In Situ Investigation of Methane Dry Reforming on Metal/Ceria(111) Surfaces: Metal–Support Interactions and C–H Bond Activation at Low Temperature

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were only seen when the dosing of CH₄ 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 containing 2 ML of Co to 50 mTorr of CH₄ at different temperatures. Both CeO²⁻ and Ce³⁺ 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.

Similar experiments to those shown in Figure 1 and Figure 2 were performed for Cu/CeO₂(111). The results of XPS and Auger spectroscopy indicate that the interaction of Cu with CeO₂(111) (Supporting Information, Figures S3 and S4) is not as strong as that seen for Co. The dissociation of CH₄ on Cu/CeO₂(111) surfaces was negligible at temperatures between 300 and 700 K (Supporting Information, Figure S5).

In this respect, the behavior of these surfaces is very similar to that found for clean CeO₂(111).[5,6] In Figure 3, we compare the reduction of CeO₂ (that is, formation of Ce³⁺) after dosing CH₄ to Co/CeO₂(111), Cu/CeO₂(111), and a Ni/CeO₂(111) system examined in a previous study.[5] In the temperature range of 500–700 K, Co/CeO₂(111) reacts better with CH₄ than Ni/CeO₂(111) or Cu/CeO₂(111). As shown in the proceeding text, the partial reduction of CeO₂ is important for the activation of CO₂ and closing the catalytic cycle for DRM.

In the case of Co/CeO₂(111), catalytic activity for DRM 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 approximately 0.15 ML. A maximum for the production of ethane/ethylene was seen at a Co coverage of 0.1 ML. At these low Co coverages, the Co/CeO₂(111) system had no problem dissociating CH₄ (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 DRM or by the generation of hydrocarbons; see [Eq. (2)]⁷,⁸.
2CH₄ → C₂H₆/C₂H₄ + nH₂  

(2)

CO and C₂H₄ can also be obtained by [Eq. (3)]:

2CH₄ + 2CO₂ → 2CO + C₂H₄ + 2H₂O  

(3)

At the maximum of catalytic activity in Figure 4, a turnover frequency (TOF) of 6–7 molecules per Co atom in a second was estimated for DRM. 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 (Supporting Information, 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/CoOₓ catalyst under reaction conditions. Figure 5 shows Ce 3d and Co 2p spectra collected while the catalyst was exposed to CH₄ or a mixture of CH₄/CO₂ at 700 K. Under pure CH₄ a surface with Co⁰ and strong peaks for Ce³⁺ is observed. Addition of CO₂ to the reactant gas leads to a weak reoxidation of Co and a substantial Ce³⁺→Ce⁴⁺ conversion. Two reaction paths, as defined by Equation (4) and Equations (5a,b), are possible for the reoxidation of the Ce³⁺ in the support:

CO₂(g) + Vac → CO(g) + O-oxide  

(4)

CO₂(g) + H(a) + Vac → HOOC(a) → HO-Vac + CO(g)  

(5a)

HO-Vac → O-oxide + H(a)  

(5b)

Both pathways could close the catalytic cycle for DRM after the process outlined by Equations (6a,b):

CH₄(g) → C(a) + 4H(a)  

(6a)

C(a) + O-oxide → CO(g) + Vac  

(6b)

Figure 6 compares the catalytic activity for DRM of Co-, Cu-, and Ni/CoOₓ catalysts. The surface with Co is clearly the best catalyst, in agreement with the trends seen in Figure 3 for the activation of pure CH₄. Among these systems, Co/CoOₓ is the only one able to catalyze the 2CH₄→C₂H₆+(1-x)H₂ reaction (x = 4.6). The negligible catalytic activity of Cu/CoOₓ results from a very poor reaction with CH₄ without the generation of the Ce³⁺ sites necessary for the activation of CO₂ (Figure 3), which shows that reducibility increases in the order Cu < Ni < Co. In a set of...
of experiments, we deposited low Co coverages (5–10 wt%) on a CeO$_2$ powder and tested the catalyst activity for DRM in a flow reactor at temperatures between 700 and 975 K. The powder system did not show signs of deactivation and the conversion of CH$_4$ by dry reforming was always close to that determined by equilibrium thermodynamics.$^{[9b]}$ These results are in agreement with the behavior seen for Co/CeO$_2$(111) at 700 K.

Decomposition of CH$_4$ is frequently cited as the most difficult step for the DRM process.$^{[7,8]}$ Herein, we apply the spin-polarized DFT + U approach to investigate the dissociative adsorption of CH$_4$ on Co and Cu nanoparticles deposited on stoichiometric and reduced cerium oxide surfaces, as well as the extended Co(0001), Co (111), and Cu(111) surfaces. Results are compared to those recently obtained for Ni/CeO$_2$ systems.$^{[5,6]}$ The metal/CeO$_2$ surfaces used for the experiments are quite complex. Co/CeO$_2$(111) displays high activity for CH$_4$ dissociation at low metal coverages with Co atoms in close contact with the CeO$_2$ support in a 2 + oxidation state; whereas Cu/CeO$_2$(111) is not active, with Cu$^{+}$ atoms aggregating to form larger metallic nanoparticles. Thus, we modeled these systems using single Co atoms and small tetrahedral Cu$_4$ clusters on CeO$_2$(111) (Supporting Information, Figure S7). We found that Co$^{+2}$ species (3d$^7$) adsorb most favorably at O-hollow sites in CeO$_2$(111), with the transfer of two electrons to the reducible support. Cu atoms transfer only one electron, yielding Cu$^{+}$ species (3d$^9$). The Cu$^{+}$ species also reduce the support, with the formation of two Ce$^{+3}$. The CeO$_2$(111) supported Co and Cu species behave similarly to the corresponding Ni$^{+}$ and Ni$^{+}$ species.$^{[5,6,9]}$ Moreover, Co/CeO$_2$(111) with a low loading of metallic cobalt is the active phase for DRM, which was modeled using single-metal Co atoms on CeO$_2$(0001) (Supporting Information, Figure S7). Hence, these M/CeO$_2$(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 CH$_4$ to Co or Cu surfaces is very weak, and dissociation (that is, CH$_4$($\epsilon$)→CH$_4$($\sigma$)+H($\epsilon$)) is difficult because of large energy barriers.$^{[10,11]}$ Our calculated barriers for Co and Cu, respectively, are 1.07 and 1.64 eV (Supporting Information, Figure S8), in agreement with previous studies.$^{[10,11]}$ This is similar to Ni(111) with a barrier of about 0.9−1.1 eV.$^{[12]}$ The molecular binding of CH$_4$ to Co$^{+2}$ and Cu$_4$ species on CeO$_2$(111) lies within the 0.1−0.2 eV range (Figure 7a; Supporting Information, Figure S9). On the Cu/CeO$_2$(111) surface, similar to Cu(111), CH$_4$ dissociation is hindered by a large energy barrier of 1.45 eV. This is consistent with the negligible CH$_4$ dissociation observed for Cu/CeO$_2$ systems at room temperature. However, on Co/CeO$_2$(111), the barrier is reduced from 1.07 to 0.87 eV, as compared to Co(0001) and from 1.02 eV if a face-centered cubic (fcc) Co(111) is considered; Supporting Information, Figure S8). Therefore, the energy barrier for Co$_2$ supported small Co nanoparticles is accessible at lower temperatures than on the extended metal surface and CH$_4$ dissociation is expected to occur, in agreement with the experiments shown in Figure 1. In this case, metal and support work in a cooperative manner 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 CH$_4$ (Supporting Information, Figure S9), but to local minima geometrically close to the transition-state structures.

Upon increasing oxygen removal from the CeO$_2$ support by reaction with CH$_4$, the Co$^{+2}$ species gradually recover their metallic state. Chemisorbed CH$_4$ molecules on both M$^{0}$/CeO$_2$(0001) (M = Co, Ni) model systems are more stable than on the corresponding M$^{+2}$/CeO$_2$(111) model systems (Figure 7), and thus the probability of reaction is expected to increase on the actual active dry reforming metal/CeO$_2$(111) catalysts. We observe that the distances between CH$_4$ and the M$^{0}$/CeO$_2$(0001) (M = Co, Ni) surfaces, as measured...
by the C–M distances, are reduced by approximately 0.6 (Co) to 1.0 (Ni) Å with respect to the same distances in the M$^{2+}$/CeO$_2$(111) systems (Supporting Information, Figures S9 and S10). Moreover, CH$_4$ adsorption on the M$^{2+}$/CeO$_2$(0001) 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$^{2+}$/CeO$_2$(0001) surfaces facilitates charge transfer to CH$_4$; for example, the increase in the Bader charge for the C atom upon CH$_4$ adsorption is 0.03 and 0.16 electrons for Co$^{2+}$/CeO$_2$(111) and Co$^{2+}$/CeO$_2$(0001), respectively, with respect to the gas-phase CH$_4$ molecule (Supporting Information, Table S1). Furthermore, the energy barrier for the dissociative adsorption of CH$_4$ on Co$^{2+}$/CeO$_2$(0001) is substantially reduced compared to Co$^{2+}$/CeO$_2$(111), becoming almost negligible—$E^0 = 0.05$ eV. This is not the case for the corresponding Ni/Co systems for which the barrier remains unchanged (ca. 0.8 eV). We interpret this unique Co behavior by inspecting the transition-state structures for the M$^{2+}$/CeO$_2$(0001) (M = Co, Ni) 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$^{2+}$/CeO$_2$(0001), the Co sites work alone during the dissociation of the first C–H bond. By contrast, on Ni$^{2+}$/CeO$_2$(0001) Ni and O sites work cooperatively. This is also consistent with the calculated adsorption energy for hydrogen atoms on the M$^{2+}$/CeO$_2$(0001) (M = Co, Ni) surfaces, which is about 0.7 eV larger on Co than on Ni (Supporting Information, Figure S12). Thus, both Co- and Ni/CeO$_2$ systems are able to cleave C–H bonds at room temperature. However, it is only for Co/CeO$_2$—as the temperature increases and CH$_4$ decomposes and reacts with the CeO$_2$ support, accompanied by the Co$^{2+}$/CeO$_2$→Co$^{3+}$/CeO$_2$ transformation—that C–H bonds are more easily cleaved. Therefore, more vacant sites and more Ce$^{3+}$ ions are expected to form on Co/CeO$_2$ catalysts as compared to Ni/CeO$_2$, in agreement with the experimental observations (Figure 3).

In summary, our results on M/CeO$_2$ (M = Co, Ni, Cu) model catalysts show that the nature of the metal is crucial for DRM activity and system stability (as recently pointed out for Ni, Co, and Co–Ni nanoparticles$^{[13,16]}$), and that the oxide support can also 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.$^{[5,6,11]}$ Single Co and Ni atoms on CoCe$_2$ 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 CeO$_2$ support stabilizes metallic Co and Ni atoms and the systems are active for CH$\alpha$ activation and dry reforming, with Co/CeO$_2$–$_{2\alpha}$ being much more active than Ni/CeO$_2$–$_{2\alpha}$. It is also seen that a low metal loading, below 0.2 ML, is crucial for the catalyst activity and stability, since deactivation arising from 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 (Supporting Information, Figure S13), for example, Co$_{2\alpha}$ and Ni$_{2\alpha}$/CeO$_2$ (−4.98/−4.12) < Co$_{2\alpha}$ and Ni$_{2\alpha}$/CeO$_2$ (−6.86/−6.54 eV). Herein, 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. Co/CeO$_2$ can be added to the short list of oxide-based systems that can activate CH$_4$ at room temperature.$^{[6,16]}$ opening the possibility for new and exciting chemistry.

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**Conflict of interest**

The authors declare no conflict of interest.

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