Photocatalytic performance of titania supported metal for CO\textsubscript{2} photoreduction using UV-A(365nm) illumination

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Introduction
Greenhouse gases such as CO\textsubscript{2}, CH\textsubscript{4} and CFCs are the primary causes of global warming. The atmospheric concentration of CO\textsubscript{2} has recently increased owing to human activity, further accelerating the greenhouse effect. Plants use solar energy to perform natural photosynthesis, but the energy transformation is low at the cost of supporting their lives. Consequently, the photoreduction of CO\textsubscript{2} is particularly interesting, and achieving a high efficiency for this reaction is highly desired. The ultimate goal is to demonstrate that artificial photosynthesis may be implemented via the photoreduction of CO\textsubscript{2} to produce hydrocarbons, such as methanol or methane. Equation 1 describes a photo reaction for methanol synthesis from CO\textsubscript{2}.

\[
\text{CO}_2 + 2 \text{H}_2\text{O} \xrightarrow{\text{hv}} \text{CH}_3\text{OH} + \frac{3}{2} \text{O}_2 \quad [1]
\]

Catalysts were prepared via the sol-gel method. The precursor was titanium (IV) butoxide (Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}, 97% in n-butanol), as purchased from Aldrich (USA). The hydrolysis process was performed in a glove box maintained at a relative humidity under 25% by purging with tank nitrogen. To avoid rapid precipitation during polycondensation and the formation of unstable colloidal sols, the hydrolyzing water was homogeneously released by the esterification of butanol and acetic acid[1]. Carbon dioxide was photocatalytically reduced to produce methanol in an aqueous solution using UV-A (365 nm) irradiation. Figure 1 schematically illustrates the reactor system. Supercritical-fluid grade CO\textsubscript{2} was purchased from Air Products (USA) to avoid any hydrocarbon contamination. Liquid sample was withdrawn and analyzed in a GC using FID. Analysis results indicated that methanol was the dominant hydrocarbon.

Results and Discussion

Figure 2 shows the methanol yields of various catalysts. The methanol yield of 5.96 wt% Cu/TiO\textsubscript{2} gave approximately 7 \text{\mu}mole/g following 30-hours of UV-A illumination, while that of Degussa P25 titania was almost un-detectable. The methanol yield of 2 wt% Cu/ TiO\textsubscript{2} was near 5 \text{\mu}mole/g, and it seems no difference after the hydrogen reduction of the catalyst. Figure 3 displays the VU-Vis spectra of P25 and 2 wt% Cu/TiO\textsubscript{2}, respectively. Cu/TiO\textsubscript{2} had higher UV absorption near 365 nm than P25 resulting in the high methanol yield. The redistribution of the electric charge and the Schottky barrier of Cu and TiO\textsubscript{2} also facilitates electron trapping via supported Cu. However, Compared with 254 nm VU-C illumination, the methanol yield was significantly reduced due to the low photon energy of 365 nm UV-A[2]. XPS analysis (Figure 4) revealed that Cu 2p\textsubscript{3/2} was at 933.6 eV and the spectrum indicated primary
Cu$^{1+}$ species on the TiO$_2$ supports. Quantitative XPS analysis also revealed that most Cu clusters were on the TiO$_2$ surface. The catalytic reduction of CO$_2$ has great advantage over green plants of not having to support a living system. Ideally, the transformation of photo to chemical energy by a non-living catalyst should be more efficient than that by a life-supporting one.

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References
