

Insights into the Nonthermal Effects of Light in Dry Reforming of Methane to Enhance the H_2/CO Ratio Near Unity over Ni/Ga₂O₃

Zhiqiang Rao, Yuehan Cao, Zeai Huang,* Zihang Yin, Wenchao Wan, Minzhi Ma, Yanxin Wu, Junbu Wang, Guidong Yang, Yi Cui, Zhongmiao Gong, and Ying Zhou*



from Ga_2O_3 to Ni to form the Ni⁰ sites, which provides the generation of abundant hot electrons from the electronic interband transition of Ni to boost the formation and desorption of H₂. This work promotes the understanding of nonthermal behaviors of light irradiation in light-driven photochemistry, which is significant for designing catalysts with high efficiency and controllable product distribution.

KEYWORDS: photothermal catalysis, dry reforming of methane, Ni/Ga₂O₃, nonthermal effect, H_2 /CO ratio

INTRODUCTION

Photothermal catalysis has emerged as a promising alternative to obtain clean, renewable fuels and chemical compounds by converting solar energy into chemical energy.^{1,2} Upon irradiation, the local improvement of the electric field, the hot electrons generated by plasmon decay, and the photothermal heating can occur due to the interband and/or intraband electronic excitations.³ Among these light-conduced effects, photothermal heating is several orders of magnitude more energy-efficient than conventional thermal processes induced by phonon interactions.⁴ Moreover, the construction of a photothermal system via photothermal heating and photogenerated hot electrons to drive and accelerate chemical reaction endows catalytic reactions with higher reaction rates and milder conditions than traditional thermal catalysis.⁵⁻⁹ However, understanding the role of light irradiation in lightinduced thermal effects and light-excited hot electrons to enhance reaction rates remains controversial in this photothermal cooperative process.^{10,11}

On the other hand, the hot electrons-mediated (nonthermal effects) catalytic process does more than just enhance reaction rates; it can also selectively modify the reaction paths, even unlocking an approach that is unachievable under purely thermal conditions.^{12,13} Specifically, the electrons with femto-

second-lifetime¹⁴ will speedily transfer to the adsorbate on the substrate and thus accelerate the bond scission of the adsorbed molecule before its desorption.^{15,16} For instance, the electrons excited by light can boost the associative desorption of H₂ from metal surfaces through the desorption induced by the electronic transitions (DIET) mechanism.¹⁷⁻¹⁹ Therefore, it is highly desirable to employ the nonthermal contributions of light irradiation to modulate the reaction pathways selectively. Photothermal catalytic dry reforming of methane (DRM: CH₄ + $CO_2 \rightleftharpoons 2H_2$ + 2CO) was an alternative to the traditional thermal DRM due to its sustainable and low-temperature advantages. Nevertheless, it still suffered from the H₂/CO ratio of less than 1.0 due to the coinstantaneous occurrence of reverse water gas shift (RWGS: $CO_2 + H_2 \rightleftharpoons H_2O + CO$) reaction, $^{20-22}$ which is not beneficial for the formation of C_{5-20} liquid fuels via the direct Fischer-Tropsch (FT) synthesis.² In this process, the formation of H_2 and the RWGS reaction

Received:November 5, 2020Revised:February 5, 2021Published:April 5, 2021







Figure 1. (a) TEM image, (b) HRTEM image, and (c, d) EDS mapping of the Ni/Ga₂O₃ catalyst. (e) Ni K-edge XANES spectra, (f) the Ni K-edge Fourier transform (FT) of k^3 -weighted $\chi(k)$ function, extended X-ray absorption fine structure (EXAFS) spectra (uncorrected for the phase shift) of the NiO reference, Ni foil reference, and Ni/Ga₂O₃.

are a competitive process for the hydrogen adsorbed on the metal surface.

Herein, we successfully regulate the reaction paths through the nonthermal effects of light irradiation during the photothermal catalytic DRM reaction to obtain syngas with a ratio near unity. We discovered that light irradiation not only plays a significant role in reversing the direction of electron transfer between Ga_2O_3 and Ni but also promotes the generation of hot electrons through the electronic interband transition of Ni. The H_2/CO ratio was increased from 0.55 of traditional thermal DRM to 0.94 of photothermal DRM at 664 K. In this process, light irradiation showed a distinct nonthermal contribution and proved to be an effective strategy to promote the C–H bond scission of CH_4 and H_2 formation during the photothermal DRM.

EXPERIMENTAL AND COMPUTATIONAL METHODS

Experimental Methods. Ni/Ga₂O₃ was synthesized using a facile impregnation method. In more detail, 1.0 g of Ga₂O₃ (99.99%) was added into 50.0 mL of an aqueous solution of 0.247 g of Ni(NO₃)₂·6H₂O (99.99%); both were obtained commercially from Aladdin Chemical Reagent Corp. Then, the extra water was evaporated at 353 K until dryness. After that, the mixture was calcined at 673 K for 2 h under air. The theoretical loading of Ni was 5.0 wt %, and the actual loading of Ni was measured to be 4.9 wt %, confirmed by inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent 5110).

The photothermal and thermal catalytic reactions were measured at atmospheric pressure in a Harrick cell reactor with a flat cover and a quartz window (Harrick Praying Mantis hightemperature reaction chamber) (Figure S1a). The reaction gases and production gases were analyzed by gas chromatography (Shimadzu GC-8A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD) and a mass spectrometer (OmniStar GSD-320, Pfeiffer Vacuum). In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was carried out on a Bruker infrared spectrometer (Tensor II) equipped with a liquid nitrogencooled mercury-cadmium-telluride (MCT) detector in a three-window diffuse-reflectance cell (Harrick) with a nonmodified dome cover. Two IR measurement windows were made of ZnSe, while the silicon oxide window was used for light irradiation (Figure S1b). The resolution was 4 cm^{-1} . The IR scanning range was 4000-600 cm⁻¹ with averaging over 100 scans. The gas composition and flow rate were consistent with the catalytic tests. The background spectra were obtained by purged the pretreated catalysts at 616 K in pure Ar gas for 30 min. The near-ambient-pressure X-ray photoelectron

spectroscopy (NAP-XPS) was performed on a commercial SPECS AP-XPS chamber equipped with a PHOIBOS 150 NAP hemispherical analyzer and monochromatic SPECS μ -FOCUS 600 NAP X-ray source, Al K α line ($h\nu$ = 1486.6 eV). The Ni/Ga₂O₃ powder catalyst was pressed on a copper plate and then loaded into the AP-XPS chamber.

Models and Computational Details. All calculations were carried out with dispersion-corrected density functional theory (DFT-D) based on Materials Studio software with Cambridge Sequential Total Energy Package (CASTEP) code.²⁵ The whole calculations employed the generalized gradient approximation (GGA) with Perdew-Burke-Ernzerhof (PBE) functional theory as part of the exchangecorrelation.²⁶⁻²⁸ The Monkhorst–Pack k-point and cut-off energy were set to be $2 \times 2 \times 1$ and 380 eV, respectively. A vacuum layer of 15 Å was used for all of the calculations to prevent the spurious interaction between periodic slabs. The monoclinic β -phase Ga₂O₃ surface was cleaved along the (100) direction of bulk Ga₂O₃. As presented in Figure S14, the surface energy was converged since 2×1 . Hence, a 2×2 supercell, including a cell composition (Ga₂O₃)8, was constructed in the subsequent calculations (Figure S2a).^{29,30} The Ni atom was bonded with two O atoms of Ga₂O₃ to form the Ni-O bonds (Figure S2b).

RESULTS AND DISCUSSION

Characterization. Ni was reported as an active catalytic component in the photothermal DRM reaction owing to its excellent catalytic activity and low price, and the hot electrons generated by both interband transition and LSPR could participate in the subsequent reaction process. 31,32 Ni/Ga_O_a exhibited photothermal catalytic DRM activity; however, it still suffered from the fact that H_2/CO was much lower than 1.0 due to the side RWGS reaction.³³ Ni/Ga₂O₃ catalysts were obtained by wet impregnation of commercial Ga₂O₃ powders presented in the Experimental and Computational Methods section. The crystal phases of both Ga2O3 and Ni/Ga2O3 catalysts were confirmed to be β -Ga₂O₃ (ICPDS PDF No. 76-0573) by X-ray diffraction (XRD). NiO was found to be formed; however, it was difficult to identify due to the overlap of the $Ga_2O_3(401)$ plane at 37.3° with the NiO(101) plane at 37.2° , and $Ga_2O_3(112)$ plane at 43.0° with NiO(012) plane at 43.2° (Figure S3). The UV-vis diffuse reflection spectrum (DRS) of pristine Ga_2O_3 exhibited an absorption edge at about 264 nm corresponding to a band gap of 4.70 eV (Figure S4), in good agreement with the previous report.³⁴ After Ni loading, a distinct additional absorption peak originating from NiO can be observed in the range of 270-370 nm.³⁵

Scanning electron microscopy (SEM) images revealed that Ga_2O_3 presented a rod-like structure (Figure S5a,b). Various uniformly distributed nanoparticles appeared on the surface of Ga_2O_3 after Ni loading (Figure S5c,d). Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images (Figure 1a,b) showed that nanoparticles over Ni/ Ga_2O_3 exhibited the face-centered cubic (FCC) lattice with a NiO(111) interlayer spacing of 0.24 nm, consistent with previous reports.^{36,37} The selected TEM-energy-dispersive spectrometry (EDS) mapping confirmed that the nanoparticles in Figure 1a,b were Ni species (Figure 1c,d). The particle size of NiO was around 10 nm according to the EDS mapping and HRTEM statistics (Figure S6).

The surface chemical state of Ni was further analyzed by X-ray photoelectron spectroscopy (XPS) (Figure S7). Ni $2p_{3/2}$

spectrum evidenced the presence of two peaks for Ni atoms at 855.2 and 853.5 eV assigned to NiO.^{38,39} The O 1s peak at 530.5 eV could be ascribed to the Ga–O bond, and the binding energies at 529.2 and 531.7 eV could be assigned to the feature of NiO.³⁹ The Ni K-edge X-ray absorption near-edge structure (XANES) spectrum of Ni/Ga₂O₃ also indicated the existence of NiO species as the spectrum is overlapped with the NiO reference, and the distinguishable Ni–O coordination in the extended X-ray absorption fine structure (EXAFS) spectra further confirmed the NiO phase in the catalyst (Figure 1e,f).

Thermal and Photothermal Catalytic DRM Reactions. Given that the increase of the catalyst surface temperature could be caused by the photogenerated thermal effect, the calibration of the temperature curve under photoirradiation was performed and shown in Figure S8. Based on this calibration, the photothermal and thermal DRM catalytic processes could be investigated on the condition that the surface temperatures of catalysts were kept consistent.^{10,11,40} The DRM catalytic performance over the Ni/Ga₂O₃ catalyst was assessed in the temperature range from 616 to 664 K (Figure 2a). The catalytic activity of the thermal process



Figure 2. DRM catalytic performances over Ni/Ga₂O₃ catalyst at different temperatures: (a) H₂ and CO yield under photothermal and thermal catalysis. (b) The H₂/CO ratio under photothermal and thermal catalysis. Reaction conditions: $CH_4/CO_2 = 1.0$, total flow rate: 20 mL min⁻¹, 40 mg of catalyst, 300 W Xe lamp.

without light irradiation increased with the increasing temperature. The formation rate of CO was obviously higher than that of H_2 , and the formation rate gap between CO and H_2 grew fast, with the increase in temperature. As for the photothermal process upon irradiation, a similar result of increasing formation rates of products with increasing temperatures was observed. However, no noticeable increase in the rate formation gap between CO and H_2 could be observed. This result indicated that heat was responsible for enhancing the catalytic activity, while the addition of light irradiation played a crucial role in augmenting the percentage of H_2 in the products for DRM.

During the photothermal DRM catalysis, the H₂/CO ratio improved with the increase of temperature, while the H_2/CO ratio showed a decreasing trend during thermal catalysis (Figure 2b). To be specific, the H_2/CO ratio was only 0.55 at 664 K in thermal catalysis, while this value reached 0.94 in photothermal catalysis, indicating that the H₂/CO ratio could achieve close to 1.0. As aforementioned, this is crucial for the application of the DRM reaction to other chemical processes, such as direct FT synthesis.^{23,24} The Arrhenius plots of $\ln(r_{H_2})$ vs 1/T were performed based on the $r_{\rm H_2}$ values of Ni/Ga₂O₃ (Figure S9a). Both thermal catalysis and photothermal catalysis showed good linear relationships between $\ln(r_{\rm H_2})$ and 1/T. The apparent activation energy value of H₂ over Ni/ Ga_2O_3 was calculated to be 83.4 kJ mol⁻¹ under thermal catalysis according to the Arrhenius equation $(k = A e^{-E_a/RT})$, consistent with the previous reported nickel-based catalysts.^{41,42} For the photothermal catalysis, the apparent activation energy value was decreased to 72.2 kJ mol⁻¹. This exhibited that the addition of light irradiation lowered the activation energy of the DRM reaction. Thus, the higher H₂ formation rate in the products and lower activation energy obtained upon light irradiation for the DRM process implied a unique pathway for methane activation as compared to that of thermal DRM. Besides, the mass spectrometry (MS) results of the reactants and products also confirmed good stability to promote catalytic activity during five cycles of light-on and light-off experiments (Figure S9b).

In Situ DRIFTS. The in situ DRIFTS technology was carried out to disclose the origin of the improvement toward H₂ in the products and to understand the effect of light on the reactants, intermediates, and products over Ni/Ga2O3. With the increase of reaction temperature, the adsorption peaks of gaseous CH_4 (3016 and 1302 cm⁻¹) and gaseous CO_2 (2340 and 2358 cm⁻¹) gradually decreased as a result of the CH_4 and CO_2 conversion (Figures 3a and S10).⁴³⁻⁴⁵ The broad peaks at 1341 and 1354 cm⁻¹ after the introduction of CH_4 and CO_2 assigned to asymmetric and symmetric deformation vibrations of adsorbed -CH3 groups,46,47 respectively, indicated that CH4 might be cleaved to form the adsorbed -CH3 and H species. This result was consistent with the previously reported work that the adsorbed CH₃ species could be generated and activated under low temperatures.^{48,49} In our case, the intensities of the adsorption peaks of methane and methyl groups significantly reduced at 616 K under light irradiation after 120 min (Figure 3b), indicating that light could promote the cracking of methane and accelerate the further cracking of the methyl group. Moreover, the reduction of the methyl group during thermal catalysis was not as significant as that during photothermal catalysis. Thus, the introduction of light could not only promote the pyrolysis of methane but also facilitate the continuous cracking of methyl groups.

On the other hand, two new broad adsorption bands at 2174 and 2113 cm⁻¹ corresponding to adsorbed gaseous $CO^{50,51}$ (Figure 3c) could be detected, ascribed to the decomposition of adsorbed carbonate species. During the thermal catalytic reaction without light irradiation, the gaseous CO showed an increasing trend after the reaction temperature increased to 616 K at 120 min. Interestingly, the gaseous CO showed an



Figure 3. In situ DRIFTS of the Ni/Ga₂O₃ catalyst during the DRM reaction at 528 K and 616 K for 120 min and under UV–vis light irradiation at 616 K for 30, 60, and 120 min in ranges of (a) $2525-2200 \text{ cm}^{-1}$, (b) $1400-1200 \text{ cm}^{-1}$, (c) $2225-1950 \text{ cm}^{-1}$, and (d) $3800-3700 \text{ cm}^{-1}$, respectively.

increasing trend after reaction for only 30 min and then decreased with the increase of light irradiation time at 616 K. This result demonstrated that light irradiation inhibited the formation of gaseous CO.

The presence of several broad peaks in the $3586-3734 \text{ cm}^{-1}$ region could be assigned to the stretching modes of isolated hydroxyl groups due to the adsorbed hydroxyl groups of H₂O on the surface of Ga₂O₃ (Figure 3d),⁵² which was usually involved in the RWGS reaction.^{53,54} The peaks of hydroxyl groups in this range still existed, but the intensities were changed due to their instability at high temperatures.⁵⁵ Interestingly, with the increase of temperature during thermal DRM, a new peak was generated at 3734 cm⁻¹ and was attributed to the asymmetric free OH of H₂O.⁵⁶ Moreover, the intensity of this peak after light irradiation for 120 min was significantly lower than that under thermal conditions alone. Such a kind of phenomenon, related to the formation of H₂O, was detected by mass spectrometry (MS) as well (Figure S11). This implied that the addition of light inhibited the production of H₂O in the products compared with the thermal DRM.

To clarify the effect of light on this side reaction during DRM, the RWGS reaction over thermal and photothermal catalysis was performed. The consumption of H_2 during thermal catalysis was obviously higher than that during photothermal catalysis with the increase of the reaction temperature (Figure S12). Also, a nearly 3-fold decrease in the yield of CO product was recorded under photothermal catalysis as compared to that under thermal catalysis at the



Figure 4. Energy profile during the DRM process over Ni/Ga_2O_3 under (a-c) ground state and (d-f) electron-rich condition. Energies are in kJ mol⁻¹.

same reaction temperature. Furthermore, the H₂O (m/z =18) production from mass spectrometry (MS) under the thermal catalysis was much higher than that under the photothermal catalysis during the RWGS reaction (Figure S13). Therefore, there is no doubt that the RWGS reaction was effectively inhibited over Ni/Ga₂O₃ after the addition of light to improve the H₂/CO ratio during photothermal DRM catalysis.

For nickel-based catalysts during DRM catalysis, it was generally accepted that the limitation step of the DRM reaction was mainly due to the disassociation of C–H bonds in methane molecules.^{57–59} Once the first hydrogen of the CH₄ molecule was removed, a rapid transformation of CH₃ \rightarrow CH₂ \rightarrow CH \rightarrow C could occur on the catalyst surface.^{60,61} After that, the deposited carbon would react with oxygen atoms to form gaseous CO. The dissociation of C–H resulted in the formation of H*, which would participate in the following two reactions: (1) the formation of H₂ and (2) the hydrogenation of CO₂.⁶² These were two competitive reactions for H disassociating from CH₄, and the latter one led to the occurrence of the RWGS reaction.⁶² Furthermore, the formed H₂ would react with CO₂, which could also promote the occurrence of the RWGS reaction. Based on the above experiments and considerations, the following three reaction paths were selected as critical steps during the DRM process to explore the effect of additional light in the DRM process among the Ni/Ga₂O₃ systems.^{63,64}

$$CH_4^* \to CH_3^* + H^*$$
 (Path 1)

$$\mathrm{H}^* + \mathrm{H}^* \to \mathrm{H}_2^* \tag{Path 2}$$

$$CO_2^* + H^* \rightarrow COOH^* \rightarrow CO^* + OH^*$$
 (Path 3)

DFT Calculations. Ni/Ga₂O₃ model was conducted (details in the SI), and the above three paths were simulated based on the DFT methods. Extra electrons were introduced into the whole system to create an electron-rich condition for simulating the effect of light addition.^{65–67} As presented in Figure 4, the dissociation of CH₄* to CH₃* and H* (Path 1) needed 179.6 kJ mol⁻¹ at the ground state. Comparatively, this value decreased to 162.3 kJ mol⁻¹ under an electron-rich condition facilitated the dissociation of CH₄, resulting in more H* participating in the subsequent reactions. This was in



Figure 5. Charge population of (a, b) the ground state and (c, d) under electron-rich condition during the DRM process of H_2 formation over the Ni/Ga₂O₃ surface. (e) NAP-XPS spectra of Ni/Ga₂O₃ pretreated with H_2 (gray, acquired in an ultrahigh vacuum), thermal (red), and photothermal (blue) catalytic DRM reaction (0.3 mbar CO₂ and CH₄ at 623 K), Ni $2p_{3/2}$.

accordance with the in situ DRIFTS analysis (Figure 3b). When H* formed, it could directly convert into H₂ (Path 2) or combine with CO₂ to convert into CO (Path 3). At the ground state, the formed H* could more possibly combine with CO₂ ($E_a = 64.3 \text{ kJ mol}^{-1}$) rather than converting into H₂ ($E_a = 117.5 \text{ kJ mol}^{-1}$) according to the related energy barriers. Under the electron-rich condition, the energy barrier of H₂ formation was decreased to 1.5 kJ mol⁻¹, reduced by almost eighty times compared with the ground state. Hence, the competition reaction was significantly changed, and the formation of H₂ would more possibly occur compared with the hydrogenation of CO₂ ($E_a = 32.5 \text{ kJ mol}^{-1}$).

Furthermore, the desorption energy of H_2 decreased from +0.2 to -100.8 kJ mol⁻¹ (Table S1) under electron-rich conditions, indicating that the light promoted the spontaneous desorption of formed H_2 . This phenomenon was observed in the previous report that light induced the formation of H_2 .^{17,68} In brief, the introduction of light promotes the reaction of H_2 formation instead of CO₂ hydrogenation in the DRM process on the Ni/Ga₂O₃ surface, resulting in generating more H_2 and inhibiting the RWGS reaction. On the other hand, the formed H_2 would spontaneously desorb from the surface after the light was introduced. As a result, the H_2 /CO ratio was significantly increased, which accorded with the results observed in the above experiments.

Based on the above results, Ni and its surrounding atoms were deemed as the main active sites for the DRM reaction. Hence, to gain further insight into the internal causes of light irradiation, the charge population analysis was employed in Ni and its surrounding atoms among the Ni/Ga2O3 systems (Table S2, Figures 5a-d and S14). When the Ni/Ga₂O₃ surface was constructed, the electrons were transferred from the Ni atom to two bonded O atoms, resulting in the oxidation state of the Ni atom (Figure S14a). This was consistent with the experimental analysis. At the ground state, Ni kept the oxidation state during the dissociation of CH4, the formation of H_2 , and the process of CO_2 conversion into CO. Under the electron-rich condition, the state of Ni had rarely changed except the process of H₂ formation (Figures 5 and S14d-f). During the process of H₂ formation, the electrons in the highest occupied molecular orbital (HOMO) of Ni 3d were transferred to the lowest unoccupied molecular orbital (LUMO) (Figure S15). As a consequence, the direction of electron transfer was reversed, and 0.17e electrons were

accumulated in the Ni atom, leading to the reduction state of the Ni atom (Figure 5c). Therefore, the adsorbed H atoms could obtain more electrons (Table S3) from the interband transition of Ni, which facilitated an almost 80 times decrease of the energy barrier for H₂ formation (Figure 4b,e).

To identify the change of Ni during the reaction process, the NAP-XPS analysis of the Ni/Ga2O3 catalyst pretreated with H₂, thermal catalysis, and photothermal catalysis was performed as shown in Figure 5e. Metallic Ni (Ni⁰) with a proportion of 29.6 atom % was observed in the Ni/Ga2O3 catalyst pretreated with H_2 (Table S4). The ratio of Ni⁰ (29.8 atom %) showed no significant change after the introduction of CH₄ and CO₂; however, the gaseous CO₂ was significantly increased at 623 K during the thermal catalysis. With light illumination, the peak of gaseous CO₂ showed a decreasing trend, indicating that light illumination accelerated the conversion of CO₂. Besides, the ratio of Ni⁰ increased to 32.1 atom % under the photothermal catalytic DRM reaction. These results were consistent with our theoretical simulations that the electron transfer reversed from Ga₂O₃ to Ni under the light illumination condition. In addition, the UV-vis absorption spectra of the catalyst after the photothermal catalytic reaction showed a significant absorption peak of metallic nickel from 350 to 800 nm (Figure S4).³⁷

The light irradiation promoted the electron transfer reversal from Ga₂O₃ to Ni during the formation of H₂. Compared with the thermal process, light irradiation promoted the formation of Ni⁰ that impelled more hot electrons excited from the interband transition of Ni to accelerate the dehydrogenation of CH₄, resulting in more production of H* that could be involved in the subsequent reactions. Meanwhile, the hot electrons also boosted the production and desorption of H₂ through the DIET mechanism and thus in turn promoted the regeneration of reactive active sites for the dissociation of CH₄. In other words, the detachment of H* from CH₄ was more inclined to participate in the H₂ formation rather than the competitive RWGS reaction to form CO and H₂O. Hence, the H₂/CO ratio near unity could be achieved.

In summary, this work demonstrated the nonthermal effects of light irradiation that enabled the enhancement of H_2/CO ratio to be near unity in the photothermal catalytic DRM reaction. The light irradiation promoted the direction of electron

transfer to be reversed from Ga_2O_3 to Ni during the formation of H_2 , promoting the formation of Ni⁰. As a result, more hot electrons from the electronic interband transition of Ni simultaneously promoted the dehydrogenation of CH_4 and the formation and desorption of H_2 . Hence, the ratio of $H_2/$ CO observed in the DRM reaction was increased from 0.55 to 0.94 after the light was introduced. Our findings offer a penetrating insight into the roles of light irradiation in the photothermal catalytic reaction and pave the way for enhancing the proportion of H_2 in the C–H activation and H_2 production reactions.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.0c04826.

Characterization details; catalytic reaction operation details; in situ DRIFTS device; crystal structure model; XRD results; UV–vis diffuse reflection spectra; SEM images; XPS spectra of Ni/Ga₂O₃; temperature calibration; Arrhenius plots and light-on and light-off experiments; photothermal and thermal catalytic RWGS reaction results; charge population; LUMO and HOMO orbits, XPS spectra of the Ni/Ga₂O₃ catalyst after pretreatment and thermal catalysis and photothermal catalysis; the surface energy convergence test; and the charge population of NAP-XPS (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Zeai Huang State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation and School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China; orcid.org/0000-0002-7079-2504; Email: zeai.huang@swpu.edu.cn
- Ying Zhou State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation and School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China; ◎ orcid.org/0000-0001-9995-0652; Email: yzhou@swpu.edu.cn

Authors

- Zhiqiang Rao State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation and School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Yuehan Cao School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Zihang Yin School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Wenchao Wan School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Minzhi Ma School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Yanxin Wu School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- Junbu Wang School of New Energy and Materials, Southwest Petroleum University, Chengdu 610500, China
- **Guidong Yang** XJTU-Oxford International Joint Laboratory for Catalysis, School of Chemical Engineering and Technology, Xi'an Jiaotong University, Xi'an 710049, China

- Yi Cui Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China; Orcid.org/ 0000-0002-9182-9038
- Zhongmiao Gong Vacuum Interconnected Nanotech Workstation, Suzhou Institute of Nano-Tech and Nano-Bionics, Chinese Academy of Sciences, Suzhou 215123, China

Complete contact information is available at: https://pubs.acs.org/10.1021/acscatal.0c04826

Author Contributions

Z.R. and Y.C. contributed equally. The experiments were conceived and designed by Y.Z., Z.H., Y.C., and G.Y. Z.R., Z.Y., W.W., M.M., Y.W., J.W., and Z.G. carried out experiments, characterizations and analyzed the data. Z.R., Z.H., and Y.Z. wrote the manuscript. The theoretical simulation was attributed to Y.C. All authors were involved in the manuscript discussion and revising.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was financially supported by the Sichuan Provincial International Cooperation Project (2019YFH0164), Chengdu International Cooperation Project (2019-GH02-00056-HZ), and the National Natural Science Foundation of China (U1862111). Y.Z. thanks the Cheung Kong Scholars Program of China and JSPS Invitational Fellowships for Research in Japan. The authors appreciate the calculation support from the National Supercomputing Center in Shenzhen. The authors thank Stanford Synchrotron Radiation Lightsource for the provision of time supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (under Contract No. DE-AC02-76SF00515).

REFERENCES

(1) Xiao, J. D.; Jiang, H. L. Metal-Organic Frameworks for Photocatalysis and Photothermal Catalysis. *Acc. Chem. Res.* **2019**, *52*, 356–366.

(2) Wang, Z. J.; Song, H.; Liu, H.; Ye, J. Coupling of Solar Energy and Thermal Energy for Carbon Dioxide Reduction: Status and Prospects. *Angew. Chem., Int. Ed.* **2020**, *59*, 8016–8035.

(3) Brongersma, M. L.; Halas, N. J.; Nordlander, P. Plasmon-Induced Hot Carrier Science and Technology. *Nat. Nanotechnol.* **2015**, *10*, 25–34.

(4) Park, J. Y.; Baker, L. R.; Somorjai, G. A. Role of Hot Electrons and Metal-Oxide Interfaces in Surface Chemistry and Catalytic Reactions. *Chem. Rev.* **2015**, *115*, 2781–817.

(5) Li, Y.; Hao, J.; Song, H.; Zhang, F.; Bai, X.; Meng, X.; Zhang, H.; Wang, S.; Hu, Y.; Ye, J. Selective Light Absorber-Assisted Single Nickel Atom Catalysts for Ambient Sunlight-Driven CO_2 Methanation. *Nat. Commun.* **2019**, *10*, No. 2359.

(6) Wang, L.; Dong, Y.; Yan, T.; Hu, Z.; Jelle, A. A.; Meira, D. M.; Duchesne, P. N.; Loh, J. Y. Y.; Qiu, C.; Storey, E. E.; Xu, Y.; Sun, W.; Ghoussoub, M.; Kherani, N. P.; Helmy, A. S.; Ozin, G. A. Black Indium Oxide a Photothermal CO_2 Hydrogenation Catalyst. *Nat. Commun.* **2020**, *11*, No. 2432.

(7) Song, C.; Liu, X.; Xu, M.; Masi, D.; Wang, Y.; Deng, Y.; Zhang, M.; Qin, X.; Feng, K.; Yan, J.; Leng, J.; Wang, Z.; Xu, Y.; Yan, B.; Jin, S.; Xu, D.; Yin, Z.; Xiao, D.; Ma, D. Photothermal Conversion of CO_2 with Tunable Selectivity Using Fe-Based Catalysts: From Oxide to Carbide. *ACS Catal.* **2020**, *10*, 10364–10374.

(8) Zhao, Y. X.; Yang, B.; Li, H. F.; Zhang, Y.; Yang, Y.; Liu, Q. Y.; Xu, H. G.; Zheng, W. J.; He, S. G. Photoassisted Selective Steam and Dry Reforming of Methane to Syngas Catalyzed by Rhodium– Vanadium Bimetallic Oxide Cluster Anions at Room Temperature. *Angew. Chem., Int. Ed.* **2020**, *59*, 21216–21223.

(9) Qiu, C.; Hao, X.; Tan, L.; Wang, X.; Cao, W.; Liu, J.; Zhao, Y.; Song, Y.-F. 500 nm Induced Tunable Syngas Synthesis from CO_2 Photoreduction by Controlling Heterojunction Concentration. *Chem. Commun.* **2020**, *56*, 5354–5357.

(10) Zhou, L. A.; Swearer, D. F.; Zhang, C.; Robatjazi, H.; Zhao, H. Q.; Henderson, L.; Dong, L. L.; Christopher, P.; Carter, E. A.; Nordlander, P.; Halas, N. J. Quantifying Hot Carrier and Thermal Contributions in Plasmonic Photocatalysis. *Science* **2018**, *362*, 69–72.

(11) Sivan, Y.; Baraban, J.; Un, I. W.; Dubi, Y. J. S. Comment on "Quantifying Hot Carrier and Thermal Contributions in Plasmonic Photocatalysis". *Science* **2019**, *364*, No. eaaw9367.

(12) Shoji, S.; Peng, X. B.; Yamaguchi, A.; Watanabe, R.; Fukuhara, C.; Cho, Y.; Yamamoto, T.; Matsumura, S.; Yu, M. W.; Ishii, S.; Fujita, T.; Abe, H.; Miyauchi, M. Photocatalytic Uphill Conversion of Natural Gas beyond the Limitation of Thermal Reaction Systems. *Nat. Catal.* **2020**, *3*, 148–153.

(13) Zhao, Y.; Zhao, B.; Liu, J.; Chen, G.; Gao, R.; Yao, S.; Li, M.; Zhang, Q.; Gu, L.; Xie, J.; Wen, X.; Wu, L.-Z.; Tung, C.-H.; Ma, D.; Zhang, T. Oxide-Modified Nickel Photocatalysts for the Production of Hydrocarbons in Visible Light. *Angew. Chem., Int. Ed.* **2016**, *55*, 4215–4219.

(14) Zhang, Y.; He, S.; Guo, W.; Hu, Y.; Huang, J.; Mulcahy, J. R.; Wei, W. D. Surface-Plasmon-Driven Hot Electron Photochemistry. *Chem. Rev.* **2018**, *118*, 2927–2954.

(15) Bonn, M. Phonon- Versus Electron-Mediated Desorption and Oxidation of CO on Ru(0001). *Science* **1999**, 285, 1042–1045.

(16) Zhang, X.; Li, X.; Zhang, D.; Su, N. Q.; Yang, W.; Everitt, H. O.; Liu, J. Product Selectivity in Plasmonic Photocatalysis for Carbon Dioxide Hydrogenation. *Nat. Commun.* **2017**, *8*, No. 14542.

(17) Yuan, L.; Lou, M.; Clark, B. D.; Lou, M.; Zhou, L.; Tian, S.; Jacobson, C. R.; Nordlander, P.; Halas, N. J. Morphology-Dependent Reactivity of a Plasmonic Photocatalyst. *ACS Nano* **2020**, *14*, 12054–12063.

(18) Juaristi, J.; Alducin, M.; Saalfrank, P. Femtosecond Laser Induced Desorption of H_2 , D_2 , and HD from Ru (0001): Dynamical Promotion and Suppression Studied with Ab Initio Molecular Dynamics with Electronic Friction. *Phys. Rev. B* **2017**, *95*, No. 125439.

(19) Zhou, L. A.; Martirez, J. M. P.; Finzel, J.; Zhang, C.; Swearer, D. F.; Tian, S.; Robatjazi, H.; Lou, M. H.; Dong, L. L.; Henderson, L.; Christopher, P.; Carter, E. A.; Nordlander, P.; Halas, N. J. Light-Driven Methane Dry reforming with Single Atomic Site Antenna-Reactor Plasmonic Photocatalysts. *Nat. Energy* **2020**, *5*, 61–70.

(20) Liu, H.; Meng, X.; Dao, T. D.; Zhang, H.; Li, P.; Chang, K.; Wang, T.; Li, M.; Nagao, T.; Ye, J. Conversion of Carbon Dioxide by Methane Reforming under Visible-Light Irradiation: Surface-Plasmon-Mediated Nonpolar Molecule Activation. *Angew. Chem., Int. Ed.* **2015**, *54*, 11545–11549.

(21) Liu, H.; Song, H.; Meng, X.; Yang, L.; Ye, J. Light Irradiation Enhanced CO_2 Reduction with Methane: A Case Study in Size-Dependent Optical Property of Ni Nanoparticles. *Catal. Today* **2019**, 335, 187–192.

(22) Takami, D.; Yamamoto, A.; Yoshida, H. Dry Reforming of Methane over Alumina-Supported Rhodium Catalysts at Low Temperatures under Visible and Near-Infrared Light. *Catal. Sci. Technol.* **2020**, *10*, 5811–5814.

(23) Li, J.; He, Y.; Tan, L.; Zhang, P.; Peng, X.; Oruganti, A.; Yang, G.; Abe, H.; Wang, Y.; Tsubaki, N. Integrated Tuneable Synthesis of Liquid Fuels via Fischer–Tropsch Technology. *Nat. Catal.* **2018**, *1*, 787–793.

(24) Li, N.; Jiao, F.; Pan, X.; Chen, Y.; Feng, J.; Li, G.; Bao, X. High-Quality Gasoline Directly from Syngas by Dual Metal Oxide–Zeolite (OX-ZEO) Catalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 7400–7404.

(25) Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. First-Principles Simulation: Ideas, Illustrations and the CASTEP Code. *J. Phys.: Condens. Matter* **2002**, *14*, 2717–2744. (26) White, J. A.; Bird, D. M. Implementation of Gradient-Corrected Exchange-Correlation Potentials in Car-Parrinello Total-Energy Calculations. *Phys. Rev. B* **1994**, *50*, 4954–4957.

(27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865–3868.

(28) Cao, Y.; Wang, F.; Wei, S.; Yang, W.; Zhou, Y. The Role of Potassium in the Activation of Oxygen to Promote Nitric Oxide Oxidation on Honeycomb-Like h-BN(001) Surfaces. *Phys. Chem. Chem. Phys.* **2018**, *20*, 26777–26785.

(29) Zhou, X.; Dong, H.; Ren, A.-M. The Mechanism of Hydrogen and Oxygen Evolution Reaction in Ni–NiO/ β -Ga₂O₃ Photocatalyst. *Int. J. Hydrogen Energy* **2016**, *41*, 5670–5681.

(30) Liu, T.; Tranca, I.; Yang, J.; Zhou, X.; Li, C. Theoretical Insight into the Roles of Cocatalysts in the Ni–NiO/ β -Ga₂O₃ Photocatalyst for Overall Water Splitting. *J. Mater. Chem. A* **2015**, 3, 10309–10319.

(31) Liu, H. M.; Meng, X. G.; Dao, T. D.; Liu, L. Q.; Li, P.; Zhao, G. X.; Nagao, T.; Yang, L. Q.; Ye, J. H. Light Assisted CO₂ Reduction with Methane over SiO₂ Encapsulated Ni Nanocatalysts for Boosted Activity and Stability. J. Mater. Chem. A **2017**, *5*, 10567–10573.

(32) Liu, H.; Dao, T. D.; Liu, L.; Meng, X.; Nagao, T.; Ye, J. Light Assisted CO_2 Reduction with Methane over Group VIII Metals: Universality of Metal Localized Surface Plasmon Resonance in Reactant Activation. *Appl. Catal., B* **201**7, 209, 183–189.

(33) Takami, D.; Ito, Y.; Kawaharasaki, S.; Yamamoto, A.; Yoshida, H. Low Temperature Dry Reforming of Methane over Plasmonic Ni Photocatalysts under Visible Light Irradiation. *Sustainable Energy Fuels* **2019**, *3*, 2968–2971.

(34) Hou, Y.; Wu, L.; Wang, X.; Ding, Z.; Li, Z.; Fu, X. Photocatalytic Performance of α -, β -, and γ -Ga₂O₃ for the Destruction of Volatile Aromatic Pollutants in Air. *J. Catal.* **2007**, *250*, 12–18.

(35) Lin, Z.; Du, C.; Yan, B.; Wang, C.; Yang, G. Two-Dimensional Amorphous NiO as a Plasmonic Photocatalyst for Solar H₂ Evolution. *Nat. Commun.* **2018**, *9*, No. 4036.

(36) Hu, Q.; Li, W.; Zhang, B.; Sun, W.; Lin, R.; Jiang, H.; He, G. Uniform NiO Nanoparticles Used as Anodes in Li-ion Batteries. *IOP Conf. Ser.: Mater. Sci. Eng.* **2019**, *490*, No. 022063.

(37) Mayedwa, N.; Mongwaketsi, N.; Khamlich, S.; Kaviyarasu, K.; Matinise, N.; Maaza, M. Green Synthesis of Nickel Oxide, Palladium and Palladium Oxide Synthesized via Aspalathus Linearis Natural Extracts: Physical Properties & Mechanism of Formation. *Appl. Surf. Sci.* **2018**, 446, 266–272.

(38) Peck, M. A.; Langell, M. A. Comparison of Nanoscaled and Bulk NiO Structural and Environmental Characteristics by XRD, XAFS, and XPS. *Chem. Mater.* **2012**, *24*, 4483–4490.

(39) Oswald, S.; Brückner, W. XPS Depth Profile Analysis of Non-Stoichiometric NiO Films. *Surf. Interface Anal.* 2004, 36, 17–22.

(40) Zhang, X.; Li, X. Q.; Reish, M. E.; Zhang, D.; Su, N. Q.; Gutierrez, Y.; Moreno, F.; Yang, W. T.; Everitt, H. O.; Liu, J. Plasmon-Enhanced Catalysis: Distinguishing Thermal and Non-thermal Effects. *Nano Lett.* **2018**, *18*, 1714–1723.

(41) Zhang, J. G.; Wang, H.; Dalai, A. K. Kinetic Studies of Carbon Dioxide Reforming of Methane over Ni-Co/Al-Mg-O Bimetallic Catalyst. *Ind. Eng. Chem. Res.* **2009**, *48*, 677–684.

(42) Ferreira-Aparicio, P.; Guerrero-Ruiz, A.; Rodri'guez-Ramos, I. Comparative Study at Low and Medium Reaction Temperatures of Syngas Production by Methane Reforming with Carbon Dioxide over Silica and Alumina Supported Catalysts. *Appl. Catal., A* **1998**, *170*, 177–187.

(43) Bachiller-Baeza, B.; Mateos-Pedrero, C.; Soria, M. A.; Guerrero-Ruiz, A.; Rodemerck, U.; Rodriguez-Ramos, I. Transient Studies of Low-Lemperature Dry Reforming of Methane over Ni-CaO/ZrO₂-La₂O₃. *Appl. Catal., B* **2013**, *129*, 450–459.

(44) Wang, Y.; Yao, L.; Wang, Y. N.; Wang, S. H.; Zhao, Q.; Mao, D. H.; Hu, C. W. Low-Temperature Catalytic CO₂ Dry Reforming of Methane on Ni-Si/ZrO₂ Catalyst. *ACS Catal.* **2018**, *8*, 6495–6506.

(45) Zhang, Q.; Mao, M. Y.; Li, Y. Z.; Yang, Y.; Huang, H.; Jiang, Z. K.; Hu, Q. Q.; Wu, S. W.; Zhao, X. J. Novel Photoactivation Promoted Light-driven CO₂ Peduction by CH₄ on Ni/CeO₂

Nanocomposite with High Light-to-Fuel Efficiency and Enhanced Stability. *Appl. Catal., B* 2018, 239, 555-564.

(46) Sutthiumporn, K.; Kawi, S. Promotional Effect of Alkaline Earth over Ni–La₂O₃ Catalyst for CO₂ Reforming of CH₄: Role of Surface Oxygen Species on H₂ Production and Carbon Suppression. *Int. J. Hydrogen Energy* **2011**, *36*, 14435–14446.

(47) Wu, T.; Lin, D.; Wu, Y.; Zhou, X.; Yan, Q.; Weng, W.; Wan, H. In-Situ FT-IR Investigation of Partial Oxidation of Methane to Syngas over Rh/SiO₂ Catalyst. *J. Nat. Gas Chem.* **2007**, *16*, 316–321.

(48) Liang, Z.; Li, T.; Kim, M.; Asthagiri, A.; Weaver, J. F. Low-Temperature Activation of Methane on the IrO_2 (110) Surface. *Science* **2017**, 356, 299–303.

(49) 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_2 on Ni-CeO₂(111) Surfaces: Effect of Ce³⁺ Sites and Metal–Support Interactions on C–H Bond Cleavage. ACS Catal. **2016**, 6, 8184–8191.

(50) Jiang, S.; Lu, Y.; Wang, S.; Zhao, Y.; Ma, X. Insight into the Reaction Mechanism of CO_2 Activation for CH_4 Reforming over NiO-MgO: A Combination of DRIFTS and DFT Study. *Appl. Surf. Sci.* **2017**, *416*, 59–68.

(51) Xu, W.; Si, R.; Senanayake, S. D.; Llorca, J.; Idriss, H.; Stacchiola, D.; Hanson, J. C.; Rodriguez, J. A. In Situ Studies of CeO₂-Supported Pt, Ru, and Pt–Ru Alloy Catalysts for the Water–Gas Shift Reaction: Active Phases and Reaction Intermediates. *J. Catal.* **2012**, 291, 117–126.

(52) Dama, S.; Ghodke, S. R.; Bobade, R.; Gurav, H. R.; Chilukuri, S. Active and Durable Alkaline Earth Metal Substituted Perovskite Catalysts for Dry Reforming of Methane. *Appl. Catal., B* **2018**, *224*, 146–158.

(53) Rodriguez, J. A.; Liu, P.; Hrbek, J.; Evans, J.; Perez, M. Water Gas Shift Reaction on Cu and Au Nanoparticles Supported on $CeO_2(111)$ and ZnO(0001): Intrinsic Activity and Importance of Support Interactions. *Angew. Chem., Int. Ed.* **2007**, *46*, 1329–32.

(54) Ratnasamy, C.; Wagner, J. P. Water Gas Shift Catalysis. *Catal. Rev.* **2009**, *51*, 325–440.

(55) Fulle, D.; Hamann, H. F.; Hippler, H.; Troe, J. High Pressure Range of Addition Reactions of HO. II. Temperature and Pressure Dependence of the Reaction HO+CO \Leftrightarrow HOCO \rightarrow H+CO₂. J. Chem. Phys. **1996**, 105, 983–1000.

(56) Inokuchi, Y.; Ohashi, K.; Honkawa, Y.; Yamamoto, N.; Sekiya, H.; Nishi, N. Infrared Photodissociation Spectroscopy of [Aniline– $(Water)_n$]⁺(n=1–8): Structural Change from Branched and Cyclic to Proton-Transferred Forms. *J. Phys. Chem. A* **2003**, *107*, 4230–4237.

(57) Liu, Z. Y.; Grinter, D. C.; Lustemberg, P. G.; Nguyen-Phan, T. D.; Zhou, Y. H.; Luo, S.; Waluyo, I.; Crumlin, E. J.; Stacchiola, D. J.; Zhou, J.; Carrasco, J.; Busnengo, H. F.; Ganduglia-Pirovano, M. V.; Senanayake, S. D.; Rodriguez, J. A. Dry Reforming of Methane on a Highly-Active Ni-CeO₂ Catalyst: Effects of Metal-Support Interactions on C-H Bond Breaking. *Angew. Chem., Int. Ed.* **2016**, *55*, 7455–7459.

(58) Horn, R.; Schlögl, R. Methane Activation by Heterogeneous Catalysis. *Catal. Lett.* **2015**, *145*, 23–39.

(59) Wei, J.; Iglesia, E. Isotopic and Kinetic Assessment of the Mechanism of Reactions of CH_4 with CO_2 or H_2O to Form Synthesis Gas and Carbon on Nickel Catalysts. J. Catal. **2004**, 224, 370–383.

(60) Nave, S.; Tiwari, A. K.; Jackson, B. Methane Dissociation and Adsorption on Ni(111), Pt(111), Ni(100), Pt(100), and Pt(110)-(1 ×2): Energetic Study. *J. Chem. Phys.* **2010**, *132*, No. 054705.

(61) Li, J.; Croiset, E.; Ricardez-Sandoval, L. Effect of Metal–Support Interface During CH₄ and H2 Dissociation on Ni/ γ -Al₂O₃: A Density Functional Theory Study. *J. Phys. Chem. C* **2013**, *117*, 16907–16920.

(62) Foppa, L.; Silaghi, M.-C.; Larmier, K.; Comas-Vives, A. Intrinsic Reactivity of Ni, Pd and Pt Surfaces in Dry Reforming and Competitive Reactions: Insights From First Principles Calculations and Microkinetic Modeling Simulations. *J. Catal.* **2016**, *343*, 196–207.

(63) Zhu, Y. A.; Chen, D.; Zhou, X. G.; Yuan, W. K. DFT Studies of Dry Reforming of Methane on Ni Catalyst. *Catal. Today* **2009**, *148*, 260–267.

(64) Fan, C.; Zhu, Y. A.; Yang, M. L.; Sui, Z. J.; Zhou, X. G.; Chen, D. Density Functional Theory-Assisted Microkinetic Analysis of Methane Dry Reforming on Ni Catalyst. *Ind. Eng. Chem. Res.* **2015**, *54*, 5901–5913.

(65) Zhang, J.; Peng, C.; Wang, H.; Hu, P. Identifying the Role of Photogenerated Holes in Photocatalytic Methanol Dissociation on Rutile $TiO_2(110)$. ACS Catal. **2017**, 7, 2374–2380.

(66) Wei, S.; Wang, F.; Dan, M.; Yu, S.; Zhou, Y. Vanadium (V) and Niobium (Nb) as the Most Promising Co-Catalysts for Hydrogen Sulfide Splitting Screened out From 3d and 4d Transition Metal Single Atoms. *Int. J. Hydrogen Energy* **2020**, *45*, 17480–17492.

(67) Li, Y.-F.; Selloni, A. Theoretical Study of Interfacial Electron Transfer from Reduced Anatase $TiO_2(101)$ to Adsorbed O_2 . J. Am. Chem. Soc. **2013**, 135, 9195–9199.

(68) Luntz, A. C.; Persson, M.; Wagner, S.; Frischkorn, C.; Wolf, M. Femtosecond Laser Induced Associative Desorption of H_2 from Ru(0001): Comparison of "First Principles" Theory with Experiment. *J. Chem. Phys.* **2006**, *124*, No. 244702.