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# Synergy of Single-Atom Ni<sub>1</sub> and Ru<sub>1</sub> Sites on CeO<sub>2</sub> for Dry Reforming of CH<sub>4</sub>

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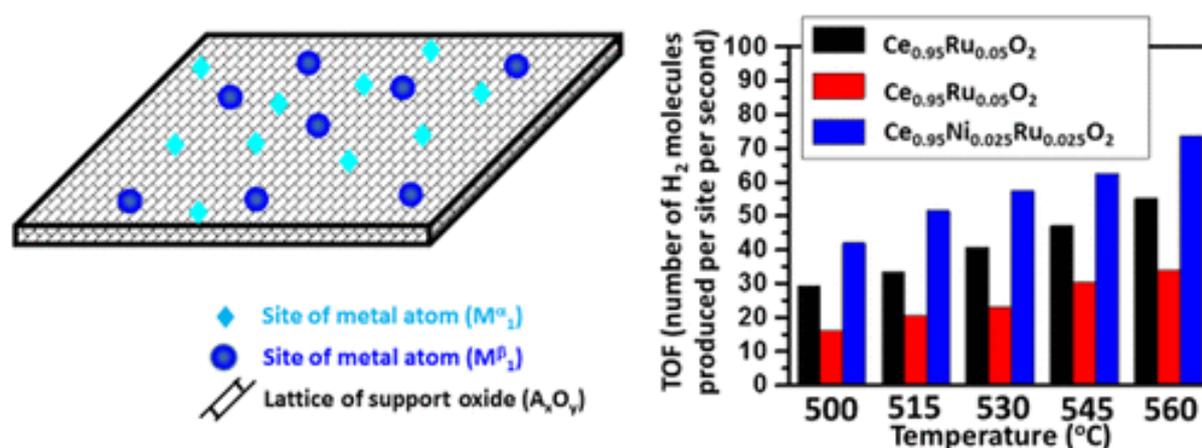
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## Abstract



Heterogeneous catalysis performs on specific sites of a catalyst surface even if specific sites of many catalysts during catalysis could not be identified readily. Design of a catalyst by managing catalytic sites on an atomic scale is significant for tuning catalytic performance and offering high activity and selectivity at a relatively low temperature. Here, we report a synergy effect of two sets of single-atom sites (Ni<sub>1</sub> and Ru<sub>1</sub>) anchored on the surface of a CeO<sub>2</sub> nanorod, Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>. The surface of this catalyst, Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>, consists of two sets of single-atom sites which are highly active for reforming CH<sub>4</sub> using CO<sub>2</sub> with a turnover rate of producing 73.6 H<sub>2</sub> molecules on each site per second at 560 °C. Selectivity for producing H<sub>2</sub> at this temperature is 98.5%. The single-atom sites Ni<sub>1</sub> and Ru<sub>1</sub> anchored on the CeO<sub>2</sub> surface of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> remain singly dispersed and in a cationic state during catalysis up to 600 °C. The two sets of single-atom sites play a synergistic role, evidenced by lower apparent activation barrier and higher turnover rate for production of H<sub>2</sub> and CO on Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> in contrast to

$\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  with only  $\text{Ni}_1$  single-atom sites and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  with only  $\text{Ru}_1$  single-atom sites. Computational studies suggest a molecular mechanism for the observed synergy effects, which originate at (1) the different roles of  $\text{Ni}_1$  and  $\text{Ru}_1$  sites in terms of activations of  $\text{CH}_4$  to form CO on a  $\text{Ni}_1$  site and dissociation of  $\text{CO}_2$  to CO on a  $\text{Ru}_1$  site, respectively and (2) the sequential role in terms of *first* forming H atoms through activation of  $\text{CH}_4$  on a  $\text{Ni}_1$  site and *then* coupling of H atoms to form  $\text{H}_2$  on a  $\text{Ru}_1$  site. These synergistic effects of the two sets of single-atom sites on the same surface demonstrated a new method for designing a catalyst with high activity and selectivity at a relatively low temperature.

## 1. Introduction

Methane, the major component of natural gas and shale gas, has attracted much attention in the production of chemical intermediates for making liquid fuels and high value chemicals.[\(1–6\)](#) Due to the increase of annual global production of shale gas, chemical industries have started to progressively switch their raw materials from crude oil to shale gas components. Reforming of methane with  $\text{CO}_2$  or  $\text{H}_2\text{O}$  has been one of the most important processes since it produces syngas, one of the most important intermediates for producing liquid fuels and synthesizing high-value chemicals through established industrial processes.[\(1,5–7\)](#)

The current industrial process of reforming methane on supported Ni metal nanoparticle catalysts undergoes at a temperature higher than  $800\text{ }^\circ\text{C}$ .[\(8–10\)](#) Unfortunately, it faces two challenges. First, the catalyst is readily deactivated due to sintering of these supported metallic Ni nanoparticles at high temperature in an environment of reducing gases ( $\text{CO} + \text{H}_2$ ).[\(11\)](#) The sintering significantly decreases dispersion of Ni atoms of a supported Ni catalyst; therefore, the number of exposed Ni atoms of the catalyst decreases dramatically. Second, a side reaction of methane pyrolysis is readily performed on the surface of metallic Ni nanoparticles.[\(12,13\)](#) Due to the very high binding energy of C atoms of  $\text{CH}_n$  ( $n = 0–3$ ) species on Ni atoms of metallic Ni nanoparticles, metallic Ni nanoparticles are very active for breaking the C–H bond of methane. The rapid catalytic pyrolysis produces layers of carbon atoms on the surface of a Ni catalyst, which is known as coke.[\(14,15\)](#) The formation of coke completely blocks methane from accessing Ni atoms of the catalyst, making the catalyst completely poisoned. In addition, the quite high catalytic temperature of supported Ni nanoparticles ( $800\text{ }^\circ\text{C}$  or higher) requires a significant amount of energy. Facing these challenges, it would be ideal if methane reforming could be done at a relative low temperature without coke formation; for this purpose, significant efforts have been made by the groups of Rodriguez and others.[\(16–18\)](#)

To avoid the formation of coke on the surface of Ni catalysts, we proposed to design a catalyst which can activate  $\text{CH}_n$  ( $n = 0–3$ ) and their intermediates.

Based on our recent studies that showed that binding energy of a methane molecule on a metal atom at a cationic state is typically lower than that on a metal atom at a metallic state,[\(19–23\)](#) here we propose to anchor Ni atoms of a cationic state instead of Ni atoms of a metallic state to activate methane or CO<sub>2</sub> molecules, avoiding strong binding to CH<sub>n</sub> ( $n = 0–3$ ) species. In addition, to spatially limit any potential coupling between carbon atoms or CH<sub>n</sub> ( $n = 0–3$ ) species adsorbed on continuously packed Ni atoms to form precursor of a coke layer, Ni atoms are spatially anchored on the surface in the format of single-atom sites as shown with bright blue diamonds (Ni atoms) in [Figure 1](#).

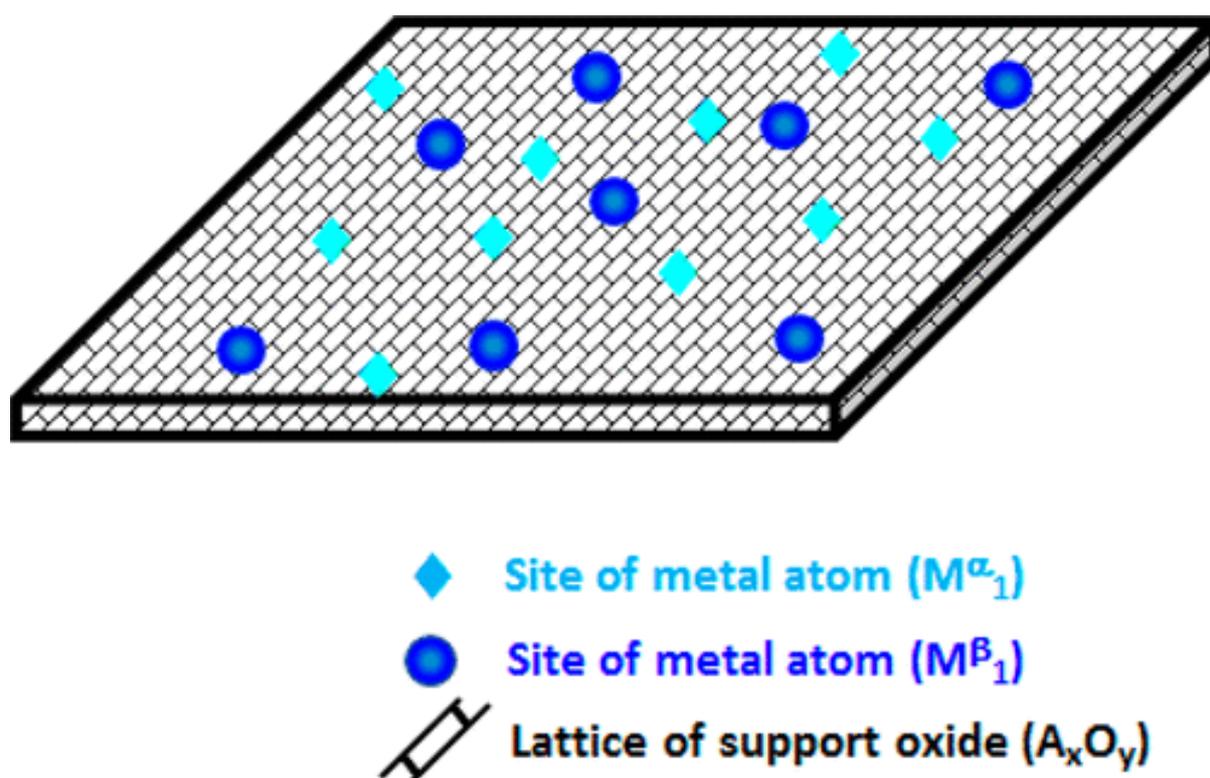


Figure 1. Schematic of a catalyst surface consists of two sets of single-atom sites including single-atom M<sup>α</sup> sites (green diamonds) and single-atom M<sup>β</sup> sites (blue balls) anchored on the surface lattice of support (black mesh). This schematic represents the surface structure of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> on which Ni<sub>1</sub> and Ru<sub>1</sub> cations are single-atom sites; CeO<sub>2</sub> is the support; both Ni<sub>1</sub> and Ru<sub>1</sub> are singly dispersed on CeO<sub>2</sub>.

Ru is active in activating CO<sub>2</sub> by dissociation of C–O of CO<sub>2</sub> to CO[\(1,8,9,18,20,24–26\)](#) Thus, it is chosen as the guest metal atom to activate CO<sub>2</sub>. The surface of CeO<sub>2</sub> has a high density of oxygen vacancies.[\(17,27,28\)](#) It is expected that oxygen vacancies of the CeO<sub>2</sub> surface could participate into the activation of CO<sub>2</sub>. In addition, the high affinity of surface lattice oxygen atoms to metal atoms could stabilize these guest cations and keep them singly dispersed. Thus, CeO<sub>2</sub> was chosen as a support to anchor the two sets of single atoms, Ni<sub>1</sub> and Ru<sub>1</sub>.

Catalysts consisting of CeO<sub>2</sub> nanorods and two sets of single-atom sites, Ni<sub>1</sub> or/and Ru<sub>1</sub>, were successfully synthesized in this work. Operando studies of chemical and coordination environments during catalysis revealed that both Ni and Ru cations are singly dispersed and remained at the cationic state during catalysis. This catalyst is highly active for reforming methane with CO<sub>2</sub>. Selectivity for producing H<sub>2</sub> reaches 98.5% at 600 °C. Synergy effects between single-atom sites Ni<sub>1</sub> and Ru<sub>1</sub> at low concentration of 2.5% Ni and 2.5% Ru were proved. Computational studies proposed a molecular mechanism for the synergistic effects of Ni<sub>1</sub> and Ru<sub>1</sub> sites in reforming CH<sub>4</sub> with CO<sub>2</sub>. This work suggests an avenue in designing new catalysts with high activity and selectivity at a relatively low temperature.

## 2. Experimental and Computational Methods

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The CeO<sub>2</sub>-based nanorods were synthesized with a modified hydrothermal method.[\(29–31\)](#) Typically, 4 mmol of metal nitrite precursors was dissolved in 10 mL of deionized water and then added to 70 mL of NaOH solution (6 mol/L) dropwise under vigorous stirring. A precipitate was formed during stirring. After being stirred for 30 min at room temperature, the slurry was transferred to a stainless-steel autoclave (100 mL) with PTFE lining and maintained at 120 °C for 24 h. Then the autoclave was cooled to room temperature naturally. The solid in the autoclave was separated by centrifugation and then washed with water until the pH was about 7.0. The solid separated upon the centrifugation was collected and then dried in an oven at 80 °C for 12 h. After the drying step, the product was ground into fine powder and then calcined at 400 °C for 2 h in air. Catalytic performances of a catalyst were measured with a fixed-bed flow reactor. Specific catalytic conditions can be found in section 1 of the [Supporting Information](#).

The high-resolution transmission electron microscope (HR-TEM) images and high angle annular dark field (HAADF) images in the STEM mode of used catalysts were taken by using a FEI Tecnai F20 XT. Powder X-ray diffraction (XRD) patterns of used catalysts were recorded with a Rigaku Ultimate IV operating in reflection mode with Cu K $\alpha$  radiation that was monochromated with a secondary graphite monochromator. Extended X-ray absorption fine structure spectra (EXAFS) at the Ru K-edge and Ni K-edge of catalysts during catalysis were collected at a beamline 2-2 at SSRL and ISS end station (8-ID) at NSLS-II. Details of characterization can be found in section 2 of the [Supporting Information](#).

Ambient-pressure X-ray photoelectron spectroscopy is an analytical method by which surface of a material in gas phase at certain pressure (mostly subtorr or a couple of torr of gas) is examined when gas is remained during data acquisition. The upper limit of gas pressure is limited to the brightness of the X-ray beam and other factors. The surface chemistry of a catalyst uncovered under this condition can be correlated with catalytic performance of the catalyst. The Ce 3d, Ni 2p, Ru 3p, and O 1s of a catalyst before catalysis were

collected at 150 °C for increasing conductivity of CeO<sub>2</sub>-based samples and thus minimizing surface charging. For in situ/operando studies of surface of the catalyst during catalysis at a temperature higher than 150 °C, there is no charging effect.

All the DFT calculations were carried out with a periodic slab model using the Vienna *ab initio* simulation program (VASP).<sup>(32–35)</sup> The generalized gradient approximation (GGA) was used with the Perdew–Burke–Ernzerhof (PBE)<sup>(36)</sup> exchange–correlation functional. The projector-augmented wave (PAW) method<sup>(37,38)</sup> was utilized to describe the electron–ion interactions; the cutoff energy for the plane-wave basis set was 450 eV. Details of DFT calculations can be found in section 3 of the [Supporting Information](#).

### 3. Results and Discussion

#### 3.1. Preparation of CeO<sub>2</sub> Nanorods with anchored Ni<sub>1</sub> and Ru<sub>1</sub> Sites or Coanchored Ni<sub>1</sub> and Ru<sub>1</sub> Sites

Three type of catalysts, namely Ru<sub>1</sub>/CeO<sub>2</sub>, Ni<sub>1</sub>/CeO<sub>2</sub>, and Ru<sub>1</sub> + Ni<sub>1</sub>/CeO<sub>2</sub>, were prepared with the specific protocol described in the [Experimental Section](#). The loading concentrations of Ru, Ni, and the total of Ru and Ni in the three catalysts are 5.0 wt % for Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, 5.0 wt % for Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, and 2.5 wt % + 2.5 wt % for Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>, respectively. Morphology and lattice fringes of the used Ru<sub>1</sub>/CeO<sub>2</sub>, Ni<sub>1</sub>/CeO<sub>2</sub>, and Ru<sub>1</sub>+Ni<sub>1</sub>/CeO<sub>2</sub> were examined with HRTEM. The observed diffraction peaks of Ru<sub>1</sub> + Ni<sub>1</sub>/CeO<sub>2</sub> catalyst in the XRD pattern in Figure S1 in the [Supporting Information](#) were indexed to (111), (200), (220), and (311) planes, which correspond to a typical fluorite structure of CeO<sub>2</sub> (JCPDS 43-1002).<sup>(29)</sup> No characteristic diffraction peaks belonging to NiO and RuO<sub>2</sub> nanoparticles could be detected, suggesting the lack of NiO and RuO<sub>2</sub> nanoparticles. Thus, these used catalysts, Ru<sub>1</sub>/CeO<sub>2</sub>, Ni<sub>1</sub>/CeO<sub>2</sub>, and Ru<sub>1</sub> + Ni<sub>1</sub>/CeO<sub>2</sub>, remain the fluorite phase of pure CeO<sub>2</sub> without formation of NiO or RuO<sub>2</sub> nanoparticles on them. XRD patterns of the used catalysts suggest that these catalysts have high structural stability during catalysis at 600 °C.

High-resolution TEM images of the used catalyst Ru<sub>1</sub> + Ni<sub>1</sub>/CeO<sub>2</sub> allow for identification of lattice fringes ([Figures 2 and 3](#)). The dominantly exposed planes of Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, and Ce<sub>0.95</sub>Ru<sub>0.025</sub>Ni<sub>0.025</sub>O<sub>2</sub> catalysts exhibit interplanar spacing of 2.80 Å, which corresponds to (200) planes of CeO<sub>2</sub>.<sup>(29)</sup> As Ni and Ru atoms have lower atomic number than a Ce atom, it is challenging to distinguish Ni or Ru atoms from Ce atoms of CeO<sub>2</sub> nanorods by the HAADF–STEM technique. Many efforts were made in checking whether NiO or/and RuO<sub>2</sub> could have been formed on the surface of CeO<sub>2</sub> nanorods. No NiO or RuO<sub>2</sub> nanoparticles were observed on the surfaces of CeO<sub>2</sub> nanorods of these catalysts even at different tilting angles of specimens in HAADF–STEM. These structural characterizations of catalysts used for reforming CH<sub>4</sub> with CO<sub>2</sub> suggest that Ru and Ni cations are highly dispersed. In fact, they are singly dispersed; their single dispersions in terms

of single-atom sites of Ni<sub>1</sub> and Ru<sub>1</sub> of these used catalysts were confirmed with operando EXAFS studies to be presented in next sections.

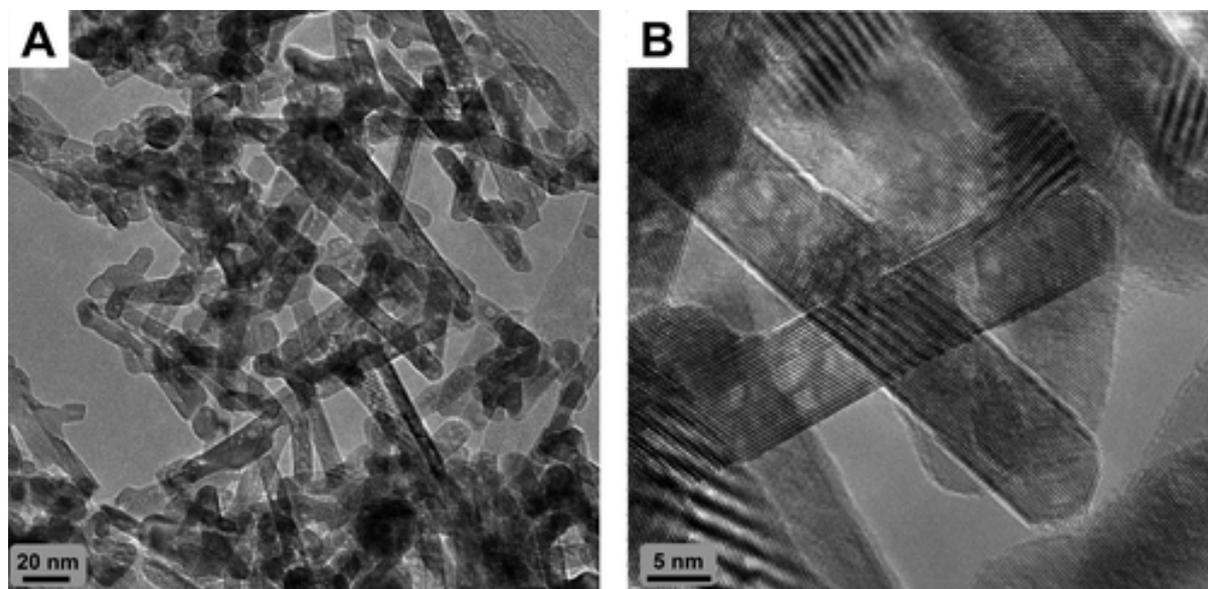


Figure 2. HRTEM images of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  catalyst after it was used for reforming of methane with  $\text{CO}_2$  at 600 °C performed in a fixed-bed flow reactor.

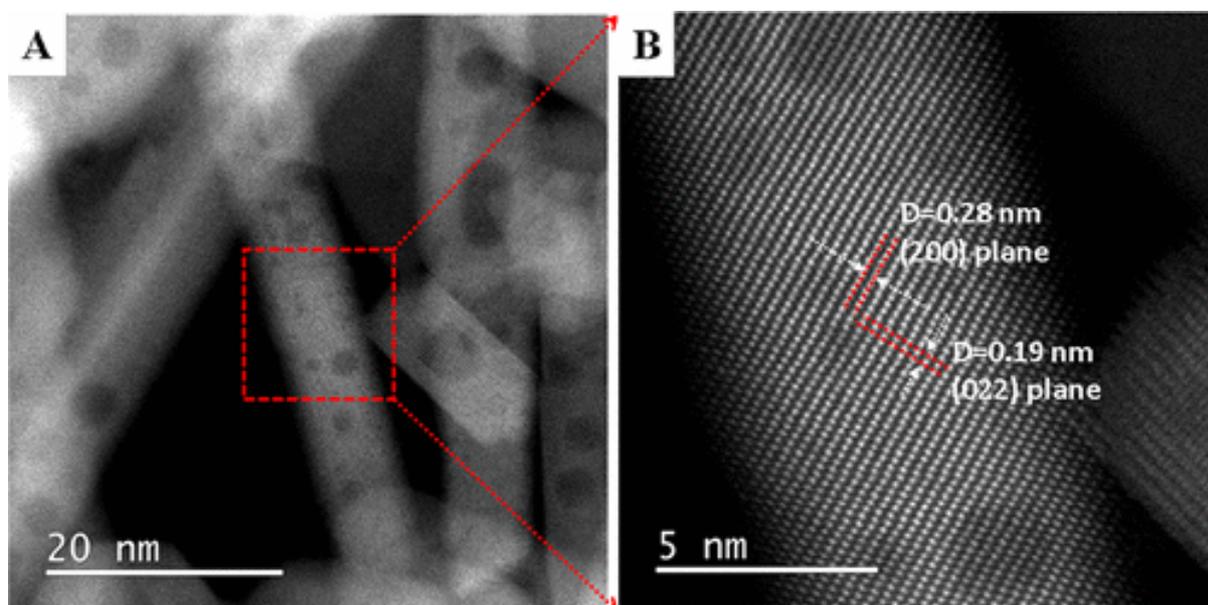


Figure 3. Aberration-corrected STEM images of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  catalyst after it was used for reforming of  $\text{CH}_4$  with  $\text{CO}_2$  at 600 °C performed in a fixed-bed flow reactor.

[Figure 3](#) presents the aberration-corrected HAADF–STEM images of a  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  catalyst which was used for reforming  $\text{CH}_4$  at 600 °C. The used  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  catalyst retains the original morphology of nanorods after catalysis at 600 °C ([Figure 3a](#)). The two-dimensional lattice fringe of the used  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  can be readily identified in [Figure 3b](#). The interplanar distances of the  $\text{CeO}_2$  nanorods of the used catalyst  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  along the two directions marked with red dashed lines in [Figure 3b](#) are 2.8 and 1.9 Å, which correspond to the interplanar distance of two adjacent planes of (200) and that of two adjacent (220) planes of  $\text{CeO}_2$ , respectively. The identification of these lattice fringes shows that (110) is one of the preferentially formed plane perpendicular to (200) and (022), consistent with that reported in literatures. ([29,31](#)) No NiO and  $\text{RuO}_2$  nanoparticles were observed from the used catalyst  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  ([Figure 3](#)). Similar to  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ , (110) planes of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  are the preferentially exposed surfaces, and there is lack of NiO or  $\text{RuO}_2$  nanoparticles formed on the surface of nanorods of the two used catalysts.

### 3.2. Catalytic Performance of Single-Atom $\text{Ru}_1$ and/or $\text{Ni}_1$ Sites on Ceria Support

Catalytic performances of three  $\text{Ce}_{1-x-y}\text{Ni}_x\text{Ru}_y\text{O}_2$  catalysts ( $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$ ,  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ ) for reforming methane with  $\text{CO}_2$  in terms of conversion of  $\text{CH}_4$  and selectivity for production of  $\text{H}_2$  and ratio of  $\text{H}_2$  to  $\text{CO}$  were studied with a fixed-bed flow reactor in the temperature range of 300–600 °C. For the measurements of catalytic performances, 50 mg of each of the three catalysts diluted with 300 mg of purified quartz was loaded to the reactor. A 40 mL/min mixture of  $\text{CH}_4$  (1% in Ar) and  $\text{CO}_2$  (1% in Ar) was mixed and flown through the catalyst bed. Selectivities for producing  $\text{H}_2$  on  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  at 600 °C are 80.0% and 82.9%, respectively (black and red lines in [Figure 4b](#)). Compared to  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$ ,  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  exhibits a higher selectivity of 98.5% for producing  $\text{H}_2$  at 600 °C (blue line in [Figure 4b](#)). As shown in [Figure 4a](#), the conversion of  $\text{CH}_4$  on 50 mg  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ , 91% is obviously higher than half of the total of conversions of 50 mg  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  (83%) and 50 mg of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  (63%) at 600 °C ([Figure 4a](#)), 73%  $\left( = \frac{83\% + 63\%}{2} \right)$ , which suggests a synergy effect of Ni and Ru cations on reforming  $\text{CH}_4$  with  $\text{CO}_2$ . In addition, the yield of  $\text{H}_2$  at 600 °C (90%) is much higher than half of total yield of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  (65%) and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  (52%), 58.5%  $\left( = \frac{65\% + 50\%}{2} \right)$ . Here, we assume that the number of sites ( $\text{Ni}_1$  or  $\text{Ru}_1$ ) on topmost layer of  $\text{CeO}_2$  is proportional to the nominal composition of the three catalysts and that the numbers of  $\text{Ni}_1$  and  $\text{Ru}_1$  sites of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  are half of the number of  $\text{Ni}_1$  sites of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and half of the number of  $\text{Ru}_1$  sites of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$ , respectively.

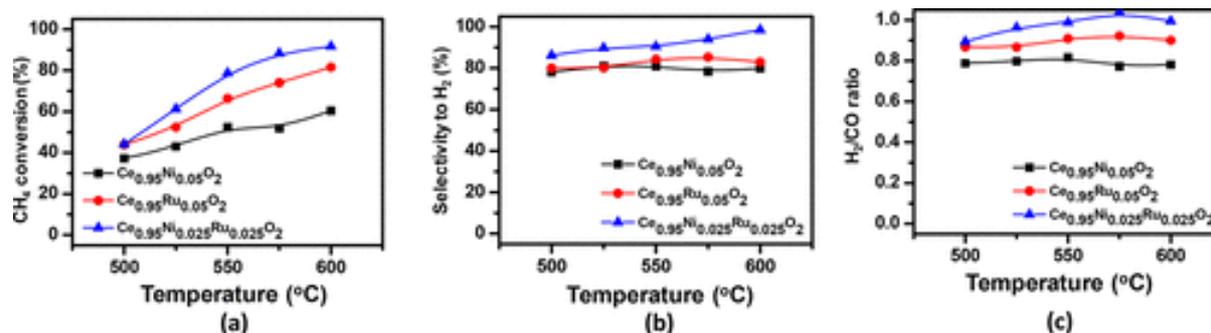


Figure 4. Catalytic performances of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$ ,  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$ , and  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  for reforming of  $\text{CH}_4$  with  $\text{CO}_2$ . (a) Conversion of  $\text{CH}_4$ , (b) selectivity for producing  $\text{H}_2$ , and (c)  $\text{H}_2/\text{CO}$  ratio.  $\text{Ce}_{1-x-y}\text{Ni}_x\text{Ru}_y\text{O}_2$  (50 mg) diluted with 300 mg purified quartz was loaded to the fixed-bed flow reactor.  $\text{CH}_4$  (20 mL/min) (1.0%) and 20 mL/min  $\text{CO}_2$  (1.0%) were mixed and then flown into the reactor.

To explore whether the observed synergistic effect is an intrinsic characteristic or just a matter of number of sites of these catalysts, kinetic studies of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  and  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  were performed under the same conditions. In these kinetic studies, a certain amount of catalyst diluted with 300 mg of purified quartz was loaded to a fixed-bed flow reactor, and a mixture of 40 mL/min 1.0%  $\text{CH}_4$  and 40 mL/min 1.0%  $\text{CO}_2$  was introduced to the reactor. Catalytic performances on these catalysts were measured in the whole temperature range of kinetics studies, 500–560 °C. Figure 5 presents Arrhenius plots of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$ ,  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$ , and  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  in the temperature range of 500–560 °C. All conversions in this temperature range are definitely lower than 20%. The Y axis of Figure 5 is the natural log of the production rate of  $\text{H}_2$  or  $\text{CO}$  (number of molecules produced per site per second). Apparent activation barriers were calculated through the slopes of these plots in Figure 5. Notably, on the basis of the production of  $\text{H}_2$ , the measured activation barrier of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  (51.7 kJ/mol) is obviously lower than those of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  (66.0 kJ/mol) and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  (75.6 kJ/mol). On the basis of the production of  $\text{CO}$ , the measured activation barrier of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  (41.5 kJ/mol) is also obviously lower than those of  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  (61.2 kJ/mol) and  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$  (71.3 kJ/mol). This intrinsic difference in dry reforming between  $\text{Ce}_{0.95}\text{Ni}_{0.05}\text{O}_2$  (or  $\text{Ce}_{0.95}\text{Ru}_{0.05}\text{O}_2$ ) and  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  confirmed the synergistic effect between anchored Ni and Ru cations; this synergistic effect of  $\text{Ni}_1$  and  $\text{Ru}_1$  sites on  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  decreases the activation barriers for reforming methane with  $\text{CO}_2$ .

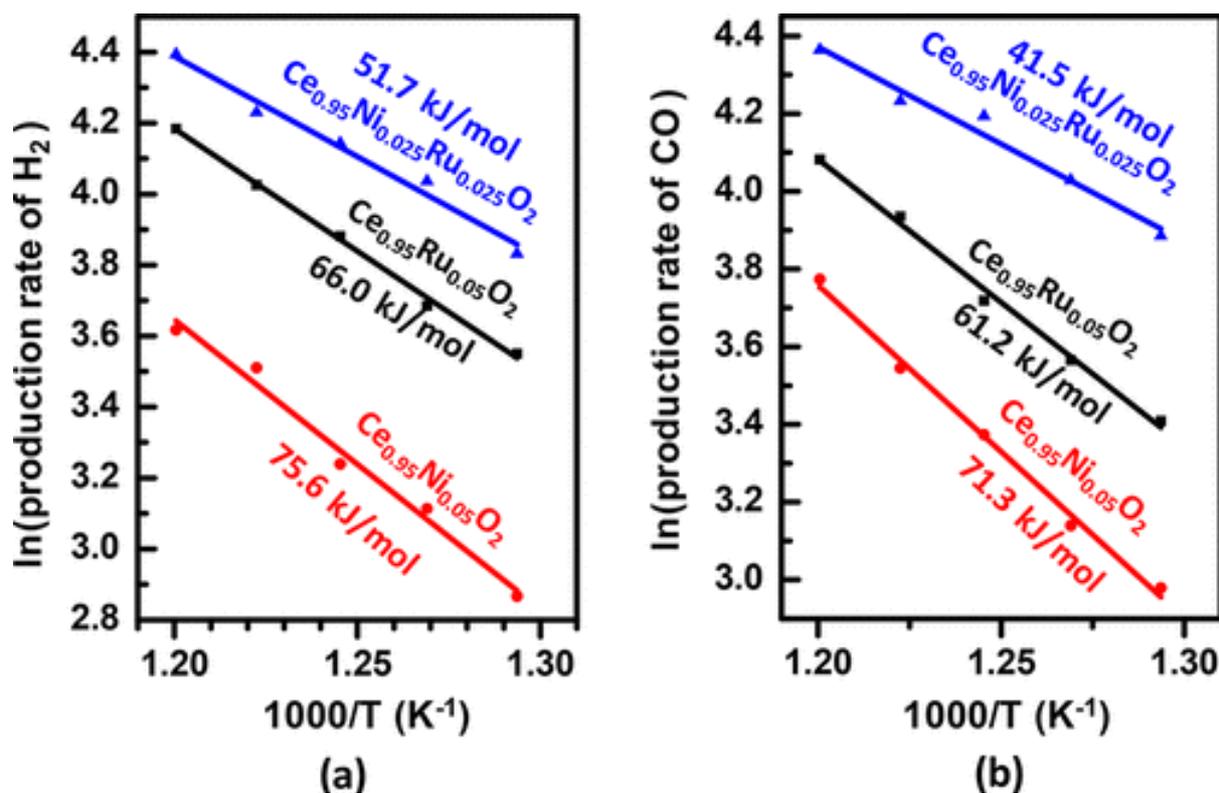


Figure 5. Arrhenius plot in terms of the rate of product of (a) H<sub>2</sub> and (b) CO catalyzed by the Ce<sub>1-x-y</sub>Ni<sub>x</sub>Ru<sub>y</sub>O<sub>2</sub> catalysts. Blue: 5 mg of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> diluted with 300 mg of purified quartz. Black: 15 mg of Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> diluted with 300 mg of purified quartz. Red: 20 mg of Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub> diluted with 300 mg of purified quartz. Mixture of 40 mL/min of 1.0% CH<sub>4</sub> and 40 mL/min of 1.0% CO<sub>2</sub> was introduced during kinetic studies. Y-axis is the natural log of the production rate of H<sub>2</sub>(a) or CO (b) in a unit: the number of H<sub>2</sub>(or CO) molecules formed on a metal site per second. For Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>, both Ni and Ru atoms of the topmost layer were counted as active sites in the calculation of production rate (the number of H<sub>2</sub> or CO molecules produced on a site per second). For Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> and Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, only Ni or Ru cations of the topmost layer were considered as active sites. The numbers of Ni<sub>1</sub> atoms of Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, Ru<sub>1</sub> atoms of Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, or both Ni<sub>1</sub> and Ru<sub>1</sub> of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> were measured with AP-XPS during catalysis.

As shown in [Figure 5](#), the measured apparent activation barrier for producing CO is different from that for producing H<sub>2</sub> on the same catalyst. It is known that for many reactions more than one step could have activation barriers close to the step of the highest activation barrier; in fact, these steps of a catalytic cycle can be considered as rate-determining steps as well. In other words, to some extent there could be more than one rate-determining step in a complete catalytic cycle. However, how these rate-determining steps collectively give a measurable apparent activation barrier is still a debatable topic in the field of computational and experimental studies. Here, the measured difference between apparent activation barriers for producing CO

and that for producing H<sub>2</sub> suggests that some of the rate-determining steps for producing CO are different from those of the rate-determining steps for producing H<sub>2</sub>. In fact, *both* the complexity of rate-determining steps for CO and H<sub>2</sub> and the unknown correlation between barriers of rate-determining steps and observable apparent activation barrier could result in the difference between the measured apparent activation barrier for producing CO and that for producing H<sub>2</sub>.

As shown in [Figure 4c](#), the ratio of H<sub>2</sub>/CO increases as a function of catalysis temperature, which is consistent with the evolution of equilibrium H<sub>2</sub>/CO ratio in reforming of CH<sub>4</sub> with CO<sub>2</sub> as a function of temperature calculated with ASPEN; in this calculation the equilibrium H<sub>2</sub>/CO ratios at different temperatures were calculated when H<sub>2</sub>O was considered as a product formed from reverse water–gas shift (RWGS) of CO<sub>2</sub> and H<sub>2</sub>. In these ASPEN calculations, we built a fixed-bed flow reactor, input the initial concentrations of CH<sub>4</sub>, (0.5%) and CO<sub>2</sub> (0.5%), and took CO, H<sub>2</sub>, and H<sub>2</sub>O as products. [Figure S5](#) plots the calculated conversion of CH<sub>4</sub> as a function of temperatures at 300–600 °C. At 600 °C, the conversion of CH<sub>4</sub> is 97%. In addition, the calculated ratios of H<sub>2</sub>/CO were plotted in [Figure S6](#); they increase as a function of catalysis temperature. This temperature evolution of H<sub>2</sub>/CO ratio calculated with ASPEN while H<sub>2</sub>O was a byproduct and RWGS as a side reaction ([Figure S6](#)) is in agreement with the one measured ([Figure 4c](#)). This consistency suggests that RWGS is definitely a side reaction of dry reforming of CH<sub>4</sub>.

Turnover frequencies (TOFs) of reforming of methane with CO<sub>2</sub> over these catalysts were calculated with yields of H<sub>2</sub> and CO measured under a kinetics-controlled regime. For catalysts Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub> or Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, the number of Ni<sub>1</sub> or Ru<sub>1</sub> atoms on the topmost layer of the catalyst was, respectively, used as a denominator in the calculation of TOF. In the case of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>, the total number of both Ni<sub>1</sub> and Ru<sub>1</sub> atoms on the topmost layer of this catalyst was counted as an active site of reforming CH<sub>4</sub> in the calculations of TOFs. The calculations of numbers of Ni<sub>1</sub> or/and Ru<sub>1</sub> sites on these catalysts and the corresponding TOFs can be found in section 2 of the [Supporting Information](#). As shown in [Figure 6](#), TOF of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> is definitely higher than that of Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub> and Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> at the same temperature in the temperature range 500–560 °C, further confirming the synergy effect between Ru<sub>1</sub> and Ni<sub>1</sub> sites on CeO<sub>2</sub> in reforming of CH<sub>4</sub> with CO<sub>2</sub>.

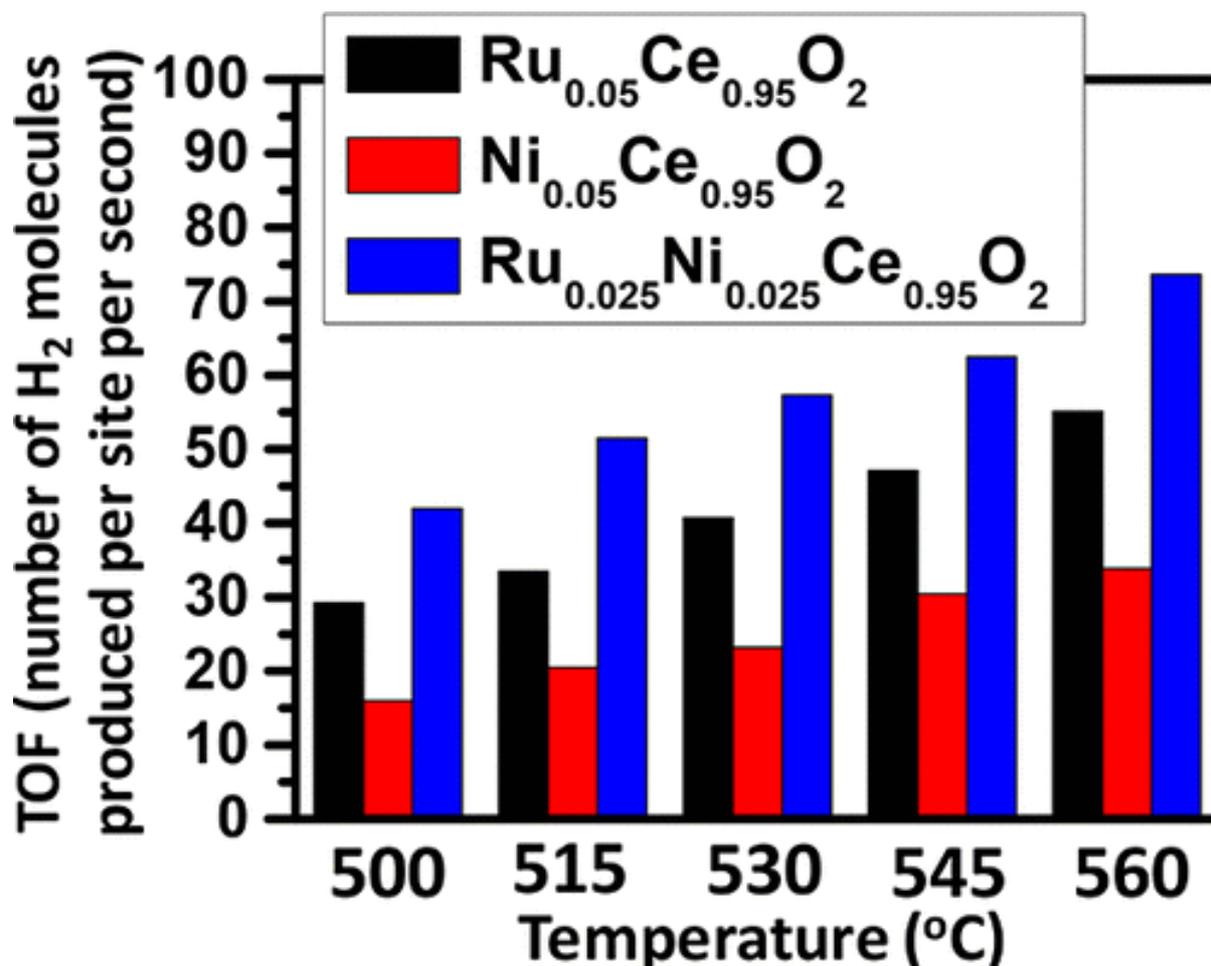


Figure 6. Turnover frequency (TOF) of reforming CH<sub>4</sub> with CO<sub>2</sub> in terms of hydrogen production per Ni<sub>1</sub> site of Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, per Ru<sub>1</sub> site of Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, and per Ni<sub>1</sub> or Ru<sub>1</sub> site for Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> at 500–560 °C. In the calculation of TOFs, the number of catalytic sites for Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> is the total number of Ni and Ru atoms of the topmost surface layer of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>. The number of Ni atoms on the topmost layer of Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>, the numbers of Ru<sub>1</sub> atoms on the topmost layer of Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub>, and the total number of Ni<sub>1</sub> and Ru<sub>1</sub> atoms on the topmost layer of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> were measured with an ambient-pressure X-ray photoelectron spectrometer during catalysis under kinetics control regime.

The distance between Ni<sub>1</sub> and Ru<sub>1</sub> cations of Ce<sub>1-x-y</sub>Ni<sub>x</sub>Ru<sub>y</sub>O<sub>2</sub> is expected to be a factor influencing catalytic performance. To address how a relative distance between Ni<sub>1</sub> and Ru<sub>1</sub> on CeO<sub>2</sub> could influence a catalytic performance, a much larger variation in concentration of Ni<sub>1</sub> (or Ru<sub>1</sub>) on surfaces of Ce<sub>1-x-y</sub>Ni<sub>x</sub>Ru<sub>y</sub>O<sub>2</sub> is necessary. To largely decrease the relative distance, one has to increase the loadings of Ni and Ru largely. Unfortunately, Ni (or Ru) at high loadings can readily form metal or oxide nanoparticles, which could readily prevent us from studying the synergistic effect between two sets of single atom sites. To largely increase the average distance between Ni<sub>1</sub> and Ru<sub>1</sub> sites, one has to largely decrease the loadings of these metal atoms. However, it is quite

challenging to characterize chemical and coordination environments of these single-atom sites if the loading of Ni or Ru is too low. Facing these challenges, how the average distance between Ni<sub>1</sub> and Ru<sub>1</sub> could influence the synergetic effect was not explored here.

### 3.3. Operando Studies of Catalyst during Catalysis

Surface chemistry of catalysts during catalysis was investigated by AP-XPS. On the basis of the literature,[\(39,40\)](#) one of the photoemission features of Ce<sup>3+</sup> is at 885.2 eV which does not overlap with photoemission features of Ce<sup>4+</sup> of CeO<sub>2</sub>.[\(39,40\)](#) As shown in [Figure 7a1](#), there is nearly lack of the photoemission feature of Ce<sup>3+</sup> at 885.2 eV. It suggests that the fraction of Ce<sup>3+</sup> in the surface region of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> before catalysis is quite low, forming a valley in the region of 885.2 ± 1.5 eV. Compared to the catalyst before catalysis, the fraction of Ce<sup>3+</sup> during catalysis at 550 °C is obviously higher than that before catalysis, as evidenced by the formation of a plateau in the region of 885.2 ± 1.5 eV during catalysis at 550 °C ([Figure 7a2](#)) instead of a valley-like feature ([Figure 7a1](#)). The deconvolution of Ce 3d collected at 550 °C during catalysis suggests that the Ce<sup>3+</sup>/(Ce<sup>3+</sup> + Ce<sup>4+</sup>) is 20.3%, which is much higher than the 2.3% of catalyst at 150 °C in UHV. In terms of the O 1s feature before catalysis, the major oxygen species represented by the O 1s feature is surface lattice oxygen. A component at 532.0 eV in the O 1s spectrum of the fresh catalyst ([Figure 7b1](#)) was observed and assigned to -OH groups formed on the surface of ceria.[\(39,41\)](#) It is formed through dissociative chemisorption of water molecules on oxygen vacancies in the cooling process in air upon calcination at a high temperature during catalyst preparation. The atomic fraction of these species of hydroxyl groups decreased along the increase of catalysis temperature. Because Ru 3d overlaps with C 1s, Ru 3p spectra were collected here to analyze Ru. As shown in the [Figure 7c1](#), Ru is at an oxidizing state in the fresh catalyst of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>. When Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> was under catalysis conditions at a specific temperature ([Figure 7c2](#)), binding energies of Ru 3p downshifted to the side of lower binding energy. This downshift of binding energy of Ru 3p indicates an increase of electron density of Ru atoms. This is due to a partial reduction of Ru atoms or a change of chemical or/and coordination environment of Ru atoms to an environment of Ru with a higher electron density. Notably, the binding energy (462.4 eV) of Ru 3p of Ru atoms during catalysis at 550 °C ([Figure 7c2](#)) is still higher than the metallic Ru 3p, which is 461.7 eV;[\(42\)](#) it suggests that Ru atoms of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> are at a cationic state.

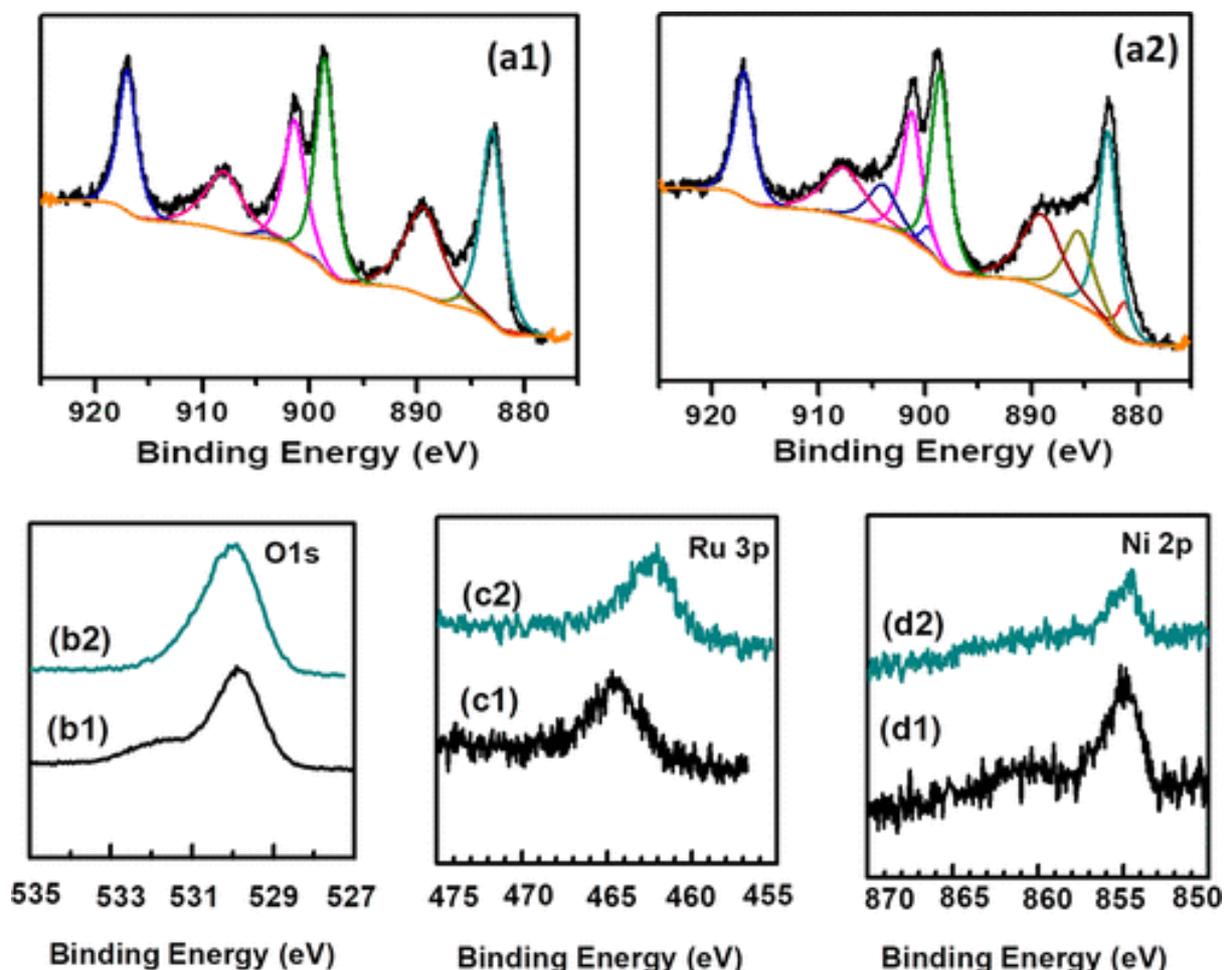
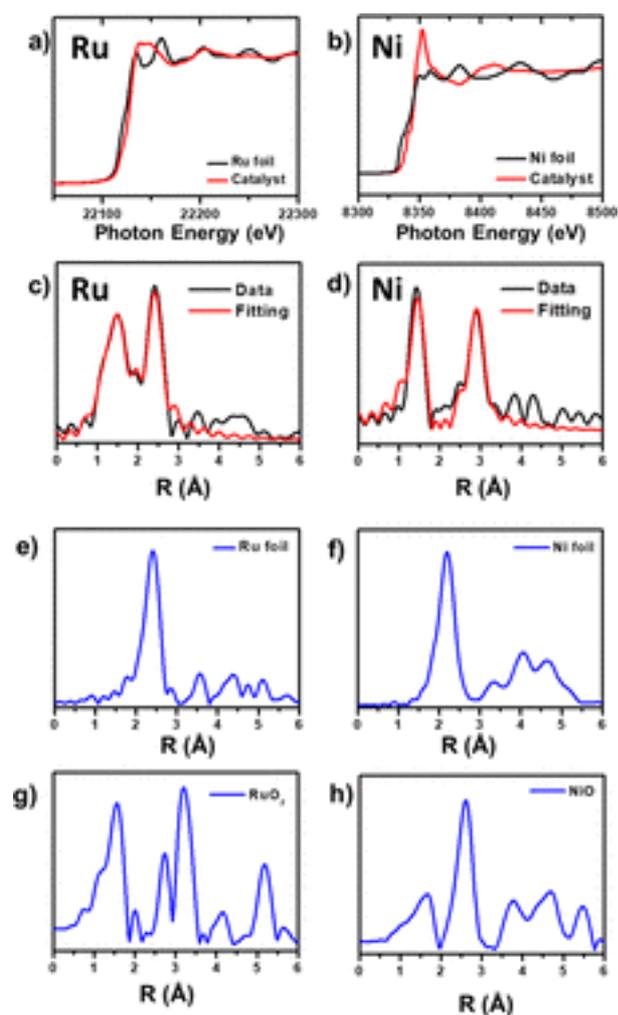


Figure 7. Ce 3d, O 1s, Ru 3p, and Ni 2p photoemission features from AP-XPS studies of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  during reforming of  $\text{CH}_4$  with  $\text{CO}_2$ . (a1, b1, c1, and d1) Photoemission feature before catalysis, (a2, b2, c2, and d2) photoemission feature during catalysis at 550 °C. The molar fractions of  $\text{CO}_2$  and  $\text{CH}_4$  in the flowing mixture are 50% and 50%.

[Figure 7d](#) presents the Ni 2p<sub>3/2</sub> of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  collected under different conditions. The photoemission feature of Ni 2p<sub>1/2</sub> was not shown in this figure so that the photoemission feature of Ni 2p<sub>3/2</sub> can be presented clearly. Although a slight down shift of Ni 2p<sub>3/2</sub> was observed during catalysis ([Figure 7d2](#)) compared to that before catalysis ([Figure 7d1](#)), Ni atoms of this catalyst during catalysis with Ni 2p<sub>3/2</sub> at 854.8 eV remained at an oxidative state based on the binding energy of Ni 2p photoelectrons of NiO at 853.8 eV.[\(43\)](#) In the case of NiO nanoparticles, a very strong satellite peak of Ni 2p<sub>3/2</sub> was clearly observed at 861.4 eV;[\(43\)](#) this satellite peak is originated at long-range scattering of structure of  $\cdots\text{Ni}-\text{O}-\text{Ni}-\text{O}-\text{Ni}-\text{O}\cdots$  in the lattice of a NiO nanoparticle whose surface region has interdigitated Ni and O atoms.[\(24,44,45\)](#) By checking this satellite peak, we can judge whether there is a Ni–O–Ni structure or not on the surface region of the catalyst. For instance, Ni 2p<sub>3/2</sub> of singly dispersed Ni atoms in micropore of ZSM-5[\(18\)](#) and on the surface of  $\text{Co}_{2.25}\text{Ni}_{0.75}\text{O}_4$  nanoparticles does not exhibit such a satellite

peak in our previous studies.<sup>(24)</sup> Here, the lack of satellite peak next to the Ni 2p<sub>3/2</sub> main peak (Figure 7d2) suggests that Ni atoms during catalysis at 550 °C are singly dispersed instead of formation of NiO lattice,  $\cdots\text{Ni}-\text{O}-\text{Ni}-\text{O}-\text{Ni}-\text{O}\cdots$ . Thus, the AP-XPS studies of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  clearly suggest that Ni and Ru atoms in this catalyst during catalysis are at a cationic state instead of a metallic state.<sup>(46)</sup> This was confirmed by inoperando studies of chemical and coordination environments of Ni and Ru atoms during catalysis with EXAFS (Figure 8).



	CN	Distance (Å)	ss
Ru-O	2.08±0.65	1.86±0.06	0.00200
Ru-O	2.41±0.63	2.11±0.05	0.00200
Ru-Ce	2.73±0.40	2.78±0.02	0.00200
Ni-O	3.38±0.35	1.90±0.02	0.00456
Ni-Ce	2.80±0.85	3.10±0.07	0.00828

i)

Figure 8. Operando studies of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  during catalysis and reference samples (Ni foil, Ru foil, NiO powder, and  $\text{RuO}_2$  powder) using X-ray

absorption spectroscopy (XANES and EXAFS) and corresponding Fourier transformed radical distribution function of Ru K edge and Ni K edge. In these studies, a certain amount of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  was loaded into the quartz reactor of EXAFS and XANES cells. A mixture of  $\text{CH}_4$ ,  $\text{CO}_2$  and He was flowed through the catalyst bed of the EXAFS cell at catalysis temperature. Data collection after sample was cooled to 50–100 °C: (a) energy space of Ru K edge of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  and Ru foil reference; (b) energy space of Ni K edge of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  and Ni foil reference. (c) Experimental (black) and fitting (red) *r*-space spectra of Ru K edge of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ . (d) Experimental (black) and fitting (red) *r*-space spectra of Ni K edge of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$ . (e) *r*-space spectrum of reference sample Ru foil. (f) *r*-space spectrum of reference sample Ni foil. (g) *r*-space spectrum of reference sample  $\text{RuO}_2$ . (h) *r*-space spectrum of reference sample NiO. All *r*-space spectra are shown without phase correction. (i) Coordination environments of  $\text{Ni}_1$  and  $\text{Ru}_1$  atoms of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  during catalysis.

From the feature of near-edge absorption of the Ru K edge and Ni K edge collected during catalysis, Ru and Ni atoms of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  during catalysis are at cationic states ([Figures 8a,b](#)). The *R*-space spectra of the Ni K edge and Ru K edge obtained from EXAFS studies of  $\text{Ce}_{0.95}\text{Ni}_{0.025}\text{Ru}_{0.025}\text{O}_2$  during catalysis show that Ni and Ru atoms are singly dispersed and coordinated with oxygen atoms during catalysis. The fitting results of the Fourier transformed radical distribution functions ([Figure 8c,d](#)) suggest that Ru and Ni are coordinated with O in the first shell and Ce in the second shell during catalysis. As shown in [Figure 8i](#), the fittings of *r*-space of Ni K-edge suggest that (1) each Ni atom bonds with three oxygen atoms on average in the first coordination shell, (2) the distance between Ni and O is  $1.90 \pm 0.02 \text{ \AA}$ , (3) each Ni atom coordinates with three Ce atoms in the closest second coordination shell (Ni–O–Ce), and (4) the direct distance between Ni and Ce in Ni–(O)–Ce is  $3.10 \pm 0.07 \text{ \AA}$ . Similar fitting of *r*-space of Ru K-edge suggests that (1) each Ru atom bonds with about four oxygen atoms in the first coordination shell, (2) the direct distances between Ru and O are  $1.86 \pm 0.06 \text{ \AA}$  and  $2.11 \pm 0.05 \text{ \AA}$ , which are close to the  $1.90 \pm 0.02 \text{ \AA}$  of Ni–O of this catalyst to some extent, (3) each Ru atom coordinates with three Ce atoms in the closest second coordination shell (Ru–O–Ce), and (4) the direct distance between Ru and Ce is  $2.78 \pm 0.02 \text{ \AA}$ , which is a reasonable distance between Ru and Ce since the ionic radii of Ru and Ce are 0.82 and 1.15 Å, respectively,[\(47\)](#) and the  $\angle\text{Ru–O–Ce}$  is about  $55^\circ$ .

The coordination number and bond distance of  $\text{Ni}_1$  and  $\text{Ru}_1$  uncovered with operando EXAFS studies ([Figure 8i](#)) are consistent with the geometries of  $\text{Ni}_1$  and  $\text{Ru}_1$  sites on the surface of  $\text{CeO}_2$  (110) optimized with DFT calculations ([Figure 9](#)). Obviously, the *r*-space spectra of Ru K-edge and Ni K-edge do not support the existence of the second shell of Ru or Ni atoms in terms of Ru–O–Ru and Ni–O–Ni structure, respectively. Thus, we concluded that Ru and Ni cations are in the format of single dispersion on  $\text{CeO}_2$  during catalysis instead of NiO,  $\text{RuO}_2$ , Ni, or Ru nanoparticles.

**Figure 9**

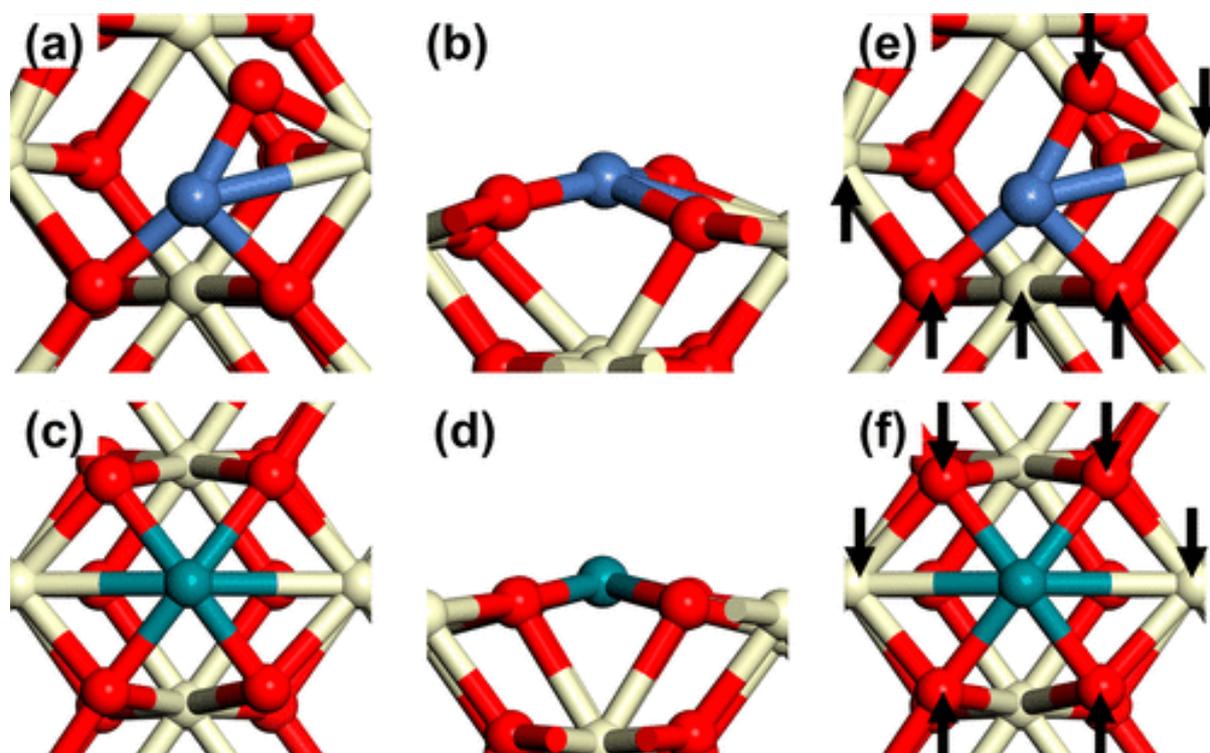


Figure 9. Most stable surface structure representing the surface of  $\text{Ru}_{0.025}\text{Ni}_{0.025}\text{Ce}_{0.95}\text{O}_2$  during catalysis. (a) Top view of  $\text{CeO}_2$  (110) anchored with a  $\text{Ni}_1$  atom. (b) Side view of  $\text{CeO}_2$  (110) anchored with the  $\text{Ni}_1$  atom. (c) Top view of  $\text{CeO}_2$  (110) anchored with  $\text{Ru}_1$  atoms. (d) Side view of  $\text{CeO}_2$  (110) anchored with  $\text{Ru}_1$  atoms. (e) Marked neighbor atoms (black arrows) coordinated with  $\text{Ni}_1$  site. (f) Marked neighbor atoms (black arrows) coordinated with  $\text{Ru}_1$  site. Ce, Ni, and Ru are shown in yellow, blue, and green, respectively. Red balls indicate oxygen atoms. These notations are used throughout this work. It is the most stable surface among four optimized surface structures with different binding environments of  $\text{Ni}_1$  and  $\text{Ru}_1$  atoms.

## 4. DFT Calculations

### 4.1. Different Anchoring Sites of $\text{Ni}_1$ and $\text{Ru}_1$ Atoms

(110) of  $\text{CeO}_2$  is the preferentially exposed surface of a  $\text{Ru}_{0.025}\text{Ni}_{0.025}\text{Ce}_{0.95}\text{O}_2$  on the basis of the above HRTEM studies ([Figures S8 and S9](#)). Thus, the (110) surface of  $\text{CeO}_2$  nanorods was chosen to build structural models for simulating activation of  $\text{CH}_4$  and  $\text{CO}_2$  on  $\text{Ru}_{0.025}\text{Ni}_{0.025}\text{Ce}_{0.95}\text{O}_2$ . Four potential doping sites for both  $\text{Ru}_1$  and  $\text{Ni}_1$  on  $\text{CeO}_2$ , respectively, were optimized. The most stable doping sites are shown in [Figure 9](#). Chemical and coordination environments of  $\text{Ni}_1$  and  $\text{Ru}_1$  atoms of the most stable sites offered through optimization with DFT ([Figure 9](#)) are listed in [Table S1](#). These bonding parameters ([Table S1](#))

are in good agreement with the coordination environments measured through operando EXAFS studies of Ni K-edge and Ru K-edge (Figure 8i). Therefore, the optimized surface structure in Figure 9 was used for simulating activations of methane and CO<sub>2</sub> molecules to form CO and H<sub>2</sub> in dry reforming of CH<sub>4</sub>.

#### 4.2. Activation of the First C–H of CH<sub>4</sub> To Form CH<sub>3</sub> on Ni<sub>1</sub>

Activation of methane is one of the most important elementary steps in catalytic transformation of CH<sub>4</sub> according to previous work.<sup>(20,48–50)</sup> On the basis of the optimized structure (Figure 9), here dissociative chemisorptions of methane on Ru<sub>1</sub> and Ni<sub>1</sub> sites were investigated. Geometries of the most favorable transition states in activation of the first C–H of methane on Ni<sub>1</sub> and Ru<sub>1</sub> atoms are shown in Figure 10a,b (for Ni<sub>1</sub>) and Figure 10c,d (for Ru<sub>1</sub>), respectively. On the basis of these DFT calculations, Gibbs free energy barriers for activations of the first C–H of CH<sub>4</sub> on Ni<sub>1</sub> and Ru<sub>1</sub> sites are 1.88 and 2.01 eV, respectively. These values suggest that Ni<sub>1</sub> is the preferred active site for activating the first C–H of methane since the barrier on Ni<sub>1</sub> is relatively lower in contrast to Ru<sub>1</sub>. In fact, the activation barrier of C–H of methane on the Ni<sub>1</sub>, 1.88 eV, is low in contrast to the activation barriers of the first C–H of methane on other catalysts,<sup>(15)</sup> which is consistent with the quite high activity of dry reforming at a relatively low temperature observed in this work. The formed CH<sub>3</sub> and H adsorb on a Ni atom and an O atom of the surface lattice, respectively (Figure 10e,f).

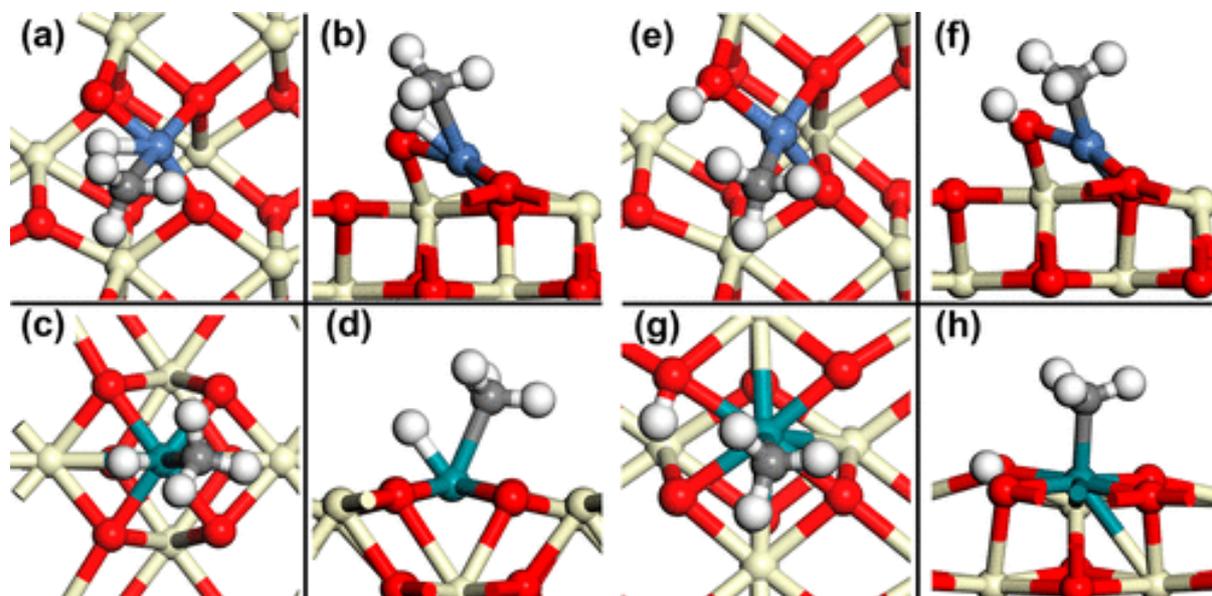


Figure 10. Top views and side views of transition-state geometries of CH<sub>4</sub> activation and intermediate structures of formed CH<sub>3</sub> and H on Ni<sub>1</sub> and Ru<sub>1</sub> sites on CeO<sub>2</sub>. Top and side views of transition-state geometries of CH<sub>4</sub> activation on Ni<sub>1</sub> ((a and b) and Ru<sub>1</sub> (c and d), intermediate geometries of CH<sub>3</sub> and H formed on Ni<sub>1</sub> site (e and f) and Ru<sub>1</sub> site (g and h).

### 4.3. Transformation of CH<sub>3</sub> to CO and H on Ni<sub>1</sub>

Transformation of CH<sub>4</sub> to CO can be done through four dehydrogenation steps to form H atoms and C atom; the formed C atom is then oxidized to form CO. Due to the high mobility of surface lattice oxygen atoms, the possibility of coupling between oxygen atom of surface lattice and carbon atom formed through activation of methane is considered here.

After the formation of CH<sub>3</sub> species, two different types of reactions including (1) dehydrogenation of CH<sub>3</sub> into CH<sub>2</sub> and H and (2) oxidation of CH<sub>3</sub> to CH<sub>3</sub>O are considered here for transforming CH<sub>3</sub> to CO. Both of them were investigated. The transition-state geometries of these two potential steps on a Ni<sub>1</sub> site and a Ru<sub>1</sub> site are shown in [Figure S8a–d](#) and [Figure S8e–h](#), respectively. The calculated activation energies of CH<sub>3</sub> dehydrogenation performed on a Ni<sub>1</sub> site ([Figure S8a,b](#)) and CH<sub>3</sub> oxidation on a Ni<sub>1</sub> site ([Figure S8c,d](#)) are 1.39 and 1.33 eV, respectively. Therefore, the dehydrogenation of CH<sub>3</sub> on a Ni<sub>1</sub> site to form CH<sub>2</sub> and H and oxidation of CH<sub>3</sub> on a Ni<sub>1</sub> site to CH<sub>3</sub>O are kinetically similar. However, the free energy changes for dehydrogenation of CH<sub>3</sub> on a Ni<sub>1</sub> site and oxidation of CH<sub>3</sub> to CH<sub>3</sub>O on a Ni<sub>1</sub> site are +0.50 and –0.03 eV, respectively. Thus, in terms of Ni<sub>1</sub> site, the oxidation of CH<sub>3</sub> to CH<sub>3</sub>O is likely to be the dominant pathway in contrast to the dehydrogenation of CH<sub>3</sub> into CH<sub>2</sub> and H on Ni<sub>1</sub> site.

Parallel to the above investigations on a Ni<sub>1</sub> site, dehydrogenation of CH<sub>3</sub> to CH<sub>2</sub> or oxidation of CH<sub>3</sub> on a Ru<sub>1</sub> site were studied as well. The activation barrier for dehydrogenation of CH<sub>3</sub> to CH<sub>2</sub> and H on a Ru<sub>1</sub> site and oxidation of CH<sub>3</sub> to CH<sub>3</sub>O on a Ru<sub>1</sub> site are 1.73 and 2.22 eV, respectively. The free energy change for the dehydrogenation and oxidation on a Ru<sub>1</sub> site is 0.69 and 0.58 eV, respectively. Thus, obviously both dehydrogenation of CH<sub>3</sub> to CH<sub>2</sub> and H and oxidation of CH<sub>3</sub> to CH<sub>3</sub>O on a Ni<sub>1</sub> site are kinetically favorable in contrast to a Ru<sub>1</sub> site. For instance, compared to the dehydrogenation of CH<sub>3</sub> to CH<sub>2</sub> on a Ru<sub>1</sub> with an activation barrier of 1.73 eV and free energy change of 0.69 eV, the oxidation of CH<sub>3</sub> to CH<sub>3</sub>O on a Ni<sub>1</sub> site (with activation barrier of 1.33 eV and free energy change of –0.03 eV) is thermodynamically favorable. Thus, upon the activation of the first C–H of CH<sub>4</sub>, a favorable step is oxidation of CH<sub>3</sub> to CH<sub>3</sub>O on a Ni<sub>1</sub> site.

With similar methods, all possible steps of dehydrogenation of CH<sub>2</sub> and CH and oxidation of CH<sub>2</sub> to CH<sub>2</sub>O, CH to CHO, and C to CO on Ni<sub>1</sub> and Ru<sub>1</sub> sites were systematically investigated. The favorable pathways from activation of the first C–H of CH<sub>4</sub> to formation of CO on Ni<sub>1</sub> sites are listed in [Table S2](#). For comparison, [Table S2](#) lists the pathways from activation of CH<sub>4</sub> to the formation of CO on the Ru<sub>1</sub> site as well.

As shown in [Table S2](#), most of the dehydrogenation steps after the third step are favorable with low free energy barriers and negative Gibbs free energy changes on a Ru<sub>1</sub> site. In addition, the steps of desorption of CO from the Ni<sub>1</sub> site and the Ru<sub>1</sub> site are endothermic and barrierless (step 6 in [Table S2](#)). Notably, the bonding of CO on a Ru<sub>1</sub> site is much stronger than on a Ni<sub>1</sub> site, which likely results in a high coverage of CO on Ru<sub>1</sub> sites and therefore limits

the reaction rate. In general, the activation energies of elementary steps on a Ni<sub>1</sub> site are lower than those on a Ru<sub>1</sub> site as shown in [Table S2](#), indicating that a Ni<sub>1</sub> site is more active in the transformation of CH<sub>3</sub> to CO. Overall, DFT calculations suggest that a Ni<sub>1</sub> site is responsible for the activation of CH<sub>4</sub> to form CO. In the potential pathway presented in [Table S2](#), the highest free energy barrier among these elementary steps is the activation of the first C–H bond of CH<sub>4</sub> on both Ni<sub>1</sub> and Ru<sub>1</sub> sites. It suggests that methane activation is the rate-determining step of reforming CH<sub>4</sub> with CO<sub>2</sub> on Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>.

#### 4.4. Activation of CO<sub>2</sub> To Form CO and O on Ru<sub>1</sub> + O<sub>vac</sub>

Due to the formation of a CO molecule from CH<sub>4</sub> on a catalyst surface, a lattice oxygen atom is consumed from the surface of CeO<sub>2</sub> and thus an oxygen vacancy is created. The oxygen vacancy needs to be filled so that the surface lattice oxygen atoms can continuously function in oxidation steps of the next catalytic cycle. For instance, the transition state of the step from CH<sub>4</sub> to CH<sub>3</sub> is a four-membered ringlike structure involving the bindings of C and H atoms of CH<sub>4</sub> to Ni and surface lattice O atom, respectively ([Figure 10a,b](#)). In dry reforming (CH<sub>4</sub> + CO<sub>2</sub> = 2CO + 2H<sub>2</sub>), carbon dioxide is the only source to provide oxygen atoms to fill oxygen vacancies of the catalyst surface. Here, activations of CO<sub>2</sub> on Ni<sub>1</sub> and Ru<sub>1</sub> sites together with refilling of oxygen vacancies were investigated. It is found that the Gibbs free energy barriers ( $G_a$ ) of dissociating CO<sub>2</sub> on a Ni<sub>1</sub> and a Ru<sub>1</sub> site are 1.23 and 0.01 eV, respectively. Thus, activation of CO<sub>2</sub> on Ru<sub>1</sub> + O<sub>vac</sub> is much more kinetically favorable than Ni<sub>1</sub> + O<sub>vac</sub>. After crossing this transition state ([Figure S9a,b](#)), the formed CO binds to Ni<sub>1</sub> and the formed O fills O<sub>vac</sub> next to Ni<sub>1</sub>. The formed CO and O atom are adsorbed on Ru<sub>1</sub> fill to O<sub>vac</sub> next to Ru<sub>1</sub> ([Figure S9g,h](#)). As shown in [Figure S9a,b](#), the activation of CO<sub>2</sub> on Ni<sub>1</sub> and Ru<sub>1</sub> involves oxygen vacancies next to Ni<sub>1</sub> and Ru<sub>1</sub> atoms, respectively. Gibbs free energy changes in dissociation of CO<sub>2</sub> on Ni<sub>1</sub> + O<sub>vac</sub> and Ru<sub>1</sub> + O<sub>vac</sub> to form the adsorbed CO and O are 0.76 and -0.99 eV, respectively, suggesting that Ru<sub>1</sub> + O<sub>vac</sub> is a thermodynamically favorable site. Thus, Ru<sub>1</sub> + O<sub>vac</sub> is kinetically and thermodynamically favorable for activation of CO<sub>2</sub> in contrast to Ni<sub>1</sub> + O<sub>vac</sub>. The activation of CO<sub>2</sub> on Ru<sub>1</sub> + O<sub>vac</sub> forms the second CO molecule of the reforming (CH<sub>4</sub> + CO<sub>2</sub> = 2CO + 2H<sub>2</sub>).

#### 4.5. Coupling of H Atoms To Form H<sub>2</sub> on Ru<sub>1</sub>

Other than formation of CO through activation of CH<sub>4</sub> to CH<sub>*n*</sub> (*n* = 0–3) along with progressive oxidation of CH<sub>*n*</sub> (*n* = 0–3) to CO, H atoms are formed in the pathway of transferring CH<sub>4</sub> to CO as shown in [Table S2](#). Coupling of these formed H atoms on surface to form H<sub>2</sub> is a necessary step. This step was simulated. Transition states for coupling hydrogen atoms on Ni<sub>1</sub> and Ru<sub>1</sub> sites are shown in [Figure S10](#). The calculated activation barriers for coupling H atoms on Ni<sub>1</sub> and Ru<sub>1</sub> are 1.96 and 0.65 eV, respectively, while the free energies changes for coupling hydrogen atoms to form a H<sub>2</sub> molecule on Ni<sub>1</sub> and Ru<sub>1</sub> sites are 0.63 and 0.26 eV, respectively. Therefore, the Ru<sub>1</sub> site

should be responsible for coupling atomic hydrogen to form H<sub>2</sub> molecules since coupling of H atoms on Ru<sub>1</sub> is thermodynamically and kinetically favorable.

#### 4.6. Synergy Effect of Ni<sub>1</sub> and Ru<sub>1</sub> in Reforming CH<sub>4</sub> with CO<sub>2</sub>

The chemical and coordination environments of Ni atoms and Ru atoms of optimized CeO<sub>2</sub>(110) with anchored Ni<sub>1</sub> and Ru<sub>1</sub> atoms proposed through DFT calculations are consistent with the catalyst structure of experimental characterization using in situ/operando approaches, suggesting that the structural model optimized with these DFT calculations is suitable for exploring mechanism of reforming of CH<sub>4</sub> with CO<sub>2</sub>. The activations of CH<sub>4</sub> and CO<sub>2</sub> and coupling of H atoms were simulated with all the possible elementary steps on Ni<sub>1</sub>, Ru<sub>1</sub>, Ni<sub>1</sub> + Vac, and Ru<sub>1</sub> + Vac. It is found that Ni<sub>1</sub> and its adjacent oxygen atom are highly active for the activation of methane to form both CO and oxygen vacancy with a low activation barrier, offering high activity of reforming methane on Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> at a relatively low temperature. Ru<sub>1</sub> + O<sub>vac</sub> is responsible for activating another reactant. The different roles of a Ni<sub>1</sub> site (for activation of CH<sub>4</sub>) and a Ru<sub>1</sub> site (for activation of CO<sub>2</sub>) of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> clearly justified the synergistic effect between Ni<sub>1</sub> and Ru<sub>1</sub> observed experimentally.

As shown in [sections 4.2](#), [4.3](#), and [4.5](#), the formed H atoms in the steps of activating CH<sub>4</sub> to form CO on a Ni<sub>1</sub> site prefer to couple each other to form a H<sub>2</sub> molecule on a Ru<sub>1</sub> site. Thus, the first formation of H atoms on a Ni<sub>1</sub> site and then coupling H atoms to form H<sub>2</sub> molecules on a Ru<sub>1</sub> site is another synergistic effect between Ni<sub>1</sub> and Ru<sub>1</sub> sites of Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>; in other words, Ni<sub>1</sub> and Ru<sub>1</sub> sites play a *sequential* role in *first* generation of H atoms on Ni<sub>1</sub> sites and *then* coupling H atoms to form H<sub>2</sub> on a Ru<sub>1</sub> site in a catalytic cycle. Thus, these DFT calculations provided molecular pictures of the two synergy effects of the two sets of single-atom sites (Ni<sub>1</sub> and Ru<sub>1</sub>) on Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>.

## 5. Summary

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Two sets of single-atom sites, Ni<sub>1</sub> and Ru<sub>1</sub>, were successfully anchored on the surface of CeO<sub>2</sub> nanorods, forming a catalyst of dual single-atom sites, Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>. It is highly active for reforming methane with CO<sub>2</sub> to produce syngas (CO + H<sub>2</sub>) with a selectivity of 98.5% for producing H<sub>2</sub> with an unprecedented high activity in terms of TOF of 73.6 H<sub>2</sub> per site per second at 560 °C. The synergistic effect between Ru<sub>1</sub> and Ni<sub>1</sub> on Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub> were confirmed by its lowest apparent activation barrier and highest turnover rate of forming CO and H<sub>2</sub> among Ce<sub>0.95</sub>Ni<sub>0.025</sub>Ru<sub>0.025</sub>O<sub>2</sub>, Ce<sub>0.95</sub>Ru<sub>0.05</sub>O<sub>2</sub> and Ce<sub>0.95</sub>Ni<sub>0.05</sub>O<sub>2</sub>. Computational studies uncovered that the molecular-level origins of synergistic effects of Ni<sub>1</sub> and Ru<sub>1</sub> sites are (1) the complementary function of Ni<sub>1</sub> (for activation of CH<sub>4</sub>) and of Ru<sub>1</sub> (for activation of CO<sub>2</sub>) and (2) the

sequential role of *first* generating H atoms in activating CH<sub>4</sub> on a Ni<sub>1</sub> site and *then* coupling H atoms to form H<sub>2</sub> on a Ru<sub>1</sub> site. These reported synergistic effects demonstrated a new avenue for designing a catalyst with high activation and selectivity at a low temperature.

## Supporting Information

The Supporting Information is available free of charge on the [ACS Publications website](#) at DOI: [10.1021/jacs.8b10910](https://doi.org/10.1021/jacs.8b10910).

Characterization data, influence of gas-phase molecules, measurement of catalytic performance, stability of catalytic activity, and DFT calculations ([PDF](#))

## References

1. Schwach, P.; Pan, X.; Bao, X. Direct Conversion of Methane to Value-Added Chemicals over Heterogeneous Catalysts: Challenges and Prospects. *Chem. Rev.* **2017**, *117* (13), 8497– 8520, DOI: 10.1021/acs.chemrev.6b00715
2. Spivey, J. J.; Hutchings, G. Catalytic aromatization of methane. *Chem. Soc. Rev.* **2014**, *43* (3), 792– 803, DOI: 10.1039/C3CS60259A
3. Guo, X.; Fang, G.; Li, G.; Ma, H.; Fan, H.; Yu, L.; Ma, C.; Wu, X.; Deng, D.; Wei, M. Direct, nonoxidative conversion of methane to ethylene, aromatics, and hydrogen. *Science* **2014**, *344* (6184), 616– 619, DOI: 10.1126/science. 1253150
4. Yi, N.; Cao, Y.; Liu, Y.-M.; Dai, W.-L.; He, H.-Y.; Fan, K.-N. Highly Efficient Ni–Ce–O Mixed Oxide Catalysts via Gel-coprecipitation of Oxalate Precursors for Catalytic Combustion of Methane. *Chem. Lett.* **2005**, *34* (1), 108– 109, DOI: 10.1246/cl.2005.108
5. Lunsford, J. H. Catalytic conversion of methane to more useful chemicals and fuels: a challenge for the 21st century. *Catal. Today* **2000**, *63* (2–4), 165– 174, DOI: 10.1016/S0920-5861(00)00456-9
6. Pena, M. A.; Gomez, J. P.; Fierro, J. L. G. New catalytic routes for syngas and hydrogen production. *Appl. Catal., A* **1996**, *144* (1–2), 7– 57, DOI: 10.1016/0926-860X(96)00108-1
7. Song, C. S.; Pan, W. Tri-reforming of methane: a novel concept for catalytic production of industrially useful synthesis gas with desired H<sub>2</sub>/CO

ratios. *Catal. Today* **2004**, *98* (4), 463– 484, DOI: 10.1016/j.cattod.2004.09.054

8. Pakhare, D.; Spivey, J. A review of dry (CO<sub>2</sub>) reforming of methane over noble metal catalysts. *Chem. Soc. Rev.* **2014**, *43* (22), 7813– 7837, DOI: 10.1039/C3CS60395D
9. Gonzalez-delaCruz, V. M.; Pereñíguez, R.; Ternero, F.; Holgado, J. P.; Caballero, A. In situ XAS study of synergic effects on Ni–Co/ZrO<sub>2</sub> methane reforming catalysts. *J. Phys. Chem. C* **2012**, *116* (4), 2919– 2926, DOI: 10.1021/jp2092048
10. Fan, M. S.; Abdullah, A. Z.; Bhatia, S. Catalytic technology for carbon dioxide reforming of methane to synthesis gas. *ChemCatChem* **2009**, *1* (2), 192– 208, DOI: 10.1002/cctc.200900025
11. Hansen, T. W.; DeLaRiva, A. T.; Challa, S. R.; Datye, A. K. Sintering of catalytic nanoparticles: particle migration or Ostwald ripening?. *Acc. Chem. Res.* **2013**, *46* (8), 1720– 1730, DOI: 10.1021/ar3002427
12. Trimm, D. L. Coke formation and minimisation during steam reforming reactions. *Catal. Today* **1997**, *37* (3), 233– 238, DOI: 10.1016/S0920-5861(97)00014-X
13. Trimm, D. L. Catalysts for the control of coking during steam reforming. *Catal. Today* **1999**, *49* (1–3), 3– 10, DOI: 10.1016/S0920-5861(98)00401-5
14. Ginsburg, J. M.; Piña, J.; El Solh, T.; De Lasa, H. I. Coke formation over a nickel catalyst under methane dry reforming conditions: thermodynamic and kinetic models. *Ind. Eng. Chem. Res.* **2005**, *44* (14), 4846– 4854, DOI: 10.1021/ie0496333
15. Wang, Z.; Cao, X.-M.; Zhu, J.; Hu, P. Activity and coke formation of nickel and nickel carbide in dry reforming: a deactivation scheme from density functional theory. *J. Catal.* **2014**, *311*, 469– 480, DOI: 10.1016/j.jcat.2013.12.015
16. Lustemberg, P. G.; Ramírez, P. J.; Liu, Z.; Gutiérrez, R. A.; Grinter, D. G.; Carrasco, J.; Senanayake, S. D.; Rodriguez, J. A.; Ganduglia-Pirovano, M. V. Room-Temperature Activation of Methane and Dry Re-forming with CO<sub>2</sub> on Ni-CeO<sub>2</sub>(111) Surfaces: Effect of Ce<sup>3+</sup> Sites and Metal–Support Interactions on C–H Bond Cleavage. *ACS Catal.* **2016**, *6* (12), 8184– 8191, DOI: 10.1021/acscatal.6b02360

17. Rodriguez, J. A.; Grinter, D. C.; Liu, Z.; Palomino, R. M.; Senanayake, S. D. Ceria-based model catalysts: fundamental studies on the importance of the metal–ceria interface in CO oxidation, the water–gas shift, CO<sub>2</sub> hydrogenation, and methane and alcohol reforming. *Chem. Soc. Rev.* **2017**, *46* (7), 1824– 1841, DOI: 10.1039/C6CS00863A
18. 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/CeO<sub>2</sub>: reaction pathway and interaction between Ni and the CeO<sub>2</sub> support. *ACS Catal.* **2013**, *3* (5), 975– 984, DOI: 10.1021/cs4000969
19. Zhang, S.; Nguyen, L.; Liang, J.-X.; Shan, J.; Liu, J.; Frenkel, A. I.; Patlolla, A.; Huang, W.; Li, J.; Tao, F. Catalysis on singly dispersed bimetallic sites. *Nat. Commun.* **2015**, *6*, 7938, DOI: 10.1038/ncomms8938
20. Tao, F. F.; Shan, J.-j.; Nguyen, L.; Wang, Z.; Zhang, S.; Zhang, L.; Wu, Z.; Huang, W.; Zeng, S.; Hu, P. Understanding complete oxidation of methane on spinel oxides at a molecular level. *Nat. Commun.* **2015**, *6*, 7798, DOI: 10.1038/ncomms8798
21. Zhang, S.; Tang, Y.; Nguyen, L.; Zhao, Y.-F.; Wu, Z.; Goh, T.-W.; Liu, J. J.; Li, Y.; Zhu, T.; Huang, W. Catalysis on Singly Dispersed Rh Atoms Anchored on an Inert Support. *ACS Catal.* **2018**, *8* (1), 110– 121, DOI: 10.1021/acscatal.7b01788
22. Nguyen, L.; Zhang, S.; Wang, L.; Li, Y.; Yoshida, H.; Patlolla, A.; Takeda, S.; Frenkel, A. I.; Tao, F. Reduction of Nitric Oxide with Hydrogen on Catalysts of Singly Dispersed Bimetallic Sites Pt<sub>1</sub>Co<sub>m</sub> and Pd<sub>1</sub>Co<sub>n</sub>. *ACS Catal.* **2016**, *6* (2), 840– 850, DOI: 10.1021/acscatal.5b00842
23. Fung, V.; Tao, F.; Jiang, D. E. Low-temperature activation of methane on doped single atoms: descriptor and prediction. *Phys. Chem. Chem. Phys.* **2018**, *20* (35), 22909– 22914, DOI: 10.1039/C8CP03191F
24. Shan, J.; Huang, W.; Nguyen, L.; Yu, Y.; Zhang, S.; Li, Y.; Frenkel, A. I.; Tao, F. Conversion of methane to methanol with a bent mono ( $\mu$ -oxo) dinickel anchored on the internal surfaces of micropores. *Langmuir* **2014**, *30* (28), 8558– 8569, DOI: 10.1021/la501184b
25. Liu, Z.; Grinter, D. C.; Lustemberg, P. G.; Nguyen-Phan, T. D.; Zhou, Y.; Luo, S.; Waluyo, I.; Crumlin, E. J.; Stacchiola, D. J.; Zhou, J. Dry Reforming of Methane on a Highly-Active Ni-CeO<sub>2</sub> Catalyst: Effects of Metal-Support Interactions on C– H Bond Breaking. *Angew. Chem., Int. Ed.* **2016**, *55* (26), 7455– 7459, DOI: 10.1002/anie.201602489

26. Yan, B.; Yang, X.; Yao, S.; Wan, J.; Myint, M.; Gomez, E.; Xie, Z.; Kattel, S.; Xu, W.; Chen, J. G. Dry reforming of ethane and butane with CO<sub>2</sub> over PtNi/CeO<sub>2</sub> bimetallic catalysts. *ACS Catal.* **2016**, 6 (11), 7283– 7292, DOI: 10.1021/acscatal.6b02176
27. Zhu, Y.; Zhang, S.; Shan, J.-j.; Nguyen, L.; Zhan, S.; Gu, X.; Tao, F. In situ surface chemistries and catalytic performances of ceria doped with palladium, platinum, and rhodium in methane partial oxidation for the production of syngas. *ACS Catal.* **2013**, 3 (11), 2627– 2639, DOI: 10.1021/cs400070y
28. Xie, Z. H.; Yan, B. H.; Kattel, S.; Lee, J. H.; Yao, S. Y.; Wu, Q. Y.; Rui, N.; Gomez, E.; Liu, Z. Y.; Xu, W. Q.; Zhang, L.; Chen, J. G. G. Dry reforming of methane over CeO<sub>2</sub>-supported Pt-Co catalysts with enhanced activity. *Appl. Catal., B* **2018**, 236, 280– 293, DOI: 10.1016/j.apcatb.2018.05.035
29. Mai, H.-X.; Sun, L.-D.; Zhang, Y.-W.; Si, R.; Feng, W.; Zhang, H.-P.; Liu, H.-C.; Yan, C.-H. Shape-selective synthesis and oxygen storage behavior of ceria nanopolyhedra, nanorods, and nanocubes. *J. Phys. Chem. B* **2005**, 109 (51), 24380– 24385, DOI: 10.1021/jp055584b
30. Jones, J.; Xiong, H.; DeLaRiva, A. T.; Peterson, E. J.; Pham, H.; Challa, S. R.; Qi, G.; Oh, S.; Wiebenga, M. H.; Hernández, X. I. P. Thermally stable single-atom platinum-on-ceria catalysts via atom trapping. *Science* **2016**, 353 (6295), 150– 154, DOI: 10.1126/science.aaf8800
31. Wu, Z.; Schwartz, V.; Li, M.; Rondinone, A. J.; Overbury, S. H. Support shape effect in metal oxide catalysis: ceria-nanoshape-supported vanadia catalysts for oxidative dehydrogenation of isobutane. *J. Phys. Chem. Lett.* **2012**, 3 (11), 1517– 1522, DOI: 10.1021/jz300513u
32. Kresse, G.; Furthmüller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, 54 (16), 11169– 11186, DOI: 10.1103/PhysRevB.54.11169
33. Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, 6 (1), 15– 50, DOI: 10.1016/0927-0256(96)00008-0
34. Kresse, G.; Hafner, J. Ab-Initio Molecular-Dynamics Simulation of the Liquid-Metal Amorphous-Semiconductor Transition in Germanium. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, 49 (20), 14251– 14269, DOI: 10.1103/PhysRevB.49.14251

35. Kresse, G.; Hafner, J. Ab initio molecular dynamics for liquid metals. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, *47* (1), 558– 561, DOI: 10.1103/PhysRevB.47.558
36. Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77* (18), 3865– 3868, DOI: 10.1103/PhysRevLett.77.3865
37. Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59* (3), 1758– 1775, DOI: 10.1103/PhysRevB.59.1758
38. Blöchl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50* (24), 17953– 17979, DOI: 10.1103/PhysRevB.50.17953
39. Mullins, D.; Overbury, S.; Huntley, D. Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces. *Surf. Sci.* **1998**, *409* (2), 307– 319, DOI: 10.1016/S0039-6028(98)00257-X
40. Paparazzo, E. On the curve-fitting of XPS Ce (3d) spectra of cerium oxides. *Mater. Res. Bull.* **2011**, *46* (2), 323– 326, DOI: 10.1016/j.materresbull.2010.11.009
41. Newberg, J. T.; Starr, D. E.; Yamamoto, S.; Kaya, S.; Kendelewicz, T.; Mysak, E. R.; Porsgaard, S.; Salmeron, M. B.; Brown, G. E.; Nilsson, A. Formation of hydroxyl and water layers on MgO films studied with ambient pressure XPS. *Surf. Sci.* **2011**, *605* (1), 89– 94, DOI: 10.1016/j.susc.2010.10.004
42. Morgan, D. J. Resolving ruthenium: XPS studies of common ruthenium materials. *Surf. Interface Anal.* **2015**, *47* (11), 1072– 1079, DOI: 10.1002/sia.5852
43. Chastain, J.; King, R. C.; Moulder, J. *Handbook of X-ray photoelectron spectroscopy: a reference book of standard spectra for identification and interpretation of XPS data*; Physical Electronics Division, Perkin-Elmer Corp., Eden Prairie, MN, **1992**.
44. Grosvenor, A. P.; Biesinger, M. C.; Smart, R. S. C.; McIntyre, N. S. New interpretations of XPS spectra of nickel metal and oxides. *Surf. Sci.* **2006**, *600* (9), 1771– 1779, DOI: 10.1016/j.susc.2006.01.041
45. Sangaletti, L.; Depero, L.; Parmigiani, F. On the non-local screening mechanisms in the 2p photoelectron spectra of NiO and La<sub>2</sub>NiO<sub>4</sub>. *Solid State Commun.* **1997**, *103* (7), 421– 424, DOI: 10.1016/S0038-1098(97)00185-3

46. Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J. Synchrotron Radiat.* **2005**, *12* (4), 537– 541, DOI: 10.1107/S0909049505012719
47. Shannon, R. D. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1976**, *32*, 751, DOI: 10.1107/S0567739476001551
48. Wang, Z.; Cao, X. M.; Zhu, J.; Hu, P. Activity and coke formation of nickel and nickel carbide in dry reforming: A deactivation scheme from density functional theory. *J. Catal.* **2014**, *311* (0), 469– 480, DOI: 10.1016/j.jcat.2013.12.015
49. Jones, G.; Jakobsen, J. G.; Shim, S. S.; Kleis, J.; Andersson, M. P.; Rossmeisl, J.; Abild-Pedersen, F.; Bligaard, T.; Helveg, S.; Hinnemann, B.; Rostrup-Nielsen, J. R.; Chorkendorff, I.; Sehested, J.; Norskov, J. K. First principles calculations and experimental insight into methane steam reforming over transition metal catalysts. *J. Catal.* **2008**, *259* (1), 147– 160, DOI: 10.1016/j.jcat.2008.08.003
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50. Tang, Y.; Li, Y.; Fung, V.; Jiang, D.-e.; Huang, W.; Zhang, S.; Iwasawa, Y.; Sakata, T.; Nguyen, L.; Zhang, X. Single rhodium atoms anchored in micropores for efficient transformation of methane under mild conditions. *Nat. Commun.* **2018**, *9* (1), 1231, DOI: 10.1038/s41467-018-03235-7