

Complete Oxidation of Methane on NiO Nanoclusters Supported on CeO₂ Nanorods through Synergistic Effect

Xiaoyan Zhang,^{†,‡,§} Stephen D. House,[⊥][®] Yu Tang,[§][®] Luan Nguyen,[§] Yuting Li,[§] Adedamola A. Opalade,[§][®] Judith C. Yang,[⊥] Zaicheng Sun,^{*,∥}[®] and Franklin Feng Tao^{*,§}

[†]State Key Laboratory of Luminescence and Applications, Changchun Institute of Optics, Fine Mechanics and Physics, Changchun, 130033 Jilin, People's Republic of China

[‡]University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China

[§]Department of Chemical and Petroleum Engineering and Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, United States

Beijing Key Laboratory for Green Catalysis and Separation, Department of Chemistry and Chemical Engineering, Beijing University of Technology, Beijing 100124, People's Republic of China

¹Department of Chemical and Petroleum Engineering, University of Pittsburgh, Pittsburgh, Pennsylvania 15261, United States

ABSTRACT: Catalytic complete oxidation of CH₄ at relatively low temperatures is significant for removing unburned CH₄ from the exhaust of combustion engines fueled with natural gas or liquefied petroleum gas. Here a nanocomposite catalyst (NiO/CeO_2) consisting of CeO₂ nanorods and supported NiO nanoclusters was prepared by a two-step wet-chemistry method. This nanocomposite catalyst exhibits high catalytic activity for the complete oxidation of CH₄ in the temperature range of 350-600 °C. A CH₃-like intermediate bound to Ni cations was observed at a relatively low temperature by ambient pressure X-ray photo-



electron spectroscopy under catalytic conditions. Parallel kinetic studies of NiO/SiO₂, CeO₂ and NiO/CeO₂ catalysts show that the apparent barrier for complete oxidation of CH₄ on NiO/CeO₂ (69.4 \pm 4 kJ/mol) is much lower than the 95.1 \pm 5 kJ/mol of pure CeO₂ and 98.4 \pm 5 kJ/mol of NiO/SiO₂, supported by the turnover frequency of NiO/CeO₂ being significantly higher than NiO/SiO₂ and CeO₂. These differences indicate a synergistic effect between the CeO₂ nanorods and the supported NiO nanoclusters. This synergistic effect occurs at the interface of NiO and CeO₂, observed in TEM. The lattice oxygen atoms at the interface exhibit high activity based on the lower reduction temperature uncovered in studies of the temperature-programmed reduction of H₂.

KEYWORDS: NiO, CeO₂, Methane, Complete oxidation, AP-XPS

INTRODUCTION

CH4 is one of the main gas components in the exhaust of vehicles using natural gas or liquefied petroleum gas as fuels for their combustion engines. Unlike gasoline-fueled engines, the engines of vehicles using natural gas or liquefied petroleum gas perform combustions of light hydrocarbons at relatively low temperatures, typically <600 °C. A catalyst that is highly active at temperatures below 600 °C for the complete transformation of methane into carbon dioxide is needed to remove the unburned methane in the exhaust line prior to release into the environment because CH4 is a much stronger greenhouse gas than CO₂.¹⁻⁶ The activation of methane and complete oxidation to CO2 and H2O at temperatures lower than 600 °C require a highly active catalyst because CH4 has the strongest C-H bond among hydrocarbons.^{3,7-10} Supported Pt and Pd are active for complete oxidation of methane to CO_2 and H_2O at a relatively low temperature.^{3,9,11-20} Due to the

prohibitive price of Pt and Pd, it is necessary to find an alternative made of earth-abundant elements.

CeO₂ is an important support in oxidative catalysis due to its high activity in activating molecular oxygen.²¹⁻²⁴ However, Ce^{3+} or Ce^{4+} does not exhibit high activity in activating C–H of CH4. On the other hand, Ni atoms in either metallic state or cationic state are active for activating C-H bond of hydrocarbons.²⁵ Unfortunately, it typically does not activate molecular oxygen. As a complete oxidation of CH₄ involves both activation of C-H of CH₄ and O-O of O₂, neither CeO₂ nor NiO could exhibit high activity in complete oxidation of CH₄. Thus, here we prepared nanocomposite catalyst NiO/ CeO₂, in which a nanoparticle consists of CeO₂ nanorods with supported NiO nanoclusters. CeO₂ was synthesized through a

```
Received: January 17, 2018
Revised:
           February 21, 2018
Published: March 5, 2018
```

Downloaded via CHINESE ACADEMY OF SCIENCES on May 20, 2019 at 03:00:51 (UTC). See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

hydrothermal method reported in literature;^{26,27} then, the NiO nanoclusters were prepared by deposition-precipitation of Ni cations onto the surface of the as-prepared CeO₂ nanorods. A subsequent calcination at 500 °C in 5% O₂ atmosphere crystallized NiO nanoclusters. The integrated NiO/CeO₂ nanocomposite catalyst particles exhibit high activity for complete oxidation of methane at 350–600 °C. A catalyst nanoparticle consisting of a CeO₂ nanorod and supported NiO nanoclusters catalyzes the complete oxidation of methane through the synergistic effect of CeO₂ and NiO. It exhibits a much lower activation barrier and much higher turnover frequency (TOF) than pure CeO₂ and NiO/SiO₂. It exhibits a relatively low T_{50} (50% conversion of CH₄) compared to the reported CeO₂-based composite oxides.^{23,28–30} These studies clearly show the synergistic effect between NiO and CeO₂ in the catalyst 15.0 wt % NiO/CeO₂.

EXPERIMENTAL SECTION

Preparation of pure CeO₂, **15.0 wt % NiO/CeO**₂ and **15.0 wt % NiO/SiO**₂. Pure CeO₂ nanorods were prepared with a modified hydrothermal method. 10 mL of 0.4 mol/L cerium nitrate solution was added to 70 mL of NaOH aqueous solution (6.0 mol/L), followed by stirring at room temperature for 30 min. The resulting mixture was transferred to a Teflon-lined stainless steel autoclave, sealed and maintained in the autoclave at 120 °C for 24 h. After cooling to room temperature naturally, the product was collected by centrifugation and washed with deionized water several times, followed by drying in a 70 °C oven overnight. The obtained catalyst precursor was calcinated at 450 °C in static air for 3 h.

15.0 wt % NiO/CeO2 catalyst was prepared by the deposition precipitation method. In a typical synthesis, 1.0 g of CeO₂ nanorods was dispersed in 100 mL of deionized water under vigorous stirring to form a pale yellow suspension solution. Then, 10 mL of nickel nitrate aqueous solution (which contains 0.743 g of nickel nitrate hydrate) was introduced to the above solution. The resulting mixture was stirred thoroughly at room temperature for 2 h. Then, the pH of the mixture was adjusted to 10.0 by dropwise adding 1 mol/L sodium hydroxide aqueous solution, followed by stirring overnight. The asprepared catalyst precursor was collected by centrifugation, washed and dried in a 70 °C oven overnight. Finally, the above sample was calcinated at 400 °C in a 5% H₂ atmosphere for 1 h and then oxidized by O₂ at 500 °C for 1 h. 15.0 wt % NiO/SiO₂ was prepared under the same procedure as preparing the 15.0 wt % NiO/CeO₂ sample. The only difference was to change the CeO₂ nanorod supports to the fumed SiO₂ (0.014 μ m) from Sigma.

Ex Situ and in Situ Characterizations. Crystallographic structures of pure CeO₂ and 15.0 wt % NiO/CeO₂ catalysts were identified using X-ray diffraction with a Mo K α (λ = 0.710 73 Å) X-ray source. The size, morphology and lattice spacings of these catalysts were studied with the transmission electron microscope (JEOL JEM 2100F) operating at an accelerating voltage of 200 kV, housed in the Petersen Institute of Nanoscience and Engineering Nanofabrication and Characterization Facility of the University of Pittsburgh. Image analysis was performed using the Digital Micrograph software (Gatan, Inc.)

Temperature-programmed reduction (H₂-TPR) was carried out with a Micromeritics Autochem 2910 instrument equipped with a thermal conductivity detector (TCD). Typically, the catalyst (50 mg) was placed in a U-shaped quartz reactor and purged with N₂ to remove the air present in the lines. The catalyst was then heated to 250 °C for 30 min in N₂ with a flow rate of 40 mL/min and cooled to room temperature. The temperature was then raised from room temperature to 1000 °C at a rate of 10 °C min⁻¹ in a 5.0% H₂/N₂ flow (flow rate 30 mL min⁻¹) for the TPR experiment.

In situ/operando characterization of the surface of the 15.0 wt % NiO/CeO₂ catalyst during catalysis was carried out using the lab-based ambient pressure X-ray photoelectron spectroscopy (AP-XPS) system built by the Tao group.³¹ This AP-XPS uses a monochromated Al K α

X-ray source to generate photoelectrons. A new high-temperature reaction cell was designed and built by the Tao group.³¹ This homebuilt AP-XPS system equipped with a new reaction cell has been previously used in tracking the surface chemistry of catalysts under reaction conditions and during catalysis.^{25,32-41} The catalyst particles were loaded on a roughened silver foil affixed onto a sample holder. The sample in 1.0 Torr O2 was heated to 500 °C and held there for approximately 1 h to remove any carbon species on the catalyst surface. The progressive removal of surface carbon-containing species was monitored by continuously scanning the C 1s peak at 284.8 eV. Once the C 1s photoemission feature at this position completely disappeared, the sample was cooled to 150 °C. Then, 0.2 Torr CH₄ was added to 1.0 Torr O_2 to form a flowing mixture of CH_4 and O_2 in the reaction cell. The Ce 3d, Ni 2p, O 1s and C 1s spectra were collected from the catalyst surface at 150 °C, 200 °C, 300 °C, 400 °C or even a higher temperature while the catalyst remained in a flowing mixture of CH4 and O2. We used the satellite peak (u''') of Ce 3d photoemission features of Ce4+ as the internal reference of binding energies⁴²⁻⁴⁷ to calibrate the peak positions of all other spectra obtained in this work. The u'' was chosen because this satellite peak of Ce 3d of Ce³⁺ of CeO₂ is independent of surface defects. The peak position and shape of this peak does not change when the atomic ratio of Ce³⁺ to Ce⁴⁺ differs at different reaction and catalysis conditions.

Evaluation of Catalytic Performance of Complete Oxidation of Methane and Kinetics Studies. The catalytic performance for the complete oxidation of methane of this catalyst was studied using a fixed bed reactor. 100 mg of the catalyst was mixed with 300 mg of quartz sand and then loaded into a quartz tube reactor. A reactant mixture of 20 mL/min 10% CH₄/Ar and 10 mL/min pure O₂ was introduced to the reactor for the dry condition experiment. For the wet condition experiment, H₂O vapor with a partial pressure 30 times that of CH4 was added to the mixture of CH4 and O2 prior to introduction into the reactor.⁴⁸ Catalyst temperature was measured using a K-type thermocouple inserted into the catalyst bed. The catalysis temperature was maintained at a set point using a proportional-integral-derivative (PID) temperature controller. In order to make the catalytic conversion of CH₄ on different catalysts comparable, the same weight hourly space velocity (WHSV) of 18 000 $mL \cdot g^{-1} \cdot h^{-1}$ was used for each catalyst in this work (100 mg). Furthermore, different WHSV (18 000, 36 000, 100 000 and 200 000 mL·g $^{-1}$ ·h $^{-1}$) and a stoichiometric CH₄/O₂ mole ratio of 1:2 were used for comparison of the catalytic performance of methane complete oxidation of the 15.0 wt % NiO/CeO₂ catalyst at different conditions. Conversion of CH₄ was measured in the temperature range of 200 to 600 °C with an interval of 50 °C. Reactants and products of this catalysis process were monitored using an online gas chromatograph with a TCD. In order to keep the reaction in the kinetic regime under the same WHSV, conversions of CH₄ of these catalysts must be lower than 15%. Thus, we chose slightly different temperature ranges in order to keep conversion of CH₄ of the three catalysts below 15%.

RESULTS AND DISCUSSION

Crystalline Phase, Morphology and Reduction Property. Pure CeO₂ nanorods were synthesized by using a modified hydrothermal method in alkali condition that was described in the Experimental section. Then, the 15.0 wt % NiO/CeO₂ catalyst was prepared via a deposition precipitation method, followed by calcinating the synthesized precursor at 500 °C for 1 h. X-ray diffraction (XRD) patterns of the pure CeO₂ and 15.0 wt % NiO/CeO₂ catalysts are shown in Figure 1. The diffraction patterns of pure CeO₂ nanorods were consistent with the CeO₂ face-centered cubic phase (JCPDS 43-1002) with peaks at 12.9°, 14.9°, 21.2°, 24.9° and 30.1°, which can be assigned to (111), (200), (220), (311) and (400) planes, respectively (red pattern in Figure 1). After formation of NiO nanoclusters on CeO₂ nanorods to produce 15.0 wt% NiO/CeO₂, additional diffraction peaks appeared (marked with "#") at 16.8°, 19.5° and 27.7°. The three peaks can be assigned



Figure 1. XRD patterns of (a) pure ${\rm CeO}_2$ and (b) 15.0 wt % NiO/ ${\rm CeO}_2$ catalyst.

to the (111), (200) and (220) of NiO (JCPDS 47-1049). This confirms that the 15.0 wt % NiO/CeO₂ catalyst consists of both CeO₂ nanorods and the loaded NiO nanoclusters. The sizes of the CeO₂ nanorods and the supported NiO nanoclusters were estimated by the Debye–Scherrer Equation.

The morphologies of the pure CeO₂ and 15.0 wt % NiO/ CeO₂ catalysts were observed with transmission electron microscopy (TEM). The as-synthesized CeO₂ nanorods (e.g., Figure 2a,b) possessed diameters of 10 ± 2 nm and lengths of 60 ± 18 nm. The lattice spacings of the rods, measured via fast Fourier transform (FFT), were in excellent agreement with pure CeO₂ (e.g., Figure 2c).

Figure 2d,e shows TEM images of 15.0 wt % NiO/CeO₂ catalyst after catalysis. Compared to the as-synthesized pure CeO₂ nanorods in Figure 2a,b, the morphology of the used catalyst 15.0 wt % NiO/CeO₂ is different. After catalysis at 600 °C, the morphology of 15.0 wt % NiO/CeO₂ is basically

nanoparticles instead of the original nanorods. This is understandable because the used 15.0 wt % NiO/CeO₂ experienced reaction temperatures up to 600 °C. As shown in Figure 2d, the average size of nanoparticles of 15.0 wt % NiO/CeO_2 is 10–12 nm, which is similar to the diameter of the as-synthesized pure CeO2 nanorods. This lack of increase in size of the used 15.0 wt % NiO/CeO2 (10-12 nm) after catalysis suggests minimal sintering occurs, if any, during catalysis. Figure 2e is one representative TEM image of a nanocomposite NiO/CeO₂ nanoparticle, in which the (100) fringes of both the NiO nanoclusters and CeO₂ nanoparticle were clearly identifiable. Figure 2f is the Fourier transformation (FFT) of the selected region (white box in Figure 2e). The FFT spots of Figure 2f were consistent with NiO (100) and CeO_2 (100). Thus, these TEM studies clearly show the coexistence of NiO nanoclusters and CeO₂ nanoparticles and the formation of a NiO/CeO₂ interface. Figure 3 shows a CeO₂ nanoparticle with supported NiO nanoclusters from 15.0 wt % NiO/CeO_2 catalyst on which the interface between CeO_2 and NiO is marked with a blue curve.

The H₂-TPR experiments were conducted on pure CeO₂, commercial NiO and 15.0 wt % NiO/CeO₂ in parallel. As shown with the black line in Figure 4a, there are two reduction peaks in the profile of pure CeO₂. The peak at 175 °C can be ascribed to the reduction of surface lattice oxygen while the peak at 760 °C^{49,50} arises from the reduction of bulk CeO₂ to Ce₂O₃. For the commercial NiO (blue line), there are two reduction peaks at 355 and 548 °C, which correspond to the stepwise reduction of NiO.⁵¹

For the supported 15.0 wt % NiO/CeO₂ sample (red line in Figure 4a,b), two reduction peaks (α and β) were present in the temperature range of 100–400 °C during the H₂-TPR process. The shoulder (α) found at 194 °C is ascribed to the reduction



Figure 2. Transmission electron microscopy (TEM) studies of CeO_2 nanorods and postreaction catalyst 15.0 wt % NiO/CeO₂. (a) Large scale TEM image of pure CeO_2 nanorods. (b) High-resolution TEM image of pure CeO_2 nanorods. (c) Fast Fourier transforms (FFT) of the selected area marked with a red square of pure CeO_2 marked in panel b. (d) Large scale TEM image of nanocomposite 15.0 wt % NiO/CeO₂ particle. (e) High-resolution TEM images of postreaction nanocomposite 15.0 wt % NiO/CeO₂ particle. (f) Fast Fourier transforms (FFT) of the selected area marked with a white box of the postreaction nanocomposite 15.0 wt % NiO/CeO₂ particle in panel e.

ACS Sustainable Chemistry & Engineering



Figure 3. TEM image of 15.0 wt %NiO/CeO₂ catalyst nanoparticles consisting of CeO₂ nanoparticles with supported NiO nanocluster. The interface is marked by the blue curve. The exposed surface of CeO₂ and NiO is (100) based on the spacing and orientation of the lattice fringes. The size of the image is 20 nm × 20 nm.

of active surface oxygen species bonded to Ni cations. These oxygen atoms are different from the original surface lattice oxygen atoms of pure CeO₂ due to the smaller radius and different oxidation state of Ni²⁺ compared to Ce⁴⁺. The unbalanced charge and lattice distortion occurring in the CeO₂ lattice gives rise to the shoulder. The low reduction temperature of the oxygen atoms at the interface of NiO and CeO₂ suggests these interfacial oxygen atoms have a high activity. As reported in literature that the active oxygen species played an important role in alkane oxidation,⁵² the active oxygen species formed at the interface of NiO and CeO₂ may lead to an easier oxidation of CH₄.

Based on the observed structure of the catalyst, the asymmetric β peak at 246 °C was attributed to the reduction of NiO nanoclusters supported on the CeO₂. Similarly, the peak at 760 °C of 15.0 wt % NiO/CeO₂ (red spectrum in Figure 4a) can be attributed to the reduction of CeO₂ to Ce₂O₃. Thus, the H₂-TPR results of the three catalysts suggest the incorporation of some Ni²⁺ cations of NiO into the surface lattice of CeO₂ at the interface of NiO and CeO₂ and high activity of the oxygen atoms at this interface.

Catalytic Activity and Kinetic Study. To explore the potential synergetic effect between NiO and CeO₂, catalytic performances of the three catalysts, NiO/SiO₂, CeO₂ and NiO/CeO₂ were studied under the same catalytic conditions and WHSV. Conversions of CH₄ through complete oxidation on the three catalysts (100 mg of CeO₂, 100 mg of 15.0 wt %

 NiO/SiO_2 and 100 mg of 15.0 wt % NiO/CeO_2) as a function of temperature over the range of 200–600 °C are plotted in Figure 5. For 100 mg of 15.0 wt % NiO/CeO_2 catalyst,



Figure 5. Catalytic performance of 100 mg of pure CeO₂ nanorod, 100 mg of 15.0 wt % NiO/CeO₂ and 100 mg of 15.0 wt % NiO/SiO₂ for complete oxidation of methane. Weight hourly space velocity (WHSV) was 18 000 mL·g^{-1·h⁻¹, 100 mg catalyst.}

conversion of CH₄ reached 12.3% at 400 °C, 74.6% at 500 °C, and 98.5% at 600 °C, which were much higher than the conversions of 4.3% at 400 °C, 25.9% at 500 °C and 72% at 600 °C with 100 mg of pure CeO₂ catalyst. The increased conversion shows that NiO plays a significant role in the complete oxidation of methane on 15.0 wt % NiO/CeO₂.

The conversion of CH₄ on 15.0 wt % NiO/CeO₂ was also much higher than 15.0 wt % NiO/SiO₂ in the temperature range of 400–600 °C, suggesting that CeO₂ plays an important role in the catalysis, as well. The 50% conversion of CH₄ on 15.0 wt % NiO/CeO₂ was achieved at a temperature of 465 °C (T_{50}) at a WHSV of 18 000 mL·g⁻¹·h⁻¹ (Figure 5); however, the T_{50} of 100 mg of pure CeO₂ was as high as 555 °C under the same WHSV. This indicates that NiO clearly participated in the reaction and enhanced the activity of the CeO₂ nanorods.

Notably, the above comparisons did not consider the number of sites of these catalysts. To check whether there is an intrinsic difference between NiO/CeO₂ and NiO/SiO₂ and between NiO/CeO₂ and pure CeO₂, kinetics studies were performed on the three catalysts. In all these kinetics studies, the conversions of CH₄ were controlled at 15% or less. Figure 6 is the Arrhenius plots of 15.0 wt % NiO/CeO₂, pure CeO₂, and 15.0 wt % NiO/ SiO₂. To make sure that the conversions of CH₄ on all the three catalysts were lower than 15% under the same WHSV, the kinetics on the three catalysts were performed in three



Figure 4. H₂-TPR profiles of pure CeO₂ (black), commercial NiO (blue) and 15.0 wt % NiO/CeO₂(red). (a) 100–1000 °C of the three catalysts. (b) 100–400 °C of the 15.0 wt % NiO/CeO₂.



Figure 6. Arrhenius plots of complete oxidation of methane on catalysts of pure CeO_2 , 15.0 wt % NiO/CeO₂ and 15.0 wt % NiO/SiO₂. In terms of ln *X*, *X* is conversion of methane. Conversion of CH₄ on these catalysts in all their corresponding temperature ranges in this figure are lower than 15%.

slightly different temperature ranges: 340-420 °C for the 15.0 wt % NiO/CeO₂, 380-460 °C for pure CeO₂, and 440-520 °C for 15.0 wt % NiO/SiO₂. The apparent activation energies calculated from the Arrhenius plots were 69.4 ± 4.0 kJ/mol for 15.0 wt % NiO/CeO₂, 95.1 ± 5.0 kJ/mol for pure CeO₂ and 98.4 ± 5.0 kJ/mol for 15.0 wt % NiO/CeO₂ had the lowest apparent activation barrier among the three, confirming the synergistic effect between NiO nanoclusters and CeO₂ nanorods for the oxidation of CH₄.

Turnover Frequency of NiO/CeO₂, Pure CeO₂ and NiO/SiO₂ and Active Sites of NiO/CeO₂. To further confirm the synergistic effect of NiO and CeO₂, turnover frequencies of the three catalysts in terms of the number of converted CH₄ molecules on each site per minute were calculated with the conversion of CH₄ in the kinetically controlled regime. The number of converted CH₄ molecules per 1 min on 0.100 g catalyst can be calculated with eq 1 according to the number of the fed CH₄ molecules (N_{CH_4}) per minute and the conversion rate of CH₄ (X_{CH_4}) at a given reaction temperature.

 $N_{
m number\,of\,converted\,CH_4}$

$$= N_{\rm CH_4} \times X_{\rm CH_4}$$
$$= N_{\rm A} \times \frac{pV}{RT} \times 0.1 \times X_{\rm CH_4}$$
(1)

where $N_{\rm A}$ is Avogadro's constant (6.022 × 10²³ mol⁻¹), *p* is the pressure of the gas, *R* is the ideal gas constant, *T* is the temperature of the gas and *V* is the partial volume of the fed total gases that pass the catalyst in 1 min. *V* is calculated with the equation: 10% CH₄ × 20 mL/min × $\frac{1 \text{ L}}{1000 \text{ mL}}$. By substituting $N_{\rm A}$, *p*, *V*, *R* and *T* into eq 1, $N_{\rm number of converted CH_4}$ can be calculated by eq 2.

$$N_{\text{number of converted CH}_4} = 5.01 \times 10^{19} \times X_{\text{CH}_4}$$
(2)

Turnover frequency can be calculated by dividing $N_{\rm number\ of\ converted\ CH_4}$ with the number of catalytic sites.

Turnover Frequency of Pure CeO₂. Extensive TEM study of postreaction CeO₂ nanoparticles suggests the predominant exposed facet is (100). Because the measured interplanar distance of (100) is 0.27 nm, the atom density of Ce on the

CeO₂ surface in terms of the number of Ce atoms per m² is the area occupied by each Ce atom of CeO₂ (100) $\rho_{Ce} = \frac{2Ce \text{ atom each } 2D \text{ unit cell}}{29.89 \times 10^{-20} \text{ m}^2 \text{ of each } 2D \text{ unit cell}} . \text{ The measured surface area}$ $= 6.69 \times 10^{18} \text{ Ce atom perm}^2$

$$= 6.69 \times 10^{10}$$
Ce atom perm²

(S) from BET characterization was 82.0 m²·g⁻¹. The total number of Ce sites (N_{Ce}) of 100 mg CeO₂ can then be calculated with eq 3.

$$N_{\rm Ce} = \rho_{\rm Ce} \times S \times W \tag{3}$$

In eq 3, ρ_{Ce} , *S* and *W* are the density of Ce atom of CeO₂ (100) in unit m⁻², surface area in unit m²·g⁻¹, and weight in unit *g*, respectively. For 0.100 g of CeO₂, the total number of Ce atoms on the surface of CeO₂ is 5.4858 × 10¹⁹. The TOF of pure CeO₂ can be calculated with eq 4.

$$TOF_{CeO_2} = \frac{N_{converted methane molecules}}{N_{number of Ce atoms on surface}}$$
(4)

By substituting eq 2 and eq 3 into eq 4, the TOF of CeO_2 can be directly calculated from the conversion of CH_4 obtained in the kinetically controlled regime with eq 5

$$TOF_{CeO_2} = \frac{5.01 \times 10^{19} \times X_{CH_4}}{\rho_{Ce} \times S \times W} = 0.91 \times X_{CH_4}$$
(5)

Using the conversion of CH_4 on 100 mg of CeO_2 at different temperatures, TOF_{CeO_2} was calculated with eq 5 and plotted in Figure 7.



Figure 7. Turnover frequencies (TOFs) of methane oxidation on 15.0 wt % NiO/CeO₂ (red); pure CeO₂ (black) and 15.0 wt % NiO/SiO₂ (blue) measured in a kinetics-controlled regime.

Turnover Frequency of 15.0 wt % NiO/SiO₂. TEM examination also revealed that the predominant exposed surface of the postreaction NiO nanoparticles was (100). Thus, NiO(100) was used to calculate the TOF of NiO/SiO₂ nanoparticle catalyst. On the NiO(100) plane, the area of each 2-D unit cell was calculated to be 17.67 × 10⁻²⁰ m². So, the atom density of Ni on each m² of NiO (100), ρ_{Ni} is $\frac{2\text{Ni} \text{ atom each } 2\text{D} \text{ unit cell}}{17.67 \times 10^{-20} \text{ m}^2 \text{ of each } 2\text{ D} \text{ unit cell}} = 1.13 \times 10^{19} \text{ Ni} \text{ atom per m}^2$.

From XRD, the size of NiO nanoparticles according to the Scherrer equation was calculated as 14.6 nm. For convenience, the morphology of the NiO nanoclusters was assumed to be a nanocube for the calculations. For each nanocube, the exposed surface area $A_{\text{each NiO NP}}$ is five times of the surface area of each plane of a nanocube, $5 \times (14.6 \times 10^{-9} \text{ m})^2 = 1.066 \times 10^{-15} \text{ m}^2$.

The number of Ni in each NiO nanocube can be calculated with eq 6.

$$N_{\text{each NiO NC}} = \rho_{\text{Ni}} \times A_{\text{each NiO NC}}$$
(6)

.From eq 6, the calculated number of Ni atoms in each NiO nanocube with size of 14.6 nm, $N_{\text{each NiO NC}}$ is 1.21×10^4 . In 0.100 g 15.0 wt % NiO/SiO₂, the number of NiO nanocube (N_{cube}) can be calculated with eq 7.

$$N_{\text{number of NiO NCs}} = \frac{W_{\text{NiO catalyst}}}{W_{\text{NiO NC}}} = \frac{W_{\text{NiO catalyst}}}{V_{\text{NiO NC}} \times D_{\text{NiO}}}$$
(7)

For the 0.100 g 15.0 wt % NiO/SiO₂, the calculated $N_{\text{number of NiO NPs}}$ is 7.23× 10¹⁴ upon substituting 0.015 g for $W_{\text{NiO catalystr}}$ 3.11 × 10⁻¹⁸ cm³ for $V_{\text{NiO NP}}$, and 6.67g·cm⁻³ for D_{NiO} into eq 7. Thus, the total number of Ni atoms on the surface of 0.100 g 15.0 wt % NiO/SiO₂ can be calculated by 7.23× 10¹⁴ NiO NPs × 1.21 × 10⁴ Ni atoms/NiO NP, which yields 8.7483 × 10¹⁸ Ni atoms. Then, the TOF of 15.0 wt % NiO/SiO₂ can be calculated with eq 8.

$$TOF_{NiO} = \frac{N_{converted methane molecules}}{N_{number of Ni atoms on surface of NiO}}$$
$$= \frac{5.01 \times 10^{19} \times X_{CH_4}}{N_{number of Ni atoms on surface of NiO}}$$
(8)

With eq 8, the TOF of 15.0 wt % NiO/SiO₂ is $5.73 \times X_{CH_4}$.

Turnover Frequency of 15.0 wt % NiO/CeO₂. The active site of the 15.0 wt % NiO/CeO₂ system was assumed to be the Ni site at the interface between NiO and CeO₂. The interface is schematically shown in Figure 8. The number of interfacial Ni



Figure 8. Schematic briefly showing activations of C–H of CH₄ and O–O of O₂ and coupling between CH_x species and atomic oxygen at the interface of NiO/CeO₂ on 15.0 wt % NiO/CeO₂ catalyst.

sites of per NiO cube supported on a CeO_2 particle can be calculated with eq 9.

$$N_{\text{Number of Ni atoms at the interface of each NiO NP}} = \frac{\text{Length of interface}}{\text{Distance of Ni-O bond}}$$
(9)

The interfacial perimeter of a NiO nanocluster supported on CeO₂ is four times of the side length of a nanocube, $4 \times (14.6 \times 10^{-9} \text{ m})$. The length of a Ni–O bond is 2.012×10^{-10} m. Thus, there are 277.8 Ni atoms at the interfacial perimeter of a NiO nanocube and CeO₂ particle. The total number of Ni atoms at the interfaces of NiO nanocubes and CeO₂ particles in 0.100 g 15.0 wt % NiO/CeO₂ can be calculated with eq 10.

 $Ni_{number of Ni atoms} = N_{number of Ni atoms at the interface of each NiO NP}$

$$\times N_{\text{number of NiO NP}}$$
 (10)

From eq 10, the number of Ni atoms at the interface between NiO and CeO₂ was calculated to be $7.23 \times 10^{14} \times 277.8 = 2.008 \times 10^{17}$. Thus, the TOF of 15.0 wt % NiO/CeO₂ can be calculated with eq 11

$$TOF_{NiO} = \frac{N_{converted methane molecules}}{N_{number of Ni atoms at interface}}$$
$$= \frac{5.01 \times 10^{19} \times X_{CH_4}}{N_{number of Ni atoms at interface}}$$
(11)

The TOF values for different temperatures were calculated and, as Figure 7 shows, the NiO/CeO₂ catalyst has much more higher TOF values than pure CeO₂ and NiO/SiO₂.

Catalytic Performance and Stability of NiO/CeO₂ under Other Catalytic Conditions. In order to examine what roles the CH_4/O_2 molar ratio, WSHV and addition of water^{22,48,53-55} might play in the complete oxidation of methane with 15.0 wt% NiO/CeO2, tests were conducted under a range of reaction conditions. As displayed in Figure 9a, when the molar ratio of CH_4/O_2 was changed from 1:5 to 1:2 (10 mL/min 10% CH₄/Ar and 20 mL/min 10% O₂) and the WHSV remained at 18 000 mL/g/h, NiO/CeO₂ exhibited the same catalytic performance (the red and blue lines in Figure 9a). In addition, upon increasing the WHSV from 18 000 to 36 000 mL·g⁻¹·h⁻¹ while the $CH_4:O_2$ remained at 1:5, the methane conversion decreased slightly to 96% at 600 °C (the red and orange lines in Figure 9a). When the WHSV was further increased to 100 000 mL·g⁻¹·h⁻¹ and the CH₄:O₂ remained at 1:5 (the dark cyan line in Figure 9a), the lightoff temperature of methane oxidation reaction on the catalyst of 15.0 wt % NiO/CeO₂ shifted to a higher temperature and the conversion of CH₄ reached 98% at 700 °C. When the WHSV was increased to 200 000 $mL{\cdot}g^{-1}{\cdot}h^{-1}$ (the pink line in Figure 9a), the light-off temperature further increased. Figure 9a suggests that a change of WHSV can vary the light-off temperature of the catalyst. A similar correlation between WHSV and light-off temperature was demonstrated earlier by Cargnello and co-workers in the complete oxidation of methane on their modular Pd@CeO2 subunits on functionalized Al₂O₃.^{22,55}

Water vapor is a significant portion of the actual exhaust of combustion engines. Its partial pressure in the exhaust is 30 times that of the CH₄. To evaluate the catalytic performance of a catalyst in exhaust containing water vapor, water vapor was introduced at a gas mixture ratio of $CH_4:O_2:H_2O:Ar$ at 1:2:30:27. Compared to the WHSV (18 000 mL·g⁻¹·h⁻¹) at dry condition (ratio of partial pressures of $CH_4:O_2:H_2O:Ar$ at 1:2:0:27), the conversion of CH_4 at wet condition decreased by nearly 10% at 600 °C, as shown in Figure 9b. By increasing the dosage of catalyst to 200 mg, the WHSV was decreased to 9000 mL·g⁻¹·h⁻¹. Compared to the WHSV at 18 000 mL·g⁻¹·h⁻¹ under wet condition (purple line in Figure 9b), CH₄ conversion was increased (dark cyan line in Figure 9b) when WHSV was 9000 mL·g⁻¹·h⁻¹.

The catalytic stability of 15.0 wt % NiO/CeO₂ catalyst was investigated at 500 °C in the mixture of 10 mL/min 10% CH₄/ Ar and 20 mL/min 10% O₂/Ar for 4 days. As shown in Figure 10, there was only minor change in the conversion of CH₄ in the first 24 h, suggesting that this catalyst exhibits a relatively



Figure 9. (a) Different weight hourly space velocity (WHSV) of 18 000 mL·g⁻¹·h⁻¹ (red line), 36 000 mL·g⁻¹·h⁻¹ (orange line), 100 000 mL·g⁻¹·h⁻¹ (dark cyan line), 200 000 mL·g⁻¹·h⁻¹ (pink line) and stoichiometric ratio of O₂/CH₄ (2:1) (blue line) were used for complete oxidation of menthane on 15.0 wt % NiO/CeO₂ catalyst. (b) Wet condition [CH₄:O₂:H₂O:Ar = 1:2:30:27] for complete oxidation of menthane on 15.0 wt % NiO/CeO₂ catalyst with different WHSV of 18 000 mL·g^{-1·h⁻¹ (purple line) and 9000 mL·g⁻¹· h⁻¹ (dark cyan) was used for comparison with the dry condition (blue line).}



Figure 10. Stability test of 0.100 g 15.0 wt % NiO/CeO₂ at 500 °C (weight hourly space velocity of 18 000 mL·g $^{-1}$ ·h⁻¹).

high stability over 1 day under high temperature treatment. It decreased by 4.9% after 48 h. The deactivation could be due to changes in surface structure and morphology at high temperature during catalysis, as dynamic structural evolution of a similar system, supported palladium–ceria core–shell catalysts, has been reported in literature.⁵⁶ Catalyst stability is a key development issue for an industrial catalyst. The deactivation of the catalyst by impurities in the exhaust gas must be considered. For instance, H₂O, sulfur, phosphorus or even boron can largely deactivate a catalyst during complete oxidation of methane of exhaust gas.^{57,58} The stability of our catalyst would certainly need to be enhanced before the 15.0 wt % NiO/CeO₂ could be commercialized. As the focus of this work is the

demonstration of the synergistic effect of NiO and CeO_2 for the complete oxidation of methane, we plan to explore how to increase stability of the catalyst in subsequent studies.

In Situ/Operando Studies of Surface of the 15.0 wt % NiO/CeO₂ Catalyst during the Catalytic Process. The surface of nanocomposite 15.0 wt % NiO/CeO2 catalyst particles during catalysis was examined with the AP-XPS built by the Tao group.⁵⁹⁻⁶¹ Figure 11a,b,c,d are the photoemission features of Ce 3d, Ni 2p, O 1s and C 1s, respectively, in the temperature range of 150-500 °C under catalytic condition. The photoemission features of Ce 3d consist of ten peaks. The six peaks at 882.6, 889.0, 898.6, 900.9, 907.7 and 916.9 eV are characteristic satellite peaks (v, v", v"", u, u" and u"") for Ce 3d for the Ce^{4+} of CeO_2 . The other four peaks at, 880.6, 885.2, 899.2 and 904.0 eV, are characteristic satellite peaks of Ce 3d of Ce^{3+} (v_{o} , v', u_o and u').^{42–47} As we can see from Figure 11a, there is a deep valley located between v and v" peak of Ce 3d of Ce⁴⁺ in the 15.0 wt % NiO/CeO₂ spectra in the temperature range of 100 to 500 °C. This indicates a lack of v' peak of Ce³⁺ in the 15.0 wt % NiO/CeO₂ catalyst during catalysis; were Ce³⁺ cations present, the valley should have been partially or even fully filled. Larger proportions of Ce³⁺ yields a shallower valley. The obvious lack of photoemission features between v and v" peaks of Ce 3d of Ce^{4+} in Figure 11a suggests a lack of Ce^{3+} on the NiO/CeO₂ surface during complete oxidation of CH₄.

In the Ni 2p spectra of 15.0 wt % Ni/CeO₂ (Figure 11b), peaks at 854.8 and 861.0 eV correspond to the main peak and satellite peak of Ni 2p_{3/2} of NiO. The peak at 872.6 eV is



Figure 11. Photoemission surface spectra of 15.0 wt % NiO/CeO₂ with a 1:5 pressure ratio of CH₄ and O₂ reactants in the temperature range of 150–500 °C. (a) Ce 3d, (b) Ni 2p, (c) O 1s and (d) C 1s of 15.0 wt % NiO/CeO₂ during catalysis.

attributed to the main and satellite peak of Ni $2p_{1/2}$ of NiO according to literature. $^{62-65}$ The satellite peak of Ni $2p_{1/2}$ was not collected owing to the overlap with the Ce 3d peaks of CeO₂.

The O 1s spectra are shown in Figure 11c. The major peak at 529.8 eV is attributed to the lattice oxygen at the surface region of NiO and CeO₂. A shoulder at 531.8 eV was clearly observed across the whole temperature range of 150-500 °C. This shoulder could be contributions from OH groups formed on the surface of CeO₂ or/and nonstoichiometric oxygen atoms binding to the Ce³⁺ due to oxygen vacancies in CeO₂.^{66–70} As discussed above, there is a lack of Ce³⁺ during catalysis. Thus, the O 1s shoulder cannot be assigned to the nonstoichiometric oxygen atoms; it is instead assigned to the OH groups. The double peaks at 538.2 eV can be attributed to photoelectrons generated from gas phase molecules of O₂ around the catalyst NiO/CeO₂.^{70–72} The observation of the O 1s peak of gas phase O₂ confirmed that the catalyst nanoparticles were in the gas phase of reactants during AP-XPS studies.

A fundamental understanding of a catalytic reaction can be achieved through computational studies. There are many potential reaction pathways that computational studies could propose, and in each of these possible reaction pathways their intermediates and transition states are typically different. Experimental observation of stable intermediates would greatly assist the effective computational screening of possible reaction pathways to find the one closest to reality. Here, the stable intermediate is prepared to be a surface species that is formed at a relatively low temperature. At this temperature, the intermediate forms but cannot cross the activation barrier leading to the next intermediate due to the relatively high activation barrier (from the observed stable intermediate to the next intermediate) and cannot cross the activation barrier of the rate-determining step of this catalytic reaction. Thus, this intermediate stays on the surface at a relatively low temperature. Similarly, its intensity should decrease with increasing reaction temperature, eventually disappearing as the intermediates can overcome the barrier to form other intermediates or products.

Infrared spectroscopy (IR) is an appropriate technique to identity carbon-containing species; however, the significant contribution of gas phase reactants to the signal makes differentiation between adsorbed intermediate and gas phase reactants very challenging, and thus the study of adsorbates during catalysis likewise challenging. One compromise method is to purge reactant gases after reaction and then examine the surface adsorbates. Compared to in situ IR, AP-XPS allows the identification of adsorbates on the surface when the catalyst remains in the mixture of reactants. This is because the signal from gaseous reactants is typically quite weak and possess very different binding energies in an XPS spectrum, rendering them readily distinguishable.

Using our home-built AP-XPS system, we studied the surface chemistry of the NiO/CeO₂ catalyst during catalysis to track the evolution of stable intermediates formed at a relatively low temperature. The C 1s spectrum was collected as a function of temperature since a stable intermediate must contain carbon atom(s). This was performed under 1 Torr O₂ at 500 °C and in the mixture of 0.2 Torr CH₄ and 1 Torr O₂ at 150, 200, 300 and 400 °C. As the Ce 4s photoemission feature is at about 290 eV, the photoemission feature of C 1s was shown as a difference spectra. By taking the photoemission intensity of C 1s (in O₂ at 500 °C) before the introduction of CH₄ as a

reference, the difference spectra of photoemission features in the energy window of 283.5–293 eV at 150 °C, 200, 300 and 400 °C were calculated (Figure 11d). As shown in Figure 11d1, a carbon-containing species was observed at 150 °C. Its relative intensity, $\frac{A_{C \text{ 1s}}}{A_{C e \text{ 3d}}}$ plotted in Figure 11d1, increased when the sample temperature was increased to 200 °C, then decreased at 300 °C before completely disappearing at 400 °C. The positions of C 1s photoemission features at 150–300 °C remained at around 285.3–285.8 eV. The observed evolution of the intensity of C 1s photoemission features and preservation of peak position were consistent with the typical temperature-dependent evolution of an intermediate reaction pathway. On the basis of existing reports in literature, we deduce that the peak at 285.3–285.8 eV observed at 150–200 °C is the CH₃ intermediate bound to a Ni cation.^{73–75}

The evolution of C 1s photoemission features with increasing catalyst temperature supports the formation of a stable intermediate in the low temperature region around 150 °C (Figure 11d1). For complete oxidation of methane on 15.0 wt % NiO/CeO₂, the intermediate can cross the energy barrier to form the next intermediate or even product molecule when the temperature increases. The identified temperature of transformation of the stable intermediate at 300–400 °C by AP-XPS in Figure 11d1 is consistent with the observed increase in catalytic activity at 400 °C or so as shown in Figure 5. Notably, this stable intermediate formed on NiO/CeO₂ (H₃C–Ni) is different from the OCHO stable intermediate formed on the surface of NiCo₂O₄ during the catalytic oxidation of methane.²⁵

It is likely that the C–H of CH₄ was activated on the Ni–O species, forming a H₃C–Ni– intermediate on the surface at relatively low temperature. The formed CH₃ could be further activated to form CH₂ or even CH species. The CH_x species could couple with surface lattice oxygen atoms to form CO₂ and H₂. H₂ TPR studies suggest that oxygen atoms at the NiO/CeO₂ interface have high activity and thus participate into this coupling between CH_x and atomic oxygen. Figure 8 is a schematic showing the reaction performed at the interface.

SUMMARY

A nanocomposite catalyst of 15.0 wt % NiO/CeO₂ synthesized through a two-step method exhibits notably higher activity than pure CeO₂ and 15.0 wt % NiO/SiO₂ for the complete oxidation of methane in the temperature range of 200–600 °C under the same catalytic conditions. Kinetic studies show that the 15.0 wt % NiO/CeO₂ has the lowest apparent activation energy (69.4 \pm 4 kJ/mol) compared to pure CeO $_2$ (95.1 \pm 5 kJ/mol) or 15 wt% NiO/SiO₂ (98.4 \pm 5 kJ/mol). This distinct difference in apparent activation barriers of these catalysts indicates that NiO nanoclusters and CeO₂ nanorods have a synergistic effect for the oxidation of methane. The interface between NiO nanoclusters and CeO₂ nanorods was characterized with highresolution TEM. The formation of a stable H₃C-like intermediate bound to the Ni cation at a relative low temperature was confirmed by the evolution of C 1s photoemission features with increasing catalyst temperature under reaction condition. This stable intermediate formed on NiO/CeO₂ is different from the OCHO intermediate formed on NiCo₂O₄ catalysts and suggests that the complete oxidation of CH₄ on NiO/CeO₂ follows a reaction mechanism different from that of NiCo₂O₄.

ACS Sustainable Chemistry & Engineering

AUTHOR INFORMATION

Corresponding Authors

*Email: franklin.feng.tao@ku.edu (F.T.). *Email: sunzc@bjut.edu.cn (Z.S.).

ORCID 0

Stephen D. House: 0000-0003-2035-6373 Yu Tang: 0000-0001-9435-9310 Adedamola A. Opalade: 0000-0001-8508-2807 Zaicheng Sun: 0000-0002-7059-3177

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was performed at University of Kansas. It was mainly supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences and Biosciences Division under Award Number DE-SC0014561 and partially National Science Foundation under the Grant Number NSF-OIA-1539105. S.D.H. and J.C.Y. acknowledge the support of NSF DMREF through contract No. CHE-1534630.

REFERENCES

(1) Solomon, S. Climate change 2007-the physical science basis; Working group I contribution to the fourth assessment report of the IPCC; Cambridge University Press: 2007; Vol. 4.

(2) Choudhary, T.; Banerjee, S.; Choudhary, V. Catalysts for combustion of methane and lower alkanes. *Appl. Catal., A* **2002**, 234 (1), 1–23.

(3) Gélin, P.; Primet, M. Complete oxidation of methane at low temperature over noble metal based catalysts: a review. *Appl. Catal., B* **2002**, *39* (1), 1–37.

(4) Chen, J.; Arandiyan, H.; Gao, X.; Li, J. Recent advances in catalysts for methane combustion. *Catal. Surv. Asia* **2015**, *19* (3), 140–171.

(5) Trimm, D. t. Catalytic combustion. Appl. Catal. 1983, 7 (3), 249–282.

(6) Pfefferle, L.; Pfefferle, W. Catalysis in combustion. *Catal. Rev.: Sci. Eng.* **1987**, 29 (2–3), 219–267.

(7) Farrauto, R. J. Low-temperature oxidation of methane. *Science* **2012**, 337 (6095), 659–660.

(8) Bendtsen, A. B.; Glarborg, P.; Dam-Johansen, K. Low temperature oxidation of methane: the influence of nitrogen oxides. *Combust. Sci. Technol.* **2000**, *151* (1), 31–71.

(9) Widjaja, H.; Sekizawa, K.; Eguchi, K. Low-temperature oxidation of methane over Pd supported on SnO2-based oxides. *Bull. Chem. Soc. Jpn.* **1999**, 72 (2), 313–320.

(10) Sekizawa, K.; Widjaja, H.; Maeda, S.; Ozawa, Y.; Eguchi, K. Low temperature oxidation of methane over Pd catalyst supported on metal oxides. *Catal. Today* **2000**, *59* (1), 69–74.

(11) Arendt, E.; Maione, A.; Klisinska, A.; Sanz, O.; Montes, M.; Suarez, S.; Blanco, J.; Ruiz, P. Structuration of Pd (2 wt%)/Fe– Al oxide catalysts on ceramic and metallic monoliths: physicochemical characterization, effect of the nature of the slurry, and comparison with LaMnO3 catalysts. J. Phys. Chem. C 2009, 113 (37), 16503–16516.

(12) Eguchi, K.; Arai, H. Low temperature oxidation of methane over Pd-based catalysts—effect of support oxide on the combustion activity. *Appl. Catal., A* **2001**, *222* (1), 359–367.

(13) Gelin, P.; Urfels, L.; Primet, M.; Tena, E. Complete oxidation of methane at low temperature over Pt and Pd catalysts for the abatement of lean-burn natural gas fuelled vehicles emissions: influence of water and sulphur containing compounds. *Catal. Today* **2003**, 83 (1), 45–57.

(14) Fujimoto, K.-i.; Ribeiro, F. H.; Avalos-Borja, M.; Iglesia, E. Structure and reactivity of PdOx/ZrO2Catalysts for methane oxidation at low temperatures. *J. Catal.* **1998**, *179* (2), 431–442.

(15) Yoshida, H.; Nakajima, T.; Yazawa, Y.; Hattori, T. Support effect on methane combustion over palladium catalysts. *Appl. Catal., B* **2007**, *71* (1), 70–79.

(16) Strobel, R.; Grunwaldt, J.-D.; Camenzind, A.; Pratsinis, S. E.; Baiker, A. Flame-made alumina supported Pd–Pt nanoparticles: structural properties and catalytic behavior in methane combustion. *Catal. Lett.* **2005**, *104* (1), 9–16.

(17) Liotta, L.; Di Carlo, G.; Pantaleo, G.; Deganello, G. Catalytic performance of Co 3 O 4/CeO 2 and Co 3 O 4/CeO 2–ZrO 2 composite oxides for methane combustion: influence of catalyst pretreatment temperature and oxygen concentration in the reaction mixture. *Appl. Catal., B* 2007, 70 (1), 314–322.

(18) Royer, S.; Duprez, D.; Can, F.; Courtois, X.; Batiot-Dupeyrat, C.; Laassiri, S.; Alamdari, H. Perovskites as substitutes of noble metals for heterogeneous catalysis: dream or reality. *Chem. Rev.* **2014**, *114* (20), 10292–10368.

(19) Choudhary, V. R.; Uphade, B. S.; Pataskar, S. G.; Keshavaraja, A. Low-Temperature Complete Combustion of Methane over Mn-, Co-, and Fe-Stabilized ZrO2. *Angew. Chem., Int. Ed. Engl.* **1996**, 35 (20), 2393–2395.

(20) Jiang, Z.; Yu, J.; Cheng, J.; Xiao, T.; Jones, M. O.; Hao, Z.; Edwards, P. P. Catalytic combustion of methane over mixed oxides derived from Co-Mg/Al ternary hydrotalcites. *Fuel Process. Technol.* **2010**, *91* (1), 97–102.

(21) Xiao, L.-h.; Sun, K.-p.; Xu, X.-l.; Li, X.-n. Low-temperature catalytic combustion of methane over Pd/CeO 2 prepared by deposition–precipitation method. *Catal. Commun.* **2005**, *6* (12), 796–801.

(22) Cargnello, M.; Jaén, J. D.; Garrido, J. H.; Bakhmutsky, K.; Montini, T.; Gámez, J. C.; Gorte, R.; Fornasiero, P. Exceptional activity for methane combustion over modular Pd@ CeO2 subunits on functionalized Al2O3. *Science* **2012**, *337* (6095), 713–717.

(23) Liotta, L.; Di Carlo, G.; Pantaleo, G.; Venezia, A.; Deganello, G. Co 3 O 4/CeO 2 composite oxides for methane emissions abatement: relationship between Co 3 O 4–CeO 2 interaction and catalytic activity. *Appl. Catal., B* **2006**, *66* (3), 217–227.

(24) Montini, T.; Melchionna, M.; Monai, M.; Fornasiero, P. Fundamentals and catalytic applications of CeO2-based materials. *Chem. Rev.* **2016**, *116* (10), 5987–6041.

(25) Tao, F. F.; Shan, J. J.; Nguyen, L.; Wang, Z. Y.; Zhang, S. R.; Zhang, L.; Wu, Z. L.; Huang, W. X.; Zeng, S. B.; Hu, P. Understanding complete oxidation of methane on spinel oxides at a molecular level. *Nat. Commun.* **2015**, *6*, DOI: 10.1038/ncomms8798.

(26) Xu, Q.; Lei, W.; Li, X.; Qi, X.; Yu, J.; Liu, G.; Wang, J.; Zhang, P. Efficient removal of formaldehyde by nanosized gold on well-defined CeO2 nanorods at room temperature. *Environ. Sci. Technol.* **2014**, *48* (16), 9702–9708.

(27) Liu, X.; Zhou, K.; Wang, L.; Wang, B.; Li, Y. Oxygen vacancy clusters promoting reducibility and activity of ceria nanorods. *J. Am. Chem. Soc.* **2009**, *131* (9), 3140–3141.

(28) Liotta, L.; Di Carlo, G.; Pantaleo, G.; Deganello, G. Co 3 O 4/ CeO 2 and Co 3 O 4/CeO 2–ZrO 2 composite catalysts for methane combustion: correlation between morphology reduction properties and catalytic activity. *Catal. Commun.* **2005**, *6* (5), 329–336.

(29) Bozo, C.; Guilhaume, N.; Garbowski, E.; Primet, M. Combustion of methane on CeO 2–ZrO 2 based catalysts. *Catal. Today* **2000**, *59* (1), 33–45.

(30) Pakulska, M. M.; Grgicak, C. M.; Giorgi, J. B. The effect of metal and support particle size on NiO/CeO 2 and NiO/ZrO 2 catalyst activity in complete methane oxidation. *Appl. Catal., A* **2007**, 332 (1), 124–129.

(31) Tang, Y.; Nguyen, L.; Li, Y.; Wang, N.; Tao, F. F. Surface of a catalyst in a gas phase. *Curr. Opin. Chem. Eng.* **2016**, *12*, 52–61.

(32) Shan, J. J.; Zhang, S. R.; Choksi, T.; Nguyen, L.; Bonifacio, C. S.; Li, Y. Y.; Zhu, W.; Tang, Y.; Zhang, Y. W.; Yang, J. C.; Greeley, J.; Frenkel, A. I.; Tao, F. Tuning Catalytic Performance through a Single or Sequential Post Synthesis Reaction(s) in a Gas Phase. ACS Catal. 2017, 7 (1), 191–204.

(33) Dou, J.; Sun, Z. C.; Opalade, A. A.; Wang, N.; Fu, W. S.; Tao, F. Operando chemistry of catalyst surfaces during catalysis. *Chem. Soc. Rev.* 2017, 46 (7), 2001–2027.

(34) Zhang, S. R.; Shan, J. J.; Nie, L. H.; Nguyen, L.; Wu, Z. L.; Tao, F. In situ studies of surface of NiFe2O4 catalyst during complete oxidation of methane. *Surf. Sci.* **2016**, *648*, 156–162.

(35) Tao, F. F.; Nguyen, L.; Zhang, S. R.; Li, Y. Y.; Tang, Y.; Zhang, L.; Frenkel, A. I.; Xia, Y. N.; Salmeron, M. Formation of Second-Generation Nanoclusters on Metal Nanoparticles Driven by Reactant Gases. *Nano Lett.* **2016**, *16* (8), 5001–5009.

(36) Nguyen, L.; Liu, L. C.; Assefa, S.; Wolverton, C.; Schneider, W. F.; Tao, F. F. Atomic-Scale Structural Evolution of Rh(110) during Catalysis. *ACS Catal.* **2017**, 7 (1), 664–674.

(37) Liu, J. J.; Zhang, S. R.; Zhou, Y.; Fung, V.; Nguyen, L.; Jiang, D. E.; Shen, W. J.; Fan, J.; Tao, F. F. Tuning Catalytic Selectivity of Oxidative Catalysis through Deposition of Nonmetallic Atoms in Surface Lattice of Metal Oxide. *ACS Catal.* **2016**, *6* (7), 4218–4228.

(38) Nguyen, L.; Zhang, S. R.; Yoon, S. J.; Tao, F. Preferential Oxidation of CO in H-2 on Pure Co3O4-x and Pt/Co3O4-x. ChemCatChem 2015, 7 (15), 2346–2353.

(39) Nguyen, L.; Zhang, S. R.; Wang, L.; Li, Y. 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 Pt1Com and Pd1Con. *ACS Catal.* **2016**, *6* (2), 840–850.

(40) Zhang, S. R.; Nguyen, L.; Liang, J. X.; Shan, J. J.; Liu, J. Y.; Frenkel, A. I.; Patlolla, A.; Huang, W. X.; Li, J.; Tao, F. Catalysis on singly dispersed bimetallic sites. *Nat. Commun.* **2015**, *6*, DOI: 10.1038/ncomms8938.

(41) Tao, F.; Stach, E. A.; Browning, N. D. Structure of catalyst particles from in-situ electron microscopy: a web themed issue. *Chem. Commun.* **2014**, *50* (83), 12417–12419.

(42) Mullins, D.; Overbury, S.; Huntley, D. Electron spectroscopy of single crystal and polycrystalline cerium oxide surfaces. *Surf. Sci.* **1998**, 409 (2), 307–319.

(43) Wen, C.; Zhu, Y.; Ye, Y.; Zhang, S.; Cheng, F.; Liu, Y.; Wang, P.; Tao, F. Water-Gas Shift Reaction on Metal Nanoclusters Encapsulated in Mesoporous Ceria Studied with Ambient-Pressure X-ray Photoelectron Spectroscopy. *ACS Nano* **2012**, *6* (10), 9305– 9313.

(44) 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.

(45) Larachi, F. ç.; Pierre, J.; Adnot, A.; Bernis, A. Ce 3d XPS study of composite CexMn 1-xO 2-y wet oxidation catalysts. *Appl. Surf. Sci.* **2002**, 195 (1), 236–250.

(46) Radutoiu, N.; Teodorescu, C. Satellites in Ce 3D X-ray photoelectron spectroscopy of ceria. *Digest J. Nanomater. Biostruc.* **2013**, *8*, 1535–1549.

(47) Bêche, E.; Charvin, P.; Perarnau, D.; Abanades, S.; Flamant, G. Ce 3d XPS investigation of cerium oxides and mixed cerium oxide (CexTiyOz). *Surf. Interface Anal.* **2008**, *40* (3–4), 264–267.

(48) Monai, M.; Montini, T.; Chen, C.; Fonda, E.; Gorte, R. J.; Fornasiero, P. Methane Catalytic Combustion over Hierarchical Pd@ CeO2/Si-Al2O3: Effect of the Presence of Water. *ChemCatChem* **2015**, 7 (14), 2038–2046.

(49) Wu, K.; Zhou, L.; Jia, C.-J.; Sun, L.-D.; Yan, C.-H. Pt-embedded-CeO 2 hollow spheres for enhancing CO oxidation performance. *Materials Chemistry Frontiers* **2017**, *1* (9), 1754–1763.

(50) Ma, C.; Wen, Y.; Yue, Q.; Li, A.; Fu, J.; Zhang, N.; Gai, H.; Zheng, J.; Chen, B. H. Oxygen-vacancy-promoted catalytic wet air oxidation of phenol from MnO x–CeO 2. RSC Adv. 2017, 7 (43), 27079–27088.

(51) Shan, W.; Luo, M.; Ying, P.; Shen, W.; Li, C. Reduction property and catalytic activity of Ce 1- X Ni X O 2 mixed oxide catalysts for CH 4 oxidation. *Appl. Catal.*, A **2003**, 246 (1), 1–9.

(52) Haneda, M.; Mizushima, T.; Kakuta, N. Synergistic effect between Pd and nonstoichiometric cerium oxide for oxygen activation in methane oxidation. *J. Phys. Chem. B* **1998**, *102* (34), 6579–6587.

(53) Li, X.; Henrich, V. E. Reaction of SO 2 with stoichiometric and defective NiO (100) surfaces. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1993**, 48 (23), 17486.

(54) Furstenau, R.; Langell, M. Adsorption of ethylene on stoichiometric and reduced NiO (100). *Surf. Sci.* **1985**, *159* (1), 108–132.

(55) Colussi, S.; Gayen, A.; Farnesi Camellone, M.; Boaro, M.; Llorca, J.; Fabris, S.; Trovarelli, A. Nanofaceted Pd□ O Sites in Pd□ Ce Surface Superstructures: Enhanced Activity in Catalytic Combustion of Methane. *Angew. Chem., Int. Ed.* **2009**, *48* (45), 8481–8484.

(56) Zhang, S. Y.; Chen, C.; Cargnello, M.; Fornasiero, P.; Gorte, R. J.; Graham, G. W.; Pan, X. Q. Dynamic structural evolution of supported palladium-ceria core-shell catalysts revealed by in situ electron microscopy. *Nat. Commun.* **2015**, *6*, DOI: 10.1038/ncomms8778.

(57) Monai, M.; Montini, T.; Melchionna, M.; Duchon, T.; Kus, P.; Chen, C.; Tsud, N.; Nasi, L.; Prince, K. C.; Veltruska, K.; Matolin, V.; Khader, M. M.; Gorte, R. J.; Fornasiero, P. The effect of sulfur dioxide on the activity of hierarchical Pd-based catalysts in methane combustion. *Appl. Catal., B* **2017**, *202*, 72–83.

(58) Monai, M.; Montini, T.; Melchionna, M.; Duchon, T.; Kus, P.; Tsud, N.; Prince, K. C.; Matolin, V.; Gorte, R. J.; Fornasiero, P. Phosphorus poisoning during wet oxidation of methane over Pd@ CeO2/graphite model catalysts. *Appl. Catal., B* **2016**, *197*, 271–279.

(59) Tao, F.; Nguyen, L.; Zhang, S. R. Design of a new reactor-like high temperature near ambient pressure scanning tunneling microscope for catalysis studies. *Rev. Sci. Instrum.* **2013**, *84* (3), 034101.

(60) Nguyen, L.; Tao, F. Development of a reaction cell for in-situ/ operando studies of surface of a catalyst under a reaction condition and during catalysis. *Rev. Sci. Instrum.* **2016**, 87 (6), 064101.

(61) Tao, F. Design of an in-house ambient pressure AP-XPS using a bench-top X-ray source and the surface chemistry of ceria under reaction conditions. *Chem. Commun.* **2012**, *48* (32), 3812–3814.

(62) Uhlenbrock, S.; Scharfschwerdt, C.; Neumann, M.; Illing, G.; Freund, H.-J. The influence of defects on the Ni 2p and O 1s XPS of NiO. J. Phys.: Condens. Matter **1992**, 4 (40), 7973.

(63) Mansour, A. Characterization of NiO by XPS. Surf. Sci. Spectra **1994**, 3 (3), 231–238.

(64) Zhang, Y.; Zhuo, Q.; Lv, X.; Ma, Y.; Zhong, J.; Sun, X. NiO-Co 3 O 4 nanoplate composite as efficient anode in Li-ion battery. *Electrochim. Acta* 2015, 178, 590–596.

(65) Xu, Y. F.; Gao, M. R.; Zheng, Y. R.; Jiang, J.; Yu, S. H. Nickel/ nickel (II) oxide nanoparticles anchored onto cobalt (IV) diselenide nanobelts for the electrochemical production of hydrogen. *Angew. Chem., Int. Ed.* **2013**, *52* (33), 8546–8550.

(66) Yamamoto, S.; Kendelewicz, T.; Newberg, J. T.; Ketteler, G.; Starr, D. E.; Mysak, E. R.; Andersson, K. J.; Ogasawara, H.; Bluhm, H.; Salmeron, M.; et al. Water Adsorption on r-Fe2O3 (0001) at near Ambient Conditions. *J. Phys. Chem. C* **2010**, *114* (5), 2256–2266.

(67) 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.; et al. Formation of hydroxyl and water layers on MgO films studied with ambient pressure XPS. *Surf. Sci.* **2011**, 605 (1), 89–94.

(68) Carson, G.; Nassir, M.; Langell, M. Epitaxial growth of Co3O4 on CoO (100). J. Vac. Sci. Technol., A 1996, 14 (3), 1637–1642.

(69) Li, K.; Gao, S.; Wang, Q.; Xu, H.; Wang, Z.; Huang, B.; Dai, Y.; Lu, J. In-situ-reduced synthesis of Ti3+ self-doped TiO2/g-C3N4 heterojunctions with high photocatalytic performance under LED light irradiation. ACS Appl. Mater. Interfaces **2015**, 7 (17), 9023–9030.

(70) Zou, J.; Gao, J.; Wang, Y. Synthesis of highly active H 2 O 2sensitized sulfated titania nanoparticles with a response to visible light. *J. Photochem. Photobiol., A* **2009**, 202 (2), 128–135.

(71) Eren, B.; Heine, C.; Bluhm, H.; Somorjai, G. A.; Salmeron, M. Catalyst chemical state during CO oxidation reaction on Cu (111) studied with ambient-pressure x-ray photoelectron spectroscopy and

near edge x-ray adsorption fine structure spectroscopy. J. Am. Chem. Soc. 2015, 137 (34), 11186–11190. (72) Yuan, K.; Zhong, J.-Q.; Zhou, X.; Xu, L.; Bergman, S. L.; Wu, K.;

(72) Yuan, K.; Zhong, J.-Q.; Zhou, X.; Xu, L.; Bergman, S. L.; Wu, K.; Xu, G. Q.; Bernasek, S. L.; Li, H. X.; Chen, W. Dynamic oxygen on surface: catalytic intermediate and coking barrier in the modeled CO2 reforming of CH4 on Ni (111). ACS Catal. **2016**, *6* (7), 4330–4339.

(73) Borasio, M.; Rodríguez de la Fuente, O.; Rupprechter, G.; Freund, H.-J. In situ studies of methanol decomposition and oxidation on Pd (111) by PM-IRAS and XPS spectroscopy. *J. Phys. Chem. B* **2005**, *109* (38), 17791–17794.

(74) Dissanayake, D.; Rosynek, M. P.; Kharas, K. C.; Lunsford, J. H. Partial oxidation of methane to carbon monoxide and hydrogen over a Ni/Al2O3 catalyst. *J. Catal.* **1991**, *132* (1), 117–127.

(75) Chorkendorff, I.; Alstrup, I.; Ullmann, S. XPS study of chemisorption of CH4 on Ni (100). Surf. Sci. 1990, 227 (3), 291–296.