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Article

Visible light-enhanced photothermal CO₂ hydrogenation over Pt/Al₂O₃ catalyst

Ziyan Zhao^{a,b}, Dmitry E. Doronkin^{c,d,#}, Yinghao Ye^b, Jan-Dierk Grunwaldt^{c,d}, Zeai Huang^{a,b}, Ying Zhou^{a,b,*}

^a State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation, Southwest Petroleum University, Chengdu 610500, Sichuan, China

^b The Center of New Energy Materials and Technology, School of Materials Science and Engineering, Southwest Petroleum University, Chengdu 610500, Sichuan, China

^c Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology, Karlsruhe (KIT), 76131 Karlsruhe, Germany

^d Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

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ABSTRACT

Light illumination has been widely used to promote activity and selectivity of traditional thermal catalysts. Nevertheless, the role of light irradiation during catalytic reactions is not well understood. In this work, Pt/Al₂O₃ prepared by wet impregnation was used for photothermal CO₂ hydrogenation, and it showed a photothermal effect. Hence, operando diffuse reflectance infrared Fourier-transform spectroscopy and density functional theory calculations were conducted on Pt/Al₂O₃ to gain insights into the reaction mechanism. The results indicated that CO desorption from Pt sites including step sites (Pt_{step}) or/and terrace site (Pt_{terrace}) is an important step during CO₂ hydrogenation to free the active Pt sites. Notably, visible light illumination and temperature affected the CO desorption in different ways. The calculated adsorption energy of CO on Pt_{step} and Pt_{terrace} sites was −1.24 and −1.43 eV, respectively. Hence, CO is more strongly bound to the Pt_{step} sites. During heating in the dark, CO preferentially desorbs from the Pt_{terrace} site. However, the additional light irradiation facilitates transfer of CO from the Pt_{step} to Pt_{terrace} sites and its subsequent desorption from the Pt_{terrace} sites, thus promoting the CO₂ hydrogenation.

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1. Introduction

With the development of industry and economy, significant attention is being paid to environmental remediation [1–4]. Emission of carbon dioxide as a primary greenhouse gas results in global temperature increase and climate changes. Among the numerous CO₂ utilization strategies, CO₂ hydrogenation has attracted extensive attention, because it is not only an im-

portant strategy for improving the environment but also a promising technology for producing renewable hydrocarbon fuels such as HCOOH, CH₃OH, and CH₄ [5–10]. However, CO₂ hydrogenation requires high temperature because of the thermodynamic stability of CO₂ [11–13].

Photothermal catalysis, a combination of photoexcitation with thermal energy to trigger chemical reactions, significantly improves in the activity and selectivity of catalytic reactions

* Corresponding author. Tel: +86-28-83037401; Fax: +86-28-83037406; E-mail: yzhou@swpu.edu.cn

Corresponding author. Tel: +49-721-60848090; Fax: +49-721-60844820; E-mail: dmitry.doronkin@kit.edu

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and the stability of the catalysts [5,14–16]. Therefore, light irradiation has been utilized to promote diverse thermal catalytic reactions such as CO oxidation [17], propylene oxidation [18], Fischer-Tropsch synthesis [19], reverse water gas shift (RWGS) reaction [20], and CO₂ hydrogenation [21]. Light irradiation can significantly improve the catalytic performance of these reactions. For instance, in our previous work, we found that light irradiation promoted CO oxidation through O₂ excitation [22]. Wang et al. [19] reported that photo-induced back donation of electrons from Co to CO facilitated CO activation and dissociation. In addition, visible light irradiation increased RWGS activity of Au nanoparticles by 1300% by decreasing the activation energy from 47 to 35 kJ/mol [20]. For CO₂ hydrogenation, light-induced electron transfer from Rh to anti-bonding orbitals of a reaction intermediate resulted in efficient CH₄ generation [15]. CO desorption was regarded as the rate-limiting step during CO₂ hydrogenation [23]. However, the effects of light and temperature on this step are still not understood in depth.

In this work, CO₂ hydrogenation was conducted over Pt/Al₂O₃ catalyst. Operando diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was used to investigate CO desorption on Pt sites during the photothermal CO₂ hydrogenation. The reaction pathway is discussed to understand the mechanism of the photothermal catalysis.

2. Experimental

2.1. Catalyst synthesis

Pt/Al₂O₃ catalysts were prepared by the wet impregnation method using aqueous H₂PtCl₆, as described in our previous work [24]. γ -Al₂O₃ (10 nm) was bought from Aladdin Co., Ltd. Briefly, 500 mg γ -Al₂O₃ was dispersed in a mixture of 5 mL H₂PtCl₆ (2 mg/mL) solution and 30 mL water to achieve 2 wt% Pt loading on γ -Al₂O₃. Then, the suspension was stirred for 6 h at 27 °C. The product was centrifuged and dried at 65 °C for 24 h. Pt/TiO₂ was prepared in the same way using hydrothermally synthesized anatase TiO₂ support, as used in our previous work [22] and described in the Supporting Information.

2.2. Characterization

X-ray diffraction (XRD) patterns were recorded on a PANalytical X'pert diffractometer using Cu K α radiation operating at 40 mA and 40 kV. Transmission electron microscopy (TEM) was carried out on an FEI Tecnai G2 20 microscope operating at 200 kV. UV-vis spectra were recorded on a Shimadzu 2600 UV-vis spectrophotometer. Raman spectra were obtained on a Horiba LabRAM HR Evolution Raman spectrometer with a 532 nm laser.

2.3. Evaluation of CO₂ hydrogenation and operando DRIFTS

Sieved powder catalysts (50 mg, 100–200 μ m) were used for the tests. The catalysts were pretreated in 5% H₂/He (100 mL/min) at 200 °C for 6 h. The temperature of the catalyst bed was calibrated by an IR camera. For evaluating the activity,

1000 ppm CO₂ and 6000 ppm H₂ in He were dosed into the reactor (Harrick Praying Mantis™ high temperature reaction chamber with a flat cover and a quartz window, Scheme 1, left) at 110 mL/min. Schott KL 2500 LCD light source with an intensity of 710 mW/cm² was used as the light source. CO and CO₂ concentrations were detected by a Hartmann & Braun Uras 10E detector. The photo-enhancement was calculated as follows: Photo-enhancement = (Rate_{photothermal} - Rate_{thermal})/Rate_{thermal}. OmniStar GSD-320 quadrupole mass spectrometer (Pfeiffer Vacuum) was used to detect CO (m/z = 28), CO₂ (m/z = 44), CH₃OH (m/z = 31), HCOOH (m/z = 46), and CH₄ (m/z = 16).

For operando DRIFTS, the gas composition was kept the same as that for catalytic tests. The spectra were measured on a VERTEX 70 FTIR spectrometer (Bruker) equipped with a mercury cadmium telluride detector. Harrick in situ cell with a dome cover with two KBr windows and a glass window was used as the reactor (Scheme 1, right). The catalyst was pretreated in 5% H₂/He at a flow rate of 100 mL/min at 200 °C for 6 h. The spectra of the pre-reduced catalysts at 30 °C in pure He gas were used as the background spectra. The reacting systems were stabilized for 30 min in the absence of light at room temperature, and then DRIFTS spectra were collected (without light) at 30, 80, 120, 160, and 200 °C. After the spectrum was obtained at each temperature, the catalyst was irradiated for 10 min. Then, it was flushed with He, and the spectrum was recorded again. At each temperature, the catalyst was flushed with He gas for 10 and 20 min, and the additional spectra were collected. The IR spectra were recorded from 4000 to 700 cm⁻¹ with 4 cm⁻¹ resolution and by averaging over 100 scans.

2.4. Thermodynamic calculation

Equilibrium concentrations of species obtained during CO₂ hydrogenation were calculated by HSC chemistry 7 [25]. The ratio of CO₂/H₂ was 1/6, and CHOOH, CH₃OH, CO, H₂O, and CH₄ were originally considered as products. Including CH₄ in the calculation led to the conclusion that is the preferred product under thermodynamic control, with an equilibrium concentra-

Scheme 1. Scheme of the setup for evaluating the CO₂ hydrogenation activity and performing the operando DRIFTS.

tion close to 100% among all the carbon-containing species at all the studied temperatures [26]. Since only a small amount of CH₄ was detected experimentally, its production was limited by kinetics. Therefore, it was excluded from further thermodynamic analysis.

2.5. Computational details

Density functional theory (DFT) calculations were performed using DMol³ software package based on Materials Studio software. The electron exchange and correlation were approximated by generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional. Dispersion correction by TS (DFT-D) was used to describe the van der Waals interaction. The valence electron configurations were 2s²2p² for C, 2s²2p⁴ for O, and 5d⁹6s¹ for Pt. As for the Monkhorst-Pack grid *k*-point in the Brillouin-zone, a 5 × 5 × 1 *k*-point was used for geometry optimization. For convergence threshold, the total energy of the system, maxforce, and displacement tolerances were set to 1 × 10^{−5} Ha, 0.02 Ha/Å, and 0.05 Å, respectively. A vacuum space of 15 Å was set between the slabs in order to avoid interaction.

The adsorption energy (*E*_{ad}) of adsorbates was calculated as follows:

$$E_{ad} = E_{CO+surface} - E_{surface} - E_{CO} \quad (1)$$

Here, *E*_{CO+surface} is the total energy of Pt surface with CO, *E*_{surface} is the total energy of the clean surface, and *E*_{CO} is the total energy of CO in the gas phase. The CO molecule was optimized in a three-dimensional (3D) box of *a* = *b* = *c* = 15 Å.

3. Results and discussion

3.1. Photothermal effects

The CO₂ conversion rate and CO production rate during CO₂ hydrogenation over Pt/Al₂O₃ at different temperatures are depicted in Fig. 1. Fig. 1(a) shows that during the thermal catalysis, CO₂ conversion rate increased from 0 to 10 μmol/(g·min) when the temperature changed from 80 to 120 °C and reached up to about 225 μmol/(g·min) at 400 °C. No CO was detected until the temperature reached 200 °C (Fig. 1(b)). Additional light irradiation significantly promoted both CO₂

conversion and CO production rate. For example, the CO₂ conversion rate in the presence of at 120 °C was about 50 μmol/(g·min), while it was only 10 μmol/(g·min) in the dark. The CO production rate was ca. 0 μmol·g^{−1}·min^{−1} at 120 °C in the dark and about 15 μmol/(g·min) under light irradiation (Fig. 1(b)). The production rates at other temperatures were also significantly promoted by light. Moreover, light irradiation decreased the temperature required for CO generation on Pt/Al₂O₃. The CO production rate at 120 °C under light was close to the thermally activated CO production rate at 250 °C, and a similar trend was also observed for CO₂ conversion rates. Photo enhancement was used to evaluate the effect of light on the thermally driven reaction. The enhancement reached the maximum value at 80 °C, which was about 9 times that of the corresponding purely thermally driven CO₂ conversion rate. As the temperature increased, the thermally induced rate further increased, while the photo-induced enhancement decreased, which may be because of mass-transfer limitations [23].

Simultaneously, the temperature increase due to light irradiation should also be taken into consideration. In our previous work, although the light intensity was 972 mW/cm², light irradiation increased the surface temperature by no more than 60 °C [22]. In this work, at a lower light intensity of 710 mW/cm², both CO₂ conversion and CO production rates over Pt/Al₂O₃ at 80 °C were much higher than the rates at 160 °C in the dark. Therefore, Pt/Al₂O₃ exhibited typical synergistic effect of photoexcitation and thermal energy. Since the γ-Al₂O₃ support used here is a typical insulator and cannot not take part in the electron transfer process under light irradiation, it is evident that the active sites for CO₂ hydrogenation are provided by Pt.

To investigate the effect of the support, the alumina support was replaced by a typical photocatalyst, TiO₂. As shown in Fig. S1(a), CO₂ conversion rate over Pt/TiO₂ increased from 10 to 250 μmol/(g·min) when the temperature was increased from 80 to 400 °C. These rates were also significantly promoted by light irradiation. For example, the CO₂ conversion rate was 50 μmol/(g·min) at 80 °C under light irradiation, while it was only about 10 μmol/(g·min) in the dark. Moreover, the light-induced CO₂ conversion rate, 50 μmol/(g·min), was identical to the rate at 250 °C in the dark. The CO₂ conversion and CO production rates over Pt/TiO₂ were similar to those of Pt/Al₂O₃. The slightly higher activity of Pt/TiO₂ may be due to the strong in-

Fig. 1. CO₂ (a) conversion and CO production rates (b) in photothermal CO₂ hydrogenation on Pt/Al₂O₃.

Fig. 2. (a) CO₂ conversion and CO production rates of Pt/Al₂O₃ induced by light irradiation (after subtracting the corresponding thermally induced rates). (b) Ion currents of the products of CO₂ hydrogenation over Pt/Al₂O₃ measured at different temperatures in the dark and under light irradiation.

teraction between the Pt and TiO₂ support, resulting in the higher dispersion of Pt and inhibition of sintering [24]. Obviously, both the catalysts exhibited very small differences in the catalytic activity. Besides, Al₂O₃ as a support with high surface area facilitates high dispersion of Pt even without strong metal-support interaction. Moreover, with the wide band gap, it cannot be excited by light, thereby allowing to decouple the photoexcitation of Pt species and photocatalytic effect of titania. Thus, the following investigations of the mechanism of CO₂ hydrogenation on Pt sites were conducted on Pt/Al₂O₃.

3.2. Products of CO₂ hydrogenation

It is clear from Fig. 2(a) that the CO₂ conversion rate of Pt/Al₂O₃ increased from 32 to 75 μmol/(g·min) and then decreased to 30 μmol/(g·min) as the temperature increased from 80 to 400 °C. Meanwhile, CO production rate increased from 8 to 25 μmol/(g·min) and then decreased to 15 μmol/(g·min). Obviously, the consumed CO₂ was not entirely converted into CO. To evaluate the composition of CO₂ hydrogenation products, the outlet gas was analyzed by mass spectrometry (Fig. 2(b)), and the ion currents of some reactants and products are summarized in Fig. S2. Once CO₂ and H₂ feed was switched on, higher H₂O, CH₄, and HCOOH background was detected. Further

heating resulted in the corresponding increase in CH₄ and H₂O signals, while CO₂ and HCOOH signals decreased. These results indicate that CO₂ and H₂ were gradually converted into CH₄ and H₂O, while HCOOH may have been consumed as the reaction intermediate.

Thermodynamic equilibrium calculation for the used gas feed (molar ratio CO₂:H₂ = 1:6) is shown in Fig. 3. Three ranges can be observed during heating process. Below 120 °C, CH₃OH is the thermodynamically preferred product of CO₂ hydrogenation (CH₄, if included in the calculation, would be the most thermodynamically stable in the entire temperature range). Although HCOOH is thermodynamically less stable than the other products, it was experimentally detected, and its concentration decreased with increasing temperature. In the range of 120 to 180 °C, CO₂ is the most thermodynamically stable component; hence, its reduction is not favored in this temperature range, as also confirmed experimentally from the low conversion rates. When the temperature was above 180 °C, CO₂ conversion rate gradually increased, and CO production (reverse water gas shift reaction) was favored, which was consistent with the experimental change in CO₂ conversion and CO production rates shown in Fig. 3(a). As shown in Fig. S2, the ion currents of reactants and products obtained from the experimental results exhibited similar trends in the calculation. Thus,

Fig. 3. Relative thermodynamic stabilities of species in the system including CO₂ (initial concentration 1), H₂ (initial concentration 6), and CO, HCOOH, CH₃OH, H₂O (initial concentrations of these four species were 0). (a) Temperature dependent equilibrium concentrations of all the considered reactants and products except CH₄; (b) Enlarged view of the trends of CO₂, CO, CH₃OH, and H₂O from (a).

Fig. 4. XRD patterns (a) and a representative HRTEM image (b) of Pt/Al₂O₃ (with a histogram showing the size distribution of Pt nanoparticles).

the thermodynamic calculation agrees well with the experimental results, indicating that CO₂ hydrogenation is not limited by kinetics (unlike the CH₄ pathway).

3.3. Structure, morphology, and optical properties

Pt was not detected in the XRD patterns (Fig. 4(a)), and all the diffraction peaks were attributed to γ -Al₂O₃ (PDF#16-0394). TEM images (Fig. 4(b)) showed Pt nanoparticles with a diameter of 0.9 ± 0.2 nm (shown in Fig. S3) deposited on Al₂O₃. The crystalline interplanar spacings of 0.226 and 0.195 nm were indexed to {111} and {200} facets of Pt, while the spacing of 0.289 nm was attributed to {117} facet of γ -Al₂O₃. As reflected in the UV-vis spectra (Fig. S4), Pt deposition promoted the light adsorption ability of Al₂O₃ in the range 200–600 nm [27]. Strong interaction at the Pt/TiO₂ interface was evidenced for Pt/TiO₂ [24]. Raman spectra showed a signal located at 145 cm⁻¹ attributable to the E_g(1) peak of anatase (spectrum given in the supporting information, Fig. S5). After Pt deposition, this peak shifted to 151 cm⁻¹, which indicated the generation of Pt-O_{vacancy}-Ti³⁺ at the interface between Pt and TiO₂ [28]. Hong et al. [29] reported that Pt-O_{vacancy}-Ti³⁺ behaved as an adsorption site for the reaction intermediates such as CO generated from HCOOH decomposition. This increased the residence time of surface intermediates, resulting in the promoted activity. It might be also the reason that Pt/TiO₂ (Fig. S1) exhibited higher activity than Pt/Al₂O₃ (Fig. 1).

Table 1

Assignments of peaks in IR spectra during CO₂ hydrogenation.

Wavenumber/cm ⁻¹	Assignment	Refs.
2326–2362	CO ₂	[30]
2058–2046	CO Pt _{terrace}	[31,32]
2038–2007	CO Pt _{step}	[31] [32]
2007	CO on Pt _{step}	[32] [33]
1760	Bridged CO	[31]
1625	–OH	[32,34]

3.4. Operando DRIFTS

Operando DRIFT spectra obtained during the photothermal catalytic CO₂ hydrogenation are shown in Fig. 5, and the assignments of IR peaks are summarized in Table 1. The maximum temperature to obtain a reasonable signal-to-noise ratio was 200 °C.

Fig. 5(a) shows that after the exposure of Pt/Al₂O₃ to CO₂ and H₂ at 30 °C, peaks emerged at 2326–2362 and 1625 cm⁻¹, which were attributed to CO₂ and –OH on Pt [30,32,34]. These signals became weaker, and the peaks at 2007 and 1760 cm⁻¹ corresponding to carbonyl and CO evolved as the temperature increased from 30 to 200 °C [31–33]. No CO production was observed when the temperature was increased to 120 °C, (Fig. S2(d)), which was in agreement with thermodynamics (Fig. 3(b)). On the other hand, HCOOH decreased (Fig. S2(e)), while the intensity of carbonyl band at 2007 cm⁻¹ (Fig. 5(a)) did not increase. Increase in the catalyst temperature resulted in higher intensity of the carbonyl band at 2007 cm⁻¹. Considering the gradual decrease in HCOOH concentration in the effluent (Fig. S2(e)) and the increase in CO concentration (Figs. 1–3), the higher band intensity was attributed to the CO produced on Pt_{step} site [31,32].

Under light illumination below 80 °C, the intensity of the band at 1624 cm⁻¹ (surface –OH) decreased (Fig. 5(b)). The signals in the range 2326–2362 cm⁻¹ (CO₂) slightly increased, while the intensity of the peaks at 2007 and 1760 cm⁻¹ (CO) obviously rose [30–33]. Besides, CO₂ and HCOOH ion currents decreased, as shown in Fig. S2(a) and Fig. S2(e). These changes indicate that CO₂ was preferably adsorbed on Pt and then formed small amount of CO under light irradiation. At temperatures above 120 °C, CO generation was promoted by temper-

Fig. 5. Operando DRIFT spectra of Pt/Al₂O₃ during thermal (a) and photothermal (b) CO₂ hydrogenation.

ature, and CO molecules gradually accumulated on Pt_{step} sites in the absence of light. When the light was turned on at the respective temperatures, CO signals increased significantly, indicating the enhanced CO generation (Fig. 5(b)). This was in accordance with the increased concentration of CO in the gas phase (Fig. 1(b) and Fig. S2(d)). It was worth noting that the CO signal at 2007 cm⁻¹ was blue shifted once the light was turned on, indicating the weakened interaction of CO molecules with Pt_{step} sites.

To further investigate the interaction between CO and Pt, He was used to flush the catalyst surface to observe the intermediate species adsorbed during the photothermal CO₂ hydrogenation (Fig. 6). CO on Pt_{step} sites (2038–2007 cm⁻¹ [31,32]) was not visible after He flushing. However, CO on Pt_{terrace} sites was detected in the range 2058–2046 cm⁻¹, which was different from the thermal catalysis shown in Fig. 5(a) [31,32]. This indicates that light and temperature have different effects on CO adsorption. The adsorption of CO on Pt_{step} sites is much stronger compared with that on Pt_{terrace} sites, the desorption from which was found to occur at 77–177 °C [35]. As shown in Fig. 1(b), a small amount of CO evolved at temperature below 200 °C in the dark; hence, the generated CO was probably desorbed from Pt_{terrace} sites, and the corresponding signals could not be observed in the IR spectra (Fig. 5(a)). On the other hand, the adsorption of CO was stronger on the undercoordinated Pt_{step} sites, resulting in clearly visible IR bands. Even when the temperature reached 200 °C, the CO produced accumulated on Pt_{step} sites, as reported previously [36]. Thus, the observed CO on Pt_{terrace} (Fig. 6) did not originate during the thermal catalysis but during light irradiation.

3.5. Effects of light and temperature on CO₂ desorption

According to the mechanism of CO₂ hydrogenation [37], CO desorption is regarded as an important step, with activation energy of CO desorption from Pt and Pd being much higher than that from other metals [23]. At low temperatures, the active sites on metal surface are usually covered by CO, which poisons or blocks the sites [38,39]. Hence, CO desorption from the active sites requires the sites to be free for catalyzing the CO₂ hydrogenation. The operando DRIFTS results indicated

Fig. 6. Operando DRIFT spectra of Pt/Al₂O₃ after 20 min of flushing with He gas after turning off light.

that light and temperature affected CO desorption in different ways. The formed CO was preferably desorbed from Pt_{terrace} sites during heating, while its distribution seem to be altered under additional light irradiation.

Compared with the terrace sites, metal step sites are more coordinatively unsaturated, which is beneficial for CO adsorption [40,41]. To further reveal the interaction between CO and Pt, energies of CO adsorption on Pt_{terrace} and Pt_{step} sites were calculated by DFT. Adsorption geometries and the corresponding energies are shown in Fig. 7. The Pt-C distances for CO adsorbed on Pt_{terrace} and Pt_{step} sites were 2.01 and 1.98 Å, and the adsorption energies were -1.24 and -1.43 eV, respectively, which were similar to the reported values of -1.39 and -1.42 eV in the previous work [42]. This indicates that CO is more strongly adsorbed on Pt_{step} sites than on Pt_{terrace} sites, consistent with the IR spectra [43,44]. Fig. 5(b) and Fig. 6 show that light irradiation weakens the interaction between CO and Pt_{step} sites. However, even after He flushing, CO on Pt_{terrace} site with weaker bonding was detected during the photothermal process in the range 30–200 °C, while the CO on Pt_{step} site was not visible. This indicates that CO was desorbed from Pt_{step} sites, while the CO produced accumulated on Pt_{terrace}. Additionally, Lawrenz et al. [45] reported that laser light could induce the spillover of CO from Pt_{step} to Pt_{terrace} sites. Thus, upon light irradiation, the CO produced first transfers from Pt_{step} sites to Pt_{terrace} sites and then desorbs from Pt_{terrace} sites.

Based on the results mentioned above, the main reactions occurring during CO₂ hydrogenation are summarized in Eqs. (2–5), and the mechanism of light- and temperature-induced activation of CO desorption from Pt during CO₂ hydrogenation is summarized in Fig. 8. CO₂ and H₂ are spontaneously converted to HCOOH because of the low activation energy [46]. Subsequently, HCOOH is decomposed to *CO adsorbed on Pt_{terrace} ($E_{\text{ads}} = -1.24$ eV) and Pt_{step} ($E_{\text{ads}} = -1.43$ eV) sites. CO desorption is regarded as a crucial step during CO₂ hydrogenation to free the active, low-coordinated Pt step sites. Considering the weaker interaction between CO and Pt_{terrace} sites, the CO generated preferably desorbed from Pt_{terrace} site in the thermally activated CO₂ hydrogenation process [36]. On the contrary, additional light irradiation induced CO desorption from Pt_{step} sites (with possible spillover to Pt_{terrace} sites), as evidenced by operando DRIFTS. As a result, the interaction between CO and Pt site became weaker, and further thermally activated CO desorption from Pt_{terrace} site was facilitated. Hence, we suggest that this, in turn, promotes CO₂ hydrogenation [45,47]. This should be further substantiated in future studies.

Fig. 7. Adsorption energies and Pt-C distances for CO adsorbed on (a) Pt_{terrace} and (b) Pt_{step}.

Fig. 8. Effects of light and temperature on the CO desorption during CO₂ hydrogenation at different Pt sites.

4. Conclusions

Pt/Al₂O₃ was synthesized through the impregnation method. It exhibited photothermal catalytic activity in CO₂ hydrogenation, with Pt being the active site. Operando DRIFTS and theoretical calculations indicated that light and temperature facilitated CO desorption from Pt in different ways. CO preferentially desorbed from Pt_{terrace} sites during thermal activation. With additional light irradiation, CO on Pt_{step} site was transferred to Pt_{terrace} site, thus facilitating its thermal desorption from Pt_{terrace} site. As a result, CO desorption activated by both heating and additional light irradiation resulted in the promotion of CO₂ hydrogenation. This work provides further understanding of the effect of light and temperature on CO desorption during CO₂ hydrogenation and may help in designing more efficient photothermal catalytic processes in future.

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Graphical Abstract

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Visible light-enhanced photothermal CO₂ hydrogenation over Pt/Al₂O₃ catalyst

Ziyan Zhao, Dmitry E. Doronkin *, Yinghao Ye, Jan-Dierk Grunwaldt, Zeai Huang, Ying Zhou *
Southwest Petroleum University, China; Karlsruhe Institute of Technology, Germany

Light illumination and temperature affected CO coverage during CO₂ hydrogenation in different ways, offering a new pathway for improving the thermal catalysis.

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光照对Pt/Al₂O₃光热CO₂加氢反应的增强作用

赵梓伊^{a,b}, Dmitry E. Doronkin^{c,#}, 叶英浩^b, Jan-Dierk Grunwaldt^{c,d}, 黄泽皓^{a,b}, 周莹^{a,b,*}

^a西南石油大学油气藏地质及开发工程国家重点实验室, 四川成都610500, 中国

^b西南石油大学材料科学与工程学院新能源材料及技术研究中心, 四川成都610500, 中国

^c卡尔斯鲁厄理工学院化学技术与高分子化学研究所, 卡尔斯鲁厄76131, 德国

^d卡尔斯鲁厄理工学院催化研究与技术研究所, 卡尔斯鲁厄76344, 德国

摘要: 在传统热催化材料的研究领域中, 光照技术已经得到了广泛的应用, 从而使传统热催化剂的催化反应活性和选择性得到优化。然而, 在光热协同催化反应过程中, 光照因素对催化反应过程的影响尚未得到很好地研究和理解。本文通过浸渍法制得Pt/Al₂O₃催化剂, 并应用于光热协同催化CO₂加氢反应。结果证明, 在光热协同CO₂加氢催化反应中, Pt/Al₂O₃催化剂表现出光热协同效应。本文结合原位漫反射红外光谱(*operando* DRIFTS)和密度泛函理论计算(DFT)对光照因素对该催化反应过程的作用机制进行了进一步深入研究。结果表明, CO气体分子从Pt纳米颗粒上的脱附过程为CO₂加氢反应的重要步骤; CO气体分子在Pt纳米颗粒上脱附的位置包含台阶位置(Pt_{step})和平台位置(Pt_{terrace})。结果表明, 反应过程中CO气体分子从Pt表面的脱附有利于催化剂暴露出Pt反应活性位点。值得注意的是, 在光热协同催化CO₂加氢反应过程中, 光照和温度因素对CO气体分子的脱附过程具有不同影响。吸附能的计算结果证明, CO气体分子吸附在Pt_{step}和Pt_{terrace}上的吸附能分别为-1.24和-1.43 eV。由此可见, CO气体分子与Pt纳米颗粒上的Pt_{step}吸附位点之间相互作用更强。在无光照作用的条件下对催化剂进行加热, CO气体分子更容易从Pt_{terrace}吸附位点发生脱附; 但是在对应的温度下加入光照作用后, 吸附在Pt_{step}位点上的CO气体分子会先转移到Pt_{terrace}吸附位点上, 随后脱附, 从而促进CO₂加氢反应的进行。

关键词: 二氧化碳加氢; 光热催化; 铂/三氧化二铝; 原位漫反射红外光谱; 密度泛函理论

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*通讯联系人. 电话: (028)83037401; 传真: (028)83037406; 电子邮箱: yzhou@swpu.edu.cn

#通讯联系人. 电话: +49-721-60848090; 传真: +49-721-60844820; 电子邮箱: dmitry.doronkin@kit.edu

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