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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In Situ Investigation of Methane Dry Reforming on Metal/Ceria(111) Surfaces: Metal-Support Interactions and C-H Bond Activation 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$_x$ 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$_{0}$/CeO$_2$(111) to 0.87 eV on Co$_{0.05}$/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$_{0.05}$/CeO$_2$(111) catalyst recombines to yield ethane or ethylene.

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$_2$ → 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$_{0.05}$/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$_{0.05}$/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

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Supporting information for this article is given via a link at the end of the document.

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Temperature activation of methane is a major technological objective. It is known that enzymes such as the methane monoxygenase and some copper- and zinc-based inorganic compounds can activate C–H bonds near room temperature.[2-4]
the ceria to yield COx species. The intensity of the C 1s peak for the CHx species increased with Co coverage up to 0.15-0.2 ML, and then decreased at higher admetal 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 Ce4+. 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 Co2+ 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 C2H6/C2H4 formed after exposing the Co-ceria surfaces to 1 Torr of CH4 and 1 Torr of CO2 at 650 K for 5 minutes.

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 CH4 (Figures 1-3). The CH4 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.
methane dry reforming after the process: \( \text{CH}_4(g) \rightarrow \text{C}(a) + 4\text{H}(a); \text{C}(a) + \text{O-oxide} \rightarrow \text{CO}(g) + \text{Vac} \).

Two reaction paths are possible for the re-oxidation of the Ce\(^{3+}\) in the support: \( \text{CO}_2(g) + \text{Vac} \rightarrow \text{CO}(g) + \text{O-oxide}, \text{or CO}_2(g) + \text{H}(a) + \text{Vac} \rightarrow \text{HOCO}(a) \rightarrow \text{HO-Vac} + \text{CO}(g) + \text{HO-Vac} \rightarrow \text{O-oxide} + \text{H}(a) \). Both of them could close the catalytic cycle for methane dry reforming after the process: \( \text{CH}_4(g) \rightarrow \text{C}(a) + 4\text{H}(a); \text{C}(a) + \text{O-oxide} \rightarrow \text{CO}(g) + \text{Vac} \).

Figure 6 compares the catalytic activity for methane dry reforming of Co-, Cu- and Ni-CeO\(_2\) catalysts.\(^{[10,11]}\) The surface with Co is clearly the best catalyst, in agreement with the trends seen in Figure 3 for the activation of pure methane. Among these systems, Co-CeO\(_2\) is the only one able to catalyze the \( 2\text{CH}_4 \rightarrow \text{C}_2\text{H}_4 + \langle(8-x)/2\rangle\text{H}_2 \) reaction \((x=4,6)\). The negligible catalytic activity of Cu-CeO\(_2\) results from a very poor reduction of \( \text{CO}_2 \), as indicated in Figure 3, which shows that reducibility increases in the order Cu < Ni < Co. In a set of experiments, we deposited small Co coverages \((5-10\ \text{wt\%})\) on a ceria powder and tested the catalytic activity for DRM in a flow reactor at temperatures between 700 and 975 K. The powder system did not show signs for deactivation and the conversion of methane through dry reforming was always close to the theoretical values seen in the XPS data shown in Figures 3 and 5.

The molecular binding of methane to Cu or Cu surfaces is very weak and dissociation, \( \text{CH}_4(a) \rightarrow \text{CH}_2(a) + \text{H}(a) \), is difficult due to large energy barriers.\(^{[10,11]}\) Our calculated barriers are 1.07 and 1.64 eV (Figure S8), respectively, in agreement with previous studies.\(^{[10,11]}\) This is similar to Ni(111) with a barrier of about 0.9–1.1 eV.\(^{[5,12]}\) The molecular binding of \( \text{CH}_4 \) to Co\(^{2+}\) and Cu\(^{4+}\) species on CeO\(_2\) lies within the 0.1-0.2 eV range (Figures 7a and S9). On the Cu/CeO\(_2\) 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. Upon increasing oxygen removal from the ceria support by the transfer of two electrons to the reducible support, Cu atoms transfer only one electron, yielding Cu\(^{3+}\) species (3d\(^{9}\)). The Cu\(^{4+}\) species also reduce the support, with the formation of two Ce\(^{3+}\). The CeO\(_2\) supported Co and Cu species behave similarly to the corresponding Ni and Ni ones.\(^{[8,6]}\) Moreover, low-loaded Co/CeO\(_2\) with metallic cobalt, is the active phase for methane dry reforming, which will be modeled using single metal Co atoms on CeO\(_2\) (Figure S7). Hence, these M-ceria \((M=\text{Co, Cu})\) model surfaces mimic the essential features of the experimental catalysts as seen in the XPS data shown in Figures 3 and 5.

Figure 6. Catalytic activity for methane dry reforming on Cu-, Ni-, Co-ceria catalysts \((\text{Contact} \sim 0.15\ \text{ML})\). The figure reports the amount of CO/H\(_2\) formed after exposing the catalysts to 1 Torr of CH\(_4\) and 1 Torr of CO\(_2\) at 650 K for 5 minutes.

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CeO_2(0001) surfaces is aided by substantial hydrogen-metal interactions that are more pronounced compared to the M^{2+}/
CeO_2(111) systems;

Figure 7. Reaction energy profile for the CH_4 → CH_3 + H reaction on a) Cu, Co, and Ni on CeO_2(111) and b) Co and Ni on CeO_2(0001). The activation barriers are hardly affected by inclusion of vdW interactions (Figure S14). The structures shown on the left, middle and right of the reaction pathways, correspond to the side views of the molecularly adsorbed, transition and structures shown on the left, middle and right of the reaction pathways, respectively (Supporting information Figures S9 and S10).

Acknowledgements

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

References

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.
1. Experimental and Theoretical sections

1.1. Experimental Section

A commercial SPECS AP-XPS chamber equipped with a PHOIBOS 150 EP MCD-9 analyzer was used for the XPS analysis. The AP-XPS chamber can take pressure up to 1 torr with heating capability up to 900 K. The Ce 4d photoemission lines were used for the binding energy calibration based on the 122.8 eV satellite feature. To generate the films used to prepare the MO$_2$/CeO$_2$(111) M= Co, Ni or Cu model catalysts, Ce metal was evaporated onto a Ru single crystal (0001) held at 700 K in the presence of 5 × 10^{-7} Torr O$_2$, and then annealed to 800 K for 10 mins at the same O$_2$ pressure.[1,2] The ceria films were estimated to be ca. 4 nm thick (10 layers of O-Ce-O) based on the attenuation of the Ru 3d XPS signal. The metals (Co, Ni or Cu) were vapor deposited on the as-prepared ceria film at 300 K under vacuum and then annealed to 700 K for 1 min.[1,2]

The catalytic tests were done in a set-up that combined a chamber for ultra-high vacuum (UHV) studies and a batch reactor.[2] In the studies of methane activation, the sample was transferred to the reactor at ~300 K, and then the reactant gas at 1 Torr of pressure was introduced. In experiments testing the activity of the MO$_2$/CeO$_2$(111) catalysts for the DRM process, the samples were exposed to a mixture of CH$_4$ (1 Torr) and CO$_2$ (1 Torr) at 300 K and were rapidly heated to the reaction temperature of 650 K. Product yields were analyzed by mass spectroscopy or chromatography. In our experiments data were collected at intervals of 5 min. The amount of molecules (CO, H$_2$, ethane) produced in the catalytic tests was normalized by the active area exposed by the sample and the total reaction time. The kinetic experiments were done in the limit of low conversion (<10%).

1.2. Theoretical Section

The spin-polarized calculations were performed using the DFT-(PBE)+U approach as implemented in the Vienna ab initio simulation package (VASP) (vasp site, http://www.vasp.at; version vasp.5.3.5). A value of 4.5 eV was used for the Hubbard U-like term. The projector augmented wave method (PAW) was employed at a plane-wave cutoff of 415 eV to decouple the core from valence electrons. The C (2s, 2p), O (2s, 2p), Ni (3p, 3d, 4s), Co(3p, 3d, 4s), Cu(3p, 3d, 4s) and Ce (4f, 5s, 5p, 5d, 6s) electrons were treated as valence states.

In order to test the effect of long-range dispersion corrections on the methane adsorption and dissociation, we have selectively used the so called DFT-DF2 approach [3] implemented in VASP by Klimeš et al. [4,5], using the algorithm of Roman-Perez and Soler [6], see Figure S14 below. The DFT-DF2 functional aims to improve the binding description around energy minima by changing both the exchange and non-local correlation components. Specifically, we report results of DFT+U-DF2 (a Hubbard-like U term added) calculations using the so called optB88-vdW functional [5,6], with the DFT(PBE)+U lattice constant.

The M/CeO$_2$(111) and M/CeO$_2$(0001) [M= Co, Ni or Cu] surfaces were modeled by (2 × 2) unit cells, with calculated ceria bulk equilibrium lattice constant (CeO$_2$: 5.485 Å ; Ce$_2$O$_3$: 5.537 Å). In the case of CeO$_2$(111) we have considered nine atomic layers (three O-Ce-O trilayers) whereas Ce$_2$O$_3$(0001) was modeled with fifteen atomic layers (six Ce atomic layers).

There are two allotropic modifications of cobalt; a hexagonal close-packed (HCP) form, stable at temperatures below 422°C, and a face-centered-cubic (FCC) form, which is stable between 422°C and its melting point of 1495°C [7]. We have considered modeling the Co(111) and Co(0001) surfaces because, O’Shea et al. and Zhang et al. in two different experiments have demonstrated that the stable phases of cobalt are very sensitive to their exposed environment such as pressure, temperature and pretreatment of the catalysts [8,9].

The Co(0001), Co(111) and Cu(111) surfaces were modeled by (3 × 3) unit cell and five metal layers. The optimized lattice constants for (hcp) Co (a = b = 2.492 Å and c = 4.028 Å) and (fcc) Co (a = 3.520 Å) Cu (a = 3.635 Å) agree well with the experimental values (hcp Co: a = b = 2.507 Å and c = 4.061 Å [10], fcc Co: a = 3.544 Å [10] fcc Cu: a = 3.597 Å [11]). In all surface models, consecutive slabs were separated by at least 12 Å of vacuum space to avoid interaction with periodic images. Monkhorst-Pack grids with a (3 × 3 × 1) and (5 × 5 × 1) k-point sampling were used for the ceria-based systems and the extended metal surfaces, respectively. All the atoms in the three bottom layers were fixed at their optimized bulk-truncated positions during geometry optimization, whereas the rest of the atoms were allowed to fully relax.

To locate the TS structures we employed the climbing image nudged elastic band method (CI-NEB)[12] with nine images for each reaction pathway. For all the TS reported in this work, we have found only one imaginary frequency, and the full geometry optimizations starting from its back and forward nearest configurations (along the reaction path) ended in a non-dissociated and dissociated state, respectively.
2. Results

Figure S1 shows the coverage dependency of Co growth on CeO$_2$(111) surface. The spectra were taken at 300 K before annealing. It can be seen that, even at 300 K, a small amount of Co already interacts strongly with the ceria substrate, resulting in the formation of Co$^{2+}$. (In XPS it is hard to distinguish Co$^{2+}$ from Co$^{3+}$, but Co$^{3+}$ probably will not form under these conditions). As the Co coverage increased, the intensities of Co$^{2+}$ peaks have saturated, and the metallic Co features start to develop, indicating Co particles are growing three dimensionally at this point. At the same time, ceria is slightly reduced as shown by the Ce$^{3+}$ features in the figure.
After depositing Co at 300 K, the surface was annealed to 700 K in UHV to generate a stabilized surface before any surface chemistry was studied. The surfaces before/after annealing are compared in Figure S2. One can see that the metallic Co feature is gone as annealing allows more charge transfer/oxygen spillover from ceria to cobalt. Interestingly, the ceria film was also slightly re-oxidized, probably due to the diffusion of the lattice oxygen from sublayers to the surface by annealing.

Figure S2: Ce 3d + Co 2p XPS spectra of the surfaces before/after annealing, $\theta_{Co} \approx 0.2$ML.
Figure S3: Ce 3d + Cu 2p XPS regions of the fresh surface (blue), as-deposited surfaces with 0.2 ML (red) and 0.3 ML Cu (black) coverages, respectively. XPS data collected at 300 K before annealing the Cu/ceria systems. Ceria is slightly reduced after Cu deposition while most of the Cu is oxidized to Cu$^{1+}$, as indicated by the Auger spectrum. No changes are seen with increased Cu coverage.

Figure S4: Ce 3d + Cu 2p XPS spectra of the surfaces before/after annealing, $\theta_{Co} \approx 0.3$ML.

In contrast to the Co deposited surface, annealing the Cu/CeO$_2$(111) surfaces leads to the reduction of Cu$^{1+}$ to Cu$^{0}$, as evident by the Auger spectrum in the inset figure. One possible explanation is that the severe
coalescence of Cu after annealing causes the reduction of Cu, which is a strong indication that the interaction between Cu with CeO$_2$(111) is much weaker than in the case of Co.

Figure S5: Ce 3d + Cu 2p XPS spectra of the surface at elevated temperatures under 50 mTorr CH$_4$, $\theta_{Co} \approx 0.2$ML.

No changes for Cu-ceria surfaces under 50 mTorr of methane.

Figure S6: Effect of Co coverage on the amount of atomic carbon (features in the 284-282 eV window) formed after exposing Co-CeO$_2$(111) surfaces to 1 Torr of methane and 1 Torr of CO$_2$ at 650 K for 5 min.

The C 1s intensity of C$_x$ species was normalized by the coverage of Co on the surface.
Figure S7: Top and side views of the model catalysts used in the calculations: a) Cu(111), b) Co(111), c) Co(0001), d) Cu$_4$/CeO$_2$(111), e) Co$^{2+}$/CeO$_2$(111) and f) Co$^0$/Ce$_2$O$_3$(0001).
Figure S8: Reaction pathways for CH₄ dissociation on Ni(111), Cu(111), Co(111) and Co(0001) as well as top and side views of the structures of the molecularly adsorbed state, transition state (TS), and dissociated state for the three reaction pathways. Selected interatomic distances (in pm) are indicated. All energies (in eV) are referenced to the total energy of CH₄(g) and the extended metal surfaces.
Figure S9: Top and side views of the molecularly adsorbed state, transition state (TS), and dissociated state for the CH$_4$→CH$_3$+H reaction on the Cu$_4$/CeO$_2$(111), Co$_1$/CeO$_2$(111), and Ni$_1$/CeO$_2$(111) model catalysts (Figure 7a in the main text). Selected interatomic distances (in pm) are indicated. All energies (in eV) are referenced to the total energy of CH$_4$(g) and the M/CeO$_2$(111) {M=Cu, Co, Ni} surfaces.
Figure S10: Top and side views of the molecularly adsorbed state, transition state (TS), and dissociated state for the CH$_4$→CH$_3$+H reaction on the Co$_1$/Ce$_2$O$_3$(0001) and Ni$_1$/Ce$_2$O$_3$(0001) model catalysts (Figure 7b in the main text). Selected interatomic distances (in pm) are indicated. All energies (in eV) are referenced to the total energy of CH$_4$(g) and the M/Ce$_2$O$_3$(0001) {M=Co, Ni} surfaces.
Table S1: Bader charge change for the C atom upon CH$_4$ adsorption on ceria and metal-ceria surfaces, with respect to the gas-phase molecule (note: a positive change denote a higher electron density).

<table>
<thead>
<tr>
<th>Surface</th>
<th>CH$_4$/Ce$_2$O$_3$</th>
<th>CH$_4$/Ni$_1$-Ce$_2$O$_3$</th>
<th>CH$_4$/Co$_1$-Ce$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$(111) Ni$^{2+}$/CeO$_2$(111)</td>
<td>0.03</td>
<td>-0.09</td>
<td>+0.03</td>
</tr>
<tr>
<td>CeO$_2$(0001) Ni$^0$/Ce$_2$O$_3$(0001)</td>
<td>-0.01</td>
<td>+0.15</td>
<td>+0.16</td>
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</tbody>
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$\Delta q_C = +0.11 \Delta q_{Ni} = -0.08$ $\Delta q_C = +0.11 \Delta q_{Co} = -0.13$

Figure S11: Top panel: Top and side views of molecularly adsorbed CH$_4$ on the Ce$_2$O$_3$(0001), Ni$^0$/Ce$_2$O$_3$(0001), and Co$^0$/Ce$_2$O$_3$(0001) surfaces. Selected interatomic distances (in pm) are indicated. Adsorption energies (in eV) are referenced to the total energy of CH$_4$(g) and the M/Ce$_2$O$_3$(0001) {M=Ni, Co} surfaces. Lower panel: Charge density isosurfaces corresponding to a charge density difference, namely, that of the chemisorbed system from which both the charge density of the clean surface and that of the isolated methane molecule (both with distances as in the chemisorbed system) have been subtracted. $\Delta q$ is the associated Bader charge difference (in electrons). The picture displays the induced effect by the adsorption of a CH$_4$ molecule on the valence charge of its neighboring metal atom on the M/Ce$_2$O$_3$(0001) {M=Ni, Co} surfaces, namely, charge is withdrawn from the metal upon CH$_4$ adsorption.
Figure S12: Top and side views of a hydrogen atom adsorbed on the M$_1$/CeO$_2$(111) and M$_1$/Ce$_2$O$_3$(0001) \( \{M=\text{Ni, Co}\} \) surfaces. Selected interatomic distances (in pm) are indicated. Adsorption energies (in eV) are referenced to the total energy of H$_2$(g) and the M/Ce$_2$O$_3$(0001) \( \{M=\text{Ni, Co}\} \) surfaces.

Figure S13: Top and side views of a carbon atom adsorbed on the M$_i$/CeO$_2$(111) and M$_i$/Ce$_2$O$_3$(0001) \( \{M=\text{Ni, Co, } i = 1, 4\} \) surfaces. Selected interatomic distances (in pm) are indicated. Adsorption energies (in eV) are referenced to the total energy of H$_2$(g) and the M$_i$/Ce$_2$O$_3$(0001) \( \{M=\text{Ni, Co}\} \) surfaces.
Figure S14: Reaction energy profile for the $\text{CH}_4 \rightarrow \text{CH}_3 + \text{H}$ reaction on Cu$_4$, Co$_1$ and Ni$_1$ on CeO$_2$(111) with and without van der Waals corrections. The structures shown on the left, middle and right of the reaction pathways, correspond to the side views of the molecular adsorbed, transition and dissociated states, respectively without vdW correction. All energies are referenced to the total energy of CH$_4$(g) and the M/ceria M=Co, Ni, Cu surfaces. Atoms color scheme: Ni in blue, Cu in brown, Co in violet, Ce$^{3+}$ in grey, Ce$^{4+}$ in white, surface/subsurface oxygen atoms in red/green.

3. Bibliography

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