Methane steam reforming (MSR) plays a key role in the production of syngas and hydrogen from natural gas. The increasing interest in the use of hydrogen for fuel cell applications demands the development of catalysts with high activity at reduced operating temperatures. Ni-based catalysts are promising systems because of their high activity and low cost, but coke formation generally poses a severe problem. Studies of ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) indicate that CH$_4$/H$_2$O gas mixtures react with Ni/CeO$_2$(111) surfaces to form OH, CH$_x$ and CH$_x$O at 300 K. All these species are easy to form and desorb at temperatures below 700 K when the rate of the MSR process accelerates. Density functional theory (DFT) modeling of the reaction over ceria-supported small Ni nanoparticles predicts relatively low activation barriers between 0.3–0.7 eV for the complete dehydrogenation of methane to carbon and the barrierless activation of water at interfacial Ni sites. Hydroxyls resulting from water activation allow CO formation via a COH intermediate with a barrier of about 0.9 eV, which is much lower than that through a pathway involving lattice oxygen from ceria. Neither methane nor water activation are rate-determining steps, and the OH-assisted CO formation through the COH intermediate constitutes a low-barrier pathway that prevents carbon accumulation. The interaction between Ni and the ceria support and the low metal loading are crucial for the reaction to proceed in a coke-free and efficient way. These results could pave the way for further advances in the design of stable and highly active Ni-based catalysts for hydrogen production.
Reaction Pathway for Coke-Free Methane Steam Reforming on a Ni/CeO$_2$

Catalyst: Active Sites and Role of Metal-Support Interactions

Agustín Salcedo$^{1,2}$, Pablo G. Lustemberg$^{3,4}$, Ning Rui$^5$, Robert M. Palomino$^5$, Zongyuan Liu$^5$, Slavomir Nemsak$^6$, Sanjaya D. Senanayake$^5$, José A. Rodríguez$^*5$, M. Verónica Ganduglia-Pirovano$^{*3}$, Beatriz Irigoyen$^{*1,2}$

$^1$Universidad de Buenos Aires (UBA), Facultad de Ingeniería, Departamento de Ingeniería Química, Ciudad Universitaria, C1428EGA Buenos Aires, Argentina

$^2$Instituto de Tecnologías de Hidrógeno y Energías Sostenibles (ITHES, CONICET-UBA), Ciudad Universitaria, C1428EGA Buenos Aires, Argentina

$^3$Instituto de Catálisis y Petroleoquímica (ICP, CSIC), 28049 Madrid, Spain

$^4$Instituto de Física Rosario (IFIR, CONICET-UNR), S2000EKF Rosario, Santa Fe, Argentina

$^5$Chemistry Division, Brookhaven National Laboratory, Upton, New York 11973, USA

$^6$Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Corresponding authors:

$^*$beatriz@di.fcen.uba.ar

$^*$vgp@icp.csic.es

$^*$rodrigez@bnl.gov
Abstract

Methane steam reforming (MSR) plays a key role in the production of syngas and hydrogen from natural gas. The increasing interest in the use of hydrogen for fuel cell applications demands the development of catalysts with high activity at reduced operating temperatures. Ni-based catalysts are promising systems because of their high activity and low cost, but coke formation generally poses a severe problem. Studies of ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) indicate that CH₄/H₂O gas mixtures react with Ni/CeO₂(111) surfaces to form OH, CHₓ and CHₓO at 300 K. All these species are easy to form and desorb at temperatures below 700 K when the rate of the MSR process accelerates. Density functional theory (DFT) modeling of the reaction over ceria-supported small Ni nanoparticles predicts relatively low activation barriers between 0.3–0.7 eV for the complete dehydrogenation of methane to carbon and the barrierless activation of water at interfacial Ni sites. Hydroxyls resulting from water activation allow CO formation via a COH intermediate with a barrier of about 0.9 eV, which is much lower than that through a pathway involving lattice oxygen from ceria. Neither methane nor water activation are rate-determining steps, and the OH-assisted CO formation through the COH intermediate constitutes a low-barrier pathway that prevents carbon accumulation. The interaction between Ni and the ceria support and the low metal loading are crucial for the reaction to proceed in a coke-free and efficient way. These results could pave the way for further advances in the design of stable and highly active Ni-based catalysts for hydrogen production.

Keywords

Methane, Steam reforming, Hydrogen, Nickel, Ceria, DFT
1. Introduction

Methane steam reforming (MSR, \(\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons 3\text{H}_2 + \text{CO}\)) is the main route for large-scale industrial manufacture of hydrogen, primarily used for the synthesis of ammonia and methanol, among other commodities,\(^1\) as well as the hydrocracking of long-chain hydrocarbons in petroleum refineries.\(^2\) In a typical industrial reformer the MSR reaction is carried out at 800–1000 °C and 14–20 atm, with a \(\text{H}_2\text{O}/\text{CH}_4\) ratio of \(\sim 2.5\).\(^1,3\) Environmental concerns about air pollution and greenhouse gases have renewed the interest in using hydrogen as a clean energy carrier for automotive applications, through its electrochemical conversion in fuel cell systems, which produces water as the only by-product. However, the severe reaction conditions of industrial MSR result in elevated capital and operating costs, which are prohibitive for small-scale fuel cell applications. Several alternative reactions have been proposed, such as methane dry reforming and partial oxidation, but their lower \(\text{H}_2/\text{CO}\) ratio compared to that of MSR makes them unfit for fuel cell applications that require high-purity \(\text{H}_2\).\(^4-6\) Therefore, it is necessary to improve MSR technology in order to reduce heating and steam requirements and achieve a cost-efficient \(\text{H}_2\) manufacture. In this sense, the capability to operate fuel cells at ambient pressure,\(^7\) and the development of hydrogen-selective membrane reactors,\(^8-10\) represent an opportunity to increase the thermodynamically limited conversion imposed by the endothermicity of the MSR reaction,\(^11\) allowing both lower operating temperatures (500–600 °C) and lower steam-to-methane ratios, while maintaining good \(\text{H}_2\) yield. Commercial catalysts in industrial reforming units, typically consisting of nickel on magnesium or aluminum oxides supports, are designed to withstand high-temperature operation without losing strength, and thus prioritize stability and thermal resistance over surface area.\(^1\) In addition, they are prone to deactivation by coking, sintering and sulfur poisoning.\(^12\) Noble metals such as Pt, Rh and Pd are also active for MSR, but more expensive than Ni.\(^11\) Therefore, the present challenge is to develop novel Ni-based catalysts to carry out the MSR reaction with high conversion at mild operating conditions for fuel cell applications. Among recently proposed alternatives, low-loaded Ni-impregnated \(\text{CeO}_2\) catalysts have shown to be promising candidates, showing improved coking and sintering resistance and excellent performance in experiments carried out at 600 °C and ambient pressure.\(^13,14\)
A complete understanding of the MSR reaction mechanism over ceria-supported Ni catalysts, which includes the identification of the active sites as well as the determination of the relevant reaction pathways, remains elusive, but it is essential to be able to modify the catalyst to enhance activity and selectivity.

Insights from density functional theory (DFT) calculations on model Ni-based MSR catalysts has so far been limited to extended Ni surfaces. It has been postulated that the activation of CH$_4$ determines the overall reaction rate, because its C–H bonds are very stable (440 kJ/mol) and pure metal surfaces tend to show low reactivity toward methane. However, experimental and computational studies have shown that the reactions of carbonaceous species with oxygen to form the C–O bond also involve high energy barriers, and could therefore be rate-controlling. Furthermore, in previous combined computational and in-situ spectroscopic studies, it was shown that well-dispersed small Ni nanoparticles supported on a non-reduced CeO$_2$ surface can in fact activate CH$_4$ at room temperature, with calculated energy barriers up to 80% lower than those for extended nickel surfaces. This highlights the need to consider both the effect of the nature of the support and the metal loading to fully understand the mechanism governing the MSR reaction over supported metal catalysts, which is necessary for the development of improved catalytic systems.

In general, dispersed metal nanoparticles on oxide surfaces tend to be more reactive than the individual components, showing great potential as novel catalytic materials. In low-loaded CeO$_2$-supported Ni catalysts, nickel is stabilized as small particles in which the Ni atoms in direct contact with ceria are partially oxidized as a consequence of strong metal-support interactions, resulting in important changes in the chemical and catalytic properties of these systems, particularly to perform C–H and O–H bond cleavage. Furthermore, the easier reducibility of the ceria support would allow it to act as an oxygen reservoir, providing unique reaction pathways such as the reverse spillover of oxygen from ceria to metal sites, which has been experimentally observed for a variety of ceria-supported metal catalysts, including Ni/CeO$_2$. Therefore, the observed superior decoking activity of ceria-supported Ni catalysts for MSR could be ascribed to a mechanism involving the oxygen supply from the support promoting carbon removal as CO, in which the role of water as one of the reactants would be the refilling of the oxygen vacancies generated in the
reverse spillover step. However, water-mediated carbon removal has also been discussed in the context of the steam reforming of CH₄. Whether carbon removal is assisted by oxygen from the support, from H₂O, or from both, is an essential question in the understanding of the MSR reaction mechanism.

Furthermore, since both reactants in the MSR reaction over Ni/CeO₂ catalysts adsorb at Ni sites and are generally in H₂O/CH₄ ratios higher than one, their potential competition for Ni sites should also be addressed. In this regard, the CH₄ conversion in the steam reforming reaction over Ni-impregnated Zr-doped CeO₂ catalysts was found to continuously increase with H₂O content, suggesting that whatever the competition, it would not be detrimental to the reaction.

It has been previously found that small coverages of nickel on CeO₂(111) produce surfaces that are able to catalyze the MSR process at temperatures above 500 K with high activity and low propensity to deactivation by coke deposition. This is a remarkable catalytic performance. Here, using a combination of ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) and molecular modeling based on density functional theory (DFT), we present a comprehensive study of the MSR reaction on the surface of model Ni/CeO₂(111) catalysts and compare with results reported for the extended Ni(111) surface in the literature. We show that low-loaded Ni/CeO₂ catalysts have sites with unique properties that result from the nature of both the metallic phase and the support as well as their interactions, which enable the facile activation of C–H and O–H bonds from CH₄ and H₂O, respectively. The calculated elementary dehydrogenation and oxidation steps along the MSR reaction reveal that the crucial step is the formation of a COH intermediate via the reaction of carbon atoms with OH groups, suppressing carbon deposition. This pathway presents much lower barriers than the one involving C oxidation with lattice oxygen from the ceria support and is promoted by the easy formation of OH groups through the barrierless dissociative adsorption of water at the Ni-CeO₂ interface. The results provide molecular insight into the interplay between C and OH species in the steam-reforming of methane on low-loaded Ni/CeO₂ catalysts for which metal–support interactions are crucial to bind and activate methane and water.
2. Methods

A. Experiments of ambient-pressure XPS

The ambient-pressure XPS studies examining the interaction of CH$_4$/H$_2$O gas mixtures with the Ni/CeO$_2$(111) surfaces were performed in instruments located at the Chemistry Division in Brookhaven National Laboratory (BNL) and at the Advanced Light Source (ALS) in Berkeley.$^{27-30}$ In both instruments, the Ni/CeO$_2$(111) surfaces were prepared and characterized following standard procedures.$^{27-29}$ Ce metal was first evaporated onto a Ru(0001) substrate at 700 K under a background pressure of 5 × 10$^{-7}$ torr of O$_2$, and then the sample was annealed at 800 K for a period of 10 mins at the same O$_2$ pressure. The CeO$_2$(111) films were estimated to be ca. 4 nm thick ($\approx$ 10 layers of O–Ce–O) based on the attenuation of the Ru 3d XPS signal. Ni was vapor-deposited on the as-prepared ceria films and the admetal coverage was estimated by the attenuation of the Ce 3d XPS signal.$^{27-29}$ The Ni/CeO$_2$(111) surfaces were exposed to CH$_4$, H$_2$O and CH$_4$/H$_2$O mixtures at temperatures between 300 and 700 K.

The AP-XPS instrument at BNL was a SPECS AP-XPS chamber equipped with a PHOIBOS 150 EP MCD-9 analyzer. Mg Kα radiation was used to collect the Ni 2p and Ce 3d spectra of the Ni/CeO$_2$(111) samples under exposure to the reacting gases. The binding energies in these AP-XPS spectra were calibrated using as reference the strongest Ce$^{4+}$ 3d feature located at 916.9 eV.

At the ALS, the AP-XPS experiments were done in beamline 9.3.2 which is equipped with a VG Scienta R4000 HiPP analyzer. Under exposure of Ni/CeO$_2$(111) to the reacting gases, the O 1s region was probed using a photon energy of 650 eV, and the C 1s, Ni 3p, and Ce 4d regions with a photon energy of 490 eV. The energy resolution in the synchrotron experiments was $\sim$0.2 eV. The Ce 4d photoemission lines were used for binding energy calibration based on the 122.8 eV satellite features. No evidence was found for the existence of beam damage in these AP-XPS studies.

B. Models and computational details

A Ni$_{13}$ cluster adsorbed on the CeO$_2$(111) surface with (3×3) periodicity$^{34}$ was used as a representative model of low-loaded ceria-supported nickel catalysts, hereinafter referred to as Ni$_{13}$CeO$_2$ (Figure S1). The size of the Ni$_{13}$ cluster is comparable to that of Ni
nanoparticles of model Ni/CeO$_2$ catalysts in experimental studies, and has metallic Ni$^0$ and oxidized Ni$^{0.55+}$ sites, both reported to be present at steam reforming conditions. The (3×3) CeO$_2$(111) surface was modeled using a supercell with the calculated ceria bulk equilibrium lattice parameter of $a_0 = 5.485$ Å, with 6 atomic layers (two O–Ce–O trilayers, TL) separated by at least a 12 Å thick vacuum-layer.

Calculations were performed within the spin-polarized density functional theory (DFT) framework as implemented in the Vienna Ab-initio Simulation Package (VASP). The Kohn–Sham equations were solved within the generalized gradient approximation (GGA), with the exchange-correlation functional of Perdew–Burke–Ernzerhof (PBE). We treated explicitly the Ce($5s^25p^66s^25d^14f^1$), Ni($3p^64s^23d^8$), O($2s^22p^4$) and C($2s^22p^2$) valence electrons using a plane wave basis with a cutoff energy of 415 eV, whereas the core electrons were represented with the projector-augmented wave (PAW) method. Total energies were calculated with a precision of 10$^{-6}$ eV. Strong correlation effects due to charge localization were considered with the DFT+U approach within the Dudarev’s scheme.

The oxidation state of a given Ce ion (Ce$^{4+}$ or Ce$^{3+}$) was determined by considering its local magnetic moment, which can be estimated by integrating the site- and angular momentum projected spin-resolved density of states over spheres with radii chosen as the Wigner–Seitz radii of the PAW potentials. The magnetic moments of the Ce$^{4+}$ (4f$^0$) and Ce$^{3+}$ (4f$^1$) ions are 0 and $\sim 1$ μB, respectively. As for the oxidation state of the Ni atoms in the supported clusters, using Bader’s atoms-in-molecules approach, we obtained that only those Ni atoms bound to surface oxygen from the ceria support are partially oxidized. The average oxidation state of these Ni atoms was calculated as the total number of electrons transferred to the ceria support divided by the number of atoms in direct contact with the support. Full relaxation of atomic coordinates was allowed for both the Ni atoms and the Ce and O ions located in the uppermost TL, and forces were converged to 0.02 eV/Å. The ions in the bottom TL where kept fixed in their bulk positions. The Brillouin zone was sampled with a (2×2×1) k-point mesh using the Monkhorst–Pack scheme.

Transition state (TS) structures were located using the climbing image nudged elastic band method (CI-NEB) with forces converged to 0.05 eV/Å. Harmonic frequencies were
calculated for all TS structures using a finite-difference method, with displacements of ±0.015 Å in the coordinates of the adsorbates and the Ni atoms, in order to verify the existence of a single imaginary frequency.

3. Results

A. Surface chemistry of the MSR process on Ni/CeO$_2$(111): AP-XPS study

Previous results of AP-XPS indicate that methane dissociates on Ni/CeO$_2$(111) surfaces at room temperature (300 K) to yield surface CH$_x$, and that part of the adsorbed CH$_4$ undergoes full decomposition that produces C atoms which react with O centers of the support to generate CO$_x$ groups (CO$_2$ or CO$_3$ species). Maximum reactivity was observed on systems that had a Ni coverage below 0.2 monolayer (ML). These systems were able to catalyze the MSR process at temperatures above 500 K with high activity and low propensity to deactivation by coke deposition. Figure S2 shows Ni 2p and Ce 3d XPS spectra collected while exposing a Ni/CeO$_2$(111) surface to 20 mTorr of methane at 300 and 700 K. At room temperature, the reaction of methane with the surface does not change the oxidation state of Ni or Ce in the system but CH$_x$ and CO$_x$ groups are deposited on the catalyst. Reaction is seen only when Ni is added to the ceria, but the total coverage of CH$_x$ and CO$_x$ groups is larger than that of nickel, suggesting that methane dissociates on Ni or the Ni-ceria interface and then part of the C-containing species migrate to the ceria. These adsorbed species are not stable at temperatures above 500 K, but the reaction with methane is very fast, and at an elevated temperature of 700 K, the decomposition products of methane reduced Ni$^{2+}$ to Ni$^0$ and part of the Ce$^{4+}$ to Ce$^{3+}$, which is accompanied by the formation of lattice oxygen vacancies. Therefore, during methane steam reforming over Ni/CeO$_2$ at T ≥ 700 K, the dissociation of water on the O vacancies would close the catalytic cycle. However, as discussed below, the Ni$^{2+}$ → Ni$^0$ and Ce$^{4+}$ → Ce$^{3+}$ reductions were not observed under a mixture of methane and water.

The bottom traces in Figure 1 show O 1s XPS spectra collected while exposing a Ni/CeO$_2$(111) surface to 100 mTorr of H$_2$O at different temperatures. The peak around 535 eV results from H$_2$O gas. Features around 531.8 eV denote the dissociation of the adsorbate and the deposition of OH groups on the surface. At 300 K, the total coverage of
OH on the surface was in the range of 0.4–0.6 ML. The OH groups were bound to Ni and Ce cations on the substrate. The formation of Ni-OH bonds leads to a binding-energy shift in the position of the Ni 2p core levels whereas the Ce 3d core levels are not significantly affected by the dissociation of the water molecule (Figure S3). In Figure 1, there is an attenuation of the signal for surface OH groups when the temperature is increased from 300 to 450 K. Thus, the OH groups are easy to form and they do not bind strongly to the metal/oxide substrate, good characteristics for intermediates in a catalytic process.

Figure 1. O 1s XPS spectra collected while exposing a Ni/CeO$_2$(111) surface ($\theta_{\text{Ni}} \sim 0.15$ ML) to 100 mTorr of H$_2$O at 300 and 450 K, and then to a gas mixture of 25 mTorr of CH$_4$ and 100 mTorr of H$_2$O at 450 and 700 K.

Figure 2 displays C 1s XPS spectra collected while exposing Ni/CeO$_2$(111) to a CH$_4$/H$_2$O mixture at 300–700 K. The pristine surface exhibits a broad feature from 293 to 288 eV coming from the Ce 4s core level. This feature overlaps with the signal seen for the surface CO$_x$ species formed by the full dissociation of methane and reaction of the carbon with surface oxygens.$^{27,28}$ The interaction of the CH$_4$/H$_2$O gas mixture with the Ni/CeO$_2$(111) yields CO$_x$, CH$_3$O and CH$_x$ groups on the surface. The CH$_3$O species were not seen when the
Ni/CeO$_2$(111) system was exposed to only methane.$^{27,28}$ Therefore, they result from the direct reaction of OH and CH$_x$ groups on the surface, pointing to an associative reaction pathway for the MSR process, in good agreement with the DFT results described in the next section. At 700 K, the CO$_x$, CH$_x$O and CH$_x$ species have all disappeared from the catalyst surface. Thus, they are reaction intermediates which are easy to form and remove and no carbon deposition is seen on the catalyst surface.

![C 1s XPS spectra](image)

**Figure 2.** C 1s XPS spectra collected while exposing a Ni/CeO$_2$(111) surface ($\theta_{\text{Ni}} \sim 0.15$ ML) to 25 mTorr of CH$_4$ and 100 mTorr of H$_2$O at the indicated temperatures.

An analysis of the O 1s XPS spectra collected under a gas mixture of CH$_4$ and H$_2$O shows interesting trends, see Figures 1 and 3. In the top traces of Figure 1, adding CH$_4$ to H$_2$O in the environment leads to an increase in the signal around 531.5–532 eV as a
consequence of the formation of CH₃O species on the Ni/CeO₂(111) surface. The OH and CH₃O species appear at similar binding energy in the O 1s region. In Figure 3, the signal

**Figure 3.** O 1s XPS spectra acquired while exposing a Ni/CeO₂(111) surface (θₙi ~ 0.15 ML) to a mixture of 25 mTorr of CH₄ and 100 mTorr of H₂O at the indicated temperatures.

for CH₃O/OH is quite strong at 300 K, with the total coverage for the CH₃O/OH groups being in the range of 0.6–0.8 ML, but these adsorbed species have a limited stability, and their features decrease when the surface is heated to 450 K. At 700 K, all the CH₃O is gone (Figure 2) and thus only a very small concentration of OH groups remains on the catalyst surface (Figures 1 and 3). The presence of these adsorbed OH groups is important because any CHₓ species generated by methane dissociation can react with them to yield the products of the MSR process. Furthermore, Ni 2p and Ce 3d XPS spectra recorded under a mixture of methane and water (Figure S4) do *not* show any evidence for Ni²⁺ → Ni⁰ and Ce⁴⁺ → Ce³⁺ reductions as seen in the case of pure methane (Figure S2). This is valid for all the temperatures examined. Therefore, the ceria lattice oxygen is probably not involved in the MSR process on this catalyst and the AP-XPS results support an associative mechanism
which involves the formation of a CH₄O intermediate, in agreement with the predictions of the DFT calculations discussed below.

### B. Reaction pathway of the MSR reaction on Ni/CeO₂(111): DFT study

Using a Ni₁₃ cluster supported on a flat CeO₂(111) surface (Figures 4a and S1), we investigated the surface chemistry of the MSR process on Ni/CeO₂. The Ni₁₃ cluster reduces the ceria support upon adsorption with the formation of five Ce³⁺ ions. The calculated electronic structure of the Ni₁₃.CeO₂ system shows that the charge transfer by Ni atoms to the support comes solely from the nine atoms in the interfacial layer, which are partially oxidized (9 × Ni⁰.₅₅⁺), whereas four neutral Ni atoms (4 × Ni⁰) are above them (Table S1), in line with previous results.³⁴ Hence, two types of Ni sites exist for adsorption and activation of reactants on the Ni₁₃.CeO₂ model catalyst, namely, oxidized interfacial sites and metallic terrace sites, hereinafter referred to as Ni₁₃.i and Ni₁₃.t respectively. The reaction pathway for methane steam reforming over the Ni₁₃.CeO₂ model catalysts is discussed below.

**CH₄ activation and dehydrogenation.** The cleavage of the first C–H bond through the dissociative adsorption of CH₄ has generally been considered a rate-controlling step for the MSR reaction on Ni-based catalysts, based on the observed low reactivity of Ni surfaces towards methane,¹⁹ and the high activation barrier for the CH₄ → CH₃+H reaction on Ni(111) obtained in DFT studies.²⁵,²⁶ However, it was recently shown that methane activation occurs even at 300 K on small ceria-supported Ni particles,²⁷–³⁰ indicating much lower activation barriers than on the extended Ni surface. The first step in CH₄ activation involves its molecular adsorption, which is very weak on the CeO₂(111) surface,⁷⁴–⁷⁷ suggesting that methane should dissociate over Ni sites instead, as shown by XPS spectra of the pristine CeO₂ and the Ni/CeO₂ surfaces under 1 Torr of methane.²⁷,²⁹ Accordingly, we considered the adsorption and dehydrogenation of CH₄ on Ni sites of the Ni₁₃.CeO₂ system.

CH₄ adsorption on the Ni₁₃ cluster is stronger by about 0.2 eV than on the extended Ni(111) surface for both the interfacial Ni₁₃.i and terrace Ni₁₃.t sites (Figures S5, S7 and S8). Moreover, the CH₄ molecule comes closer to the surface of the Ni cluster, with C–Ni distances of 218 (Ni₁₃.i) and 228 pm (Ni₁₃.t), compared to 315 pm on Ni(111)³⁰ (Figure 4b). Inspection of the atom- and orbital-projected density of states (PDOS) onto the d-states of
the Ni$_{13}$.i and Ni$_{13}$.t sites where CH$_4$ adsorbs (Table S2), reveals that the d$_{xz}$ states become less occupied upon adsorption of the Ni$_{13}$ cluster onto the ceria support. The consequence of such effect is that the Pauli repulsion to the methane’s frontier orbital is reduced, enabling the molecule to come closer to the surface. The states are then occupied upon CH$_4$ adsorption as measured by the decrease in the number of empty d$_{xz}$ states on both Ni$_{13}$.i and Ni$_{13}$.t sites in the CH$_4$/Ni$_{13}$.CeO$_2$ system. As a result of the close approach of CH$_4$, the C–H bond pointing towards the surface becomes pre-activated, resulting in an increase in the bond length, from 110 pm in the gas-phase CH$_4$ molecule to 115 and 113 pm at the Ni$_{13}$.i and Ni$_{13}$.t sites, respectively (Figure 4b). Note that upon methane adsorption on the Ni(111) surface, the C–H bond is not stretched,$^{23,30}$ and the occupation of d$_{xz}$ states remains unchanged (Table S3).

**Figure 4.** (a) Top and side view of the Ni$_{13}$.CeO$_2$ model catalyst surface. Surface/subsurface oxygen atoms in the outermost O–Ce–O trilayer are depicted in light/dark red, Ce$^{4+}$/Ce$^{3+}$ in light/dark gray, and Ni in blue. (b) Structure of the molecular adsorption of CH$_4$ at Ni$_{13}$.i and Ni$_{13}$.t sites of the Ni$_{13}$.CeO$_2$ system, as well as on
the Ni(111) surface. Selected interatomic distances (in pm) are indicated. (c) Activation energies ($E_a$) for all CH$_x$ dehydrogenation steps.

The first dehydrogenation step of these pre-activated CH$_4$ molecules takes place with low activation energy barriers of 0.34 eV at the Ni-CeO$_2$ interface (Ni$_{0.55+}^0$) and 0.36 eV at the Ni terrace (Ni$^0$) (Figure 4c). We note that although interfacial Ni sites are partially oxidized whereas Ni atoms in the 2nd layer of the cluster have metallic character, the barriers are comparable. Hence, low-temperature CH$_4$ activation on low-loaded Ni/CeO$_2$ systems is expected to take place both at the perimeter of the Ni-CeO$_2$ interface and on Ni atoms with no direct bonds to the support. The latter, however, are not the same as surface Ni atoms in Ni(111) with an activation barrier for the CH$_4$ → CH$_3$+H reaction that is larger by 0.56 eV (0.90 eV, Figure S5). The combined effects of metal-support interactions and low metal loading contribute to the improved catalytic activity of Ni/CeO$_2$ compared to Ni(111). Importantly, ceria-deposited small Ni clusters exhibit higher local fluxionality than Ni(111), i.e. Ni–Ni bonds are less rigid for the metal atoms in the clusters and can lead to stronger stabilizing interactions and lower activation energies on catalytic pathways (cf. the change in the average Ni–Ni bond length upon CH$_4$ adsorption on Ni$_{13}$.t: +11.7 pm and on Ni(111): +0.2 pm, Table S4). Further dehydrogenation steps (CH$_3$ → CH$_2$ → CH → C) also proceed with relatively low barriers on the supported Ni$_{13}$ cluster. The activation barriers ($E_a$) for the elementary steps involved in CH$_4$ dehydrogenation are shown in Figure 4c. The corresponding reaction energies ($\Delta E$) and a comparison with previously published values for the Ni(111) surface are shown in Table S5, whereas the structures of the initial, final and transition states are shown in Figures S7 and S8. The highest energy barrier at the Ni$_{13}$.t sites corresponds to the CH$_3$ → CH$_2$+H dehydrogenation (0.72 eV), whereas at the Ni$_{13}$.i sites, it is associated to the CH → C+H dehydrogenation (0.72 eV). Similarly to the above-discussed case of the first H abstraction from CH$_4$, the comparison with the extended Ni(111) surface (Table S5) reveals that the last H abstraction from CH on Ni$_{13}$.CeO$_2$ has an activation barrier that is smaller by at least 0.6 eV than on the extended surface, whereas the barriers for the second and third dehydrogenation steps in both systems are comparable.

The binding of isolated CH$_x$ species ($x$=0–3) on Ni$_{13}$.CeO$_2$ is stronger than on Ni(111) (Table S6), with the largest difference of about 1 eV for the C atom. At both Ni$_{13}$.i and Ni$_{13}$.t
sites, CH$_3$ binds on a 2-fold bridge position and, although CH$_2$ also binds on a bridge site upon its formation, it changes to a 3-fold site after the removal of the co-adsorbed H atoms (Figures S7 and S8). Note that on the extended Ni(111) surface, CH$_3$ and CH$_2$ adsorb on a 3-fold fcc site. CH and C species bind to four Ni sites of the Ni$_{13}$ cluster producing a significant structural distortion (Figures S7 and S8), which might explain their higher stability compared to the more rigid Ni(111) surface. The 4-fold binding is ascribed to the higher degree of unsaturation of the CH and C species, and it is also seen in the Ni(111) surface, where CH and C adsorb on hcp-hollow sites (instead of fcc), enabling their coordination with an additional Ni atom in the subsurface layer. In spite of the easy formation and increased stability of C atoms on Ni sites of the Ni$_{13}$.CeO$_2$ system, a low tendency towards carbon deposition is observed in the AP-XPS experiments performed over model Ni/CeO$_2$ catalysts (cf. Figure 2), as well as in prior experimental studies. In this regard, it has been argued that carbon deposition on extended Ni surfaces depends strongly on the concentration of oxygen on the catalytic surface. In an oxygen-lacking environment, the interaction between CH$_x$ intermediates and oxygen does not occur at a rate sufficient to convert the carbon produced from CH$_4$ dehydrogenation to CO, thus resulting in carbon accumulation and subsequent deactivation of the catalysts. We show below that the Ni$_{13}$.CeO$_2$ surface provides unique sites and pathways suitable to convert carbon to CO in the MSR reaction with barriers below 0.9 eV.

**H$_2$O dissociative adsorption.** H$_2$O dissociates at the Ni-CeO$_2$ interface through a virtually barrierless process, as previously shown for ceria-supported Ni single-atoms and planar Ni$_4$ clusters. The dissociative adsorption involves sites from both the Ni cluster and the CeO$_2$ surface, with the OH group adsorbing monodentate (OH$_m$) on Ni$_{13}$.i and the dissociated proton on lattice oxygen from the ceria support (H$_s$) (Figure 5). A hydrogen bond between OH$_m$ and H$_s$ is formed, stabilizing the structure ($d$(OH$_m$–H$_s$) = 179 pm). On the other hand, the dissociation of H$_2$O on terrace sites of the Ni$_{13}$ cluster does not involve lattice oxygen, producing a bidentate OH species on Ni$_{13}$.t (OH$_t$) and a H atom nearby on the cluster, and it is hindered by a barrier of 0.79 eV.
Figure 5. H$_2$O dissociative adsorption on the Ni$_{13}$,CeO$_2$ surface. The yellow pathway describes the reaction over terrace sites of the Ni$_{13}$ cluster, whereas the blue pathway shows the barrierless dissociation at the Ni-CeO$_2$ interface. TS are indicated by a double dagger ‡. Energies are referenced to the total energy of H$_2$O$_{gas}$ and the pristine Ni$_{13}$,CeO$_2$ surface.

For comparison, the dissociative adsorption of water on Ni(111) is significantly less exothermic with $\Delta E = -0.41$ eV, and it is hindered by a high barrier of 0.90–1.11 eV, whereas on the non-defective CeO$_2$(111) surface, no true dissociation occurs and the molecular state coexists with a OH-pair-like configuration that easily recombines and desorbs at reaction temperature. Therefore, these calculations show that H$_2$O will dissociate preferentially over the Ni-CeO$_2$ interface, undergoing barrierless activation and easily producing adsorbed OH groups.

CO formation and carbon removal. Since chemisorbed CH$_4$ on Ni/CeO$_2$ will easily lose all its hydrogens (Figure 4c), we first explore the oxidation of carbon on interfacial Ni$_{13}$,i sites via its direct reaction with surface lattice oxygen (O$_s$), resulting in a CO molecule adsorbed on the Ni cluster, and an oxygen vacancy on the ceria support, which could later be reoxidized by water. This type of Mars-van Krevelen redox cycle has been suggested to be the route for many catalytic reactions involving CeO$_2$. We note the C atoms adsorbed on terrace sites can easily migrate to the Ni-CeO$_2$ interface with a barrier of 0.37 eV (Figure S8), and therefore they could be available for oxidation by lattice oxygen, even if CH$_4$ activation
and dehydrogenation take place on terrace sites. The formation of CO through the direct reaction of C with lattice oxygen has a very high barrier of 2.17 eV (Figure 6), and thus this pathway is deemed unlikely to take place. Instead, the adsorbed carbon atom could react with O or OH species chemisorbed on the Ni cluster, to directly form CO from C+O or an oxidized COH intermediate that could then dehydrogenate to CO, which would be in line with the results of the AP-XPS study. Therefore, we investigated next the energy barriers involved in the formation of CO through these pathways.

**Figure 6.** Formation of CO via a Mars-van Krevelen process, involving the migration of lattice oxygen from the ceria surface to Ni-CeO₂ interface, leaving an oxygen vacancy. The TS is indicated by a double dagger ‡. Energies are referred to the clean surface and gas-phase species according to the stoichiometry of the MSR reaction.

Regarding the existence of chemisorbed O species, as discussed above, H₂O dissociates (OH₅+H₂O Figure 5) at the Ni-CeO₂ interface through a practically barrierless process. The monodentate OH₅ species can migrate to a bidentate position OH₂ (I → II in Figure 7, cf. Figure S9) to then dissociate in O and H species on the Ni cluster with a barrier of 1.33 eV (II → III), which is close to that reported for the Ni(111) surface (1.16–1.31 eV). ²¹,²³,²⁴ We note that the possibility of forming OH and O species at interfacial Ni sites by migration of lattice O from the support to the Ni cluster (oxygen reverse spillover) has also been considered (red pathway in Figure 7). In this pathway, a surface lattice oxygen ion migrates to the cluster, leaving an oxygen vacancy on the CeO₂(111) surface (IV), in an endothermic process with ΔE=0.56 eV and Eₐ=0.77 eV. Subsequently, H₂O is activated at the oxygen vacancy site, ⁸²–⁸⁵ forming two H₂ groups (V), this step is barrierless. The
migration of H from the support to the Ni cluster involves a barrier of 1.00 eV to reach the O + H + H state (V → III). Alternatively, the H atom could bind to chemisorbed O with a barrier of 0.57 eV (V → II), resulting in an OH$_5$ group on the Ni$_{13}$ cluster. In summary, O species chemisorbed on the Ni cluster are difficult to form and thus would not be easily available for the direct oxidation of C atoms. Moreover, the direct formation of CO from C and O atoms on the Ni cluster is hindered by a high barrier of 1.47 eV (cf. R8 in Table S7), further discouraging a pathway involving the direct oxidation of carbon with chemisorbed oxygen.

Figure 7. Formation of Ni–O species on the Ni$_{13}$, CeO$_2$ system. A pathway involving H$_2$O dehydrogenation is shown in blue. The oxygen reverse spillover pathway is shown in red. H-diffusion steps have been omitted for simplicity. TS structures are indicated by a double dagger ‡. Energies are referenced to the total energy of H$_2$O$_{gas}$ and the pristine Ni$_{13}$, CeO$_2$ surface. H$_s$ denotes H adsorbed on surface lattice oxygen (O$_s$), OH$_m$ and OH$_b$ represent monodentate and bidentate binding at Ni$_{13}$,i, respectively.

However, the reaction of C with OH groups readily available from the dissociation of H$_2$O at the Ni-CeO$_2$ interface produces the COH intermediate with an energy barrier of 0.89 eV, which is significantly lower than that of the above-mentioned reaction of C with chemisorbed O (1.47 eV). This may be related to the significantly lower binding of the OH species compared to the O species (−3.97 and −5.86 eV, respectively, Table S6). The COH
formation on the Ni$_{13}$ cluster has also a lower barrier than the one reported in the literature for Ni(111), of 1.14–1.46 eV.\textsuperscript{21,24,26}

Overall, these results allow us to propose a reaction pathway for the production of CO via the direct reaction of C with OH groups through a COH intermediate (Figure 8), and thus the formation of O species chemisorbed on the Ni cluster would not be required to oxidize carbon. The first step (I in Figure 8) corresponds to the barrierless activation of water at the Ni-CeO$_2$ interface near a C atom on Ni$_{13}$, with $\Delta E = -1.75$ eV. Next, C and OH react to form the COH intermediate in an endothermic step ($\Delta E = 0.43$ eV) with an energy barrier of 0.89 eV (I $\rightarrow$ II in Figure 8). Finally, a similar barrier of 0.88 eV must be overcome to dehydrogenate the COH intermediate and produce CO (II $\rightarrow$ III in Figure 8).

**Figure 8.** COH intermediate pathway for the MSR reaction over the Ni$_{13}$-CeO$_2$ system. TS are indicated by a double dagger ‡. Energies of all states are referred to the clean surface and gas-phase species according to the stoichiometry of the MSR reaction.

Structures and energies of all the states involved in the COH intermediate pathway are detailed in Figure S10. Reaction and activation energies are summarized and compared with literature values for Ni(111) in Table S7. We note that the that the reaction of CH$_x$ ($x=1$–3) and OH to form CH$_x$OH intermediates was also considered, but the barriers ($E_a \geq 0.81$ eV) are larger than those of the dissociation of the CH$_x$ species ($E_a \leq 0.72$ eV), as shown in Figure S11. This indicates that CH$_x$ could preferentially dehydrogenate fully to C and then
react with OH, in line with the COH pathway presented above. However, it should be noted that adsorbate coverage effects can slow down the rate of CHₙ dehydrogenation steps, particularly at low temperatures (≤ 450 K) at which higher coverage of adsorbates (CHₙ, OH, H) is expected, reducing the availability of free active sites for the decomposition of methyl species. Thus, at such temperatures, various CHₙ (x=1–3) species can coexist on the catalyst surface (cf. Figure 2).

In a final step, CO and H₂ must desorb to close the catalytic cycle of the endothermic MSR reaction. We observe that the XPS spectra do not show adsorbed CO (Figure 2), therefore, the desorption of CO should not be too difficult. It must be noted that gradient-corrected exchange-correlation functionals, such as PBE, overestimate the binding of CO on metal surfaces, so desorption of the molecule is predicted more difficult than it actually is. For instance, the calculated CO adsorption on Ni(111) (Table S6) is overestimated by about 0.5 eV compared to the experimental value. On the other hand, H₂ molecules can be easily formed from the bonding of two H species chemisorbed on the Ni₁₃ cluster, with ΔE= 0.47 eV, and a barrier Eₐ= 0.62 eV (Figure S12). As for the H species adsorbed on surface lattice oxygen (Hₙ), which are formed by water dissociation at the Ni-CeO₂ interface, they would have to migrate from the support to the cluster before reacting with other H species to form H₂. The direct migration is hindered by a high energy barrier of 1.48 eV, but the process becomes easier when assisted by additional water dissociated at terrace sites of the Ni₁₃ cluster, providing a pathway with a highest barrier of Eₐ= 0.75 eV (Figure S12).

The results presented above reveal that the activation of CH₄ and H₂O and the formation of H₂ occur with relatively small energy barriers of about 0.7 eV on Ni/CeO₂, and the oxidation of carbon through an associative pathway involving the COH intermediate would take place with an activation energy below 0.9 eV. This is quite different from the case of the extended Ni(111) surface for which both the activation of methane and water as well as the oxidation of carbonaceous intermediates to form CO involve high energy barriers (≥ 1 eV, cf. Table S7). Furthermore, the barrierless activation of water at the Ni-CeO₂ interface allows for a higher supply of OH species and consequently lower steam-to-methane ratios would be required to achieve the same OH formation rate than extended Ni surfaces.
and traditional Ni catalysts supported on aluminum or magnesium oxides, for which H₂O dissociation is not easy.

4. Conclusions

We conclude that the selectivity of the MSR reaction can be steered to prevent coke formation by choosing the “right” metal-oxide combination as well as controlling the effects of metal loading. Well-dispersed Ni nanoparticles supported on ceria are active and efficient MSR catalysts. The interactions between the reducible support in combination with the small size of the nanoparticles are crucial to the facile methane dehydrogenation and water dissociation at the Ni-CeO₂ interface. Studies of AP-XPS indicate that CH₄/H₂O gas mixtures react with Ni/CeO₂(111) surfaces to form OH, CH, and CH₃O at 300 K. All these species are easy to form and desorb at temperatures below 700 K when the rate of the MSR process accelerates. In line with the experiments, DFT calculations reveal a MSR reaction pathway with barriers below 1 eV that would enable reduced operating temperatures. The path proceeds via the formation of a COH intermediate species from chemisorbed C atoms and OH groups, hindering carbon accumulation and catalyst deactivation, even with a low steam-to-methane ratio in the reactants feed. Water also facilitates the removal of hydrogen from the support at the Ni-CeO₂ interface.

In summary, when undertaking the rational design and improvement of novel ceria-supported metal catalysts for the MSR reaction, it has to be taken into account that both CH₄ and H₂O activation steps occur very easily on low-loaded Ni/CeO₂, and therefore the goal should be to modify the catalyst in order to decrease the barrier for the oxidation steps to form CO, for which one possibility may be to use Ni-based bimetallic catalysts. The properties of the ceria support material may also be chemically modified by, for example, doping with zirconium in order to improve its oxygen storage/transport characteristics, which would promote MSR pathways involving the participation of lattice oxygen that were found unlikely in this study using pure ceria. This is in line with the recently observed promising performance of Ni catalysts supported on Zr-doped ceria for MSR at low temperatures. We anticipate that these strategies could represent an opportunity to further improve Ni/CeO₂ catalysts and to guide the design of novel catalysts with lower kinetic barriers for the MSR reaction.
Associated content

**Supporting Information.** This information is available free of charge on the ACS Publications website. Ni 2p and Ce 3d spectra of AP-XPS for the interaction of methane, water and methane/water mixtures with Ni/CeO$_2$(111) catalysts. Ni$_{13}$/CeO$_2$(111) model catalyst surface. Structures and energies of all initial states, transition states, and final states. Selected projected density of states and Bader charge analysis.

**Data availability**

The DFT data that support the findings of this study are available in Materials Cloud Archive [https://www.materialscloud.org/home](https://www.materialscloud.org/home) with the identifier doi: 10.24435/materialscloud:ct-c6. The repository contains the calculations described in Figures S1 and S7–S12 in the Supporting Information. The data is also available from the authors upon reasonable request.

**Acknowledgments**

Computer time provided by the RES (Red Española de Supercomputación) at MareNostrum 4 (BSC, Barcelona), Altamira (IFCA, Cantabria) and La Palma (IAC, Canarias) nodes, by DECI resources at Finis Terrae II (CESGA, Spain) with the support from PRACE aislb, and by CSC (CONICET, Argentina) is acknowledged. A.S. thanks FIUBA for the Peruilh doctoral fellowship. B.I. acknowledges financial support from Universidad de Buenos Aires (UBACyT–20020190100167BA) and ANPCyT (PICT-2015-2135). M.V.G.P. thanks the support by the MICINN-Spain (RTI2018-101604-B-I00). This project also received funding from the European Union’s Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No 832121. The work carried out at Brookhaven National Laboratory was supported by the US Department of Energy (Chemical Sciences Division, DE-SC0012704). S.D.S. is supported by a US Department of Energy Early Career Award. This research used resources of the Advanced Light Source (Beamline 9.3.2), which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. Authors thank David C. Grinter and Mykhailo Vorokhta,
for their help in preliminary experiments examining the interaction of CH₄/H₂O with Ni-
CeO₂(111) surfaces.
References

(1) Rostrup-Nielsen, J. R.; Christiansen, L. J. Concepts in Syngas Manufacture; Imperial College Press: London, 2011.

(2) Jagannath, A.; Elkamel, A.; Karimi, I. A. Improved Synthesis of Hydrogen Networks for Refineries. *Ind. Eng. Chem. Res.* 2014, 53 (44), 16948–16963. https://doi.org/10.1021/ie5005042.

(3) Iulianelli, A.; Liguori, S.; Wilcox, J.; Basile, A. Advances on Methane Steam Reforming to Produce Hydrogen through Membrane Reactors Technology: A Review. *Catal. Rev.* 2016, 58 (1), 1–35. https://doi.org/10.1002/1080-01614940.2015.1099882.

(4) Oyama, S. T.; Hacarlioglu, P.; Gu, Y.; Lee, D. Dry Reforming of Methane Has No Future for Hydrogen Production: Comparison with Steam Reforming at High Pressure in Standard and Membrane Reactors. *Int. J. Hydrogen Energy* 2012, 37 (13), 10444–10450. https://doi.org/10.1016/j.ijhydene.2011.09.149.

(5) Alves, H. J.; Bley Junior, C.; Niklevicz, R. R.; Frigo, E. P.; Frigo, M. S.; Coimbra-Araújo, C. H. Overview of Hydrogen Production Technologies from Biogas and the Applications in Fuel Cells. *Int. J. Hydrogen Energy* 2016, 58 (1), 1–35. https://doi.org/10.1016/j.ijhydene.2015.12.057.

(6) Subramanian, N.; Caravaca, A.; García-García, F. R.; Bowker, M. Sustainable Hydrogen and/or Syngas Production: New Approaches to Reforming. In *Modern Developments in Catalysis*; World Scientific: Singapore, 2017; pp 1–39. https://doi.org/10.1142/9781786341228_0001.

(7) Lu, J. B.; Wei, G. H.; Zhu, F. J.; Yan, X. H.; Zhang, J. L. Pressure Effect on the PEMFC Performance. *Fuel Cells* 2019, 19 (3), 211–220. https://doi.org/10.1002/fuce.201800135.

(8) Matsumura, Y.; Nakamori, T. Steam Reforming of Methane over Nickel Catalysts at Low Reaction Temperature. *Appl. Catal. A Gen.* 2004, 258 (1), 107–114. https://doi.org/10.1016/j.apcata.2003.08.009.

(9) Kusakabe, K.; Sotowa, K.; Eda, T.; Iwamoto, Y. Methane Steam Reforming over Ce–ZrO2–Supported Noble Metal Catalysts at Low Temperature. *Fuel Process. Technol.* 2004, 86 (3), 319–326. https://doi.org/10.1016/j.fuproc.2004.05.003.

(10) Angeli, S. D.; Monteleone, G.; Giaconia, A.; Lemonidou, A. A. State-of-the-Art Catalysts for CH4 Steam Reforming at Low Temperature. *Int. J. Hydrogen Energy* 2014, 39 (5), 1979–1997. https://doi.org/10.1016/j.ijhydene.2013.12.001.

(11) Rostrup-Nielsen, J. R.; Sehested, J.; Nørskov, J. K. Hydrogen and Synthesis Gas by Steam- and CO2 Reforming. *Adv. Catal.* 2002, 47, 65–139. https://doi.org/10.1002/chin.200317288.

(12) Sehested, J. Four Challenges for Nickel Steam-Reforming Catalysts. *Catal. Today* 2006, 111 (1–2), 103–110. https://doi.org/10.1016/j.cattod.2005.10.002.

(13) Iglesias, I.; Baronetti, G.; Mariño, F. Ni/Ce0.95M0.05O2-d (M = Zr, Pr, La) for Methane Steam Reforming at Mild Conditions. *Int. J. Hydrogen Energy* 2017, 42 (50), 29735–29744. https://doi.org/10.1016/j.ijhydene.2017.09.176.

(14) Iglesias, I.; Baronetti, G.; Alemany, L.; Mariño, F. Insight into Ni/Ce0.97–Zr0.03O2–δ Support Interplay for Enhanced Methane Steam Reforming. *Int. J. Hydrogen Energy* 2019, 44 (7), 3668–3680. https://doi.org/10.1016/j.ijhydene.2018.12.112.

(15) Wei, J.; Iglesia, E. Structural Requirements and Reaction Pathways in Methane Activation and Chemical Conversion Catalyzed by Rhodium. *J. Catal.* 2004, 225 (1),
Ross, J. R. H.; Steel, M. C. F. Mechanism of the Steam Reforming of Methane over a Coprecipitated Nickel-Alumina Catalyst. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1973**, *69*, 10. https://doi.org/10.1039/f19736900010.

(16) Horn, R.; Schlögl, R. Methane Activation by Heterogeneous Catalysis. *Catal. Letters* **2015**, *145* (1), 23–39. https://doi.org/10.1007/s10562-014-1417-z.

(17) Schwarz, H.; Shaik, S.; Li, J. Electronic Effects on Room-Temperature, Gas-Phase C–H Bond Activations by Cluster Oxides and Metal Carbides: The Methane Challenge. *J. Am. Chem. Soc.* **2017**, *139* (48), 17201–17212. https://doi.org/10.1021/jacs.7b10139.

(18) Choudhary, T. V.; Aksoylu, E.; Wayne Goodman, D. Nonoxidative Activation of Methane. *Catal. Rev.* **2003**, *45* (1), 151–203. https://doi.org/10.1081/CR-120017010.

(19) Xu, J.; Froment, G. F. Methane Steam Reforming, Methanation and Water-Gas Shift: I. Intrinsic Kinetics. *AIChE J.* **1989**, *35* (1), 88–96. https://doi.org/10.1002/aic.690350109.

(20) Niu, J.; Wang, Y.; Qi, Y.; Dam, A. H.; Wang, H.; Zhu, Y.-A.; Holmen, A.; Ran, J.; Chen, D. New Mechanism Insights into Methane Steam Reforming on Pt/Ni from DFT and Experimental Kinetic Study. *Fuel* **2020**, *266* (October 2019), 117143. https://doi.org/10.1016/j.fuel.2020.117143.
Methane on a Highly-Active Ni-CeO₂ Catalyst: Effects of Metal-Support Interactions on C−H Bond Breaking. Angew. Chemie Int. Ed. 2016, 55 (26), 7455–7459. https://doi.org/10.1002/anie.201602489.

(29) Lustemberg, P. G.; Palomino, R. M.; Gutiérrez, R. A.; Grinter, D. C.; Vorokhta, M.; Liu, Z.; Ramírez, P. J.; Matolín, V.; Ganduglia-Pirovano, M. V.; Senanayake, S. D.; Rodriguez, J. A. Direct Conversion of Methane to Methanol on Ni-Ceria Surfaces: Metal-Support Interactions and Water-Enabled Catalytic Conversion by Site Blocking. J. Am. Chem. Soc. 2018, 140 (24), 7681–7687. https://doi.org/10.1021/jacs.8b03809.

(30) Lustemberg, P. G.; Zhang, F.; Gutiérrez, R. A.; Ramírez, P. J.; Senanayake, S. D.; Rodriguez, J. A.; Ganduglia-Pirovano, M. V. Breaking Simple Scaling Relations through Metal–Oxide Interactions: Understanding Room-Temperature Activation of Methane on M/CeO₂ (M = Pt, Ni, or Co) Interfaces. J. Phys. Chem. Lett. 2020, 2 (111), 9131–9137. https://doi.org/10.1021/acs.jpcllett.0c02109.

(31) Lian, Z.; Olanrele, S. O.; Si, C.; Yang, M.; Li, B. Critical Role of Interfacial Sites between Nickel and CeO₂ Support in Dry Reforming of Methane: Revisit of Reaction Mechanism and Origin of Stability. J. Phys. Chem. C 2020, 124 (9), 5118–5124. https://doi.org/10.1021/acs.jpcc.9b09856.

(32) Freund, H.-J.; Pacchioni, G. Oxide Ultra-Thin Films on Metals: New Materials for the Design of Supported Metal Catalysts. Chem. Soc. Rev. 2008, 37 (10), 2224. https://doi.org/10.1039/b718768h.

(33) Carrasco, J.; Barrio, L.; Liu, P.; Rodriguez, J. A.; Ganduglia-Pirovano, M. V. Theoretical Studies of the Adsorption of CO and C on Ni(111) and Ni/CeO₂(111): Evidence of a Strong Metal–Support Interaction. J. Phys. Chem. C 2013, 117 (16), 8241–8250. https://doi.org/10.1021/jp400430r.

(34) Mao, Z.; Lustemberg, P. G.; Rumptz, J. R.; Ganduglia-Pirovano, M. V.; Campbell, C. T. Ni Nanoparticles on CeO₂(111): Energetics, Electron Transfer, and Structure by Ni Adsorption Calorimetry, Spectroscopies, and Density Functional Theory. ACS Catal. 2020, 10 (9), 5101–5114. https://doi.org/10.1021/acscatal.0c00333.

(35) Ganduglia-Pirovano, M. V. The Non-Innocent Role of Cerium Oxide in Heterogeneous Catalysis: A Theoretical Perspective. Catal. Today 2015, 253, 20–32. https://doi.org/10.1016/j.cattod.2015.01.049.

(36) Carrasco, J.; López-Durán, D.; Liu, Z.; Duchoň, T.; Evans, J.; Senanayake, S. D.; Crumlin, E. J.; Matolín, V.; Rodríguez, J. A.; Ganduglia-Pirovano, M. V. In Situ and Theoretical Studies for the Dissociation of Water on an Active Ni/CeO₂ Catalyst: Importance of Strong Metal-Support Interactions for the Cleavage of O-H Bonds. Angew. Chemie Int. Ed. 2015, 54 (13), 3917–3921. https://doi.org/10.1002/anie.201410697.

(37) Trofarelli, A. Catalytic Properties of Ceria and CeO₂-Containing Materials. Catal. Rev. 1996, 38 (4), 439–520. https://doi.org/10.1080/016149496080006464.

(38) Conner, W. C.; Falconer, J. L. Spillover in Heterogeneous Catalysis. Chem. Rev. 1995, 95 (3), 759–788. https://doi.org/10.1021/cr00035a014.

(39) Zafiris, G. S.; Gorte, R. J. Evidence for Low-Temperature Oxygen Migration from Ceria to Rh. J. Catal. 1993, 139 (2), 561–567. https://doi.org/10.1006/jcat.1993.1049.

(40) Vayssilov, G. N.; Lykhach, Y.; Migani, A.; Staudt, T.; Petrova, G. P.; Tsud, N.; Skála, T.; Bruix, A.; Illas, F.; Prince, K. C.; Matolín, V.; Neyman, K. M.; Libuda, J. Support Nanostructure Boosts Oxygen Transfer to Catalytically Active Platinum Nanoparticles. Nat. Mater. 2011, 10 (4), 310–315. https://doi.org/10.1038/nmat2976.
(41) Ruiz Puigdollers, A.; Schlexer, P.; Tosoni, S.; Pacchioni, G. Increasing Oxide Reducibility: The Role of Metal/Oxide Interfaces in the Formation of Oxygen Vacancies. ACS Catal. 2017, 7 (10), 6493–6513. https://doi.org/10.1021/acscatal.7b01913.

(42) Lykhach, Y.; Kubát, J.; Neitzel, A.; Tsud, N.; Vorokhta, M.; Skála, T.; Dvořák, F.; Kosto, Y.; Prince, K. C.; Matolin, V.; Johánek, V.; Mysliveček, J.; Libuda, J. Charge Transfer and Spillover Phenomena in Ceria-Supported Iridium Catalysts: A Model Study. J. Chem. Phys. 2019, 151 (20), 204703. https://doi.org/10.1063/1.5126031.

(43) Ouyang, M.; Boldrin, P.; Maher, R. C.; Chen, X.; Liu, X.; Cohen, L. F.; Brandon, N. P. A Mechanistic Study of the Interactions between Methane and Nickel Supported on Doped Ceria. Appl. Catal. B Environ. 2019, 248, 332–340. https://doi.org/10.1016/j.apcatb.2019.02.038.

(44) H.-S. Roh; K.-W. Jun; W.-S. Dong; S.-E. Park; Y.-S. Baek. Highly Stable Ni Catalyst Supported on Ce–ZrO2 for Oxy-Steam Reforming of Methane. Catal. Letters 2001, 74 (1), 31–36. https://doi.org/10.1023/a:1016699317421.

(45) Damyanova, S.; Pawelec, B.; Palcheva, R.; Karakirova, Y.; Sanchez, M. C. C.; Tyuliev, G.; Gaigneaux, E.; Fierro, J. L. G. Structure and Surface Properties of Ceria-Modified Ni-Based Catalysts for Hydrogen Production. Appl. Catal. B Environ. 2018, 225 (December), 340–353. https://doi.org/10.1016/j.apcatb.2017.12.002.

(46) Arcotumapathy, V.; Alenazey, F. S.; Al-Otaibi, R. L.; Vo, D.-V. N.; Alotaibi, F. M.; Adesina, A. A. Mechanistic Investigation of Methane Steam Reforming over Ce-Promoted Ni/SBA-15 Catalyst. Appl. Petrochemical Res. 2015, 5 (4), 393–404. https://doi.org/10.1007/s13203-015-0121-2.

(47) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. Electronic Structure Calculations and Dynamics of Methane Activation on Nickel and Cobalt. J. Chem. Phys. 1994, 101 (12), 11012–11020. https://doi.org/10.1063/1.467852.

(48) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. Methane Activation and Dehydrogenation on Nickel and Cobalt: A Computational Study. Surf. Sci. 1995, 324 (2–3), 345–356. https://doi.org/10.1016/0039-6028(94)00716-0.

(49) Kratzer, P.; Hammer, B.; No/rskov, J. K. A Theoretical Study of CH4 Dissociation on Pure and Gold- alloyed Ni(111) Surfaces. J. Chem. Phys. 1996, 105 (13), 5595–5604. https://doi.org/10.1063/1.472399.

(50) Watwe, R. M.; Bengaard, H. S.; Rostrup-Nielsen, J. R.; Dumesic, J. A.; Nørskov, J. K. Theoretical Studies of Stability and Reactivity of CH Species on Ni(111). J. Catal. 2000, 189 (1), 16–30. https://doi.org/10.1006/jcat.1999.2699.

(51) Bengaard, H. S.; Nørskov, J. K.; Sehested, J.; Clausen, B. S.; Nielsen, L. P.; Molenbroek, A. M.; Rostrup-Nielsen, J. R. Steam Reforming and Graphite Formation on Ni Catalysts. J. Catal. 2002, 209 (2), 365–384. https://doi.org/10.1006/jcat.2002.3579.

(52) Abild-Pedersen, F.; Greeley, J.; Nørskov, J. K. Understanding the Effect of Steps, Strain, Poisons, and Alloying: Methane Activation on Ni Surfaces. Catal. Letters 2005, 105 (1–2), 9–13. https://doi.org/10.1007/s10562-005-7998-9.

(53) Wang, S.-G.; Cao, D.-B.; Li, Y.-W.; Wang, J.; Jiao, H. CO2 Reforming of CH4 on Ni(111): A Density Functional Theory Calculation. J. Phys. Chem. B 2006, 110 (20), 9976–9983. https://doi.org/10.1021/jp060992g.

(54) Wang, S.-G.; Liao, X.-Y.; Hu, J.; Cao, D.-B.; Li, Y.-W.; Wang, J.; Jiao, H. Kinetic Aspect of CO2 Reforming of CH4 on Ni(111): A Density Functional Theory
Calculation. *Surf. Sci.* **2007**, *601* (5), 1271–1284. https://doi.org/10.1016/j.susc.2006.12.059.

(55) Kresse, G.; Hafner, J. Ab Initio Molecular Dynamics for Liquid Metals. *Phys. Rev. B* **1993**, *47* (1), 558–561. https://doi.org/10.1103/PhysRevB.47.558.

(56) Kresse, G.; Furthmüller, J. Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set. *Phys. Rev. B* **1996**, *54* (16), 11169–11186. https://doi.org/10.1103/PhysRevB.54.11169.

(57) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865–3868. https://doi.org/10.1103/PhysRevLett.77.3865.

(58) Blöchl, P. E. Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953–17979. https://doi.org/10.1103/PhysRevB.50.17953.

(59) Kresse, G.; Joubert, D. From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758–1775. https://doi.org/10.1103/PhysRevB.59.1758.

(60) Dudarev, S. L.; Botton, G. A.; Savrasov, S. Y.; Humphreys, C. J.; Sutton, A. P. Electron-Energy-Loss Spectra and the Structural Stability of Nickel Oxide: An LSDA+U Study. *Phys. Rev. B* **1998**, *57* (3), 1505–1509. https://doi.org/10.1103/PhysRevB.57.1505.

(61) Nolan, M.; Parker, S. C.; Watson, G. W. The Electronic Structure of Oxygen Vacancy Defects at the Low Index Surfaces of Ceria. *Surf. Sci.* **2005**, *595* (1–3), 223–232. https://doi.org/10.1016/j.susc.2005.08.015.

(62) Ganduglia-Pirovano, M. V.; Hofmann, A.; Sauer, J. Oxygen Vacancies in Transition Metal and Rare Earth Oxides: Current State of Understanding and Remaining Challenges. *Surf. Sci. Rep.* **2007**, *62* (6), 219–270. https://doi.org/10.1016/j.surfrep.2007.03.002.

(63) Loschen, C.; Carrasco, J.; Neyman, K. M.; Illas, F. First-Principles LDA+U and GGA+U Study of Cerium Oxides: Dependence on the Effective U Parameter. *Phys. Rev. B - Condens. Matter Mater. Phys.* **2007**, *75* (3), 1–8. https://doi.org/10.1103/PhysRevB.75.035115.

(64) Skorodumova, N. V.; Simak, S. I.; Lundqvist, B. I.; Abrikosov, I. A.; Johansson, B. Quantum Origin of the Oxygen Storage Capability of Ceria. *Phys. Rev. Lett.* **2002**, *89* (16), 166601. https://doi.org/10.1103/PhysRevLett.89.166601.

(65) Ganduglia-Pirovano, M. V.; Da Silva, J. L. F.; Sauer, J. Density-Functional Calculations of the Structure of Near-Surface Oxygen Vacancies and Electron Localization on CeO$_2$(111). *Phys. Rev. Lett.* **2009**, *102* (2), 026101. https://doi.org/10.1103/PhysRevLett.102.026101.

(66) Fabris, S.; Vicario, G.; Balducci, G.; de Gironcoli, S.; Baroni, S. Electronic and Atomistic Structures of Clean and Reduced Ceria Surfaces. *J. Phys. Chem. B* **2005**, *109* (48), 22860–22867. https://doi.org/10.1021/jp0511698.

(67) Cococcioni, M.; de Gironcoli, S. Linear Response Approach to the Calculation of the Effective Interaction Parameters in the LDA+U Method. *Phys. Rev. B* **2005**, *71* (3), 035105. https://doi.org/10.1103/PhysRevB.71.035105.

(68) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu. *J. Chem. Phys.* **2010**, *132* (15), 154104. https://doi.org/10.1063/1.3382344.
(69) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the Damping Function in Dispersion Corrected Density Functional Theory. *J. Comput. Chem.* **2011**, *32* (7), 1456–1465. https://doi.org/10.1002/jcc.21759.

(70) Bader, R. F. W. A Quantum Theory of Molecular Structure and Its Applications. *Chem. Rev.* **1991**, *91* (5), 893–928. https://doi.org/10.1021/cr00005a013.

(71) Henkelman, G.; Arnaldsson, A.; Jónsson, H. A Fast and Robust Algorithm for Bader Decomposition of Charge Density. *Comput. Mater. Sci.* **2006**, *36* (3), 354–360. https://doi.org/10.1016/j.commatsci.2005.04.010.

(72) Monkhorst, H. J.; Pack, J. D. Special Points for Brillouin-Zone Integrations. *Phys. Rev. B* **1976**, *13* (12), 5188–5192. https://doi.org/10.1103/PhysRevB.13.5188.

(73) Krcha, M. D.; Mayernick, A. D.; Janik, M. J. Periodic Trends of Oxygen Vacancy Formation and C–H Bond Activation over Transition Metal-Doped CeO$_2$(111) Surfaces. *J. Catal.* **2012**, *293*, 103–115. https://doi.org/10.1016/j.jcat.2012.06.010.

(74) Salcedo, A.; Iglesias, I.; Mariño, F.; Irigoyen, B. Promoted Methane Activation on Doped Ceria via Occupation of Pr(4f) States. *Appl. Surf. Sci.* **2018**, *458*, 397–404. https://doi.org/10.1016/j.apsusc.2018.07.090.

(75) Vohs, J. M. Site Requirements for the Adsorption and Reaction of Oxygenates on Metal Oxide Surfaces. *Chem. Rev.* **2013**, *113* (6), 4136–4163. https://doi.org/10.1021/cr300328u.

(76) Chen, H.-T.; Choi, Y. M.; Liu, M.; Lin, M. C. A Theoretical Study of Surface Reduction Mechanisms of CeO$_2$(111) and (110) by H$_2$. *ChemPhysChem* **2007**, *8* (6), 849–855. https://doi.org/10.1002/cphc.200600598.

(77) Yang, Z.; Wang, Q.; Wei, S.; Ma, D.; Sun, Q. The Effect of Environment on the Reaction of Water on the Ceria(111) Surface: A DFT+U Study. *J. Phys. Chem. C* **2010**, *114* (35), 14891–14899. https://doi.org/10.1021/jp101057a.

(78) Marrocchelli, D.; Yildiz, B. First-Principles Assessment of H$_2$S and H$_2$O Reaction Mechanisms and the Subsequent Hydrogen Absorption on the CeO$_2$(111) Surface. *J. Phys. Chem. C* **2012**, *116* (3), 2411–2424. https://doi.org/10.1021/jp205573v.
(85) Salcedo, A.; Irigoyen, B. Unraveling the Origin of Ceria Activity in Water–Gas Shift by First-Principles Microkinetic Modeling. *J. Phys. Chem. C* 2020, 124 (14), 7823–7834. https://doi.org/10.1021/acs.jpcc.0c00229.

(86) Abild-Pedersen, F.; Andersson, M. P. CO Adsorption Energies on Metals with Correction for High Coordination Adsorption Sites – A Density Functional Study. *Surf. Sci.* 2007, 601 (7), 1747–1753. https://doi.org/10.1016/j.susc.2007.01.052.

(87) Schimka, L.; Harl, J.; Stroppa, A.; Grüneis, A.; Marsman, M.; Mittendorfer, F.; Kresse, G. Accurate Surface and Adsorption Energies from Many-Body Perturbation Theory. *Nat. Mater.* 2010, 9 (9), 741–744. https://doi.org/10.1038/nmat2806.

(88) Patra, A.; Peng, H.; Sun, J.; Perdew, J. P. Rethinking CO Adsorption on Transition-Metal Surfaces: Effect of Density-Driven Self-Interaction Errors. *Phys. Rev. B* 2019, 100 (3), 035442. https://doi.org/10.1103/PhysRevB.100.035442.

(89) Stuckless, J. T.; Al- Sarraf, N.; Wartnaby, C.; King, D. A. Calorimetric Heats of Adsorption for CO on Nickel Single Crystal Surfaces. *J. Chem. Phys.* 1993, 99 (3), 2202–2212. https://doi.org/10.1063/1.465282.

(90) Iglesias, I.; Forti, M.; Baronetti, G.; Mariño, F. Zr-Enhanced Stability of Ceria Based Supports for Methane Steam Reforming at Severe Reaction Conditions. *Int. J. Hydrogen Energy* 2019, 44 (16), 8121–8132. https://doi.org/10.1016/j.ijhydene.2019.02.070.
SUPPORTING INFORMATION

Reaction Pathway for Coke-Free Methane Steam Reforming on a Ni/CeO$_2$ Catalyst: Active Sites and Role of Metal-Support Interactions

Agustín Salcedo$^{1,2}$, Pablo G. Lustemberg$^{3,4}$, Ning Rui$^{5}$, Robert M. Palomino$^{5}$, Zongyuan Liu$^{5}$, Slavomir Nemsak$^6$, Sanjaya D. Senanayake$^5$, José A. Rodríguez*,$^5$ M. Verónica Ganduglia-Pirovano*,$^3$, Beatriz Irigoyen*,$^{1,2}$

$^1$Universidad de Buenos Aires (UBA), Facultad de Ingeniería, Departamento de Ingeniería Química, Ciudad Universitaria, C1428EGA Buenos Aires, Argentina

$^2$Instituto de Tecnologías de Hidrógeno y Energías Sostenibles (ITHES, CONICET-UBA), Ciudad Universitaria, C1428EGA Buenos Aires, Argentina

$^3$Instituto de Catálisis y Petroleoquímica (ICP, CSIC), 28049 Madrid, Spain

$^4$Instituto de Física Rosario (IFIR, CONICET-UNR), S2000EKF Rosario, Santa Fe, Argentina

$^5$Chemistry Division, Brookhaven National Laboratory, Upton, New York 11973, USA

$^6$Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA

Corresponding authors:
*beatriz@di.fcen.uba.ar
*vgp@icp.csic.es
*rodriguez@bnl.gov
Ni$_{13}$/CeO$_2$(111) Model

Figure S1. Top and side view of the Ni$_{13}$/CeO$_2$(111) model catalyst surface, referred as Ni$_{13}$CeO$_2$. The cartesian axes of the slab calculation are shown on the left. Surface/subsurface oxygen atoms in the outermost O–Ce–O trilayer are depicted in light/dark red, Ce$^{4+}$/Ce$^{3+}$ in light/dark gray, and Ni in blue. The Ni sites at the Ni-CeO$_2$ interface (#8, Ni$_{13}$.i) and at the terrace of the Ni$_{13}$ cluster (#13, Ni$_{13}$.t) where CH$_4$ is adsorbed are indicated.
Ni 2p and Ce 3d XPS Spectra

Figure S2. Ni 2p and Ce 3d XPS spectra collected while exposing a Ni/CeO₂(111) surface (θ_Ni ~ 0.15 ML) to 20 mTorr of methane at different temperatures. At 700 K, there is a coexistence of Ce^{4+} and Ce^{3+} cations in the oxide support as shown by curve-fitting the corresponding Ce 3d XPS spectrum.
**Figure S3.** Ni 2p and Ce 3d XPS spectra collected while exposing a Ni/CeO$_2$(111) surface ($\theta_{\text{Ni}} \sim 0.15$ ML) to 40 mTorr of water at different temperatures.
Figure S4. Ni 2p and Ce 3d XPS spectra collected while exposing a Ni/CeO$_2$(111) surface ($\theta_{\text{Ni}} \sim 0.15$ ML) to 20 mTorr of methane and 40 mTorr of water at different temperatures.
Table S1. Bader charges (in $|e|$) for the Ni atoms of the Ni$_{13}$ cluster (cf. Figure S1) before (Ni$_{13}$.gas) and after (Ni$_{13}$.CeO$_2$) its adsorption on the CeO$_2$(111) surface. Ni$_{13}$.gas corresponds to the gas-phase cluster resulting from the removal of the CeO$_2$ support from the Ni$_{13}$.CeO$_2$ system, without further geometry optimization. For Ni, 16 electrons (3$p^63d^84s^2$) were considered as valence. The difference in Bader charge upon adsorption is also listed.

| # Ni atom | Ni$_{13}$.gas | Ni$_{13}$.CeO$_2$ | Ni$_{13}$.gas$-$Ni$_{13}$.CeO$_2$ |
|-----------|---------------|------------------|-------------------------------|
| 1         | 15.9926       | 15.7760          | $-0.22$                       |
| 2         | 15.9945       | 15.7686          | $-0.23$                       |
| 3         | 16.0759       | 15.7584          | $-0.32$                       |
| 4         | 15.8241       | 15.6206          | $-0.20$                       |
| 5         | 15.9925       | 15.7271          | $-0.27$                       |
| 6         | 15.9845       | 15.7570          | $-0.23$                       |
| 7         | 16.0961       | 15.7783          | $-0.32$                       |
| 8         | 16.0833       | 15.4933          | $-0.59$                       |
| 9         | 16.0713       | 15.7255          | $-0.35$                       |
| 10        | 15.9764       | 16.0614          | $0.08$                        |
| 11        | 15.9647       | 16.0312          | $0.07$                        |
| 12        | 15.9785       | 16.0361          | $0.06$                        |
| 13        | 15.9656       | 15.9869          | $0.02$                        |
| Total     | 208.0000      | 205.5204         | $-2.48$                       |

Table S2. Integration of the projected density of states onto the d-states of a Ni atom at the interface (Ni$_{13}$.i) and on the terrace (Ni$_{13}$.t) of the Ni$_{13}$ cluster (cf. Figure S1), within the 0 ($E_F$) to +1.0 eV energy interval. The principal axes for the $lm$ decomposition are the cartesian axes of the calculation slab. The z-axis is aligned with the direction perpendicular to the surface, whereas the x- and y- axes are parallel to the surface. Ni$_{13}$.gas corresponds to the gas-phase cluster resulting from the removal of the CeO$_2$ support from the Ni$_{13}$.CeO$_2$ system, without further geometry optimization. CH$_4$/Ni$_{13}$.CeO$_2$ corresponds to the CH$_4$ adsorption on Ni$_{13}$.CeO$_2$.

| Site   | Band   | Empty states | Difference of empty states |
|--------|--------|--------------|----------------------------|
| Ni$_{13}$.i | dxy     | 0.19         | 0.21                       | 0.16             | 0.02 | $-0.05$               |
|        | dyz     | 0.15         | 0.12                       | 0.07             | $-0.04$ | $-0.04$               |
|        | dz$^2$  | 0.07         | 0.04                       | 0.12             | $-0.03$ | 0.09                 |
|        | dxz     | 0.30         | 0.35                       | 0.23             | 0.05 | $-0.12$               |
|        | dx$^2$y$^2$ | 0.19        | 0.10                       | 0.09             | $-0.09$ | $-0.01$               |
|        | dtotal  | 0.90         | 0.81                       | 0.67             | $-0.09$ | $-0.14$               |
|        | dxy     | 0.23         | 0.16                       | 0.28             | $-0.08$ | 0.12                 |
|        | dyz     | 0.24         | 0.06                       | 0.13             | $-0.18$ | 0.07                 |
|        | dz$^2$  | 0.14         | 0.06                       | 0.21             | $-0.08$ | 0.15                 |
|        | dxz     | 0.12         | 0.39                       | 0.10             | 0.27 | $-0.29$               |
|        | dx$^2$y$^2$ | 0.10        | 0.13                       | 0.03             | 0.03 | $-0.10$               |
|        | dtotal  | 0.83         | 0.79                       | 0.75             | $-0.04$ | $-0.04$               |

S6
**Figure S5.** Structure and energy (relative to CH₄ in the gas phase and the pristine surface) of the initial state (IS), transition state (TS), and final state (FS) for the first dehydrogenation of CH₄ on the Ni(111) surface.¹ Selected interatomic distances (in pm) are indicated.

**Table S3.** Integration of the projected density of states onto the d-states of the Ni atom of the Ni(111) surface where CH₄ is adsorbed, within the 0 ($E_F$) to +1.0 eV energy interval. The principal axes for the lm decomposition are the cartesian axes of the calculation slab. The z-axis is aligned with the direction perpendicular to the surface, whereas the x- and y-axes are parallel to the surface.

| Band    | Empty states Ni(111) | Empty states CH₄/Ni(111) | Difference of empty states CH₄/Ni(111)−Ni(111) |
|---------|----------------------|---------------------------|--------------------------------------------------|
| dxy     | 0.172                | 0.171                     | −0.001                                           |
| dyz     | 0.119                | 0.116                     | −0.003                                           |
| dz²     | 0.183                | 0.202                     | 0.018                                            |
| dxz     | 0.119                | 0.117                     | −0.003                                           |
| dx²−y²  | 0.172                | 0.171                     | −0.001                                           |
| dtotal  | 0.765                | 0.776                     | 0.011                                            |
Figure S6. Projected density of states onto the d-states of a Ni atom on the terrace (Ni\textsubscript{13.t}, left) and at the interface (Ni\textsubscript{13.i}, middle) of the Ni\textsubscript{13} cluster, as well as on the Ni(111) surface (right) (cf. Tables S2 and S3). The energy is referred to the Fermi level. The curves are smoothed by a Gaussian level broadening of 0.05 eV.
Table S4. Ni–Ni bond lengths in the first coordination shell of a 9-fold coordinated Ni atom at the Ni(111) surface and a 6-fold coordinated Ni terrace site of the Ni$_{13}$CeO$_2$ system (Ni$_{13}$t, cf. Figure S1, Ni atoms forming the Ni$_{13}$t–Ni bonds are labelled according to Figure S1), before and after CH$_4$ adsorption. Changes upon CH$_4$ adsorption are shown, reflecting the higher flexibility of the ceria-supported Ni$_{13}$ cluster.

| Ni-Ni bond | Length (pm) | Change (pm) | Change (pm) |
|------------|-------------|-------------|-------------|
| Ni(111) | Ni$_{13}$t | CH$_4$/Ni(111) | CH$_4$/Ni$_{13}$t | CH$_4$/Ni(111) – Ni(111) | CH$_4$/Ni$_{13}$t – Ni$_{13}$t |
| 1 (Ni$_{8B}$) | 249.0 | 264.9 | 249.2 | 308.8 | 0.2 | 43.9 |
| 2 (Ni$_{6A}$) | 249.0 | 227.6 | 249.1 | 232.7 | 0.1 | 5.0 |
| 3 (Ni$_{11B}$) | 249.0 | 239.2 | 249.3 | 241.4 | 0.2 | 2.2 |
| 4 (Ni$_{10A}$) | 249.1 | 236.0 | 249.4 | 234.2 | 0.3 | –1.8 |
| 5 (Ni$_{11}$) | 249.1 | 232.2 | 249.5 | 236.1 | 0.4 | 4.0 |
| 6 (Ni$_{8A}$) | 249.0 | 275.0 | 249.4 | 291.8 | 0.4 | 16.8 |
| 7 | 245.8 | - | 245.8 | - | 0.0 | - |
| 8 | 245.8 | - | 245.8 | - | 0.0 | - |
| 9 | 245.9 | - | 245.9 | - | 0.0 | - |
| Average | 248.0 | 245.8 | 248.2 | 257.5 | 0.2 | 11.7 |

Table S4 reveals the higher fluxionality of ceria supported small clusters compared to the extended metal surface. Upon CH$_4$ adsorption, larger changes in the Ni–Ni bond lengths are observed for the active Ni sites in the Ni$_{13}$ cluster compared to Ni(111) (cf. an average change of 11.7 pm for Ni$_{13}$t and 0.2 pm for a surface site of Ni(111)).
**CH₄ Dehydrogenation**

**Table S5.** Summary of reaction energies (ΔE) and activation energies (Eₐ) of all elementary steps involved in CH₄ dehydrogenation (cf. Figures 1, S7 and S8) on Ni₁₃.CeO₂ compared with literature values for Ni(111). H atoms resulting from R2 and R3 were removed from the cluster before the calculation of R4.

| Number | Equation | ΔE (eV) | Eₐ (eV) |
|--------|----------|---------|---------|
|        |          | Ni₁₃.i  | Ni₁₃.t  | Ni(111) | Ni₁₃.i | Ni₁₃.t | Ni(111) |
| R1     | CH₄gas → CH₄ | -0.44   | -0.36   | -0.26,₁ -0.21² | 0.00   | 0.00   | 0.00   |
|        | CH₄ → CH₃ + H | 0.32    | 0.02    | 0.09,₁ 0.31,² 0.55³ | 0.34   | 0.36   | 0.90,¹ 1.24,² 1.21,³ |
|        |           |         |         |         |        |        | 1.32,⁶ 1.13,⁵ 1.18,⁹ |
|        |           |         |         |         |        |        | 1.05,⁷ 1.09,⁸ |
|        |           |         |         |         |        |        | 0.91,¹⁰ 1.15¹¹ |
| R3     | CH₃ → CH₂ + H | 0.34    | 0.18    | 0.19,² 0.33,³ 0.07¹⁰ | 0.68   | 0.72   | 0.76² 0.87,³ 0.71,⁶ |
|        |           |         |         |         |        |        | 0.86,⁹ 0.70¹⁰ |
| R4     | CH₂ → CH + H | -0.78   | -0.37   | -0.21², -0.16,³ -0.34¹⁰ | 0.36   | 0.60   | 0.38² 0.43,³ 0.29,⁶ |
|        |           |         |         |         |        |        | 0.46,⁹ 0.35¹⁰ |
| R5     | CH → C + H | -0.16   | -0.63   | 0.80², 0.57,³ 0.52¹⁰ | 0.72   | 0.53   | 1.44² 1.45,³ 1.44,⁶ |
|        |           |         |         |         |        |        | 1.47,⁹ 1.33¹⁰ |
Figure S7. Structures and energies (relative to CH$_4$ in the gas phase and the clean system) of the initial states (IS), transition states (TS), and final states (FS) for CH$_4$ dehydrogenation steps on interfacial sites of the Ni$_{13}$ cluster supported on CeO$_2$(111). Note that two H atoms were removed before R4, which were balanced by adding a free-standing H$_2$ molecule in the calculation of the energies ($E[\text{state}] + E[H_2\text{gas}] - E[\text{CH}_4\text{gas}] - E[\text{Ni}_{13}\cdot\text{CeO}_2]$). Selected interatomic distances (in pm) are indicated.
Figure S8. Structures and energies (relative to CH$_4$ in the gas phase and the clean system) of the initial states (IS), transition states (TS), and final states (FS) for CH$_4$ dehydrogenation steps on terrace sites of the Ni$_{13}$ cluster supported on CeO$_2$(111). Carbon migration from terrace to interface sites is also shown (bottom panel). Note that two H atoms were removed before R4 and another two before carbon migration, which were balanced by adding one and two free-standing H$_2$ molecules in the calculation of the energies, respectively ($E_{\text{state}} + (1 \text{ or } 2) \ E[H_{2\text{gas}}] - E[\text{CH}_4\text{gas}] - E[\text{Ni}_{13}\text{.CeO}_2]$). Selected interatomic distances (in pm) are indicated.
**Binding energy of isolated adsorbates**

**Table S6.** Binding energies ($BE$) of isolated chemisorbed CH$_x$ ($x$=0–4), H, H$_2$, O, OH, CO and COH species relative to the species in gas phase and the clean systems (for a species A, $BE$(A) = $E[A/Ni_{13}.CeO_2] - E[A] - E[Ni_{13}.CeO_2]$). For CH$_x$ intermediates, co-adsorbed H atoms were removed in each CH$_4$ → CH$_3$ → CH$_2$ → CH → C step (cf. R1–R5 in Table S5, and Figures S7 and S8) and the structures were reoptimized. H species corresponds to the removal of CH$_3$ from the CH$_3$ + H states, followed by geometry optimization. CO and COH species correspond to the systems resulting from removing the H atom adsorbed on lattice oxygen (H$_o$) in the COH intermediate pathway (cf. Figure 4, and R8 and R9 in Figure S10). O and OH species were adsorbed separately on the same sites where they adsorb when formed via the H$_2$O dehydrogenation pathway (III and II in Figure 7 for O and OH, respectively, i.e., OH corresponds to the 2-fold-bound OH$_o$ species).

| Species | Ni$_{13}.i$/ CeO$_2$(111) | Ni$_{13}.t$/ CeO$_2$(111) | Ni(111) |
|---------|----------------------------|--------------------------|---------|
| CH$_4$  | -0.44                      | -0.36                    | -0.26$^1$–0.21$^2$|
| CH$_3$  | -2.57                      | -2.36                    | -2.02$^2$–1.81$^9$–1.91$^{10}$–1.91$^{12}$|
| CH$_2$  | -4.52                      | -4.25                    | -4.40$^2$–3.85$^9$–4.01$^{10}$–3.99$^{12}$|
| CH      | -7.20                      | -6.40                    | -6.66$^2$–6.35$^9$–6.43$^{10}$|
| C       | -7.88                      | -7.70                    | -7.03$^2$–6.61$^9$–6.78$^{10}$|
| H       | -2.68                      | -2.77                    | -2.68$^2$–2.77$^9$–2.81$^{10}$|
| H$_2$   | -0.47                      | -0.64                    | -0.38$^2$–0.22$^{10}$|
| OH      | -3.97                      | -                       | -3.12$^2$–3.11$^9$–3.42$^{10}$|
| O       | -5.86                      | -                       | -5.94$^2$–5.07$^9$–5.67$^{10}$|
| COH     | -5.02                      | -                       | -4.95$^2$–4.33$^9$–4.39$^{10}$|
| CO      | -2.18                      | -                       | -1.98$^2$–1.91$^9$–1.92$^{10}$|
OH and O Formation

Figure S9. Structures and energies (relative to H$_2$O in the gas phase and the clean system in all cases but one, namely, the O$_s$ $\rightarrow$ O+$V_O$) of the initial states (IS), transition states (TS), and final states (FS) for steps involved in O and OH formation on the Ni$_{13}$ cluster supported on CeO$_2$(111). Selected interatomic distances (in pm) are indicated.
CO formation

**Table S7.** Reaction energies ($\Delta E$) and activation energies ($E_a$) for CO formation steps evaluated on Ni$_{13.}$CeO$_2$ (cf. Figure S10) compared with literature values for Ni(111) when available.

| Number | Equation                  | $\Delta E$ (eV) | $E_a$ (eV) |
|--------|---------------------------|-----------------|------------|
|        |                           | Ni$_{13.}$CeO$_2$ | Ni(111)   | Ni$_{13.}$CeO$_2$ | Ni(111)   |
| R6     | C + O$_s$ → CO + Vo       | 0.10            | -          | 2.17             | -         |
| R7     | C + O → CO               | -0.31           | -2.50$^2$ | -1.72$^3$       | 1.47      | 0.59$^2$ | 1.30$^3$ |
|        |                           |                 | -1.35$^{10}$ |                 |           | 1.59$^{10}$ | 2.07$^{11}$ |
| R8     | C + OH + H$_s$ → COH + H$_s$ | 0.43             | -0.61$^3$ | -0.55$^{10}$   | 0.89      | 1.14$^3$ | 1.46$^{10}$ |
| R9     | COH + H$_s$ → CO + H + H$_s$ | -1.01           | -0.98$^2$ | -0.99$^{10}$   | 0.88      | 1.14$^2$ | 0.98$^{10}$ |
Figure S10. Structures and energies of the initial states (IS), transition states (TS), and final states (FS) for the CO formation steps evaluated on the Ni$_{13}$ cluster supported on CeO$_2$(111). Selected interatomic distances (in pm) are indicated. Note that in the IS of R6, O$_s$ is lifted and there are 6 Ce$^{3+}$ cations. The energies of IS, TS and FS were calculated according to the stoichiometry of the reaction, i.e., for R6: $E[\text{state}] + 2 E[\text{H}_2\text{gas}] - E[\text{CH}_4\text{gas}] - E[\text{Ni}_{13}\text{.CeO}_2]$, for R7: $E[\text{state}] + 3 E[\text{H}_2\text{gas}] - E[\text{CH}_4\text{gas}] - E[\text{H}_2\text{O}_\text{gas}] - E[\text{Ni}_{13}\text{.CeO}_2]$, and for R8 and R9: $E[\text{state}] + 2 E[\text{H}_2\text{gas}] - E[\text{CH}_4\text{gas}] - E[\text{H}_2\text{O}_\text{gas}] - E[\text{Ni}_{13}\text{.CeO}_2]$. 
Figure S11. Structures of the initial states (IS), transition states (TS), and final states (FS) for CH$_x$OH ($x$=1–3) formation reactions on the Ni$_{13}$ cluster supported on CeO$_2$(111). Selected interatomic distances (in pm) are indicated. The energies of the IS, TS, and FS states were calculated as $E_{\text{state}} + (3-m/2) E_{\text{H$_2$gas}} - E_{\text{CH$_4$gas}} - E_{\text{H$_2$O$_{\text{gas}}}} - E_{\text{Ni$_{13}$CeO$_2$}}$ where $m$ is the number of H atoms in the system. Note: a H atom adsorbed on lattice oxygen (H$_s$) is present but it does not participate in the CH$_x$OH formation reactions. In R10, the H resulting from the first H abstraction from CH$_4$ is also present.
H₂ formation

| IS         | TS         | FS         |
|------------|------------|------------|
| ![](image1) | ![](image2) | ![](image3) |
| -1.11 eV   | -0.49 eV   | -0.64 eV   |
| 5 Ce³⁺     | 5 Ce³⁺     | 5 Ce³⁺     |

| H₂ + H → H₂ |
|-------------|
| ![](image4) |
| -1.87 eV    |
| 6 Ce³⁺      |

| H₂O + OHₐ + H → OH₁ + H + OHₐ + Hₛ |
|-----------------------------------|
| ![](image5)                       |
| -2.31 eV                          |
| 5 Ce³⁺                            |

| OH₁ + H + OHₐ + Hₛ → H₂O + OH₁ + H |
|-----------------------------------|
| ![](image6)                       |
| -2.81 eV                          |
| 5 Ce³⁺                            |

**Figure S12.** Structures and energies (relative to H₂ in the gas phase in the top two panels and to two H₂O molecules in the gas phase in the bottom two panels, as well as the pristine Ni₁₃.CeO₂ surface) of the initial states (IS), transition states (TS), and final states (FS) for steps involved in H₂ formation on the Ni₁₃ cluster supported on CeO₂(111). OH₁ indicates binding on the terrace of the Ni₁₃ cluster. Selected interatomic distances (in pm) are indicated.
The top panel in Figure S12 shows the formation of H\textsubscript{2} from H species chemisorbed on the Ni\textsubscript{13} cluster, whereas the second panel shows the direct migration of H\textsubscript{s} to the cluster, both described in the main text. The third and fourth panel show an alternative water-assisted pathway. Starting from H\textsubscript{2}O dissociative adsorption at the Ni-CeO\textsubscript{2} interface (OH\textsubscript{m} + H\textsubscript{s}), firstly a second H\textsubscript{2}O molecule adsorbs on a Ni\textsuperscript{0} terrace site with $\Delta E_{\text{ads}}=−0.68$ eV. Subsequently, that molecule dissociates into OH (on the terrace, OH\textsubscript{t}) and H, releasing 0.50 eV with a barrier of 0.75 eV (third panel). Finally, H\textsubscript{s} migrates towards the OH\textsubscript{m} group forming a H\textsubscript{2}O molecule at the interface, stabilized by a hydrogen bond with the OH\textsubscript{t} group. This last step takes place with $\Delta E=0.35$ eV and an energy barrier of 0.37 eV (fourth panel). After the water molecule is desorbed, the net result is the conversion of OH + H\textsubscript{s} into OH + H, that is, the H migration from surface lattice oxygen to the Ni\textsubscript{13} cluster.
References

(1) Lustemberg, P. G.; Zhang, F.; Gutiérrez, R. A.; Ramírez, P. J.; Senanayake, S. D.; Rodríguez, J. A.; Ganduglia-Pirovano, M. V. Breaking Simple Scaling Relations through Metal–Oxide Interactions: Understanding Room-Temperature Activation of Methane on M/CeO₂ (M = Pt, Ni, or Co) Interfaces. *J. Phys. Chem. Lett.* 2020, 2 (111), 9131–9137. https://doi.org/10.1021/acs.jpcl.0c02109.

(2) Han, Z.; Yang, Z.; Han, M. Comprehensive Investigation of Methane Conversion over Ni(111) Surface under a Consistent DFT Framework: Implications for Anti-Coking of SOFC Anodes. *Appl. Surf. Sci.* 2019, 480 (September 2018), 243–255. https://doi.org/10.1016/j.apsusc.2019.02.084.

(3) Niu, J.; Wang, Y.; Qi, Y.; Dam, A. H.; Wang, H.; Zhu, Y.-A.; Holmen, A.; Ran, J.; Chen, D. New Mechanism Insights into Methane Steam Reforming on Pt/Ni from DFT and Experimental Kinetic Study. *Fuel* 2020, 266 (October 2019), 117143. https://doi.org/10.1016/j.fuel.2020.117143.

(4) Burghgraef, H.; Jansen, A. P. J.; van Santen, R. A. Methane Activation and Dehydrogenation on Nickel and Cobalt: A Computational Study. *Surf. Sci.* 1995, 324 (2–3), 345–356. https://doi.org/10.1016/0039-6028(94)00716-0.

(5) Kratzer, P.; Hammer, B.; Nørskov, J. K. A Theoretical Study of CH₄ Dissociation on Pure and Gold-alloyed Ni(111) Surfaces. *J. Chem. Phys.* 1996, 105 (13), 5595–5604. https://doi.org/10.1063/1.472399.

(6) Watwe, R. M.; Bengaard, H. S.; Rostrup-Nielsen, J. R.; Dumesic, J. A.; Nørskov, J. K. Theoretical Studies of Stability and Reactivity of CH₃ Species on Ni(111). *J. Catal.* 2000, 189 (1), 16–30. https://doi.org/10.1006/jcat.1999.2699.

(7) Bengaard, H. S.; Nørskov, J. K.; Sæhested, J.; Clausen, B. S.; Nielsen, L. P.; Molenbroek, A. M.; Rostrup-Nielsen, J. R. Steam Reforming and Graphite Formation on Ni Catalysts. *J. Catal.* 2002, 209 (2), 365–384. https://doi.org/10.1006/jcat.2002.3579.

(8) Abild-Pedersen, F.; Greeley, J.; Nørskov, J. K. Understanding the Effect of Steps, Strain, Poisons, and Alloying: Methane Activation on Ni Surfaces. *Catal. Letters* 2005, 105 (1–2), 9–13. https://doi.org/10.1007/s10562-005-7998-9.

(9) Wang, S.-G.; Cao, D.-B.; Li, Y.-W.; Wang, J.; Jiao, H. CO₂ Reforming of CH₄ on Ni(111): A Density Functional Theory Calculation. *J. Phys. Chem. B* 2006, 110 (20), 9976–9983. https://doi.org/10.1021/jp060992g.

(10) Zhu, Y.-A.; Chen, D.; Zhou, X.-G.; Yuan, W.-K. DFT Studies of Dry Reforming of Methane on Ni Catalyst. *Catal. Today* 2009, 148 (3–4), 260–267. https://doi.org/10.1016/j.cattod.2009.08.022.

(11) Blaylock, D. W.; Ogura, T.; Green, W. H.; Beran, G. J. O. Computational Investigation of Thermochemistry and Kinetics of Steam Methane Reforming on Ni(111) under Realistic Conditions. *J. Phys. Chem. C* 2009, 113 (12), 4898–4908. https://doi.org/10.1021/jp806527q.

(12) Fajín, J. L. C.; Gomes, J. R. B.; D. S. Cordeiro, M. N. Mechanistic Study of Carbon Monoxide Methanation over Pure and Rhodium- or Ruthenium-Doped Nickel Catalysts. *J. Phys. Chem. C* 2015, 119 (29), 16537–16551. https://doi.org/10.1021/acs.jpcc.5b01837.

(13) Wang, S.-G.; Liao, X.-Y.; Hu, J.; Cao, D.-B.; Li, Y.-W.; Wang, J.; Jiao, H. Kinetic Aspect of CO₂ Reforming of CH₄ on Ni(111): A Density Functional Theory Calculation. *Surf. Sci.* 2007, 601 (5), 1271–1284. https://doi.org/10.1016/j.susc.2006.12.059.
