

In situ FTIR Study of Photocatalytic CO₂ Reduction on Photocatalysts

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Introduction

The use of transition-metal loaded titania (TiO₂) has been extensively studied as a photo catalyst in photoreactions. Unlike traditional catalysts drive chemical reactions by thermal energy, semiconducting photocatalysts can induce chemical reactions by inexhaustible sunlight. Greenhouse gases such as CO₂, CH₄ and CFCs are the primary causes of global warming. CO₂ can be transformed into hydrocarbons in a photocatalytic reaction. The advantage of photo reduction of CO₂ is to use inexhaustible solar energy. One of the most promising photocatalysts for CO₂ photoreduction was supported copper titania which was previously synthesized using sol-gel method in our lab. Our previous results showed that Cu promoted CO₂ reduction activity and improved the selectivity of the product toward methanol [1]. However, the mechanisms of photocatalytic CO₂ reduction on TiO₂ under UV irradiation have not explored widely. Knowledge of elementary steps in photocatalytic CO₂ reduction under UV irradiation is required in order to improve the photo efficiency of the photocatalyst.

A heterogeneously photocatalytic reaction usually takes a longer time, i.e., hours or days, than a thermal reaction. In our previous study, the intermediates of photocatalytic NO oxidation was successfully analyzed by in situ FTIR spectroscopy [2]. In the present work, we applied diffuse reflectance technique to study photocatalytic CO₂ reduction on the TiO₂ surface via in situ Fourier Transform Infrared (FTIR) spectroscopy in time sequence. Copper loaded TiO₂ photocatalyst was also included in this work to elucidate the metal effect. The focus was placed on the intermediates and products generated on the surface by photo excited TiO₂. Possible mechanism of the photocatalytic CO₂ reduction was also proposed.

Materials and Methods

The photoreduction of CO₂ on TiO₂ and Cu/TiO₂ was studied using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) under UV irradiation. Zero-grade air, high-purity He and ultra-purity CO₂ (99.999 v% from Air Products USA) were used in the reaction system. In order to reduce water interference, air and He passed through a moisture adsorbent before entering the photoreactor. A clear IR signal was obtained using these dehumidifying apparatus. A catalyst of 140 ~170 mg was pretreated inside the photoreactor under air flow and UV irradiation at 500°C to remove residue hydrocarbons. The IR scanning range was 4000 ~ 650 cm⁻¹ with 4 cm⁻¹ resolution using a Mercury-Cadmium-Telluride detector in a Nexus 470 IR spectrometer (Thermo Nicolet). Each IR spectrum was obtained by 16-64 scans.

Results and Discussion

As well known in photocatalysis, electron-hole pairs are photogenerated in a semiconductor such as TiO₂ under UV irradiation, then a photocatalytic reaction would be initiated. Water molecule is first dissociated into H⁺ and OH⁻ ions. Hydrogen atom is produced

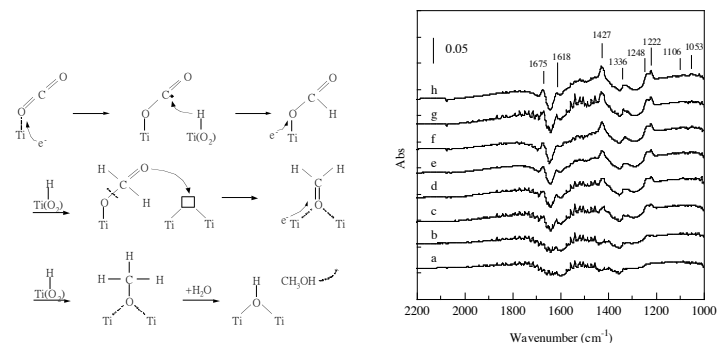
from H⁺ by accepting an electron and adsorbed on the surface. Surface adsorbed hydrogen will be used to reduce adsorbed CO₂ to hydrocarbons as shown in the Scheme.

As shown in the Figure, UV irradiation quickly induces the increasing of bicarbonate (1675, 1427 cm⁻¹) and carbonate (1336 cm⁻¹). The photo generated OH group and oxygen vacancy further increase the amount of bicarbonate and carbonate which are converted from gas-phase CO₂. However, once bicarbonate or carbonate are formed, they become very stable on the TiO₂ surface and no further conversion is possible. Formic acid (1618 cm⁻¹), formaldehyde (1106 cm⁻¹) and methoxy (1053 cm⁻¹) emerge and increase after UV irradiation as shown in the Figure. Obviously these species are produced from the photoreduction of adsorbed CO₂. They are the intermediates in the elementary steps of CO₂ photoreduction on TiO₂. Other possible intermediates may also exist but cannot be detected due to the limitation of IR measurement.

The scheme illustrates the mechanism of adsorbed CO₂ which is further photocatalytically reduced to hydrocarbons under UV irradiation. Starting from the adsorbed CO₂, format (HCOO) is formed by accepting an electron and adding one hydrogen atom. Dioxymethylene (H₂COO) is formed from the format by adding one hydrogen atom, then migrates to the adjacent oxygen vacancy to form formaldehyde (H₂CO) by accepting one electron. In this step, one oxygen is detached from dioxymethylene and left on the previous TiO₂ site. Methoxy (CH₃O) is then formed by adding another hydrogen atom. Finally methoxy reacts with free surface H₂O and converts to methanol, then leaves one OH group on TiO₂ surface after methanol is desorbed from the surface.

Significance

Various intermediates and species on TiO₂ were observed during the CO₂ photoreduction using in situ FTIR. The mechanism of photoreduction of CO₂ is revealed.



Scheme : Proposed mechanism of enhanced photocatalytic CO₂ reduction on CuTiO₂

Figure: IR spectra of CO₂ photoreduction on TiO₂ under UV irradiation (a)10sec,(b)1min,(c)10min,(d)20min,(e)30min,(f)1hr,(g)1hr30min,(h)2hrs, CO₂ adsorbed TiO₂ before the UV irradiation is used as the background.

References

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2. J. C. S. Wu, Y.-T. Cheng, *J. Catal.*, 237, 393 (2006)