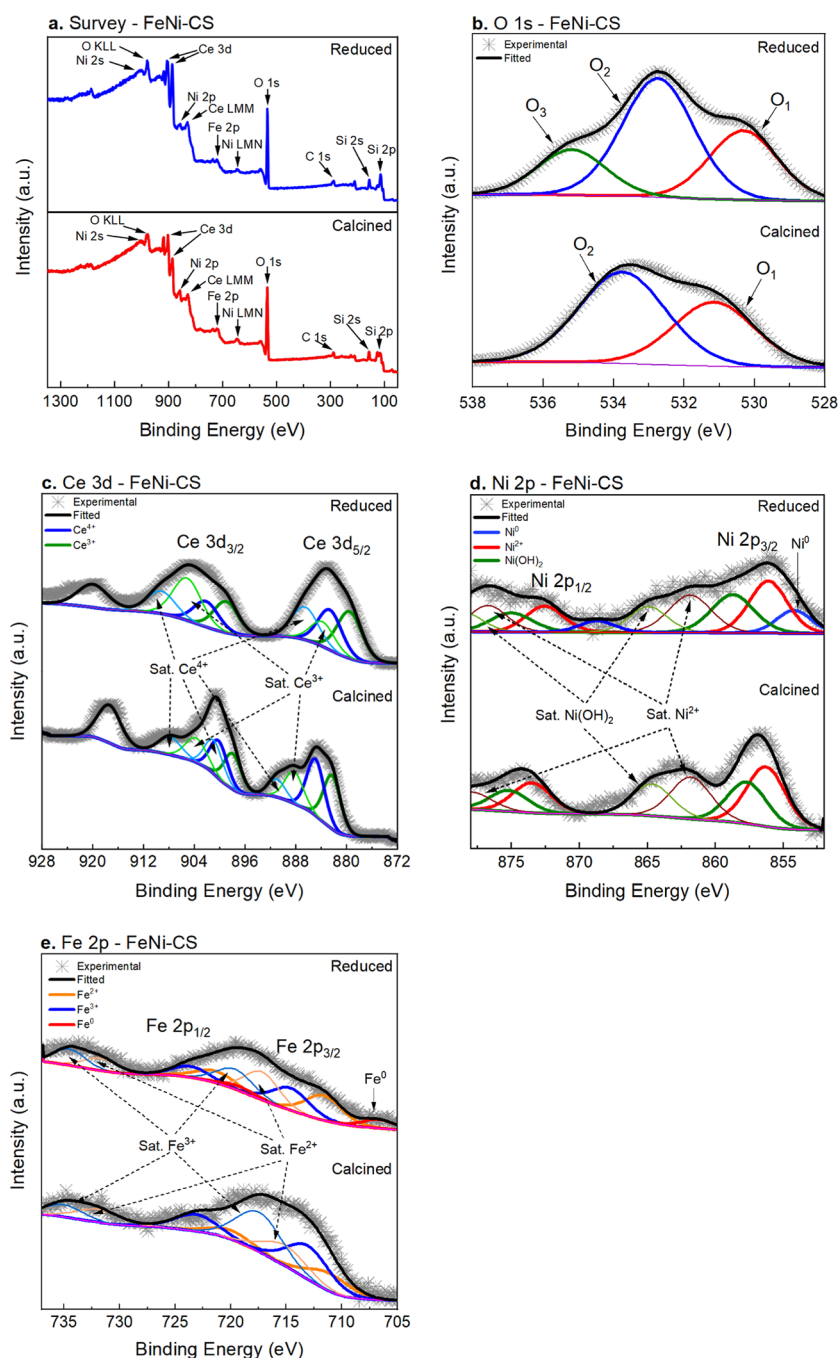


Figure 4. XPS spectra of the calcined and reduced FeNi/CS samples: (a) survey spectra, (b) O 1s, (c) Ce 3d (d) Ni 2p, and (e) Fe 2p.

active metallic species. Chemical analysis by EDS elemental mapping was conducted, as shown in Figure 3.

The TEM micrographs in Figure 3a and b, corresponding to the calcined and reduced FeNi/SiO₂ samples, respectively, reveal nanoparticles dispersed on the SiO₂ support. These particles have irregular shape with a large size distribution, with average size <20 nm. The EDS analyses of FeNi/SiO₂ samples (Figure 3a) indicate isolated regions with pure NiO and other regions with mixed phases of nickel and iron oxides. Notably, areas containing both metallic oxides facilitated the formation of alloy phases, as observed in the XRD data (Figure 1c). This is corroborated by the EDS map of the reduced sample (Figure 3b), which shows regions with isolated Ni⁰ nanoparticles, attributed to the higher nickel concentration relative to iron,

and other regions where metallic iron and nickel are simultaneously present.

In contrast, the micrographs of the calcined and reduced FeNi/CS (Figure 3c and d) display a distinct layer coating the SiO₂ spheres. That corresponds to the CeO₂ phase, confirmed by EDS mapping. Metallic particles are less evident in Figure 3d due to the CeO₂ shell layer. The microstructure of the core-shell sample revealed by the micrographs and elemental maps aligns with the H₂-TPR data, which revealed a shielding effect that hindered the reduction of metallic particles in the FeNi/CS sample. Thus, the observed microstructure is consistent with the properties expected for a core-shell structure, confirming the successful synthesis of such architecture catalyst. For a complete overview of the data

obtained by EDS, the individual maps of each element for all samples are available in the Supporting Information (Figures S3–S6).

Microstructural analyses indicate that the distinct architectures of FeNi/SiO₂ and FeNi/CS may justify their catalytic behavior. The FeNi/CS catalyst presents a continuous CeO₂ layer that confines the active phase (Fe–Ni) and suppresses sintering,^{29,30,32} while also potentially enhancing the redox response of ceria and promoting oxygen-vacancy formation.^{42,43} In contrast, FeNi/SiO₂ exposes highly dispersed Ni and Fe oxide nanoparticles, which exhibit higher reducibility but also greater susceptibility to carbon deposition.⁴⁴ The encapsulation of Fe and Ni beneath the CeO₂ layer facilitates oxygen migration and carbon gasification, consistent with the well-established role of ceria in suppressing coke in core–shell catalysts.^{27,29,31} These microstructural attributes account for the superior stability and reduced coke accumulation of FeNi/CS during ESR.

The surface properties of the calcined and reduced FeNi/CS samples were investigated by XPS, as shown in Figure 4. To elucidate the chemical transformations induced by the reduction treatment and their impact on catalytic performance, the quantitative surface composition of the elements was determined and is detailed in Table 2. Quantitative surface composition (atomic %) and relative species distribution of the catalysts determined by XPS.

Table 2. Quantitative Surface Composition (Atomic %) and Relative Species Distribution of the FeNi/CS Catalyst Determined by XPS

element	surface species	calcined (at %)	reduced (at %)
O (O 1s)	O _{lattice}	39.9	29.0
	O _{surface}	60.1	71.0
	ratio (O _{surface} /O _{lattice})	1.51	2.45
Ce (Ce 3d)	Ce ³⁺	40.7	49.6
	Ce ⁴⁺	59.3	50.4
Ni (Ni 2p)	NiO	54.8	51.0
	Ni(OH) ₂	45.2	38.1
	Ni ⁰	-	10.9
Fe (Fe 2p)	Fe ²⁺	37.4	48.3
	Fe ³⁺	62.6	43.0
	Fe ⁰	-	8.7

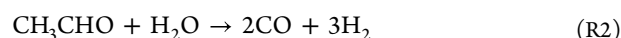
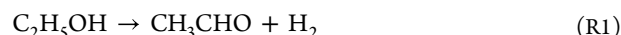
The XPS spectrum of the O 1s region for the calcined sample (Figure 4b) reveals distinct contributions that can be deconvoluted into lattice oxygen (O_{lattice}) at lower binding energies (~529.5 eV), attributed to surface lattice oxygen (O²⁻ in metal–oxygen bonds), and surface oxygen species (O_{surface}) at higher binding energies (~531.5 eV and above), corresponding to oxygen vacancies, defect sites, and weakly bound oxygen species such as hydroxyl groups, carbonates, and/or adsorbed water.^{45,46} As shown in Table 2, the reduction process increases the O_{surface}/O_{lattice} ratio from 1.51 to 2.45. This enrichment in surface defects is directly coupled with the partial reduction of the ceria shell, evidenced by the Ce 3d spectra (Figure 4c), where the peak broadening confirms the coexistence of Ce⁴⁺ and Ce³⁺ species.^{47–49} Quantitative analysis indicates that the Ce³⁺ fraction increases from 40.7% to 49.6% upon reduction. The simultaneous generation of Ce³⁺ and oxygen vacancies is relevant for the catalytic performance, as these defects act as preferential adsorption sites for water dissociation.⁴³

For the calcined sample in the Ni 2p region (Figure 4d), quantitative analysis confirms that nickel exists entirely in oxidized states, specifically NiO (54.8%) and Ni(OH)₂ (45.2%). The shift to higher binding energies compared to the typical range for NiO (853 to 855 eV³⁸), reflects the presence of these mixed nickel environments and ligand effects.⁵⁰ Additionally, the spin–orbit splitting of 17.3 eV is characteristic of Ni²⁺ species.⁵¹ Following the reduction treatment, the surface composition changes as the Ni 2p_{3/2} peak shifts to lower binding energies. The emergence of a new component at 854.8 eV confirms the partial reduction of nickel, yielding a metallic Ni⁰ surface concentration of 10.9% alongside the remaining NiO (51.0%) and Ni(OH)₂ (38.1%).⁵⁰

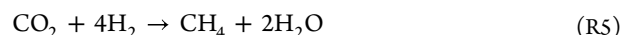
In the Fe 2p spectrum (Figure 4e), peaks corresponding to the Fe 2p_{3/2} and Fe 2p_{1/2} core levels, along with satellite peaks, are identified. Based on the quantitative analysis, the calcined sample is composed of Fe³⁺ (62.6%) and Fe²⁺ (37.4%) species. Notably, in the reduced sample, a peak at ~706 eV aligns with the binding energy region for metallic iron, confirming the partial reduction to Fe⁰ (8.7%). The remaining oxidized iron in the reduced sample consists of Fe²⁺ (48.3%) and Fe³⁺ (43.0%).^{51,52}

To evaluate and compare the catalytic performance of studied materials, both FeNi/SiO₂ and FeNi/CS catalysts were tested in an 80 h ethanol steam reforming reaction (ESR), as shown in Figure 5.

The FeNi/SiO₂ catalyst (Figure 5a) initially exhibited an ethanol conversion rate of 100% and H₂ production of 70%. This behavior is attributed to Ni, given its ability to cleave the C–C bond in ethanol, thereby favoring the steam reforming mechanism.⁵³ In addition to H₂, CO, and CO₂ were detected among the reaction products. These results indicate that ethanol dehydrogenation (Reaction R1) occurs as an initial step, followed by acetaldehyde (CH₃CHO) steam reforming (Reaction R2) and the water–gas shift reaction (Reaction R3). The formation of CO and CO₂ is therefore consistent with the main pathway of ESR.^{53,54}



The synergistic effect of Ni and Fe in bimetallic catalysts may suppress methane and carbon formation. The formation of a Ni-rich alloy with Fe₂O₃ species minimizes secondary CO and CO₂ methanation reactions (Reactions R4 and R5, respectively), reducing the CH₄ formation.



Furthermore, Fe facilitates the conversion of ethoxy groups into acetate species, preventing carbon deposition and enhancing long-term catalyst stability.²⁰ However, a gradual decrease in H₂ production over time and a proportional increase in acetaldehyde are observed, suggesting deactivation of this catalyst.

The FeNi/CS catalyst (Figure 5b) fully converted ethanol with a hydrogen selectivity close to the equilibrium. More importantly, the core–shell sample exhibited a significantly enhanced stability in ethanol conversion and H₂ production compared to FeNi/SiO₂. Ethanol conversion and H₂

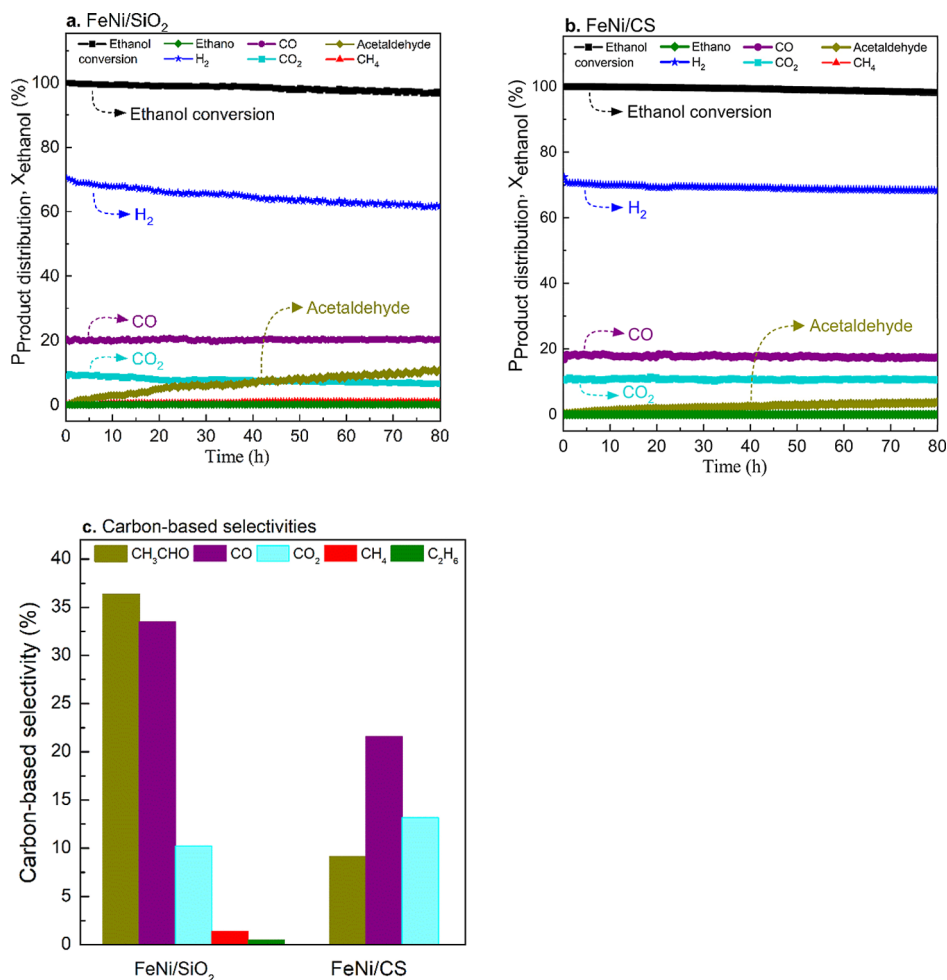


Figure 5. Ethanol conversion and distribution of products of the ESR reaction at 600 °C under H₂O/ethanol molar ratio of 3:1 for 80 h of samples (a) FeNi/SiO₂ and (b) FeNi/CS. (c) Selectivity in carbon basis for product *i*, derived from the distribution and feed flow of the ESR reaction for FeNi/SiO₂ and FeNi/CS samples.

production remained stable at approximately 100% and 70%, respectively, over a period of 80 h. CO and CO₂ were observed, with values around 17% and 10%, respectively. Notably, no significant amounts of ethene or methane were detected, indicating the absence of secondary reactions.

The combination of Ni and Fe enhances catalytic performance: Ni promotes C–C bond cleavage in ethanol, favoring the primary ESR pathway, while Fe assists in gasifying carbon intermediates, mitigating rapid deactivation via coke deposition.^{20,54,55} The core–shell architecture ensures effective diffusion of reactants and products during the reaction, improving FeNi/CS performance. This structure provides a mechanical barrier of the ceria oxide that prevents carbonaceous deposits on active sites, preserving the catalyst's structural integrity and carbon formation.³²

To further evaluate the role of the catalyst architecture, a control experiment was performed using a physical mixture of FeNi/SiO₂ and commercial CeO₂ under identical ESR conditions (Figure S7, Supporting Information). The physical mixture exhibited significantly lower H₂ selectivity (~45%) compared to the FeNi–CS catalyst (~70%), along with a higher acetaldehyde formation, indicating incomplete ethanol conversion and accumulation of intermediate species. In contrast, the FeNi/CS sample showed enhanced conversion of intermediates toward hydrogen production. These results

indicate that the simple presence of CeO₂ as a separate phase is not sufficient to reproduce the catalytic performance of the core–shell system. Instead, the improved performance is attributed to the intimate interaction between the Ni–Fe active phase and the CeO₂ shell, which promotes interfacial processes and facilitates the conversion of reaction intermediates. This comparison highlights the importance of the core–shell architecture in achieving improved catalytic performance during ethanol steam reforming.

The inclusion of CeO₂ in FeNi/CS catalyst contributes to suppressing carbon formation through its redox properties. The reversibly Ce⁴⁺/Ce³⁺ transition enables oxygen storage and release, promoting the gasification of carbonaceous species and maintaining a dynamic balance between carbon formation and removal. Additionally, CeO₂ enhances metal dispersion and stabilization, acting as an anchoring phase for Ni–Fe species. These effects are strongly influenced by oxygen vacancies on the catalyst surface, which are provided by CeO₂, further improving performance.^{27,32}

Figure 5c shows the carbon-based selectivity of the reaction products obtained during the 80 h experiment over FeNi/SiO₂ and FeNi/CS catalysts. FeNi/SiO₂ exhibits high selectivity toward CH₃CHO and CO, with values of approximately 36% and 33%, respectively, indicating that ethanol dehydrogenation and decomposition pathways are favored on this catalyst. In

contrast, FeNi/CS shows significantly lower selectivity toward CH_3CHO and CO , around 9% and 22%, respectively, together with an increased CO_2 selectivity, suggesting that the water–gas shift reaction is more favored over this material.

These results indicate that the core–shell structure formed by the CeO_2 layer can promote carbon reforming and oxidation reactions, likely associated with the redox properties of ceria and the formation of oxygen vacancies.²⁵ In addition, the formation of CH_4 and ethane (C_2H_6) is observed only for FeNi/ SiO_2 , indicating a higher tendency toward the formation of carbonaceous species on this catalyst.

Table 3 lists the ethanol conversion, H_2 molar yield, and postreaction carbon formation quantified by thermogravimetric

Table 3. Catalytic Results of Ethanol Conversion and H_2 Yield. Amount of Carbon Formed for all Spent Catalyst After ESR Reaction

samples	conversion ethanol (%)	H_2 yield (mol/mol ethanol)	carbon formed ($\text{mgC g}_{\text{cat}}^{-1} \text{h}^{-1}$)
FeNi/ SiO_2 (80 h)	98.3 ± 0.8	1.7 ± 0.8	20.7 ± 0.5
FeNi/CS (80 h)	99.2 ± 0.5	2.1 ± 0.9	11.7 ± 0.3

analysis. The FeNi/CS catalyst exhibits slightly higher ethanol conversion and H_2 yield compared to FeNi/ SiO_2 . However, despite the complete ethanol conversion, the H_2 yield remained below the stoichiometric maximum. The gap between the experimental H_2 yield and the theoretical value is a consequence of the selectivity toward byproducts like acetaldehyde and CO , which consume hydrogen atoms or limit their release via the water–gas shift reaction.

Raman spectroscopy was employed to identify carbon species in the spent catalysts (Figure 6). The spectra reveal

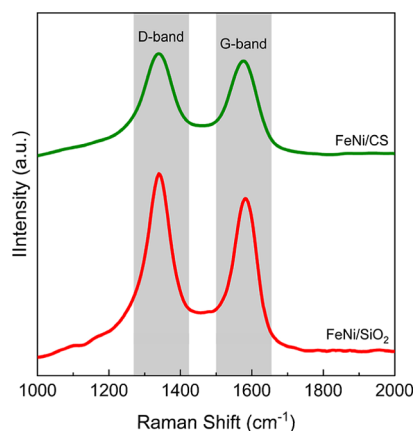


Figure 6. Raman spectra for all spent catalyst after ESR reaction.

the D and G bands, characteristic of carbonaceous materials at $\sim 1350 \text{ cm}^{-1}$ and $\sim 1580 \text{ cm}^{-1}$, respectively. The D band corresponds to disordered carbon (e.g., amorphous or defective filamentous carbon), whereas the G band is associated with ordered graphitic carbon.^{20,56} The quantitative determination of the carbon deposition rate was performed by thermogravimetric analysis of the spent catalysts, where the FeNi/ SiO_2 sample presented $\sim 21 \text{ mgC g}_{\text{cat}}^{-1} \text{h}^{-1}$, whereas the FeNi/CS sample presented $\sim 12 \text{ mgC g}_{\text{cat}}^{-1} \text{h}^{-1}$. This behavior can be attributed to the presence of the CeO_2 shell in the FeNi/CS catalyst, which can store and release active oxygen

species. These species promote water and oxygen activation and can react with deposited carbon to form CO_x , thereby suppressing surface carbon accumulation and contributing to enhanced catalytic stability over time.²⁰

In addition to suppressing carbon deposition, the CeO_2 shell may contribute to additional catalytic functions. The high concentration of oxygen vacancies associated with the $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple can enhance water–gas shift activity, facilitating CO conversion and improving hydrogen production during ethanol steam reforming. Moreover, the strong interaction between CeO_2 and metallic species may stabilize the dispersion of Ni–Fe alloy particles under reaction conditions, limiting sintering and maintaining active catalytic sites. The metal–oxide interface between Ni–Fe species and the ceria shell can also promote the activation of water molecules and oxygen-containing intermediates, further contributing to the removal of surface carbon species.^{19,20,25}

Considering that the FeNi/CS sample exhibits higher ethanol conversion, increased H_2 production, and lower carbon deposition, the incorporation of CeO_2 into the catalyst structure appears beneficial for improving catalyst stability, especially because deactivation caused by carbon deposition remains a major challenge in the development of ESR catalysts.

4. CONCLUSION

Bimetallic catalysts with a rational microstructural design were developed for hydrogen production via the ethanol steam reforming reaction (ESR). Structural and morphological characterizations confirmed the successful assembly of a core–shell architecture, in which the bimetallic active phase is supported on spherical silica and encapsulated by a ceria shell. The presence of the ceria layer reduces H_2 consumption during reduction, suggesting partial coverage of the metal nanoparticles and limited accessibility of reducible species. Postreduction XRD and TEM/EDS analyses confirmed the formation of a FeNi alloy formation in FeNi/ SiO_2 and a uniform ceria coating in FeNi/CS, while XPS results revealed oxygen vacancies and partial reduction of Ni and Fe species in FeNi/CS, which are critical for redox activity. Such microstructure confers to the produced materials a protective coverage of ceria that prevents the metallic active sites from agglomeration and carbon formation. Such effects are related to both the architecture microstructure of the catalyst and the redox properties of ceria.

The catalytic performance of FeNi/ SiO_2 and FeNi/CS in ESR highlights the advantages of the core–shell design. In both catalysts, the FeNi alloy promotes the conversion of the ethoxy species to acetates, contributing to the mitigation of carbon formation. However, the FeNi/CS catalyst exhibits superior performance due to the presence of the CeO_2 shell, which, rather than acting as conventional support, forms an encapsulating layer that directly interfaces with the Fe–Ni active phase.

This configuration promotes a synergistic interaction between CeO_2 and the FeNi alloy, enhancing oxygen transfer at the metal–oxide interface and facilitating the continuous removal of carbonaceous intermediates. In this system, Fe contributes to suppressing coke formation, while the CeO_2 shell provides mobile oxygen species that assist in carbon gasification, resulting in a cooperative effect that improves catalyst stability.

As a result, the FeNi/CS catalyst achieves higher ethanol conversion, sustained H_2 production, lower selectivity toward

carbonaceous products, and reduced carbon deposition compared to FeNi/SiO₂ during prolonged ESR operation. These findings demonstrate that the improved catalytic behavior is not solely due to the presence of CeO₂, but rather to its role as a shell that enhances metal–support interactions and promotes synergistic effects with the FeNi phase.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.energyfuels.6c00504>.

Schematic representation of catalyst synthesis; Nitrogen adsorption and desorption isotherms and pore size distribution for all samples; Elemental map in detail for all samples; Catalytic performance of FeNi/SiO₂ and CeO₂ catalyst prepared by physical mixture (PDF)

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Notes

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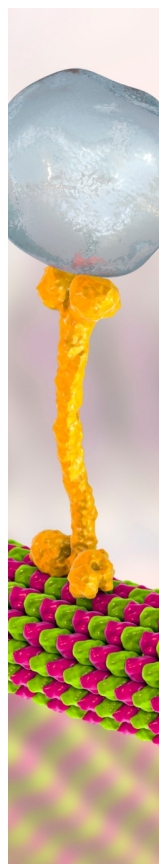
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