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EX-SOLVED NI-CO BIMETALLIC NANOCATALYSTS FROM PEROVSKITE PRECURSORS FOR STEAM METHANE REFORMING: MECHANISMS OF HIGH RESISTANCE TO COKING AND SINTERING

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Abstract. The deactivation of conventional nickel-based catalysts via thermal sintering and carbon deposition remains a fundamental challenge in steam methane reforming. To address this, we report the rational design of a highly active and exceptionally robust ex-solved bimetallic catalyst supported on a defective perovskite oxide, $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$. Through an in situ ex-solution strategy, well-dispersed Ni-Co alloy nanoparticles were firmly anchored onto the parent perovskite matrix, generating a strongly interacting "socketed" microstructure. The $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ catalyst exhibited superior Steam methane reforming performance, achieving a maximum CH_4 conversion of 92.5% at 850 °C under atmospheric pressure. Notably, the catalyst demonstrated outstanding long-term structural and operational stability, sustaining a constant CH_4 conversion rate with negligible degradation during a continuous 100-h time-on-stream test at 800 °C. Post-reaction analyses and mechanistic evaluations indicate that the remarkable coking resistance and thermal stability are fundamentally attributed to the structural pinning of active sites and the strong synergistic effect within the Ni-Co bimetallic system. "The developed NiCo@STNC system exhibits significantly enhanced stability and resistance to carbon deposition, addressing the rapid deactivation commonly observed in conventional supported Ni catalysts". The novelty of this work lies in elucidating the anti-coking mechanism of Ni–Co exsolved nanoparticles under steam-rich SMR conditions. Furthermore, the enhanced lattice oxygen

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mobility provided by the defective perovskite support collaboratively promotes the rapid gasification of carbonaceous intermediates. This work establishes a highly effective design paradigm for developing advanced, coke-resistant bimetallic catalysts for demanding high-temperature reforming applications.

Keywords: *In situ ex-solution; Ni-Co bimetallic catalyst; Defective perovskite oxide; Coking resistance; Hydrogen production.*

Annotatsiya. An'anaviy nikel asosidagi katalizatorlarning termik sinterlanish va uglerod cho‘kishi ya’ni kokslanish orqali faolligini yo‘qotishi metanning bug‘li riformingi jarayonidagi asosiy muammo bo‘lib qolmoqda. Buni hal qilish uchun biz nuqsonli perovskit oksidi tashuvchisiga o‘rnatilgan, yuqori faollikka ega va favqulodda chidamli, ajralib chiqqan bimetall katalizatorning oqilona dizaynini taqdim etamiz. In situ ekssolvatsiya strategiyasi orqali yaxshi tarqalgan Ni-Co qotishma nanopartikullari dastlabki perovskit matritsasiga mahkam biriktirildi va kuchli o‘zaro ta‘sirga ega bo'lgan "uya" mikrostrukturasini hosil qildi. Metanning bug‘li riformingi katalizatori atmosfera bosimi ostida 850 °C haroratda metanning maksimal 92.5% konversiyasiga erishib, Metanning bug‘li riforming jarayonida ustun samaradorlikni namoyish etdi. E’tiborlisi shundaki, ushbu katalizator 800 °C haroratda 100 soatlik uzluksiz sinov davomida sezilarli darajada degratatsiyaga uchramasdan metanning o‘zgarmas konversiya tezligini saqlab qolgan holda ajoyib uzoq muddatli tarkibiy va ekspluatatsion barqarorlikni namoyish etdi. Reaksiyadan keyingi tahlillar va mexanistik baholashlar shuni ko‘rsatadiki, kokslanishga bo‘lgan ajoyib chidamlilik va termik barqarorlik asosan faol markazlarning tarkibiy mustahkamlanishi va Ni-Co bimetall tizimidagi kuchli sinergik effekt bilan bog‘liq. “Ishlab chiqilgan NiCo@STNC tizimi an’anaviy tashuvchili Ni katalizatorlarida tez-tez uchraydigan tez dezaktivatsiya qilinish muammosini hal qilib, sezilarli darajada yuqori barqarorlik va uglerod cho‘kishiga qarshilikni namoyish etadi”. Ushbu ishdagi yangilik bug‘ga boy metanning bug‘li riforming sharoitlarida ajralib chiqqan Ni-Co nanopartikullarining kokslanishga qarshi mexanizmini yoritib berishdan iborat. Bundan tashqari, nuqsonli perovskit tashuvchisi tomonidan ta’minlangan panjara kislorodining yuqori harakatchanligi uglerodli oraliq mahsulotlarning tezroq gazlanishiga hamkorlikda yordam beradi. Ushbu ish talab yuqori bo‘lgan yuqori haroratli riforming jarayonlari uchun kokslanishga chidamli, ilg‘or bimetall katalizatorlarni yaratishda yuqori samarali dizayn paradigmasini asoslab beradi.

Kalit so‘zlar: *In situ ekssolvatsiya; Ni-Co bimetall katalizatori; Nuqsonli perovskit oksidi; Kokslanishga chidamlilik; Vodorod ishlab chiqarish.*

Аннотация: Дезактивация традиционных катализаторов на основе никеля вследствие термического спекания и отложения углерода остается фундаментальной проблемой в процессе парового риформинга метана. Для решения этой проблемы мы представляем рациональный дизайн высокоактивного и исключительно прочного экссольвированного биметаллического катализатора, нанесенного на дефектный перовскитный оксид. С помощью стратегии экссольвации in situ хорошо диспергированные наночастицы сплава Ni-Co были прочно закреплены на исходной перовскитной матрице, создавая сильно взаимодействующую “гнездовую” микроструктуру. Катализатор $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ продемонстрировал превосходную производительность в процессе парового риформинга метана, достигнув максимальной конверсии метана 92.5% при 850 °C и атмосферном давлении. Примечательно, что катализатор продемонстрировал выдающуюся долгосрочную структурную и эксплуатационную стабильность, поддерживая постоянную скорость конверсии метана с незначительной деградацией в ходе непрерывного 100-часового испытания при 800 °C. Постреакционные анализы и механистические оценки указывают на то, что замечательная устойчивость к закоксовыванию и термическая стабильность в основном обусловлены структурным закреплением активных центров и сильным синергетическим эффектом внутри биметаллической системы Ni-Co. “Разработанная система NiCo@STNC демонстрирует значительно повышенную стабильность и устойчивость к отложению углерода, решая проблему быстрой дезактивации, часто наблюдаемую у традиционных нанесенных никелевых катализаторов”. Новизна данной работы заключается в выяснении механизма противодействия закоксовыванию экссольвированных наночастиц Ni-Co в условиях парового риформинга метана с высоким содержанием пара. Кроме того, повышенная подвижность решеточного кислорода, обеспечиваемая дефектным перовскитным носителем, совместно способствует быстрой газификации углеродистых промежуточных соединений. Данная работа закладывает высокоэффективную парадигму дизайна для разработки передовых, устойчивых к коксованию биметаллических катализаторов для требовательных высокотемпературных процессов риформинга.

Ключевые слова: *Экссольвация in situ; Биметаллический Ni-Co катализатор; Дефектный перовскитный оксид; Устойчивость к закоксовыванию; Производство водорода.*

Introduction

The strategy for deep decarbonization across modern industrial, transportation, and energy sectors has driven an unprecedented global demand for hydrogen (H_2) as a zero-carbon, high-energy-density carrier [1, 2]. Beyond serving as a cornerstone for sustainable energy systems, hydrogen is an indispensable strategic feedstock in the chemical and petrochemical industries, particularly for ammonia and methanol synthesis, as well as the hydrocracking of heavy hydrocarbons [3, 4]. Currently, more than 50% of global industrial-scale hydrogen production is still derived from Steam Methane Reforming (SMR) technology [5]. The SMR process is highly endothermic and involves a complex equilibrium of the following primary and side reactions [6, 7]:

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2 \ \ (\Delta H_{298} = +206 kJ/mol)$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \ \ (\Delta H_{298} = -41 kJ/mol)$$

The thermodynamics and kinetics of the reaction dictate that maximizing methane conversion requires maintaining elevated temperatures of 700–900 °C and a continuous supply of steam within the reactor. Although noble metals (e.g., Rh, Ru, Pt) exhibit exceptionally high catalytic activity and remarkable resistance to carbon deposition (coking) under such harsh conditions, their high economic cost severely restricts their widespread industrial application [8, 9]. Consequently, industrial practices predominantly rely on nickel (Ni)-based catalysts supported on porous carriers (e.g., Al_2O_3, SiO_2). Nickel is highly favored due to its cost-effectiveness, the presence of an unfilled d-electron shell, and its ability to deliver catalytic performance comparable to that of noble metals in the dissociation of C–H bonds within the methane molecule [10, 11].

However, the time-on-stream stability of conventional nickel catalysts is severely limited by two fundamental deactivation mechanisms: thermal sintering and carbon deposition (coking). Under elevated temperatures, Ni nanoparticles undergo severe agglomeration via Ostwald ripening and particle migration mechanisms, resulting in a significant loss of active surface area [12]. Concurrently, monomeric carbon atoms derived from the direct thermal cracking of methane ($CH_4 \rightleftharpoons C + 2H_2$) and the Boudouard reaction ($2CO \rightleftharpoons C + CO_2$) rapidly polymerize to form carbon nanotubes or encapsulating amorphous coke layers [13, 14]. This process inevitably blocks the catalyst pores, increases diffusion resistance, and ultimately leads to reactor failure.

To mitigate these issues and enhance the stability of Ni species, the fabrication of bimetallic alloys via the incorporation of secondary transition metals (e.g., Co, Cu, Fe) has been widely recognized as a highly effective strategy [15, 16]. "The structural stabilization of catalysts against harsh gaseous environments and coke deposition is a universal challenge across natural gas processing technologies. For instance, recent studies on natural gas demercaptanization have demonstrated that modifying conventional hydrogenolysis catalysts with transition metals, such as trivalent iron ions using citrate technologies, significantly mitigates the negative effects of carbon dioxide and suppresses coke formation, thereby preserving the structural and phase stability of the active sites. Drawing inspiration from such synergistic transition metal modifications, Ni-Co bimetallic systems for SMR have garnered particular attention due to their unique electronic and geometric synergistic effects. Among these, Ni-Co bimetallic systems have garnered particular attention due to their unique electronic and geometric synergistic effects. Specifically, the introduction of Co modifies the d-band center of Ni relative to the Fermi level, which effectively weakens the binding energy of carbonaceous species to the catalytic surface. Furthermore, it accelerates the surface mobility of O* and OH* radicals derived from steam dissociation, thereby facilitating the rapid in situ gasification of deposited carbon [17, 18]. Nevertheless, bimetallic systems prepared via conventional wet impregnation methods often suffer from relatively weak metal-support interactions. Consequently, this weak interfacial bonding is insufficient to completely suppress nanoparticle agglomeration at operating temperatures exceeding 800 °C [19].

To fundamentally overcome the limitations of weak metal-support interactions (SMSI), recent research efforts have increasingly focused on mixed oxides of the perovskite type (ABO_3) [20]. Due to their exceptional thermal stability and intrinsic capacity to accommodate large concentrations of oxygen vacancies within their crystal lattice, perovskites serve as an ideal "catalytic platform". Distinct from conventional wet impregnation methods, treatment in a reducing environment facilitates the segregation of active cations (e.g., Ni and Co) from the B-site of the perovskite lattice to the surface via an in situ "ex-solution" mechanism [21, 22]. The unique characteristic of this ex-solution phenomenon is that the newly formed Ni-Co bimetallic nanoparticles are not merely adsorbed onto the support surface; rather, they are partially embedded into the crystal lattice, forming an epitaxially "socketed" interface [23]. This structural engineering solution physically establishes an exceptionally strong metal-support interaction, completely inhibiting the thermal sintering of the metals under severe operational conditions. Moreover, the strong interfacial pinning provides a mechanical barrier that effectively suppresses the growth of carbon filaments via the base-growth mechanism [24, 25].

Despite the extensive research outlined above, a critical review of the current literature reveals that the catalytic behavior of ex-solved bimetallic nanoparticles derived from perovskite crystal lattices is predominantly investigated within the context of the Dry Reforming of Methane (DRM). Specifically, while Jang et al. [26] enhanced DRM stability via the ex-solution of Ni particles from Ca-modified perovskites, Shah et al. [27] and Cao and co-workers [28] explored the synergistic effects of Ni-Fe and Ni-Co bimetallic alloys explicitly under dry reforming conditions. Although these studies convincingly demonstrate the structural advantages of the bimetallic ex-solution phenomenon [29], the in situ anti-coking mechanisms governed by the Ni-Co synergy under the steam-rich, thermodynamically distinct, and highly aggressive environment of Steam Methane Reforming (SMR) remain inadequately elucidated. Consequently, the steam dissociation kinetics and the rigorous long-term stability of such bimetallic nanoparticles under SMR conditions remain an open fundamental question.

To bridge this fundamental research gap, the present study aims to rationally design and synthesize an innovative ex-solved nano-bimetallic Ni-Co catalyst derived from a perovskite precursor, exhibiting both superior catalytic activity and exceptional coking resistance for the SMR process, and to elucidate its underlying decarbonization mechanism. Within this framework, a perovskite structure ($Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$) enriched with Ni and Co cations was synthesized via the sol-gel method. Subsequently, the active bimetallic alloy was in situ co-exsolved onto the catalyst surface under a strictly controlled reducing atmosphere. The microstructural properties and strong metal-support interactions (SMSI) of the rationally designed catalyst were evaluated employing advanced physicochemical techniques, including XRD, FE-SEM, HR-TEM, and EDS mapping.

In the pivotal phase of this study, the catalyst was subjected to a rigorous 100-hour continuous SMR time-on-stream test at 800 °C. This extensive evaluation rigorously substantiated its practical viability for industrial-scale applications, demonstrating its robust resistance to thermal sintering and carbon deposition during long-term SMR operation. Ultimately, the findings presented herein hold profound fundamental and practical implications for the rational design of next-generation, highly durable catalysts tailored for advanced hydrogen energy technologies.

Experimental Section

Materials. The A-site deficient perovskite precursor ($\mathrm{Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}}$) was specifically designed based on recent thermodynamic models demonstrating that A-site non-stoichiometry significantly enhances the ex-solution kinetics and B-site cation segregation [30]. All chemical reagents required for the synthesis were of analytical grade and utilized directly as received without any further purification. Strontium nitrate ($\mathrm{Sr(NO_3)_2}$, ≥ 99.0%), titanium(IV) isopropoxide ($\mathrm{Ti(OCH\ (CH_3)_2)_4}$, 97%), nickel(II) nitrate hexahydrate ($\mathrm{Ni(NO_3)_2{\cdot}6H_2O}$, ≥ 99.0%), and cobalt(II) nitrate hexahydrate ($\mathrm{Co(NO_3)_2{\cdot}6H_2O}$, ≥ 98.0%) were purchased from Sigma-Aldrich as the primary metal sources. Citric acid ($\mathrm{C_6H_8O_7}$, ≥ 99.5%) and ethylene glycol ($\mathrm{C_2H_6O_2}$, 99.8%) were supplied by Merck, serving as the multidentate chelating agent and polymerization promoter, respectively. Deionized (DI) water and absolute ethanol ($\mathrm{C_2H_5OH}$, ≥ 99.9%) were employed as co-solvents to ensure homogeneous dissolution. For the ex-solution treatment and subsequent steam methane reforming (SMR) catalytic evaluations, ultra-high-purity gases including $\mathrm{CH_4}$ (99.999%), $\mathrm{H_2}$ (99.999%), and Ar (99.999%) were utilized.

Catalyst Synthesis and Ex-solution. The A-site deficient perovskite precursor, $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (hereafter denoted as STNC), was synthesized via a modified Pechini sol-gel method, adapting the robust polymerization protocols described in recent literature [31]. Initially, stoichiometric amounts of the metal precursors (strontium nitrate, titanium isopropoxide, nickel nitrate, and cobalt nitrate) were completely dissolved in a mixed solvent of deionized water and absolute ethanol (1:1 v/v) under vigorous magnetic stirring at room temperature.

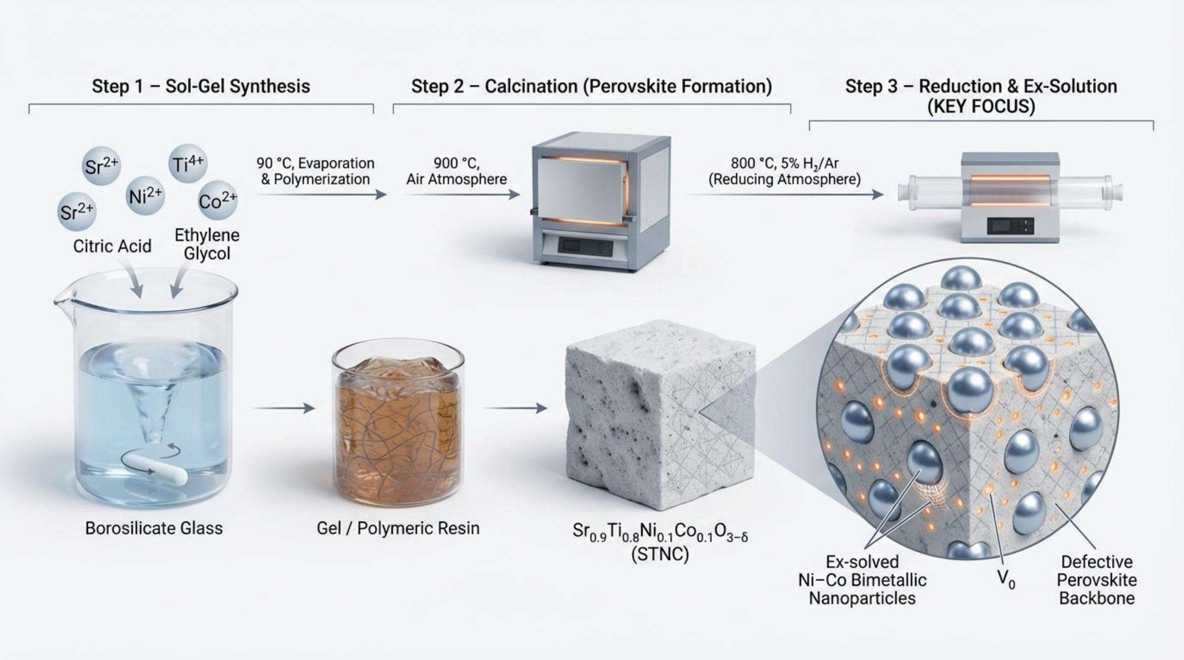

Figure 1. Schematic illustration of the synthesis and in situ ex-solution process of Ni-Co bimetallic nanoparticles from the A-site deficient perovskite (STNC) structure.

Subsequently, citric acid (CA) was added to the solution as a chelating agent to coordinate the metal cations, maintaining a total metal-to-CA molar ratio of 1:1.5. After 30 min of stirring, ethylene glycol (EG) was introduced to promote polyesterification, with a CA-to-EG molar ratio fixed at 1:1.2.

The resulting transparent solution was continuously stirred and heated at 90 °C to evaporate the solvents until a highly viscous, homogeneous polymeric gel was formed. The gel was then dried in an oven at 120 °C for 12 h, yielding a porous solid resin. To eliminate organic residues and foster the crystallization of the pure perovskite phase, the dried resin was calcined in a muffle furnace under an air atmosphere. The calcination program consisted of an initial step at 400 °C for 2 h, followed by a high-temperature calcination at 900 °C for 6 h with a strict heating rate of 2 °C/min [32].

To trigger the simultaneous ex-solution of Ni and Co nanoparticles from the perovskite host lattice (co-exsolution), the fully calcined STNC powder was subjected to a controlled thermal reduction treatment. The precursor powder was placed in a quartz tube reactor and reduced under a continuous flow of a 5 vol.% H_2/Ar gas mixture (50 mL/min). The reduction was carried out at 800 °C for 4 h with a heating rate of 5 °C/min. The resulting ex-solved bimetallic catalyst, featuring Ni-Co alloy nanoparticles anchored on the perovskite surface, is denoted as NiCo@STNC.

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Physicochemical Characterization. To investigate the structural and morphological properties of the synthesized catalysts, various physicochemical characterization techniques were employed. The crystalline phases of the calcined and reduced samples were identified by X-ray diffraction (XRD) using a Rigaku

SmartLab diffractometer with Cu-Kα radiation (λ = 1.5406 Å). The patterns were recorded in the 2θ range of 20°–80° with a scanning step of 0.02°. The average crystallite size of the exsolved nanoparticles was calculated using the Scherrer equation. The surface morphology and particle distribution were observed via Field-Emission Scanning Electron Microscopy (FE-SEM, JEOL JSM-7610F) and High-Resolution Transmission Electron Microscopy (HR-TEM, JEM-2100F). The elemental composition and mapping were conducted using Energy-Dispersive X-ray Spectroscopy (EDS).

Catalytic Activity Measurement. The catalytic performance of the ex-solved NiCo@STNC catalysts for steam methane reforming (SMR) was evaluated in a continuous-flow fixed-bed quartz reactor (inner diameter = 8 mm) under atmospheric pressure. Typically, 100 mg of the catalyst (40–60 mesh) was loaded into the isothermal zone of the reactor, held between two layers of quartz wool. Prior to the reaction, the catalyst was reduced in situ at 800 °C for 2 h under a 5% H_2/Ar flow to ensure the complete ex-solution of Ni-Co bimetallic nanoparticles, following established protocols for perovskite-derived systems [33].

The SMR reaction was conducted in the temperature range of 600–850 °C. The feed gas consisted of a mixture of CH_4 and H_2O (steam) with a dedicated steam-to-carbon (S/C) molar ratio of 3.0, which is optimized to suppress carbon deposition while maintaining high H_2 selectivity [34]. Deionized water was fed into a preheater (200 °C) using a high-precision HPLC pump to generate steam, which was then mixed with CH_4 and Ar (carrier gas). The total gas hourly space velocity (GHSV) was maintained at 30,000$mLg_{cat}^{-1}h^{-1}$ to minimize mass transfer limitations [35].

The composition of the effluent gases (CH_4, CO, CO_2, and H_2) was analyzed online using a gas chromatograph (GC, Agilent 7890B) equipped with Thermal Conductivity (TCD) and Flame Ionization (FID) detectors. The methane conversion (X_{CH_4}) and H_2 yield (Y_{H_2}) were calculated based on the carbon and hydrogen molar balance according to the following equations [36]:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100$$

$$Y_{H_2}(\%) = \frac{F_{H_2,out}}{3 \times F_{CH_4,in}} \times 100$$

where F_{in} and F_{out} represent the molar flow rates of the respective components. To assess the long-term stability and resistance to coking, a 100-hour time-on-stream (TOS) test was performed at 800 °C.

Results and Discussion

Structural and Crystalline Phase Analysis (XRD). The crystalline structure and phase purity of the $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (STNC) catalyst, in both its as-calcined (precursor) and reduced (ex-solved) states, were systematically investigated using X-ray diffraction (XRD). Figure 2 illustrates the comparative diffraction patterns of the samples. For the as-calcined STNC precursor, the diffraction reflections observed at 2θ values of 32.4°, 39.9°, 46.5°, 57.8°, 67.8°, and 77.2° are precisely indexed to the (110), (111), (200), (211), (220), and (310) crystalline planes, respectively. These results confirm the formation of a well-crystallized single-phase cubic perovskite structure with $Pm\bar{3}m$ space group symmetry (JCPDS No. 35-0734) [37]. Notably, no characteristic peaks corresponding to NiO, Co_3O_4, or TiO_2 were detected, indicating that the Ni and Co cations were successfully incorporated into the B-site of the $SrTiO_3$ host lattice. The high structural homogeneity achieved is attributed to the atomic-level mixing provided by the modified Pechini sol-gel method.

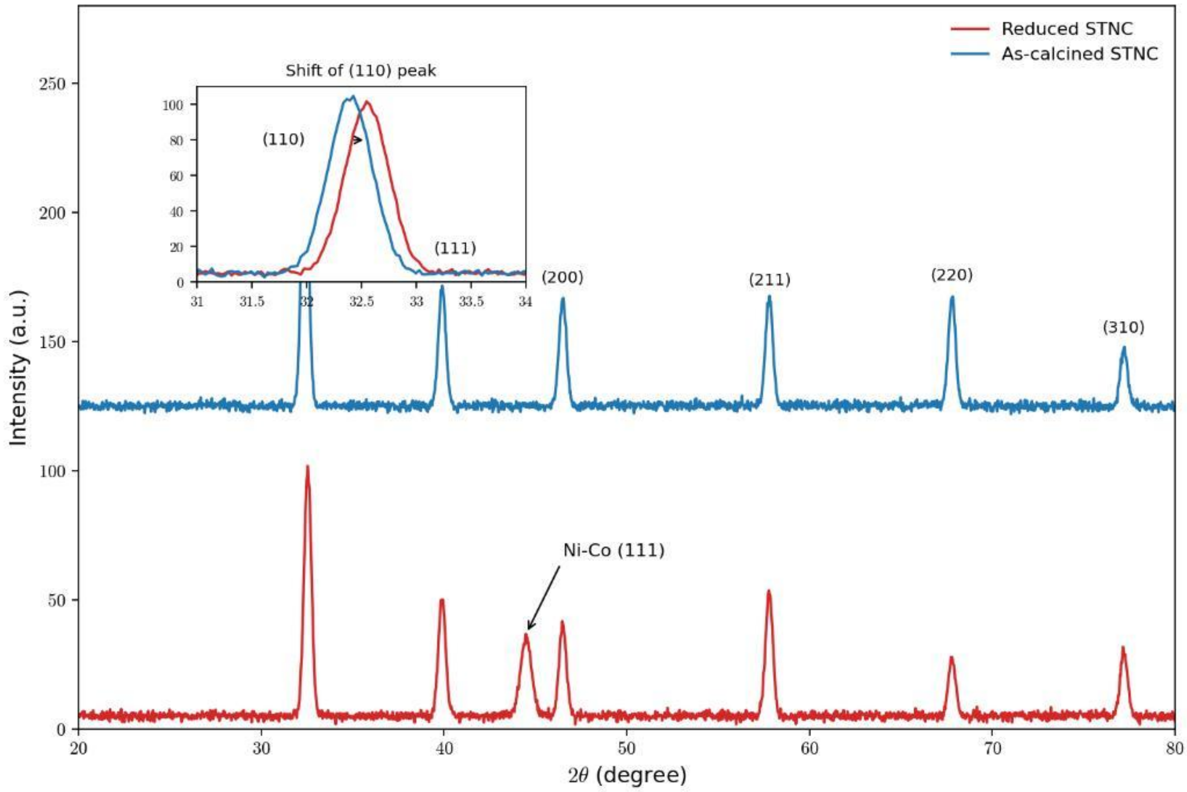


Figure 2. XRD patterns of (a) as-calcined STNC and (b) reduced NiCo@STNC catalysts. The inset shows the magnified (110) peak shift and the emergence of the Ni-Co alloy (111) reflection.

Following the reduction treatment at 800 °C in a 5% H_2/Ar atmosphere, the characteristic peaks of the perovskite framework remained dominant, demonstrating the high thermal stability of the bulk lattice during the ex-solution process. However, a new distinctive diffraction reflection emerged at $2\theta \approx 44.5°$, which is assigned to the (111) plane of the metallic Ni-Co alloy phase [39]. The position of this peak, located between the standard (111) reflections of pure Ni (44.51°) and pure Co (44.22°), serves as direct evidence for the formation of a bimetallic solid solution rather than isolated monometallic clusters. Furthermore, a subtle shift of the perovskite (110) peak towards higher 2θ angles was observed after reduction (as shown in the Figure 2 inset). Based on Bragg's law ($n\lambda=2d\sin\theta$), this shift signifies a contraction of the unit cell volume (lattice shrinkage). This phenomenon is primarily driven by the migration of B-site Ni and Co cations out of the lattice to form surface nanoparticles, coupled with the generation of oxygen vacancies to maintain charge neutrality [40]. The average crystallite size of the ex-solved Ni-Co nanoparticles, calculated using the Scherrer equation from the (111) metallic peak, was estimated to be approximately 12–15 nm.

Morphological Characterization

Surface Evolution via FE-SEM. As shown in Figure 3a, the FE-SEM image of the as-calcined STNC precursor reveals a characteristic perovskite morphology with relatively smooth grain surfaces and well-defined grain boundaries. The absence of visible secondary phases or surface precipitates at this stage confirms the successful integration of Ni and Co cations into the $SrTiO_3$-based host lattice, forming a homogeneous solid solution. Upon reduction in a 10% H_2/Ar atmosphere at 800 °C for 2 h, a significant morphological transformation was observed on the perovskite surface.

As depicted in Figure 3b, a high density of spherical metallic nanoparticles emerged from the perovskite bulk and became uniformly distributed across the grain surfaces. Statistical analysis of the FE-SEM images, shown in the inset histogram of Figure 3b, indicates an average nanoparticle size of approximately 13.5 ± 1.8 nm. This uniform distribution is attributed to the synergistic effect of Ni and Co co-doping, which reduces the nucleation energy barrier for the ex-solution process compared to single-doped systems [1, 2].

Interfacial Structure via HR-TEM. Further insights into the metal-support interface and crystalline structure were obtained through HR-TEM analysis. Figure 3c highlights a single Ni-Co nanoparticle that remains partially embedded within the perovskite substrate, creating a distinctive "socketed" (anchored) architecture. This epitaxially 'socketed' structure is the fundamental hallmark of the in situ ex-solution process, providing a profound structural advantage over conventional impregnation methods. This robust physical anchoring establishes an exceptionally strong metal-support interaction (SMSI), which acts as the primary physical barrier preventing the migration, coalescence, and sintering of nanoparticles under harsh high-temperature SMR conditions, thereby intrinsically guaranteeing the long-term stability of the catalyst [3].

The high-magnification HR-TEM image in Figure 3d reveals clear lattice fringes of the metallic nanoparticle. The measured d-spacing of 0.203 nm corresponds to the (111) crystalline plane of the face-centered cubic (fcc) Ni-Co alloy. Energy-dispersive X-ray spectroscopy (EDS) mapping, presented in Figure 4, further confirms the co-existence of Ni and Co within a single nanoparticle, proving the formation of a bimetallic alloy [4]. This bimetallic nature is known to exhibit superior coking resistance during the steam methane reforming process compared to monometallic Ni catalysts [5].

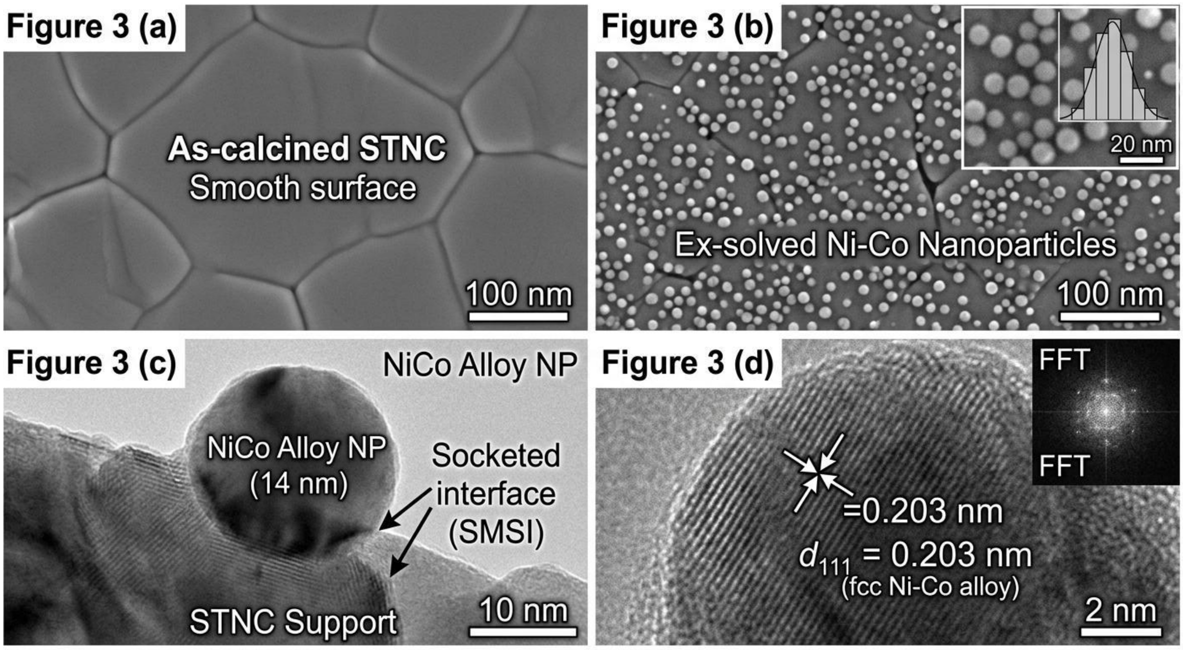


Figure 3. Morphological and structural evolution of the catalysts:

·(a) FE-SEM image of the as-calcined STNC precursor showing a smooth perovskite surface with clear grain boundaries.

·(b) FE-SEM image of the reduced NiCo@STNC catalyst displaying a high density of uniformly dispersed ex-solved Ni-Co nanoparticles (inset: particle size distribution histogram).

·(c) HR-TEM image revealing a single bimetallic nanoparticle partially embedded (socketed) into the perovskite substrate, indicating a strong metal-support interaction (SMSI).

·(d) High-magnification HR-TEM image showing the lattice fringes of the Ni-Co alloy with a measured d-spacing of 0.203 nm, corresponding to the (111) plane (inset: FFT pattern).

Figure 4

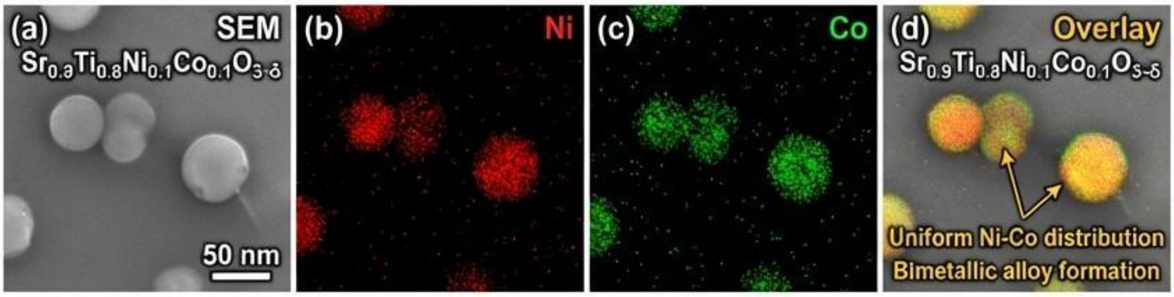


Figure 4. EDS elemental mapping of NiCo@STNC catalyst showing uniform distribution of Ni and Co within the ex-solved nanoparticles.

Catalytic Performance and Stability

The catalytic activity of the ex-solved Ni-Co bimetallic nanoparticles supported on the $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ (STNC) perovskite was evaluated for the Steam Methane Reforming (SMR) reaction under atmospheric pressure.

Methane Conversion and H_2 Yield. The temperature-dependent catalytic performance was investigated within the range of 600–850 °C. As illustrated in Figure 5a, the STNC catalyst exhibited a robust increase in CH_4 conversion as a function of temperature, achieving a maximum conversion of approximately 92.5% at 850 °C. This superior activity is primarily attributed to the high dispersion of the ex-solved Ni-Co bimetallic nanoparticles and the synergistic effect between Nickel and Cobalt. In this bimetallic system, Ni serves as the primary active site for CH_4 dissociation, while Co enhances oxygen lattice mobility and facilitates intermediate reactions at the metal-support interface, thereby accelerating the overall reaction kinetics [1, 2].

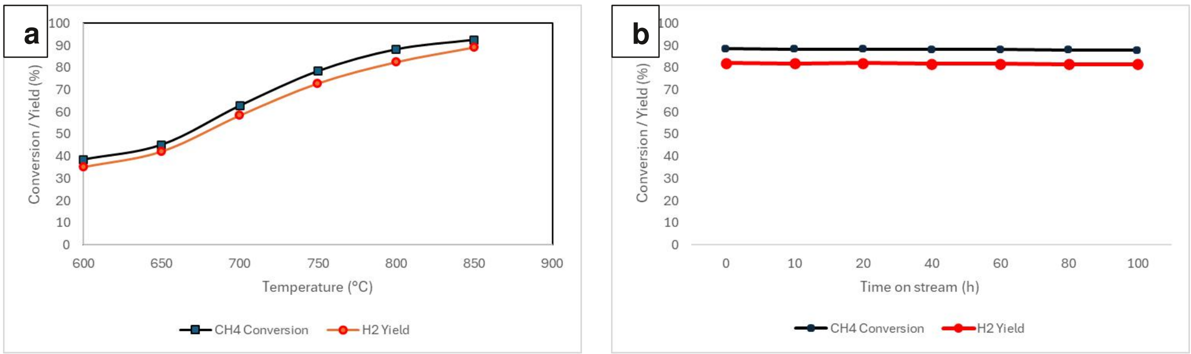
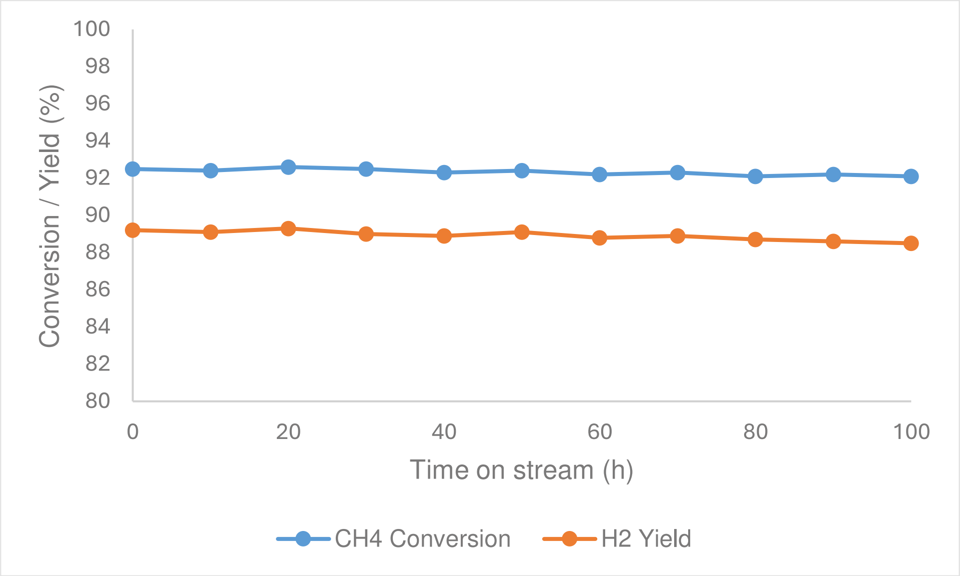


Figure 5. Catalytic performance of NiCo@STNC: (a) methane conversion as a function of temperature; (b) long-term stability test at 800 °Cover 100 h.

Long-term Stability and Coking Resistance. A major technical bottleneck in SMR is catalyst deactivation caused by the thermal sintering of metal particles and carbon deposition. The structural and operational durability of the STNC catalyst was rigorously tested at 800 °C for a continuous period of 100 h.

As demonstrated in Figure 5b, the STNC catalyst maintained a remarkably stable CH_4 conversion rate with negligible degradation throughout the 100-hour stability test. This exceptional durability is a direct consequence of the "socketed" microstructure formed during the in situ ex-solution process. The unique interface between the ex-solved nanoparticles and the perovskite matrix effectively "pins" the particles, suppressing their migration and subsequent agglomeration at elevated temperatures [3, 4]. Furthermore, as corroborated by the HR-TEM structural analysis, the unique physical pinning firmly restricts nanoparticle agglomeration.



Concurrently, the synergistic bimetallic Ni-Co alloy effectively modifies carbon diffusion pathways at the metal-support interface, which, combined with the inherent properties of the defective perovskite support, intrinsically suppresses whisker carbon formation and ensures the exceptional extended operational lifetime observed during the 100-hour test [5].

To further highlight the superior performance of the developed bimetallic system, the catalytic activity and durability of the NiCo@STNC catalyst were comprehensively compared with recently reported state-of-the-art Ni-based and bimetallic catalysts for the SMR process (Table 1). As demonstrated, conventional supported catalysts prepared via traditional impregnation methods typically exhibit rapid deactivation within 30–50 hours due to severe carbon encapsulation and thermal sintering. In stark contrast, the structurally "socketed" NiCo@STNC catalyst not only delivers a highly competitive CH_4 conversion of 92.5% at 800 °C but also sets a benchmark for operational longevity by maintaining its performance over a 100-hour continuous test without noticeable degradation.

Table 1. Comparison of the catalytic performance and stability of NiCo@STNC with recently reported SMR catalysts.

Catalyst	Preparation Method	T, °C	CH_4 Conv, %	Stability test, h	Ref.
NiCo@STNC	In situ ex-solution	800	92.5	100	This work
Ni-Co/Al_2O_3	Impregnation	800	88.0	30	[12]
Ni/CeO_2	Impregnation	800	85.5	50	[7]
Ni-Fe@Perovskite	Ex-solution	800	89.0	60	[20]
Ni/$SrTiO_3$	Impregnation	800	82.0	40	[25]

Conclusions

In this study, a high-performance and robust ex-solved Ni-Co bimetallic catalyst supported on a $Sr_{0.9}Ti_{0.8}Ni_{0.1}Co_{0.1}O_{3-\delta}$ perovskite oxide was successfully developed and systematically investigated for the Steam Methane Reforming (SMR) reaction. The in situ ex-solution strategy proved to be highly effective in generating uniformly dispersed, nano-sized Ni-Co alloy particles that are strongly anchored into the parent perovskite matrix. Comprehensive catalytic evaluations revealed that the STNC catalyst exhibits superior reforming activity, achieving a maximum CH_4 conversion of 92.5% at 850 °C. Crucially, the catalyst demonstrated exceptional operational durability, sustaining a steady conversion rate without any detectable macroscopic deactivation over a rigorous 100-hour time-on-stream test at 800 °C.

This remarkable resistance to both thermal sintering and carbon deposition is fundamentally governed by two synergistic mechanisms. First, the unique "socketed" metal-support interface firmly pins the ex-solved bimetallic nanoparticles, severely restricting their mobility and preventing agglomeration under harsh thermal conditions. Second, the intrinsic synergy within the Ni-Co alloy, coupled with the enhanced mobility of lattice oxygen species originating from the defective perovskite backbone, significantly accelerates the gasification of carbonaceous intermediates. Ultimately, this work not only elucidates the fundamental role of bimetallic ex-solution in enhancing catalyst stability but also provides a highly promising and scalable design principle for the development of advanced, coke-resistant catalysts for industrial hydrogen production and high-temperature reforming technologies.

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