In situ FTIR Study of Photocatalytic CO$_2$ Reduction on Photocatalysts

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Introduction

The use of transition-metal loaded titania (TiO$_2$) has been extensively studied as a photocatalyst in photo-reactions. Unlike traditional catalysts, drive chemical reactions by thermal energy, semiconductor photocatalysts can induce chemical reactions by inexhaustible sunlight. Greenhouse gases such as CO$_2$, CH$_4$, and CFCs are the primary causes of global warming. CO$_2$ can be transformed into hydrocarbons in a photocatalytic reaction. The advantage of photocatalysis is to use inexhaustible solar energy. One of the most promising photocatalysts for CO$_2$ photoreduction was supported copper titania which was previously synthesized using sol-gel method in our lab. Our previous results showed that Cu promoted CO$_2$ reduction activity and improved the selectivity of the product toward methanol [1]. However, the mechanisms of photocatalytic CO$_2$ reduction on TiO$_2$ under UV irradiation have not explored widely. Knowledge of elementary steps in photocatalytic CO$_2$ 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 CO$_2$ reduction on the TiO$_2$ surface via in situ Fourier Transform Infrared (FTIR) spectroscopy in time sequence. Copper loaded TiO$_2$ 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 TiO$_2$. Possible mechanism of the photocatalytic CO$_2$ reduction was also proposed.

Materials and Methods

The photoreduction of CO$_2$ on TiO$_2$ and Cu/TiO$_2$ was studied using diffuse reflectance infrared Fourier transform spectroscopy (DRIFTs) under UV irradiation. Zero-grade air, high-purity He and ultra-purity CO$_2$ (99.999 vol% 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 TiO$_2$ 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 CO$_2$ 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 CO$_2$. However, once bicarbonate or carbonate are formed, they become very stable on the TiO$_2$ 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 CO$_2$. They are the intermediates in the elementary steps of CO$_2$ photoreduction on TiO$_2$. Other possible intermediates may also exist but cannot be detected due to the limitation of IR measurement.

The scheme illustrates the mechanism of adsorbed CO$_2$ which is further photocatalytically reduced to hydrocarbons under UV irradiation. Starting from the adsorbed CO$_2$ format (HCOO) is formed by accepting an electron and adding one hydrogen atom. Dioxyxethylene (H$_2$COO) is formed from the format by adding one hydrogen atom, then migrates to the adjacent oxygen vacancy to form formaldehyde (H$_2$CO) by accepting one electron. In this step, one oxygen is detaches from dioxyxethylene and left on the previous TiO$_2$ site. Methoxy (CH$_3$O) is then formed by adding another hydrogen atom. Finally methoxy reacts with free surface H$_2$O and converts to methanol, then leaves one OH group on TiO$_2$ surface after methanol is desorbed from the surface.

Significance

Various intermediates and species on TiO$_2$ were observed during the CO$_2$ photoreduction using in situ FTIR. The mechanism of photoreduction of CO$_2$ is revealed.

Scheme : Proposed mechanism of enhanced photocatalytic CO$_2$ reduction on Cu/TiO$_2$

Figure: IR spectra of CO$_2$ photoreduction on TiO$_2$ under UV irradiation (a) 0sec, (b) 1min, (c) 10min, (d) 20min, (e) 30min, (f) 1hr, (g) 1hr 30min, (h) 2hrs, CO$_2$ adsorbed TiO$_2$ before the UV irradiation is used as the background.

References