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Mechanistic Insights of Ethanol Steam Reforming over Ni-CeO_x(111): The Importance of Hydroxyl Groups for Suppressing Coke Formation

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Abstract

We have studied the reaction of ethanol and water over Ni-CeO_{2-x}(111) model surfaces to elucidate the mechanistic steps associated with the ethanol steam reforming (ESR) reaction. Our results provide insights about the importance of hydroxyl groups to the ESR reaction over Ni-based catalysts. Systematically, we have investigated the reaction of ethanol on Ni-CeO_{2-x}(111) at varying Ce³⁺ concentrations (CeO_{1.8-2.0}) with absence/presence of water using a combination of soft X-ray photoelectron spectroscopy (sXPS) and temperature programmed desorption (TPD). Consistent with previous reports, upon annealing, metallic Ni formed on reduced ceria while NiO was the main component on fully oxidized ceria. Ni⁰ is the active phase leading to both the C-C and C-H cleavage of ethanol but is also responsible for carbon accumulation or coking. We have identified a Ni₃C phase that formed prior to the formation of coke. At temperatures above 600K, the lattice oxygen from ceria and the hydroxyl groups from water interact cooperatively in the removal of coke, likely through a strong metal-support interaction between nickel and ceria that facilitates oxygen transfer.

Keywords: Ethanol, reforming, H₂ production, ceria, nickel, X-ray photoelectron spectroscopy, temperature programmed desorption.

INTRODUCTION

The steam reforming of ethanol, $\text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O} \rightarrow 6\text{H}_2 + 2\text{CO}_2$, is of interest to the chemical industry and fuel cell applications as it provides an alternative route to obtain renewable hydrogen through ethanol (or bio-ethanol), which can be readily extracted from sources such as biomass.¹⁻² Typically, it involves the use of metal/oxide catalysts (i.e. Pt, Rh or Pd supported on CeO_x), and the reaction occurs by a complex series of mechanistic steps which are strongly coupled to a combination of factors, including the structural, chemical and electronic properties of the catalyst.²⁻³ It has been postulated that this process requires both the metal and oxide parts of the catalyst to work co-operatively, with the metal component contributing to the C–C and C–H bond scissions of ethanol, and the oxide support promoting the dehydrogenation (or dehydration) reaction as well as the dissociation of H_2O .²⁻⁶

Catalysts based on nickel have emerged as promising candidates for the ethanol steam reforming reaction and have been reported to exhibit activity and selectivity comparable to that of noble metals such as Rh and Pd.⁷⁻⁸ However, the drawback of nickel based catalysts is the high propensity for the loss in selectivity (i.e. through methanation), and deactivation which occurs through metal sintering and coke formation.^{2-3, 8-11} Particularly, for coke formation, it could occur through the following side reactions during the steam reforming processes:

- ① Dehydrogenation of the hydrocarbon groups from ethanol: $-\text{CH}_x(\text{ad}) \rightarrow \text{C} + \text{H}(\text{ad})$;
- ② Boudouard reaction: $\text{CO}(\text{ad}) + \text{CO}(\text{ad}) \rightarrow \text{CO}_2(\text{g}) + \text{C}$;
- ③ Polymerization: $n\text{C}_2\text{H}_4 \rightarrow \text{polymer} \rightarrow \text{C}$.²⁻³

In principle, minimizing the coke deposition could be achieved by perturbing the electronic properties of the metal through interactions with the oxide support,^{7, 12} by controlling particle

size¹³⁻¹⁴, by alloying with another metal,¹⁵⁻¹⁶ and by enhancing the capacity for oxygen storage and mobility within the oxide support.¹⁷⁻¹⁹ Reducible substrates such as ZnO and CeO₂, can act as an oxygen storage reservoir to the supported metal by cyclically regenerating the oxygen from dissociation of water, and thereby facilitate the oxidation of the surface carbon species. Previously, in our study of Ni-CeO₂ powder catalysts, we have investigated the role of ceria as a promoter of water dissociation and we identified that the generation of –OH groups is essential for the oxidation of surface carbon species.⁵ Nevertheless, since few techniques utilized in the powder system study can directly observe the formation of coke during the reaction, more mechanistic insights is still needed to prove how ethanol, water and associated hydroxyl groups evolved in the surface process of carbon oxidation and leads to the subsequent production of H₂.

In this study, to gain insights into the role of water and related hydroxyl groups during the reaction of ethanol on Ni-CeO₂, we have expanded our study to a Ni-CeO_{2-x}(111) model system and experiments were carried out using soft X-ray photoelectron spectroscopy (sXPS) to examine the surface adsorbed species as well as temperature programmed desorption (TPD) to investigate the desorbed products. So that, with this knowledge, catalysts can be constructed to specifically target the suppression of coke formation by enhancing the chemical, electronic and redox interactions between the active metal and the oxide support.

EXPERIMENTAL SECTION

Experiments were performed in two separate UHV chambers. Soft X-ray photoelectron spectroscopy was conducted using synchrotron radiation at beamline U12a at the National Synchrotron Light Source (NSLS). O 1s and C 1s sXPS were recorded using 700 and 395 eV

excitation, respectively. The instrumental resolution was ca. 0.2 eV. The Ce 4d photoemission lines were used for binding energy calibration using the 122.8 eV satellite features.²⁰ The temperature programmed desorption was performed in a separate chamber at the Chemistry Department of Brookhaven National Lab (BNL).

Previous studies have been devoted to understanding the growth and the formation of well-defined CeO₂(111) films.²¹ Briefly, Ce metal was evaporated onto a Ru single crystal (0001) held at 700K in the presence of 5×10^{-7} Torr O₂, and then annealed to 800K for 10 mins at the same O₂ pressure. For sub-stoichiometric film, 2×10^{-8} Torr O₂ pressure was used during the Ce deposition at 700K,²¹ and a reduced surface containing ~40% Ce³⁺ was obtained, as determined by XPS. After deposition, the surface was subsequently annealed to 800K for 10 mins in UHV. The ceria films were estimated to be ca. 2-4nm thick (7-10 layers of O-Ce-O) based on the attenuation of the Ru 3d XPS signal, which can eliminate the interference of Ru 3d_{3/2} (284 eV) with the C 1s signal. Ni was vapor deposited on the as-prepared ceria film at 300K under vacuum and then annealed to 700K for 1min. Ni coverage was estimated by thermal desorption of CO/Ni-CeO_{2-x} (see SI figure 1), whereas desorption peak area was calibrated by the 0.58 monolayer (ML) saturation coverage of CO on clean Ru(0001).²² The deposition rate of Ni was estimated to be 0.20 ML/min.

Temperature programed desorption data were collected with a shielded and differentially pumped UIT 100C mass spectrometer using a heating rate of 3K/s. The crystal was placed in “line-of-sight” geometry about 0.5 cm from the aperture of the UTI. The ethanol source (Pharmco-aaper, ACS/USP grade) was freeze-pumped-thawed in liquid nitrogen to remove gaseous contaminants. The adsorbate was introduced to the UHV chamber using a “backfilling”

method via a high precision leak valve. 2 Langmuir (L) exposure of ethanol was sufficient to saturate the surface as was evident in both sXPS and TPD.

RESULTS and DISCUSSION

1.1. Chemical state of Ni nanoparticles on CeO_{2-x}(111) film.

The growth of Ni nanoparticles on the well-defined ceria film and the identification of oxidation states have been studied in detail previously.²³⁻²⁴ Upon deposition of Ni on CeO₂(111) at 300K, Ni predominantly remains metallic. Heating the surface to 700K causes extensive Ni oxidation to NiO due to the existence of strong metal-support interaction between Ni and ceria.^{9, 23-24} Ni forms two-dimensional particles with an average height of 0.3 nm on CeO₂ film at 300 K as shown in the scanning tunneling microscopy (STM) images (Figure 1). After heating to 700 K, Ni sinters into larger particles that are 2.7 nm wide and 0.5 nm high at the cost of particle density. As shown in our previous study, smaller Ni particles with a higher particle density can form on reduced ceria due to the presence of surface defects.²⁵ In order to control reproducibility of the Ni-ceria system and ensure morphological stability in our study of ethanol reaction, all the Ni-Ceria surfaces used for the study were annealed to 700K.

Figure 1. Scanning Tunneling Microscopy images of 0.13ML Ni deposited on to $\text{CeO}_2(111)$ film at 300 K and after heating to 700 K, respectively. The image size is $100 \times 100 \text{ nm}^2$.

The Ce 4d + Ni 3p region of XPS results from the 0.2 ML Ni- $\text{CeO}_{2-x}(111)$ system after preparation (black line) and after ethanol reaction (red line) are shown in Figure 2a. A closer detail of the Ni 3p region is shown in Figure 2b. Before ethanol exposure, fully oxidized ceria and reduced ceria could be identified in the Ce 4d region by comparing the intensities of the peaks at 122.8 eV and 126.1 eV, labeled as X''' and W''' , respectively. These two features are associated with Ce^{4+} spin-orbit splitting.²⁰ Deconvolution of the Ce 4d spectrum (SI figure 2) indicates that the reduced film contained $\sim 40\%$ of Ce^{3+} , designated as Ni- $\text{CeO}_{1.8}(111)$. In the Ni 3p region, our results match well with previous studies.²³⁻²⁵ When pre-annealed to 700K, most of the Ni was oxidized to Ni^{2+} on the stoichiometric CeO_2 surface while significant amount of Ni still remained metallic on the reduced ceria surface. Peak fitting of the Ni 3p region in Figure 2b illustrates different ratios of the two components on the two surfaces. The two peaks at 65.9 eV and 67.1 eV are attributed to Ni^0 $3p_{3/2}$ and $3p_{1/2}$, respectively,²⁶ whereas the Ni^{2+} exhibits an additional two peaks located at 68.0 eV ($3p_{3/2}$) and 69.5 eV ($3p_{1/2}$).²⁷ Integrating the peak area of

each component identifies that ~80 % and ~10% of Ni^0 are present in the Ni nanoparticles on reduced ceria and fully oxidized ceria, respectively. It's noteworthy that the reduction of ceria, in addition to the oxidation of Ni nanoparticles is negligible here, which is not surprising considering only 6% of the ceria will be reduced by deposition of ~0.5 ML of Ni on the CeO_2 surface as reported previously.²³

2L of ethanol was dosed onto the surface at 300K and a step-wised heating up to 700K was carried out by 100K. The XPS spectra that were recorded after heating up to 700K are shown as a red line in Figure 2a. No significant changes of the oxidation states of Ni were observed on either surfaces, and only ~8% of the ceria is further reduced to Ce^{3+} in the $\text{Ni-CeO}_{1.8}$ system. The sustained oxidation states of Ni reinforces the existence of a strong metal-oxide interaction between Ni and ceria, so that Ni^{2+} is not easily reduced by 2L ethanol exposure. However, the stable oxidation state of Ni during the reaction under UHV conditions allows us to study the surface mechanisms of ethanol reaction by comparing the two surfaces (Ni-CeO_2 vs $\text{Ni-CeO}_{1.8}$), correlating the adsorbed surface species and the desorption products from the two surfaces using sXPS and TPD.

Figure 2. a) black line: as-prepared Ni-Ce_{2-x}(111) surface, red line: Ni-Ce_{2-x}(111) surface after ethanol reaction. b) Deconvolution in Ni 3p region of as-prepared Ni-Ce_{2-x}(111) surface, and a Shirley background was used for fitting. The components are indicated as: blue dash line (Ni²⁺), red dash line (Ni⁰), black line (envelope) and black dots (data points).

1.2. Identification of Surface Intermediates.

1.2.1. Ethanol Reaction on Ni-CeO₂(111).

XPS results for ethanol adsorption on Ni-CeO₂(111) in the C 1s and O 1s regions are shown in Figure 3. The surface was exposed to 2L of ethanol at 300K and then sequentially heated up to 700K by 100K increments. In the O 1s region, the lattice O of ceria is centered at 530.3 eV with a small shoulder at ~532.2 eV. Mullins et al.²⁸⁻²⁹ and Siokou et al.³⁰ have studied several alcohol (methanol, ethanol etc.) surface reactions on metal free fully oxidized CeO₂(111), and they showed that the formation of alkoxy species could occur on the fully oxidized ceria surface with relatively low concentration of O vacancies by adsorption on the under-coordinated Ce⁴⁺ sites. These sites are the seven-coordinated Ce⁴⁺ cations located in the second layer underneath the O-terminated CeO₂(111) surface. Additionally, their studies have shown that the alkoxy species could form on CeO₂ film at temperatures lower than 300K and no molecularly absorbed ethanol was observed on the surface at 300K. Therefore in agreement with those results, the small shoulder located at 532.3 eV can be attributed to the dissociative adsorption of ethanol on Ni-CeO₂(111) and the peak can be composed of the contributions from the O in the ethoxy species as found in CH₃CH₂O- and also the -OH that forms upon binding of the dissociated H to lattice O of ceria. By 600K, all the -OH or ethoxy species has desorbed from the surface. Similarly, this desorption process follows the same trend upon heating in the C 1s region shown

in Figure 3. At 300K, the two peaks located at 285.9 eV and 287.0 eV are attributed to the methyl carbon (CH_3^-) and methylene carbon ($-\text{CH}_2\text{O}-$) in the ethoxy species, respectively, in agreement with previous studies of ethanol on pure $\text{CeO}_2(111)$.^{29, 31} It is noteworthy that a previous TPD study of alcohols on $\text{NiO}(100)$ film showed that ethanol has a desorption temperature threshold below 300K.³² Moreover, in our study of Ni-CeO_2 , ~90% of the 0.2ML deposited Ni is in the form of NiO . Therefore, under UHV conditions, we assume that the adsorption of ethanol on Ni sites is negligible at 300K and all the observed carbon features are related to the ethoxy species on ceria sites. By heating up to 600K, all C-containing species gradually desorbed from the surface, no trace of C-C scission or conversion of ethoxy is observed during the heating process.

Figure 3. Dot line: O 1s and C 1s spectra of 2L ethanol dose on Ni-CeO₂(111) surface at 300K followed by heating up to 400K, 500K and 600K, solid line: O 1s and C 1s spectra of the pristine surface.

1.2.2. Ethanol Reaction on Ni-CeO_{1.8}(111).

Ethanol adsorption was also studied on Ni-CeO_{1.8}(111) surface, following the same procedure upon 2L of ethanol exposure. The results from the O 1s and C 1s regions are depicted in Figure 4. In the O 1s region, a peak related to –OH/ethoxy contributions at 532.3 eV is observed alongside the lattice O peak after ethanol exposure at 300K. The intensity of the –OH/ethoxy species resulting from the dissociative adsorption of ethanol is significantly higher than the one we observed on the fully oxidized ceria since more O vacancies are available on the reduced ceria surface for adsorption. These –OH/ethoxy features are gradually attenuated with heating up to 500K, and eventually disappeared at 600K, indicating the desorption or transformation of the ethoxy species. The C 1s region of Figure 4 further confirms this evolution of ethoxy species. First, at 300K, the two peaks that are indicative of the ethoxy species are evident at 286.6 eV and 287.6 eV for methyl C and methoxy C, respectively. The shift to higher binding energy of these two peaks on the reduced ceria surface has also been observed in previous studies.^{29,33} In addition to the two peaks for the ethoxy species, a new feature at 283.2 eV appears and it gradually increases in intensity upon heating up to 500K. This peak can be assigned to the carbidic carbon of Ni₃C species formed on the surface.³⁴⁻³⁵ Nickel carbide was similarly observed in the study of other hydrocarbon related species on Ni.³⁵⁻³⁸ Also, in our previous study of the Ni-CeO₂ powder catalysts, the in-situ X-ray Diffraction (XRD) clearly shows the existence of a crystalline intermediate phase during the reduction from NiO to metallic

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2
3 Ni by exposing Ni-CeO₂ nanoparticles to a steam of ethanol. This transition phase has a clearly
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5 refined hexagonal diffraction pattern, however it could be assigned to a Ni₃C phase or a
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7 hexagonal polymorph of a metallic Ni phase. Our XPS results on Ni-CeO_{1.8}(111) provide new
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9 evidence that this species is likely Ni₃C.
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13 As the carbide feature is developing, the ethoxy species are attenuated in parallel and
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15 eventually disappear at 500K. This transformation is a strong indication of the C-C bond
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17 cleavage of the ethoxy species, which is not observed on the fully oxidized Ni-CeO₂ system and
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19 can be attributed to Ni-Ce³⁺ interactions. Since the surface contains significant amounts of
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21 metallic Ni as shown in Figure 2, it also proves that, at 300K, metallic Ni nanoparticles can
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23 readily break the C-C bond, which is consistent with the previous study of ethanol on a Ni(111)
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25 film by Gates et al.³⁹ Their TPD data show that CO, arising from the C-C bond scission, could be
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27 produced at 350K, which means that the carbon bond breaking of ethanol occurs below 350K on
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29 the Ni(111) surface. Subsequently, the formed methyl groups (CH₃-) are not stable on the Ni(111)
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31 surface at 300K, and most of them will be further dehydrogenated to surface carbon and
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33 hydrogen.⁴⁰⁻⁴³ In our case, over Ni-CeO_{1.8}, surface carbon was generated through the formation
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35 of carbidic Ni, which reveals a strong interaction between the surface hydrocarbons and Ni metal
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37 particles. Furthermore, one can also conclude that the ethoxy species shown here in the C 1s
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39 spectra are mainly due to the dissociative adsorption of ethanol on ceria sites, whereas small
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41 amount of ethoxy species that forms on the Ni sites may decompose to form Ni₃C.
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50 Further increasing the temperature to 600K shows a second transformation from NiC
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52 (283.2eV) to coke (C⁰, 284.5 eV), as Ni₃C is metastable and it will decompose to metallic Ni and
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54 surface carbon at higher temperature around 733K.⁴⁴ By 700K, a significant amount of coke with
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56 minor amounts of Ni₃C is still retained on the surface, although there is a minor decrease in
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intensity of the coke/ Ni_3C features, suggesting a limited capability for coke removal from the surface under these conditions. Thus, this result demonstrates a dramatic impact of the metal-oxide interaction on the surface chemistry of ethanol at elevated temperatures and the role of metallic Ni and reduced ceria here for its contribution to C-C and C-H bond breaking in ethanol, in agreement with previous studies of Ni-CeO₂ powder catalysts.^{5, 45}

Figure 4. Dot line: O 1s and C 1s spectra of 2L ethanol dose on Ni-CeO_{1.8}(111) surface at 300K followed by heating up to 400K, 500K, 600K and 700K, solid line: O 1s and C 1s spectra of the pristine surface.

1.2.3. Ethanol + H₂O on Ni-CeO_{1.8}(111).

Previous studies have identified that generation of hydroxyl groups from water is favored on reduced ceria.⁴⁶ These hydroxyl groups are likely to impart a strong interaction with oxide supported metal particles.⁴⁷ In addition, Ni/Ni²⁺ in Ni-CeO_x(111) can also dissociate water

readily to form OH on the surface.⁴⁸ Here, to study the effects of hydroxyl groups on the reforming reaction of ethanol, 2L of ethanol was initially dosed onto the Ni-CeO_{1.8}(111) surface at 300K, then -OH groups were introduced to the system by exposing the surface to 2x10⁻⁸ Torr of water. Since the -OH groups will not remain on the ceria surface above ~550K, and to ensure the hydroxyl groups can evolve into the reaction at higher temperature,⁴⁶ a 2x10⁻⁸ Torr background pressure of water was maintained during the heating process between each temperature step. XPS data were collected after each heating step when the water was pumped out, as shown in Figure 5. In the O 1s region, a stronger hydroxyl peak is observed at 532.4 eV in comparison to the spectra prior to water exposure, indicating the surface was more hydroxylated due to the presence of water. When the temperature was increased to 600K, only a small portion of the -OH groups was left on the surface. It should be noted that even though the -OH groups on the surface were almost gone at 600K, the interaction between the water and the Ni-CeO_{1.8} surface could still be occurring dynamically, as a background of 2x10⁻⁸ Torr of water was always maintained during the heating process. In the C 1s spectra, the two C peaks related to the ethoxy species at 300K are clearly visible and then, with increased temperature, the evolution from ethoxy species to Ni₃C/coke emerged, similarly to the trend shown in Figure 4. However, further increasing the temperature to 700K leads to removal of all the carbon related species from the surface, leaving the surface free of coke. This implicates that the presence of water vapor and/or additional OH groups not only completes the catalytic cycle in the steam reforming of ethanol to produce more hydrogen product, but it is also crucial to prevent the formation of coke through oxidation of the surface carbon at higher temperature (>700K), as will be further elucidated below from TPD data.

Figure 5. O 1s and C 1s spectra of 2L ethanol dose on Ni-CeO_{1.8}(111) surface at 300K followed by heating up to 400K, 500K, 600K and 700K under a background of 2x10⁻⁸ Torr pressure of water.

1.3.Desorption of Products.

The TPD of ethanol on plain CeO₂(111) surfaces has been previously reported^{29, 49} and we have also performed this as a control before we investigated the desorption products of ethanol on Ni-CeO_{2-x}(111). Desorption products were calibrated with respect to cracking fragments and included: ethanol (m/z=31), acetaldehyde (m/z=29), CO (m/z=28), water (m/z=18), ethylene (m/z=27), methane (m/z=15) and CO₂ (m/z=44). The contribution from the fragmentation of the parent masses were subtracted by a normalized factor of the corresponding mass. These scaled factors were derived based on the fragmentation of the molecules, the ionization probability, and the mass-dependent response of the spectrometer. The total and relative yield of each desorption products was estimated by integrating the TPD peak area of its corresponding mass, as shown in Table 1.

Figures 6a-c shows the TPD data obtained from fully oxidized $\text{CeO}_2(111)$, reduced $\text{CeO}_{1.8}(111)$ and $\text{Ni-CeO}_2(111)$ following a 2L dose of ethanol at 300K. On the fully oxidized film (Figure 6a), in addition to a small amount of molecularly desorbed ethanol, the primary desorption products are ethylene, acetaldehyde and H_2O with a desorbing temperature threshold at 515K (505K for acetaldehyde), which is in agreement with the previously reported TPD of CeO_{2-x} .^{29, 49} H_2 production is not evident on the fully oxidized surface even though a small amount of acetaldehyde is observed. This might be owed to recombination of adsorbed H with the lattice O and subsequent desorption as H_2O instead of H_2 . In contrast, the ethanol TPD results on reduced ceria film in Figure 6b clearly shows the production of H_2 as a consequence of the O deficiency of the reduced ceria surface and presence of Ce^{3+} . Additionally, as shown in Table 1, no molecularly desorbed ethanol is detected, and the amount of product formation through either dehydration or dehydrogenation processes rises significantly because of the increased amount of adsorbed ethoxy due to the surface defects (oxygen vacancies) on the reduced ceria. These defects are essential to the dissociative adsorption of ethanol on ceria.

TPD results of ethanol after adding 0.2 ML of Ni on fully oxidized ceria are displayed in Figure 6c, showing a similar set of desorption profiles followed as on the metal free oxidized ceria surface. No evidence of C-C bond breaking is observed here. This result supports the XPS data, which shows that the adsorbed ethoxy species are likely to be on ceria sites and that ethanol does not adsorb on NiO at 300K. By this, we could assume that, on the 0.2 ML Ni- CeO_2 system, most of the surface exposed sites are Ni^{2+} and Ce^{4+} and that they are inert for the reforming of ethanol through C-C bond scission. The possible reaction pathway for desorption profiles shown in Figure 6 a-c could be interpreted as follows:

Figure 6. TPD results from 2L ethanol adsorbed at 300K on a) $\text{CeO}_2(111)$, b) $\text{CeO}_{1.8}(111)$ and c) $\text{Ni-CeO}_2(111)$ film.

However, the desorption profiles from the $\text{Ni-CeO}_{1.8}$ surface shown in Figure 7 exhibit drastic changes with respect to the $\text{Ni-CeO}_2(111)$ surface. Two reaction conditions were undertaken here in order to match the XPS experiments: the 2L ethanol TPD (black line) and the 2L ethanol TPD under 2×10^{-8} torr of D_2O vapor background (red line). First, following the ethanol TPD without D_2O , three distinguishable peaks for CO are observed with desorption temperatures at 346K, 500K and 596K. The CO desorption peak at $\sim 360\text{K}$ threshold is similar to

the one observed on Ni(111) film by Gates et al.³⁹ The observation of CO (g) production requires the C-C cleavage of the surface adsorbed ethoxy, and with an isotope study, Gates et al assigned this ~360K CO peak to methylene C (-CH₂-O-) desorbed from the ethoxy species due to C-C bond breaking. In our Ni-CeO_{1.8} case, the similarity of the temperature for the emergence of Ni₃C from 300K~500K reinforces the argument that C-C bond scission has already taken place on the metallic Ni sites at 300K. Therefore, the CO produced at 346K here is attributed to the decarbonylation of the methylene C (-CH₂-O-) of the ethoxy species adsorbed on metallic Ni. Moreover, H₂ is simultaneously produced with CO at 346K to form a small broad peak. Considering both dehydrogenation of ethoxy species as well as the surface adsorbed -H from C-C bond scission in methyl groups, the H₂ production at 346K here is mainly from the recombination of surface -H(ad) on different sites originating from the methylene H (-CH₂-O-) as well as the methyl H (-CH₃). Additionally, no CO₂ production was detected and negligible CH₄ was produced at ~500K (not shown here), indicating that the coke formation was mainly due to the dehydrogenation of the surface methyl groups instead of the Boudouard reaction.

The remaining two CO desorption peaks with temperature threshold at 500K and 596K were not observed in the previous study of ethanol on the plain Ni film,^{39, 50} suggesting that they are associated with the ceria substrate and its interfaces formed with Ni. Also note that the reported temperature regime for CO desorption from Ni film is below 450K.⁵¹⁻⁵³ These two higher temperature peaks are, therefore, reaction-limited. As mentioned above, at 500K, only Ni₃C and coke remain on the surface, no hydrocarbon related species are evident in the C 1s, which suggests that all the C-H bonds have been broken by this temperature. Furthermore, coincident with the CO evolution at 500K temperature threshold, H₂ is also produced in the TPD data. These results all imply that the surface retained ethoxy species on ceria sites could either

dehydrogenate/dehydrate followed by desorption as acetaldehyde/ethylene, or diffuse to the metal and further react in the same manner. As a result, more surface carbon will be accumulated on the surface as indicated by the 500K C 1s spectra in Figure 4.

The oxidation of the surface Ni₃C/C requires oxygen transfer from the ceria substrate to the Ni nanoparticles via the reduction of ceria. This process can be simply described as $\text{Ni} + 2\text{CeO}_2 \rightarrow 2\text{Ce}_2\text{O}_3 + \text{NiO}$, and it is thermodynamically unfavorable at low temperature ($\Delta H_f = 136.9$ kJ/mol).⁵⁴ Also, computational studies show that migration of O from ceria to Ni is an endothermic process associated with a thermodynamic barrier of 18 kcal/mol,⁵⁵ which indicates that the transfer of oxygen from ceria to Ni is only favored at higher temperatures. Furthermore, the 8% reduction of ceria for the post-reaction surface shown in Figure 2 is reasonably consistent with the consumption of O by 0.2ML of Ni, since only 2L of ethanol was dosed to the surface. Hence, the observation of the CO peak at 596K could be attributed to the surface Ni₃C/C on Ni nanoparticles combining with the O transferred from the support ceria oxides at higher temperature. It is worth to note that although some of the surface C could react and desorb as CO with the oxygen from ceria, substantial amount of coke is still accumulated on the surface as proved by the 700K C 1s spectra in Figure 4. The possible reaction routes for the desorption profiles in Figure 7 in the absence of water can be explained as follows:

- ① $\text{CH}_3\text{CH}_2\text{OH}(\text{ad}) \rightarrow \text{CH}_3\text{CH}_2\text{O}(\text{ad}) + \text{-H}(\text{ad})$, 300K
- ② On Ni sites: $\text{CH}_3\text{CH}_2\text{O-} \rightarrow \text{CH}_3(\text{ad}) + \text{CO}(\text{g}) + 2\text{-H}(\text{ad})$, 300K-450K;
 $\text{CH}_3(\text{ad}) \rightarrow \text{C}(\text{coke}) + 3\text{-H}(\text{ad})$, 300K-450K;
 $2\text{-H}(\text{ad}) \rightarrow \text{H}_2(\text{g})$, 300K-450K;
- ③ On ceria sites: $\text{CH}_3\text{CH}_2\text{O-} \rightarrow \text{CH}_3\text{CHO}(\text{ad}) + \text{-H}(\text{ad})$ ~500K;

Then diffuse to Ni sites: $\text{CH}_3\text{CHO}(\text{ad}) \rightarrow \text{CH}_3(\text{ad}) + \text{CO}(\text{g}) + \text{-H}(\text{ad})$, $\sim 500\text{K}$;

$\text{-O}(\text{lattice}) + \text{Ni}_3\text{C/C} \rightarrow \text{Ni}^0 + \text{CO}(\text{g})$, $> 600\text{K}$;

To study the effects of hydroxyl groups on the ethanol reaction, ethanol TPD under D_2O vapor pressure (2×10^{-8} torr) over $\text{Ni-CeO}_{1.8}$ is presented as red lines in Figure 7. D_2O was used here to distinguish the hydrogen from ethanol from that of water. First, at temperatures below 500K, the surface in the presence of D_2O exhibits a TPD profile comparable to the one of pure ethanol, showing that there is no apparent effect of hydroxyls on the ethanol reaction at lower temperature. However, at temperature above 500K, D_2 and DH were detected in addition to the CO and H_2 production, indicating that D_2O has been involved in the reaction at this temperature. The occurrence of DH here is not surprising since mobile surface hydrogens are available for isotopic exchange with the deuterated hydroxyls during thermal desorption, which could also explain the lower production of H_2 , as some of the adsorbed H desorbs as $\text{DH}(\text{g})$. For the CO evolution, two peaks appears at 500K and 600K with a slight peak shift compared to the one in pure ethanol. The peak area of the 600K CO peaks resulting from the oxidation of surface $\text{Ni}_3\text{C}/\text{coke}$ are estimated to be 40% larger than those from the D_2O free surface. The fact that the XPS data shows a coke free surface at 700K in the C 1s spectra of Figure 5, and also noting that a significant amount of D_2 is produced from D_2O simultaneously at $\sim 600\text{K}$ due to the transfer of oxygen to ceria/Ni, one can draw the conclusion that the -OD groups formed upon D_2O exposure, as water is prone to be dissociated on reduced ceria,⁴⁶ and can play a vital role here in assisting the removal of coke from surface as in the form of CO. At this temperature ($> 600\text{K}$), considering the mobility of the surface oxygen and the strong interaction between Ni and ceria, the lattice O from ceria and the -OD groups from D_2O could have a synergistic interplay during the oxidation of the $\text{Ni}_3\text{C/C}$ phases, which can be interpreted as follows:

Our results highlight a strong interaction between Ni and Ceria, and present important insights into the mechanism of ethanol steam reforming. Model surfaces studied here can have a strong correlation to steady state conditions of the ESR over powder samples, at temperatures above 600K. It is likely that two competing processes will occur on the surface: the surface carbon accumulation and the oxidation of surface carbon by water/hydroxyls. The ability to sustain sites that can do both steps including C-C bond breaking and –OH formation is critical and can now be joined with additional step which includes the remediation of coke formation. The later process relies heavily on the redox nature of the oxide substrate as well as the metal-oxide interaction facilitating the oxygen transport.

Figure 7. TPD results from 2L ethanol adsorbed at 300K on Ni-CeO_{1.8}(111) film, black line: temperature ramping without D₂O, red line: temperature ramping under 2×10⁻⁸ Torr D₂O background pressure.

Table 1. Total and relative (in brackets) product yields of desorption products estimated by peak integration from the TPD results shown in Figure 6 and 7.

	H ₂ O	CO			H ₂				CH ₄	CH ₂ =CH ₂	CH ₃ CHO	EtOH
CeO ₂	13 (0.29)	-			-				-	12 (0.27)	8 (0.18)	12 (0.27)
CeO _{1.8}	25 (0.4)	-			-				-	20 (0.32)	7 (0.11)	10 (0.16)
Ni-CeO ₂	77 (0.38)	-			40 (0.2)				-	45 (0.22)	39 (0.19)	-
Ni-CeO _{1.8}	-	150 (0.22) <500K	98 (0.14) 500- 600K	184 (0.26) >600K	58 (0.08) <500K	140 (0.20) >500K			12 (0.02)	22 (0.032)	32 (0.05)	-
Ni-CeO _{1.8} (with D ₂ O)	-	149 (0.16) <500K	110 (0.12) 500- 600K	260 (0.28) >600K	60 (0.06) (H ₂) < 500K	76 (0.08) (H ₂) 500- 600K	58 (0.06) (DH) 500- 600K	160 (0.17) (D ₂) >600K	10 (0.01)	20 (0.02)	28 (0.03)	-

CONCLUSIONS

Ethanol and ethanol with water reactions on Ni-CeO_x(111) surface were studied using a combination of sXPS and TPD. The scission of the C-C and C-H bonds is only observed on the Ni-CeO_{1.8} surface, demonstrating the importance of the Ni⁰ and Ce³⁺ interplay as an active components in the reaction. A Ni₃C phase was formed prior to the surface coke formation. The oxidation of surface carbon requires the transfer of oxygen from ceria to nickel at higher temperature (>600K) and the addition of water and hydroxyls essentially assist in the removal of surface coke. With these aspects, we hypothesize that developing catalysts capable of higher water dissociation efficiency as well as strong metal-oxides interaction could enhance the transfer of oxygen and thus improve the oxidation of surface carbon.

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Supporting Information Available: CO TPD from clean Ru(0001) as calibration for coverages of Ni over CeO_x(111); XPS of Ce 4d showing deconvolution of Ce⁴⁺ vs Ce³⁺ species. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References

1. Huber, G. W.; Iborra, S.; Corma, A., Synthesis of Transportation Fuels from Biomass: Chemistry, Catalysts, and Engineering. *Chem. Rev.*, **2006**, *106*, 4044-4098.
2. Mattos, L. V.; Jacobs, G.; Davis, B. H.; Noronha, F. B., Production of Hydrogen from Ethanol: Review of Reaction Mechanism and Catalyst Deactivation. *Chem. Rev.*, **2012**, *112*, 4094-4123.
3. Piscina, P. R. D. L.; Homs, N., Use of Biofuels to Produce Hydrogen (Reformation Processes). *Chem. Soc. Rev.*, **2008**, *37*, 2459-2467.
4. Divins, N. J.; Casanovas, A.; Xu, W.; Senanayake, S. D.; Wiater, D.; Trovarelli, A.; Llorca, J., The Influence of Nano-Architected CeOx Supports in RhPd/CeO₂ for the Catalytic Ethanol Steam Reforming Reaction. *Catal. Today*, **2015**, *In press* DOI:10.1016/j.cattod.2014.12.042.
5. Xu, W.; Liu, Z.; Johnston-Peck, A. C.; Senanayake, S. D.; Zhou, G.; Stacchiola, D.; Stach, E. A.; Rodriguez, J. A., Steam Reforming of Ethanol on Ni/CeO₂: Reaction Pathway and Interaction between Ni and the CeO₂ Support. *ACS Catalysis*, **2013**, *3*, 975-984.
6. Llorca, J.; Homs, N. S.; Sales, J.; de la Piscina, P. R. R., Efficient Production of Hydrogen over Supported Cobalt Catalysts from Ethanol Steam Reforming. *J. Catal.*, **2002**, *209*, 306-317.
7. Zhou, G., et al., High Activity of Ce_{1-x}Ni_xO_{2-y} for H₂ Production through Ethanol Steam Reforming: Tuning Catalytic Performance through Metal–Oxide Interactions. *Angew. Chem.*, **2010**, *122*, 9874-9878.
8. Frusteri, F.; Freni, S.; Spadaro, L.; Chiodo, V.; Bonura, G.; Donato, S.; Cavallaro, S., H₂ Production for Mc Fuel Cell by Steam Reforming of Ethanol over MgO Supported Pd, Rh, Ni and Co Catalysts. *Catal. Commun.*, **2004**, *5*, 611-615.

9. 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*, 8241-8250.
10. Vannice, M. A., The Catalytic Synthesis of Hydrocarbons from H₂CO Mixtures over the Group VIII Metals: Iv. The Kinetic Behavior of CO Hydrogenation over Ni Catalysts. *J. Catal.*, **1976**, *44*, 152-162.
11. Rodriguez, J.; Wayne Goodman, D., High-Pressure Catalytic Reactions over Single-Crystal Metal Surfaces. *Surf. Sci. Rep.*, **1991**, *14*, 1-107.
12. Senanayake, S. D.; Rodriguez, J. A.; Stacchiola, D., Electronic Metal–Support Interactions and the Production of Hydrogen through the Water-Gas Shift Reaction and Ethanol Steam Reforming: Fundamental Studies with Well-Defined Model Catalysts. *Top. Catal.*, **2013**, *56*, 1488-1498.
13. Ávila-Neto, C. N.; Zanchet, D.; Hori, C. E.; Ribeiro, R. U.; Bueno, J. M. C., Interplay between Particle Size, Composition, and Structure of MgAl₂O₄-Supported Co–Cu Catalysts and Their Influence on Carbon Accumulation During Steam Reforming of Ethanol. *J. Catal.*, **2013**, *307*, 222-237.
14. Soykal, I. I.; Sohn, H.; Singh, D.; Miller, J. T.; Ozkan, U. S., Reduction Characteristics of Ceria under Ethanol Steam Reforming Conditions: Effect of the Particle Size. *ACS Catalysis*, **2014**, *4*, 585-592.
15. Chen, L.-C.; Lin, S. D., The Ethanol Steam Reforming over Cu-Ni/SiO₂ Catalysts: Effect of Cu/Ni Ratio. *Appl. Catal. B*, **2011**, *106*, 639-649.
16. Wang, F.; Li, Y.; Cai, W.; Zhan, E.; Mu, X.; Shen, W., Ethanol Steam Reforming over Ni and Ni–Cu Catalysts. *Catal. Today*, **2009**, *146*, 31-36.

17. Song, H.; Ozkan, U. S., Ethanol Steam Reforming over Co-Based Catalysts: Role of Oxygen Mobility. *J. Catal.*, **2009**, *261*, 66-74.
18. Gupta, A.; Waghmare, U. V.; Hegde, M. S., Correlation of Oxygen Storage Capacity and Structural Distortion in Transition-Metal-, Noble-Metal-, and Rare-Earth-Ion-Substituted CeO₂ from First Principles Calculation. *Chem. Mater.*, **2010**, *22*, 5184-5198.
19. Liu, Z., et al., Superior Performance of Ni–W–Ce Mixed-Metal Oxide Catalysts for Ethanol Steam Reforming: Synergistic Effects of W- and Ni-Dopants. *J. Catal.*, **2015**, *321*, 90-99.
20. Mullins, D.; Overbury, S.; Huntley, D., Electron Spectroscopy of Single Crystal and Polycrystalline Cerium Oxide Surfaces. *Surf. Sci.*, **1998**, *409*, 307-319.
21. Mullins, D. R.; Radulovic, P. V.; Overbury, S. H., Ordered Cerium Oxide Thin Films Grown on Ru(0001) and Ni(111). *Surf. Sci.*, **1999**, *429*, 186-198.
22. Hoffmann, F.; Weisel, M.; Peden, C., In-Situ FT-IRAS Study of the CO Oxidation Reaction over Ru (001): II. Coadsorption of Carbon Monoxide and Oxygen. *Surf. Sci.*, **1991**, *253*, 59-71.
23. Zhou, Y.; Zhou, J., Interactions of Ni Nanoparticles with Reducible CeO₂ (111) Thin Films. *J. Phys. Chem. C*, **2012**, *116*, 9544-9549.
24. Senanayake, S. D.; Evans, J.; Agnoli, S.; Barrio, L.; Chen, T.-L.; Hrbek, J.; Rodriguez, J. A., Water–Gas Shift and CO Methanation Reactions over Ni–CeO₂ (111) Catalysts. *Top. Catal.*, **2011**, *54*, 34-41.
25. Zhou, Y.; Perket, J. M.; Crooks, A. B.; Zhou, J., Effect of Ceria Support on the Structure of Ni Nanoparticles. *J. Phys. Chem. Lett.*, **2010**, *1*, 1447-1453.

26. Mansour, A. N., Nickel Mg K α XPS Spectra from the Physical Electronics Model 5400 Spectrometer. *Surf. Sci. Spectra*, **1994**, 3, 211-220.
27. Jeon, Y.; Park, D.-H.; Park, J.-I.; Yoon, S.-H.; Mochida, I.; Choy, J.-H.; Shul, Y.-G., Hollow Fibers Networked with Perovskite Nanoparticles for H₂ Production from Heavy Oil. *Sci. Rep.*, **2013**, 3.
28. Mullins, D. R.; Robbins, M. D.; Zhou, J., Adsorption and Reaction of Methanol on Thin-Film Cerium Oxide. *Surf. Sci.*, **2006**, 600, 1547-1558.
29. Mullins, D. R.; Senanayake, S. D.; Chen, T. L., Adsorption and Reaction of C1–C3 Alcohols over CeO_x(111) Thin Films. *J. Phys. Chem. C*, **2010**, 114, 17112-17119.
30. Siokou, A.; Nix, R. M., Interaction of Methanol with Well-Defined Ceria Surfaces: Reflection/Absorption Infrared Spectroscopy, X-Ray Photoelectron Spectroscopy, and Temperature-Programmed Desorption Study. *J. Phys. Chem. B*, **1999**, 103, 6984-6997.
31. Senanayake, S. D.; Mudiyanse, K.; Bruix, A.; Agnoli, S.; Hrbek, J.; Stacchiola, D.; Rodriguez, J. A., The Unique Properties of the Oxide-Metal Interface: Reaction of Ethanol on an Inverse Model CeO_x–Au (111) Catalyst. *J. Phys. Chem. C*, **2014**, 118, 25057-25064.
32. Wu, M. C.; Truong, C. M.; Goodman, D. W., Interactions of Alcohols with a Nickel Oxide(100) Surface Studied by High-Resolution Electron Energy Loss Spectroscopy and Temperature-Programmed Desorption Spectroscopy. *J. Phys. Chem.*, **1993**, 97, 9425-9433.
33. Zhou, J.; Mullins, D. R., Adsorption and Reaction of Formaldehyde on Thin-Film Cerium Oxide. *Surf. Sci.*, **2006**, 600, 1540-1546.
34. Kovács, G. J.; Bertóti, I.; Radnóczy, G., X-Ray Photoelectron Spectroscopic Study of Magnetron Sputtered Carbon–Nickel Composite Films. *Thin Solid Films*, **2008**, 516, 7942-7946.

35. Czekaj, I.; Loviat, F.; Raimondi, F.; Wambach, J.; Biollaz, S.; Wokaun, A., Characterization of Surface Processes at the Ni-Based Catalyst During the Methanation of Biomass-Derived Synthesis Gas: X-Ray Photoelectron Spectroscopy (XPS). *Appl. Catal. A*, **2007**, 329, 68-78.
36. Sarr, M.; Bahlawane, N.; Arl, D.; Dossot, M.; McRae, E.; Lenoble, D., Tailoring the Properties of Atomic Layer Deposited Nickel and Nickel Carbide Thin Films Via Chain-Length Control of the Alcohol Reducing Agents. *J. Phys. Chem. C*, **2014**, 118, 23385-23392.
37. Ducati, C.; Alexandrou, I.; Chhowalla, M.; Robertson, J.; Amaratunga, G. A. J., The Role of the Catalytic Particle in the Growth of Carbon Nanotubes by Plasma Enhanced Chemical Vapor Deposition. *J. Appl. Phys.*, **2004**, 95, 6387-6391.
38. Klink, C.; Stensgaard, I.; Besenbacher, F.; Lægsgaard, E., An Stm Study of Carbon-Induced Structures on Ni(111): Evidence for a Carbide-Phase Clock Reconstruction. *Surf. Sci.*, **1995**, 342, 250-260.
39. Gates, S.; Russell, J.; Yates, J., Bond Activation Sequence Observed in the Chemisorption and Surface Reaction of Ethanol on Ni(111). *Surf. Sci.*, **1986**, 171, 111-134.
40. Tjandra, S.; Zaera, F., A Study of the Thermal Reactions of Methyl Iodide Coadsorbed with Hydrogen on Ni(111) Surfaces: Hydrogenation of Methyl Species to Methane. *J. Catal.*, **1994**, 147, 598-600.
41. Tjandra, S.; Zaera, F., Methyl Iodide Thermal Reactions When Chemisorbed on Nickel(100) Surfaces. *Langmuir*, **1992**, 8, 2090-2097.
42. Guo, H.; Zaera, F., Thermal Chemistry of Iodomethane on Ni(110). 1. Clean and Hydrogen-Predosed Surfaces. *J. Phys. Chem. B*, **2004**, 108, 16220-16225.

43. Wang, J.-H.; Lee, C. S.; Lin, M. C., Mechanism of Ethanol Reforming: Theoretical Foundations. *J. Phys. Chem. C*, **2009**, *113*, 6681-6688.
44. Tanaka, T.; Ishihara, K. N.; Shingu, P. H., Formation of Metastable Phases of Ni-C. *Metall. Trans. A*, **1992**, *23*, 2431-2435.
45. Fatsikostas, A. N.; Verykios, X. E., Reaction Network of Steam Reforming of Ethanol over Ni-Based Catalysts. *J. Catal.*, **2004**, *225*, 439-452.
46. Mullins, D. R.; Albrecht, P. M.; Chen, T.-L.; Calaza, F. C.; Biegalski, M. D.; Christen, H. M.; Overbury, S. H., Water Dissociation on CeO₂(100) and CeO₂(111) Thin Films. *J. Phys. Chem. C*, **2012**, *116*, 19419-19428.
47. Addou, R.; Senftle, T. P.; O'Connor, N.; Janik, M. J.; van Duin, A. C. T.; Batzill, M., Influence of Hydroxyls on Pd Atom Mobility and Clustering on Rutile TiO₂(011)-2 × 1. *ACS Nano*, **2014**, *8*, 6321-6333.
48. 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. Chem. Int. Ed.*, **2015**, *54*, 3917-3921.
49. Martono, E.; Vohs, J. M., Support Effects in Cobalt-Based Ethanol Steam Reforming Catalysts: Reaction of Ethanol on Co/CeO₂/YSZ (100) Model Catalysts. *J. Catal.*, **2012**, *291*, 79-86.
50. Skoplyak, O.; Barteau, M. A.; Chen, J. G., Reforming of Oxygenates for H₂ Production: Correlating Reactivity of Ethylene Glycol and Ethanol on Pt(111) and Ni/Pt(111) with Surface D-Band Center. *J. Phys. Chem. B*, **2006**, *110*, 1686-1694.

- 1
2
3 51. Netzer, F. P.; Madey, T. E., The Structure of CO on Ni (111). *J. Chem. Phys.*, **1982**, *76*,
4 710-715.
5
6
7
8 52. Öfner, H.; Zaera, F., Surface Defect Characterization in Oxygen-Dosed Nickel Surfaces
9 and in NiO Thin Films by Co Adsorption–Desorption Experiments. *J. Phys. Chem. B*, **1997**, *101*,
10 9069-9076.
11
12
13
14
15 53. Surnev, L.; Xu, Z.; Yates Jr, J. T., IRAS Study of the Adsorption of CO on Ni(111):
16 Interrelation between Various Bonding Modes of Chemisorbed CO. *Surf. Sci.*, **1988**, *201*, 1-13.
17
18
19
20 54. Lide, D. R., *Crc Handbook of Chemistry and Physics*, *84th Ed.*; CRC Press: Boston, MA,
21 2003-2004.
22
23
24
25 55. Shishkin, M.; Ziegler, T., The Electronic Structure and Chemical Properties of a Ni/CeO₂
26 Anode in a Solid Oxide Fuel Cell: A Dft + U Study. *J. Phys. Chem. C*, **2010**, *114*, 21411-21416.
27
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