Influence of mid-infrared laser irradiation conditions on CO_2 photoreduction performance of Au/TiO_2 catalyst

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Abstract: We carried out CO_2 photoreduction with an Au/TiO_2 photocatalyst and simultaneous irradiation with UV light and a 2 μm wavelength mid-infrared laser at several cooling temperatures. This work's purpose was to observe the relationship between the CH_4 production efficiency and the laser irradiation. We analyzed the generated components using FT-IR spectroscopy and found that CH_4 production rate with laser irradiation at 40 ℃ was 1.7 times larger than that at 15 ℃. We assumed that the CH_4 production rate increased because the number of vibrationally excited CO_2 molecules at 40 ℃ was more than that at 15 ℃.
Keywords: CO_2 photoreduction, Au/TiO_2, Mid-infrared laser

1. Introduction

Photocatalysis is an important technology that can solve some environmental issues related to global warming, because photoreduction of the photocatalyst can convert CO_2 into hydrocarbons such as CH_4. It was reported that Au/TiO_2 could convert CO_2 into hydrocarbons (e.g., CH_4 and CO) under photoirradiation.[1],[2] We studied the CO_2 photoreduction performance of the Au/TiO_2 catalyst under simultaneous irradiation with UV light and a 2.05 μm wavelength mid-infrared laser and confirmed that the CH_4 generation efficiency increased as a result of irradiation with the mid-infrared laser.[3],[4] In this work, we carried out simultaneous irradiation with UV light and a 2 μm wavelength mid-infrared laser at cooling temperature of 15 ℃ and 40 ℃.

2. Experimental

Au/TiO_2 (anatase) was produced by deposition precipitation method and fixed on a 20 × 20 mm quartz filter paper. The sample was sintered at 200 ℃ for 2 hours in an air atmosphere before irradiation. We then placed the sample in a gas reactor and carried out simultaneous irradiation with UV light and a 2 μm wavelength mid-infrared laser. After 1 hour of irradiation, we analyzed the generated components by FT-IR spectrometer and repeated the irradiation and analysis five times. The atmosphere in the gas reactor was CO_2 at 50% R.H. Figure 1 shows the experimental setup. We adjusted the mid-infrared laser light to irradiate the surface of the quartz filter paper in the gas reactor.

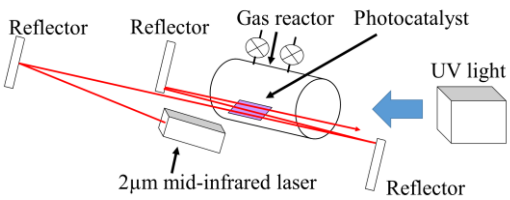

Figure 1. Experimental setup

3. Results and discussion

Scanning electron microscope (SEM) and Transmission electron microscope (TEM) images of the Au/TiO_2 (anatase) are shown in Figure 2. The Au/TiO_2 (anatase) particle diameter was approximately 0.5 μm from Figure 2(A) and the Au nanoparticle diameter was approximately 14 nm from Figure 2(C). We analyzed the generated components using FT-IR spectroscopy. We calculated the amounts of CH_4 produced from the absorbance differences around 3017 cm^{-1}. Figure 3 shows the relationship between the CH_4 concentration calculated from absorbance differences and the irradiation times for each irradiation condition. The CH_4 production rate was calculated from the production amount per unit time from 2~5 hour, considering the influence of

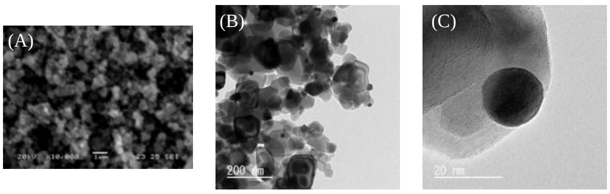

Figure 2. SEM and TEM images of Au/TiO_2 (anatase) (A)SEM (B)TEM, and (C) TEM of Au nanoparticle

sample surface impurities. The CH_4 production rate without the laser is 0.12 μmol/(g·h), and the rates with laser cooling temperature of 15 ℃ and 40 ℃ are 0.23 μmol/(g·h) and 0.39 μmol/(g·h), respectively. The CH_4 production rate with laser irradiation at 40 ℃ was 1.7 times larger than that at 15 ℃. We found that the laser wavelength at a cooling temperature of 40 ℃ red-shifted compared to that at 15 ℃ (2.05 μm). Figure 4 shows the CO_2 infrared absorption spectrum and probable 2 μm mid-infrared laser spectra at 15 ℃ and 40 ℃. Since the CO_2 infrared absorption exists in the 2.05~2.06 μm range, when the mid-infrared laser wavelength shifts to above 2.05 μm, the overlap between the CO_2 infrared absorption range and the mid-infrared laser wavelength increases. From Figure 4, the intensity of the absorbed infrared light is given by equation (1). Equation (1) approximates by Taylor expansion of the first approximation.

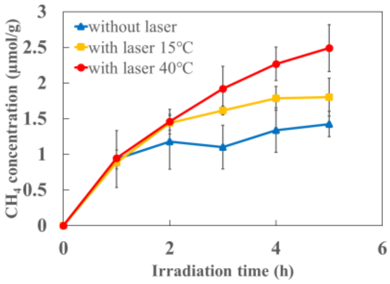

Figure 3. Relationship between CH_4 concentration calculated from absorbance differences and irradiation time

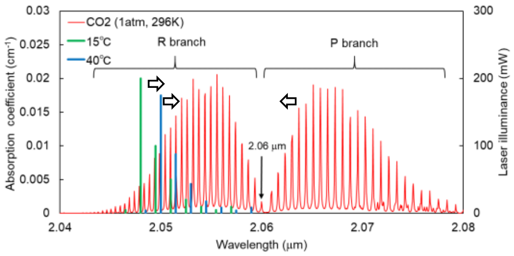

Figure 4. CO_2 infrared absorption spectrum and probable 2 μm mid-infrared laser spectra at 15 ℃ and 40 ℃

$$I_{abs} = \Sigma I_{0i} (1 - \exp(-\alpha_i \cdot l)) \approx \Sigma I_{0i} \cdot \alpha_i \cdot l \quad (1)$$

In equation (1), I_{abs} is the intensity of absorbed infrared light (mW), I_{oi} is the intensity of the irradiating infrared light at ν_i (mW), α_i is the CO_2 absorption coefficient at ν_i (cm^{-1}), l is the gas reactor length (cm), ν_i is the wavenumber (cm^{-1}). The number of vibrationally excited CO_2 molecules is given by equation (2).

$$N_{CO2} = I_{abs} / E_i \quad (2)$$

In equation (2), N_{CO2} is the number of vibrationally excited CO_2 molecules and E_i is the photon energy at ν_i (J). From equations (1) and (2), we could calculate the number of vibrationally excited CO_2 molecules. Figure 5 shows the number of vibrationally excited CO_2 molecules at each wavelength. We calculated the number of vibrationally excited CO_2 molecules at each wavelength at 15 ℃ and 40 ℃ as 1.4×10^{17} and 3.4×10^{17}, respectively. We assumed that the CH_4 production rate increased because the number of vibrationally excited CO_2 molecules at a cooling temperature of 40 ℃ was more than that at 15 ℃ and the excitation allowed electron transfer from Au nanoparticles on the TiO_2 to CO_2 molecules.

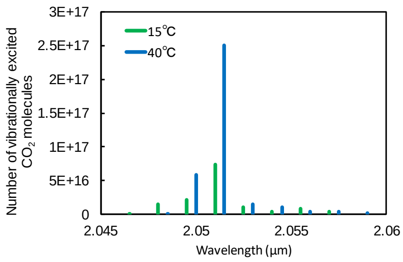

Figure 5. Number of vibrationally excited CO_2 molecules

4. Conclusions

We carried out CO_2 photoreduction on Au/TiO_2 under simultaneous irradiation with UV light and a 2 μm mid-infrared laser. It was found that the CH_4 production rate with laser irradiation at 40 ℃ was approximately 1.7 times larger than that at 15 ℃. We assumed that the CH_4 production rate increased because the number of vibrationally excited CO_2 molecules at a cooling temperature of 40 ℃ was more than that at 15 ℃.

References

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