In situ Investigation of Methane Dry Reforming on M-CeO$_2$(111) \(\{\text{M=} \text{Co, Ni, Cu}\}\) Surfaces: Metal-Support Interactions and the activation of C-H bonds at Low Temperature

**Titel:**

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In situ Investigation of Methane Dry Reforming on M-CeO$_2$(111) \{M= Co, Ni, Cu\} Surfaces: Metal-Support Interactions and the activation of C-H bonds at Low Temperature


Abstract: Studies with a series of M-CeO$_2$(111) \{M= Co, Ni, Cu\} surfaces indicate that metal-oxide interactions can play a very important role for the activation of methane and its reforming with CO$_2$ at relatively low temperatures (600-700 K). Among the systems examined, Co-CeO$_2$(111) exhibits the best performance and Cu-CeO$_2$(111) has negligible activity. Experiments using ambient pressure XPS indicate that methane dissociates on Co-CeO$_2$(111), at temperatures as low as 300 K, generating CH$_x$ and CO$_2$ species on the catalyst surface. The results of density-functional calculations show a reduction in the methane activation barrier from 1.07 eV on Co(0001) to 0.87 eV on Co/CeO$_2$(111), and to only 0.05 eV on Co/CeO$_2$(111). At 700 K, under methane dry reforming conditions, CO$_2$ dissociates on the oxide surface and a catalytic cycle is established without coke deposition. A significant part of the CH$_x$ formed on the Co/CeO$_2$(111) catalyst recombines to yield ethane or ethylene.

Natural gas can transform the energy landscape of the world since it is a cheap and abundant fuel stock and a good source of carbon for the chemical industry. CH$_4$ is the primary component of natural gas but is difficult to convert it to upgraded fuels or chemicals due to the strength of the C-H bonds in the molecule (104 kcal/mol) and its non-polar nature.[1] Enabling low-temperature activation of methane is a major technological objective. It is known that enzymes such as the methane monooxygenase and some copper- and zinc-based inorganic compounds can activate C-H bonds near room temperature.[2-4]

In recent studies, we found that a Ni$^{2+}$/CeO$_2$(111) system activates CH$_4$ at room temperature as a consequence of metal-support interactions.[5,6] The methane reforming with CO$_2$ (DRM; CH$_4 + CO_2 \rightarrow 2CO + 2H_2$) then takes place at a moderate temperature of about 700 K. Over this surface, Ni and O sites of ceria work in a cooperative way during the dissociation of the first C-H bond in methane. Can this useful phenomenon be seen with other admetal-ceria combinations? In this article we compare the behavior of Co, Ni and Cu on CeO$_2$(111) using ambient-pressure X-ray photoelectron spectroscopy (AP-XPS), kinetic testing, and theoretical calculations based on density-functional theory.

The deposition of small amounts of Co (< 0.3 ML) on a CeO$_2$(111) film at 300 K produced a partial reduction of the oxide surface and adsorbed Co/CeO$_2$ species (Figure S1 in Supporting Information). Upon annealing from 300 to 700 K, most of the Co$^0$ transformed into Co$^{2+}$ (Figure S2). This particular type of metal-oxide surface was exposed to methane at 300, 500 and 700 K. Figure 1 shows C 1s XPS spectra collected before and after exposing a Co/CeO$_2$(111) surface to 1 Torr of methane at 300 K for 5 minutes. The strong peak near 285 eV can be attributed to CH$_x$ groups formed by the partial dissociation of methane on the metal/oxide interface.[5,6] This peak was not seen when a pure CeO$_2$(111) substrate was exposed to CH$_4$ at 300 K. In Figure 1 there is a second strong peak near 289.5 eV. This likely corresponds to a CO$_x$ species.[5,6] Some of the CH$_x$ molecules fully dissociated producing C atoms that eventually reacted with oxygen atoms of...
the ceria to yield CO₂ species. The intensity of the C 1s peak for the CH₅ species increased with Co coverage up to 0.15-0.2 ML, and then decreased at higher metal coverages. Thus, small clusters of Co on ceria are the best for C-H bond activation. The dissociative adsorption of methane on the Co²⁺/CeO₂(111) surface at room temperature did not induce a change in the oxidation state of Co²⁺ or Ce³⁺. Such changes were only seen when the dosing of methane was done at temperatures of 500 and 700 K.

Figure 2 displays Ce 3d and Co 2p AP-XPS spectra recorded while exposing a CeO₂(111) surface with 0.2 ML of Co to 50 mTorr of CH₄ at different temperatures. Both ceria and Co³⁺ species undergo reduction at 500-700 K as indicated by the emergence of Ce³⁺ and Co⁰ features. Once the first hydrogen is removed from the reactant molecule, a quick CH₃ → CH₂ → CH → C transformation occurs on the surface and oxygen atoms from the sample react to form CO and H₂O gas.

Figure 3. Ce³⁺ concentration measured in XPS as a function of temperature under reaction conditions (i.e. exposure to 50 mTorr of methane) on ceria pre-covered with ~0.2 ML of Co, Ni or Cu.

Figure 4. Catalytic activity for methane dry reforming and ethane production on Co-ceria catalysts as a function of Co coverage. The figure reports the amount of CO/H₂ and ethane/ethylene formed after exposing the Co-ceria surfaces to 1 Torr of CH₄ and 1 Torr of CO₂ at 650 K for 5 minutes.

Similar experiments to those shown in Figures 1 and 2 were performed for Cu/CoO₂(111). The results of XPS and Auger spectroscopy indicate that the interaction of Cu with CoO₂(111), Figures S3 and S4, is not as strong as that seen for Co. The dissociation of methane on Cu/CoO₂(111) surfaces was negligible at temperatures between 300 and 700 K (Figure S5). In this aspect, the behavior of these surfaces is very similar to that found for clean CeO₂(111). In Figure 3, we compare the reduction of ceria (i.e. formation of Ce³⁺) after dosing methane to Co-CeO₂(111), Cu-CeO₂(111) and Ni-CeO₂(111) system examined in a previous study. In the temperature range of 500-700 K, Co-CeO₂(111) reacts better with methane than Ni-CeO₂(111) or Cu-CeO₂(111). As we will see below, the partial reduction of ceria is important for the activation of CO₂ and closing the catalytic cycle for methane dry reforming.

In the case of Co-CeO₂(111), catalytic activity for methane dry reforming and C₂ (ethane/ethylene) production was seen at 650 K (Figure 4). Clean CeO₂(111) did not display significant catalytic activity. However, the catalytic activity substantially increased when Co was added, reaching a maximum for the generation of CO/H₂ at a coverage of ~0.15 ML. A maximum for the production of ethane/ethylene was seen at a Co coverage of 0.1 ML. At these small Co coverages, the Co-CeO₂(111) system had no problem dissociating CH₃ (Figures 1-3). The CH₃ groups generated on the surface underwent full decomposition to yield syngas or formed carbon-carbon bonds to produce ethane or ethylene. In Figure 4, the hydrogen is produced by methane dry reforming or by the generation of hydrocarbons (2CH₄ → C₂H₆/C₂H₄ + nH₂). CO and C₂H₄ also can be obtained through the reaction: 2CH₄ + 2CO₂ → 2CO + C₂H₄ + 2H₂O. At the maximum of catalytic activity in Figure 4, one can estimate a turnover frequency (TOF) of 6-7 molecules/Co atom · sec for methane dry reforming. At Co coverages above 0.2 ML, there was a steady decline in the catalytic activity. At the same time, postreaction characterization of the catalysts with XPS showed an increase in the amount of atomic carbon present in the surface (Figure S6). This carbon could eventually lead to the formation of coke and catalyst deactivation. Thus, the optimum Co coverage is below 0.2 ML, when the interactions with the oxide support are important and the strength and number of the Co-Co interactions is limited.
AP-XPS was used to study the chemical changes in the best Co/CeO₂(111) catalyst under reaction conditions. Figure 5 shows Ce 3d and Co 2p spectra collected while the catalyst is exposed to CH₄ or a mixture of CH₄/CO₂ at 700 K. Under pure methane one sees a surface with Co⁰ and strong peaks for Ce³⁺. The addition of CO₂ to the reactant gas leads to a weak reoxidation of Co and a substantial Ce⁰ → Ce³⁺ conversion. Two reaction paths are possible for the re-oxidation of the Ce³⁺ in the support: CO(g) + Vac → CO(g) + O-oxide, or CO₂(g) + H(a) + Vac → HOCO(a) → HO-Vac + CO(g) and HO-Vac → O-oxide + H(a). Both of them could close the catalytic cycle for methane dry reforming after the process: CH₄(g) → C(a) + 4H(a); C(a) + O-oxide → CO(g) + Vac.

Figure 6 compares the catalytic activity for methane dry reforming of Co-, Cu- and Ni-CeO₂(111) surfaces. The scale of the Co 2p region has been multiplied by a factor of 3 (θ_{Cu} = 0.2 ML).

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Methane decomposition is frequently cited as the most difficult step for the DRM process. Here, we apply the spin-polarized DFT+U approach to investigate the dissociative adsorption of CH₄ on Co and Cu nanoparticles deposited on stoichiometric and reduced cerium oxide surfaces, plus the extended Co(0001), Co (111) and Cu(111) surfaces. Results will be compared to those recently obtained for Ni-ceria systems. The metal-ceria surfaces used for the experiments are quite complex. Co/CeO₂(111) displays high activity for methane dissociation at low metal coverages with Co atoms in close contact with the ceria support in a 2+ oxidation state, whereas Cu/CeO₂(111) is not active, with Cu⁺ atoms aggregating to form larger metallic nanoparticles. Thus, we model these systems using single Co atoms and small tetrahedral Cu₄ clusters on CeO₂(111), Figure S7. We found that Co²⁺ species (3d³) adsorb most favorably at O-hollow sites in CeO₂(111), with the transfer of two electrons to the reducible support, Cu atoms transfer only one electron, yielding Cu¹⁺ species (3d⁴). The Cu⁴⁺ species also reduce the support, with the formation of two Ce³⁺. The CeO₂(111) supported Co₁ and Cu₄ species behave similarly to the corresponding Ni₁ and Ni₄ ones. Moreover, low-loaded Co/CeO₂(111) with metallic cobalt, is the active phase for methane dry reforming, which will be modeled using single metal Co atoms on CeO₂(0001) (Figure S7). Hence, these M-ceria (M=Co, Cu) model surfaces mimic the essential features of the experimental catalysts as seen in the XPS data shown in Figures 3 and 5.

The molecular binding of methane to Co or Cu surfaces is very weak and dissociation, CH₄(a) → CH₃(a) + H(a), is difficult due to large energy barriers. Our calculated barriers are 1.64 eV (Figure S8), respectively, in agreement with previous studies. This is similar to Ni(111) with a barrier of about 0.9–1.1 eV. The molecular binding of CH₄ to Co²⁺ and Cu⁴⁺ species on CoO₂(111) lies within the 0.1-0.2 eV range (Figures 7a and S9). On the Cu₄/CeO₂(111) surface, similar to Cu(111), methane dissociation is hindered by a large energy barrier of 1.45 eV. This is consistent with the negligible methane dissociation observed for Cu-ceria systems at room temperature. However, on Co/CeO₂(111), the barrier is reduced from 1.07 to 0.87 eV, as compared to CoO₂(111) (and from 1.02 eV if fcc Co(111) is considered, Figure S8). Therefore, the energy barrier for ceria supported small Co nanoparticles is accessible at lower temperatures than on the extended metal surface and methane dissociation is expected to occur, in agreement with the experiments shown in Figure 1. Here, metal and support work in a cooperative way in the dissociation of the C–H bond. Note that the final states shown in Figure 7a do not necessarily correspond to the lowest energy structures of the dissociated methane (Figure S9), but to local minima geometrically close to the transition state structures.

Upon increasing oxygen removal from the ceria support by reaction with methane, the Co²⁺ species gradually recover their metallic state. Chemisorbed methane molecules on both M⁰/CeO₂(0001) (M=Co, Ni) model systems are more stable than on the corresponding M²⁺/CeO₂(111) model systems (Figure 7), and thus the probability of reaction is expected to increase on the actual active dry reforming metal-CeO₂-x catalysts. We observe that the distances between methane and the M⁰/CeO₂(0001) (M=Co, Ni) surfaces, as measured by the C–M distances, are reduced by approx. 0.8 (Co) to 1.0 (Ni) Å with respect to the same distances in the M²⁺/CeO₂(111) systems (Figures S9 and S10). Moreover, CH₄ adsorption on the M⁰/
CeO$_2$(001) surfaces is aided by substantial hydrogen-metal interactions that are more pronounced compared to the M$^{2+}$/CeO$_2$(111) systems;

The closer approach to the M$^0$/CeO$_2$(0001) surfaces facilitates charge transfer to methane, e.g., the increase in the Bader charge for the C atom upon CH$_4$ adsorption is 0.03 and 0.16 electrons for Co$^0$/CeO$_2$(111) and Co$^0$/CeO$_2$(0001), respectively, with respect to the gas-phase CH$_4$ molecule (Table S1). Furthermore, the energy barrier for the dissociative adsorption of methane on Co$^0$/CeO$_2$(0001) is substantially reduced compared to Co$^{2+}$/CeO$_2$(111), becoming almost negligible – $E^*$ = 0.05 eV. This is not the case for the corresponding Ni-ceria systems for which the barrier remains unchanged ($\approx$ 0.8 eV). We interpret this unique Co behavior by inspecting the transition state structures for the M$^0$/CeO$_2$(0001) (M=Co, N=) surfaces (Figure 7b): the marked differences in activation barriers relate to the ability of the metals to form strong M–H bonds. Figure 7b shows that on Co$^0$/CeO$_2$(0001), the Co sites work alone during the dissociation of the first C–H bond. By contrast, on Ni$^0$/CeO$_2$(0001), Ni and O sites work cooperatively. This is also consistent with the calculated adsorption energy for hydrogen atoms on the M$^0$/CeO$_2$(0001) (M=Co, Ni) surfaces, which is larger by about 0.7 eV on Co than on Ni (Figure S12). Thus, both Co- and Ni-ceria systems are able to cleave C–H bonds at room temperature. However, it is only for Co-ceria that as the temperature increases, and methane decomposes and reacts with the CeO$_2$ support, accompanied by the Co$^{2+}$/CeO$_2$ $\rightarrow$ Co$^{2+}$/Ce$_3$O$_4$ transformation, that C–H bonds are more easily cleaved. Therefore, more vacant sites and more Ce$^{2+}$ ions are expected to form on Co-ceria catalysts as compared to Ni-ceria, in agreement with the experimental observations (Figure 3).

Our results on M-ceria (M=Co, Ni, Cu) model catalysts show that not only the nature of the metal is crucial for DRM activity and system stability, as recently pointed out for Ni, Co and Co-Ni nanoparticles,[13,14] but also the oxide support can play an essential role. An oxide support can modify the electronic properties of an admetal in substantial ways making its chemical properties very different from those of the corresponding bulk metal.[8,15] Single Co and Ni atoms on CeO$_2$ interact strongly with the reducible support while adopting a +2 oxidation state, and exhibit room temperature activity for C–H bond dissociation. Moreover, reducing the ceria support stabilizes metallic Co and Ni atoms and the systems are active for methane activation and dry reforming, with Co–CeO$_2$ being much more active than Ni–CeO$_2$. It is also seen that a low metal loading, below 0.2 ML, is crucial for the catalyst activity and stability since deactivation due to carbon deposition is observed at higher loading. This is consistent with the calculated trend in the adsorption energy of C atoms on the supported metal clusters of varying size (Figure S13), for example, Co$_3$/Ni$_3$-CeO$_2$ (-4.98/-4.12) $<$ Co$_4$/Ni$_4$-CeO$_2$ (-6.86/-6.54 eV). Here, we show that by choosing the “right” metal-oxide combination and manipulating metal-oxide interactions, as well as controlling the effects of metal loading, an improved catalytic activity can be obtained. Our findings should be useful in the rational design of catalysts for reactions involving C–H bond dissociation. Cobalt-ceria can be added to the short list of oxide-based systems that can activate methane at room temperature,[8,15] opening the possibility for new and exciting chemistry.

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Keywords: cobalt-ceria • methane dissociation • X-ray photoelectron spectroscopy • density functional theory

Low-loaded Co-CeO$_2$ is a highly efficient, stable and non-expensive catalyst for methane activation at RT and dry reforming at relative low temperatures (700 K), as revealed by experiments of ambient pressure XPS in combination with DFT calculations. Ethane/ethylene formation is also observed. Upon temperature increase the Co$^{2+}$/CeO$_2$ $\rightarrow$ Co$^{0}$/CeO$_{2-x}$ transformation occurs, making the latter extremely active. The DRM activity strongly depends on the metal-ceria combination, with Co-ceria $>$ Ni-ceria, and Cu-ceria being inactive.