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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

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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(0001) to 0.87 eV on Co^{2+}/CeO$_2$(111), *and to only* 0.05 eV on Co^0/CeO$_{2-x}$(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/CeO$_{2-x}$ (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$_2$ → 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/CoO$_x$ 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$_4$ molecules fully dissociated producing C atoms that eventually reacted with oxygen atoms of

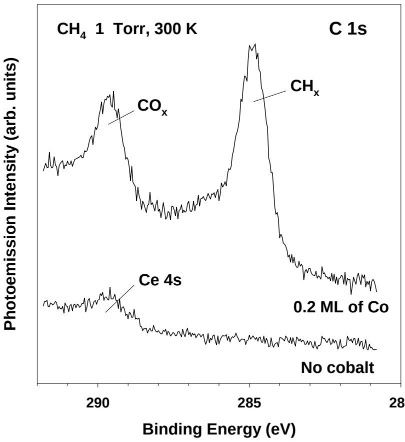

Figure 1. C 1s XPS spectra collected before and after exposing a CeO$_2$(111) surface containing 0.2 ML of Co to 1 Torr of methane at 300 K for 5 minutes.

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Supporting information for this article is given via a link at the end of the document the ceria to yield CO_x species. The intensity of the C 1s peak for the CH_x 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 for C-H bond activation. The dissociative adsorption of methane on the $Co^{2+}/CeO_2(111)$ surface at room temperature did not induce a change in the oxidation state of Co^{2+} or Ce^{4+}. 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 $CeO_2(111)$ surface with 0.2 ML of Co to 50 mTorr of CH_4 at different temperatures. Both ceria and Co^{2+} species undergo reduction at 500-700 K as indicated by the emergence of Ce^{3+} and Co^0 features. Once the first hydrogen is removed from the reactant molecule, a quick $CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C$ transformation occurs on the surface and oxygen atoms from the sample react to form CO and H_2O gas.

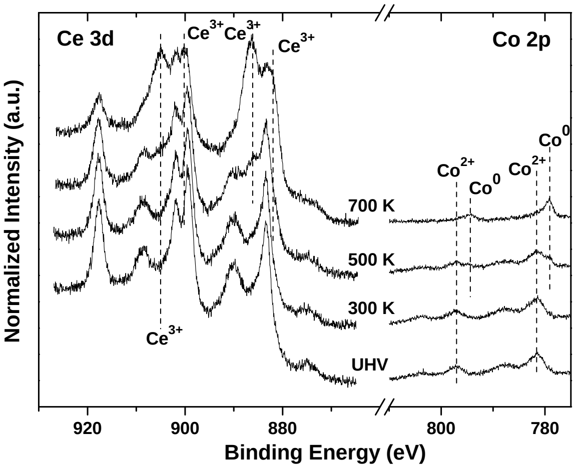

Figure 2. Ce 3d + Co 2p spectra for a $Co/CeO_2(111)$ ($\Theta_{Co} \approx 0.2$ ML) surface under 50 mTorr of CH_4 at 300, 500 and 700 K.

Similar experiments to those shown in Figures 1 and 2 were performed for $Cu/CeO_2(111)$. The results of XPS and Auger spectroscopy indicate that the interaction of Cu with $CeO_2(111)$, Figures S3 and S4, is not as strong as that seen for Co. The dissociation of methane on $Cu/CeO_2(111)$ 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 $CeO_2(111)$.[5,6] In Figure 3, we compare the reduction of ceria (i.e. formation of Ce^{3+}) after dosing methane to $Co\text{-}CeO_2(111)$, $Cu\text{-}CeO_2(111)$ and a $Ni\text{-}CeO_2(111)$ system examined in a previous study.[5] In the temperature range of 500-700 K, $Co/CeO_2(111)$ reacts better with methane than $Ni/CeO_2(111)$ or $Cu/CeO_2(111)$. As we will see below, the partial reduction of ceria is important for the activation of CO_2 and closing the catalytic cycle for methane dry reforming.

In the case of $Co/CeO_2(111)$, catalytic activity for methane dry reforming and C2 (ethane/ethylene) production was seen at 650 K (Figure 4). Clean $CeO_2(111)$ did not display significant catalytic activity. However, the catalytic activity substantially increased when Co was added, reaching a maximum for the generation of CO/H_2 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 $Co/CeO_2(111)$ system had no problem dissociating CH_4 (Figures 1-3). The CH_3 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 ($2CH_4 \rightarrow C_2H_6/C_2H_4 + nH_2$).[7,8] CO and C_2H_4 also can be obtained through the reaction: $2CH_4 + 2CO_2 \rightarrow 2CO + C_2H_4 + 2H_2O$. 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.

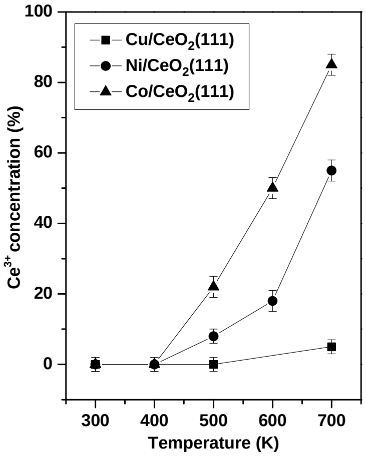

Figure 3. Ce^{3+} concentration measured in XPS as a function of temperature under reaction conditions (i.e. exposure to 50 mTorr of methane) on ceria pre-covered with ~ 0.2 ML of Co, Ni or Cu.

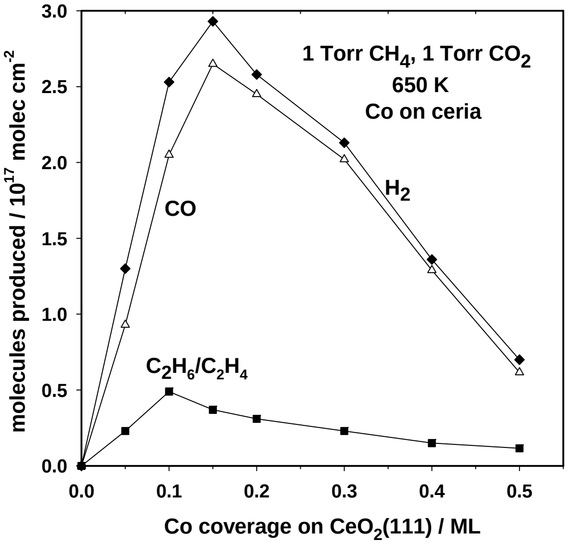

Figure 4. Catalytic activity for methane dry reforming and ethane production on Co-ceria catalysts as a function of Co coverage. The figure reports the amount of CO/H_2 and ethane/ethylene formed after exposing the Co-ceria surfaces to 1 Torr of CH_4 and 1 Torr of CO_2 at 650 K for 5 minutes.

AP-XPS was used to study the chemical changes in the best Co/CeO_2(111) catalyst under reaction conditions. Figure 5 shows Ce 3d and Co 2p spectra collected while the catalyst is exposed to CH_4 or a mixture of CH_4/CO_2 at 700 K. Under pure methane one sees a surface with Co^0 and strong peaks for Ce^{3+}. The addition of CO_2 to the reactant gas leads to a weak reoxidation of Co and a substantial $Ce^{3+} \rightarrow Ce^{4+}$ conversion. Two reaction paths are possible for the re-oxidation of the Ce^{3+} in the support: CO_2(g) + Vac → CO(g) + O-oxide, or CO_2(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: CH_4(g) → C(a) + 4H(a); C(a) + O-oxide → CO(g) + Vac.

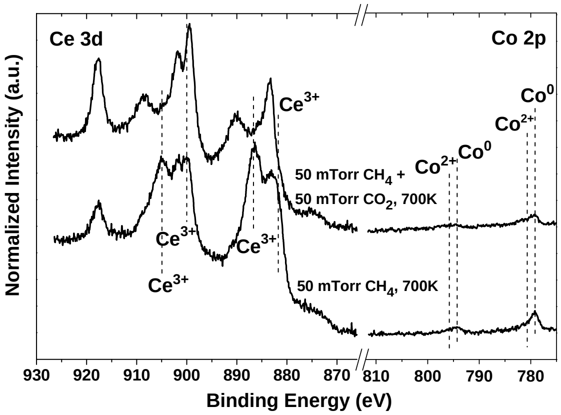

Figure 5. Ce 3d + Co 2p XPS spectra of the surface at 700 K under 50 mTorr of methane w/o the addition of 50 mTorr CO_2. The scale of the Co 2p region has been multiplied by a factor of 3 (θ_{Co} ~ 0.2 ML).

Figure 6 compares the catalytic activity for methane dry reforming of Co-, Cu- and Ni-CeO_2(111)[6]. 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(111) is the only one able to catalyze the $2CH_4 \rightarrow C_2H_x + \{(8\text{-}x)/2\}H_2$ reaction (x= 4,6). The negligible catalytic activity of Cu/CeO_2(111) results from a very poor reaction with CH_4 without the generation of the Ce^{3+} sites necessary for the activation of 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 wt%) on a ceria 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 for deactivation and the conversion of methane through dry reforming was always close to that determined by equilibrium thermodynamics.[8b] These results are in agreement with the behaviour seen for Co/CeO_2(111) at 700 K.

Methane decomposition is frequently cited as the most difficult step for the DRM process.[7,8] Here, 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, plus the extended Co(0001), Co (111) and Cu(111) surfaces. Results will be compared to those recently obtained for Ni-ceria systems.[5,6] The metal-ceria surfaces used for the experiments are quite complex. Co/CeO_2(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/CeO_2(111) is not active, with Cu^{1+} atoms aggregating to form larger metallic nanoparticles. Thus, we model these systems using single Co atoms and small tetrahedral Cu_4 clusters on CeO_2(111), 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^{1+} species ($3d^{10}$). The Cu_4 species also reduce the support, with the formation of two Ce^{3+}. The CeO_2(111) supported Co_1 and Cu_4 species behave similarly to the corresponding Ni_1 and Ni_4 ones. [5,6,9] Moreover, low-loaded Co/$CeO_{2\text{-}x}$(111) with metallic cobalt, is the active phase for methane dry reforming, which will be modeled using single metal Co atoms on Ce_2O_3(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.

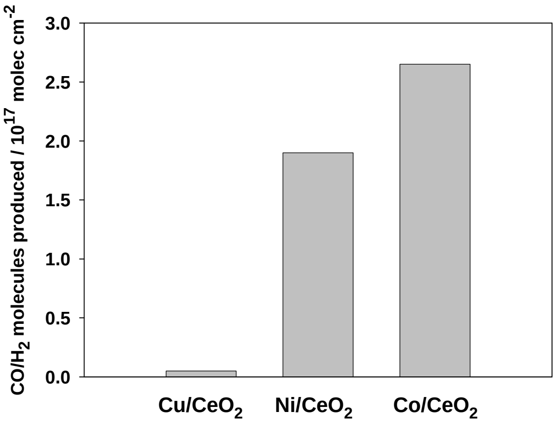

Figure 6. Catalytic activity for methane dry reforming on Cu-, Ni-, Co-ceria catalysts ($\theta_{Admetal}$ ~ 0.15 ML). The figure reports the amount of CO/H_2 formed after exposing the catalysts to 1 Torr of CH_4 and 1 Torr of CO_2 at 650 K for 5 minutes.

The molecular binding of methane to Co or Cu surfaces is very weak and dissociation, $CH_4(a) \rightarrow CH_3(a) + H(a)$, 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 CH_4 to Co^{2+} and Cu_4 species on CeO_2(111) lies within the 0.1-0.2 eV range (Figures 7a and S9). On the Cu_4/CeO_2(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_1/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 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 Co^{2+} species gradually recover their metallic state. Chemisorbed methane molecules on both M^0/Ce_2O_3(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-$CeO_{2\text{-}x}$ catalysts. We observe that the distances between methane and the M^0/Ce_2O_3(0001) {M=Co, Ni} surfaces, as measured by the C–M distances, are reduced by approx. 0.6 (Co) to 1.0 (Ni) Å with respect to the same distances in the M^{2+}/CeO_2(111) systems (Figures S9 and S10). Moreover, CH_4 adsorption on the M^0/

Ce_2O_3(0001) surfaces is aided by substantial hydrogen-metal interactions that are more pronounced compared to the M^{2+}/CeO_2(111) systems;

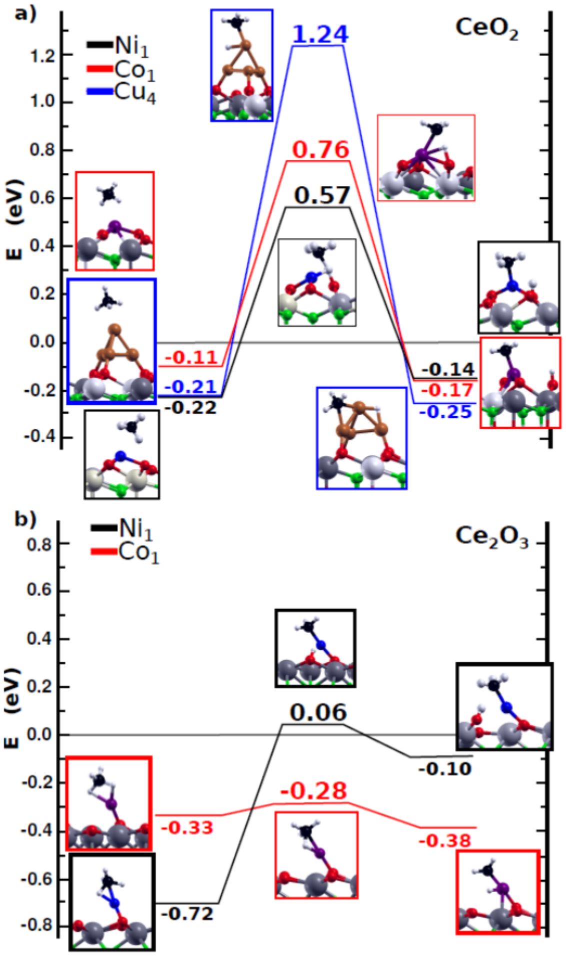

Figure 7. Reaction energy profile for the $CH_4 \rightarrow CH_3 + H$ reaction on: a) Cu_4, Co_1 and Ni_1 on CeO_2(111) and b) Co_1 and Ni_1 on Ce_2O_3(0001). The activation barriers are hardly affected by inclusion of vdW interactions (Figure S14). The structures shown on the left, middle and right of the reaction pathways, correspond to the side views of the molecularly adsorbed, transition and dissociated states, respectively (Supporting information Figures S9 and S10). All energies are referenced to the total energy of CH4(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. The CH_4-Ni^0/Ce_2O_3(0001) structure is by 0.15 eV more stable than the corresponding one in Ref. 5.

The closer approach to the M^0/Ce_2O_3(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^{2+}/CeO_2(111) and Co^0/Ce_2O_3(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/Ce_2O_3(0001) is substantially reduced compared to Co^{2+}/CeO_2(111), becoming almost negligible – E^a = 0.05 eV. This is not the case for the corresponding Ni-ceria systems for which the barrier remains unchanged (~0.8 eV). We interpret this unique Co behavior by inspecting the transition state structures for the M^0/Ce_2O_3(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^0/Ce_2O_3(0001), the Co sites work alone during the dissociation of the first C–H bond. By contrast, on Ni^0/Ce_2O_3(0001), Ni and O sites work cooperatively. This is also consistent with the calculated adsorption energy for hydrogen atoms on the M^0/Ce_2O_3(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 $Co^{2+}/CeO_2 \rightarrow Co^0/CeO_{2-x}$ transformation, that C–H bonds are more easily cleaved. Therefore, more vacant sites and more Ce^{3+} 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.[5,6,15] 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-x} being much more active than Ni-CeO_{2-x}*. 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_1/Ni_1-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,[6,16] opening the possibility for new and exciting chemistry.

Acknowledgements

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

[1] *Methane in the Environment: Occurence, Uses and Pollution*, A. Basile (Editor), Nova Science Publication Inc, 2013.
[2] S.I. Chan, S.S.F, Yu, Acc. Chem. Res. **2008**, *41*, 969-979.
[3] S.I. Chan, Y.-J. Lu, P. Nagababu, S. Maiji, M.-C. Hung, M.M. Lee, I-J. Hsu, P.D. Minh, J.C.H. Lai, K.Y. Ng, S. Ramalingam, S.S.F. Yu, M.K. Chan, *Angew. Chem. Int. Ed.* **2013**, *52*, 3731-3735.
[4] J. Xu, A. Zheng, X. Wang, G. Qi, J. Su, J. Du, Z. Gan, J. Wu, W. Wang, F. Deng, *Chem. Sci.* **2012**, *3,* 2932-2940.
[5] Z. Liu, D.C. Grinter, P.G. Lustemberg, T.-D. Nguyen-Pan, Y. Zhou, S. Luo, I. Waluyo, E.J. Crumlin, D.J. Stacchiola, J. Zhou, J, Carrasco, H,F. Busnengo, M.V. Ganduglia-Pirovano, S.D. Senanayake, J.A. Rodriguez *Angew. Chem. Int. Ed.* **2016**, *55*, 7455-7459.
[6] P.G. Lustemberg, P. J. Ramírez, Z. Liu, R. A. Gutiérrez, D. G. Grinter, J. Carrasco, S. D. Senanayake, J. A. Rodriguez, M. V. Ganduglia-Pirovano, *ACS Catal.* **2016**, *6*, 8184-8191.
[7] T. Choudhary, D.W.Goodman, *J. Mol. Catal. A-Chem.* **2000**, *163*, 9-18.
[8] a) J. Wei, E. Iglesia, *J. Phys. Chem. B*, **2004**, *108*, 4094-4103; b) D.

Pakhare, J. Spivey, *Chem. Soc. Rev*. **2014**, *43*, 7813-7837.
[9] J. Carrasco, L. Barrio, P. Liu, J. A. Rodriguez, M. V. Ganduglia-Pirovano, *J. Phys. Chem. C* **2013**, *117*, 8241-8250.
[10] a) Z. J. Zuo, W. Huang, P. D. Han and Z. H. Li, *Appl. Surf. Sci.* **2010**, *256*, 5929–5934; b) X. Hao, Q. Wang, D. Li, R. Zhang, B. Wang, *RSC Adv.* **2014**, *4*, 43004-43011.
[11] a)H.-Y. Li, Y.-L. Guo, Y. Guo, G.-Z. Lu, *J. Chem. Phys.* **2008**, *128*, 051101; b) G. Gajewski, C.-W. Pao, *J. Chem. Phys.* **2011**, *135*, 064707; c) W. Zhang, P. Wu, Z. Li and J. Yang, *J. Phys. Chem. C* **2011**, *115*, 17782–17787.
[12] a) F. Abild-Pedersen, O. Lytken, J. Engbak, G. Nielsen, I. Chorkendorff, J. K. Nørskov, *Surf. Sci.* **2005**, *590*, 127–137; b) Y.-A. Zhu, D. Chen, X.-G. Zhou, W.-K. Yuan, *Catal. Today* **2009**, *148*, 260–267; c) S. Nave, A. K. Tiwari, B. Jackson, *J. Chem. Phys.* **2010**, *132*, 054705; d) B. Jiang, R. Liu, J. Li, D. Xie, M. Yang, H. Guo, *Chem. Sci.* **2013**, *4*, 3249–3254; e) J. Li, E. Croiset, L. Ricardez-Sandoval, *Chem. Phys. Lett.* **2015**, *639*, 205–210.
[13] B. AlSabban, L. Falivene, S. M. Kozlov, A. Aguilar-Tapia, S. Ould-Chikh, J.-L. Hazemann, L. Cavallo, J.-M. Basset, K. Takanabe, *Applied Catalysis B: Environmental* **2017**, *213,* 177-189.
[14] W. Tu, M. Ghoussoub, C. V. Singh, Y.-H. C. Chin, *J. Am. Chem. Soc.* **2017**, *139*, 6928–6945.
[15] a) M. Sterrer, T. Risse, U. Martinez Pozzoni, L. Giordano, M. Heyde, H.-P. Rust, G. Pacchioni, H.-J. Freund, *Phys. Rev. Lett.* **2007**, *98*, 096107; b) A. Bruix, J. A. Rodriguez, P. J. Ramirez, S. D. Senanayake, J. Evans, J. B. Park, D. Stacchiola, P. Liu, J. Hrbek, F. Illas, *J. Am. Chem. Soc.* **2012**, *134*, 8968 – 8974; c) V. Simic-Milosevic, M. Heyde, N. Nilius, T . Konig, H.P. Rust, M. Sterrer, T. Risse, H.J.Freund, L. Giordano, G. Pacchioni, *J. Am. Chem. Soc.* **2008**, *130*, 7814-7815.
[16] a) Z. Liang, T. Li, M. Kim, A. Asthagiri, J.F. Weaver, *Science*, **2017**, *356*, 299-303; b) C.-C. Wang, S.S. Siao, J.-C. Jiang, *J. Phys. Chem. C*, **2012**, *116*, 6367-6370; c) G. Kumar, S.L.J. Lau, M.D. Krcha, M.J. Janik, *ACS Catal.* **2016**, *6,* 1812-1821.; d) A.A. Latimer, A.R. Kulkarni, H. Aljama, J.H. Montoya, J.S. Yoo, C. Tsai, F. Abild-Pedersen, F. Studt, J.K. Nørskov , *Nature Materials*, **2017**, *16*, 225-229.

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Text for Table of Contents:

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.