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Correlating Nanostructure and Activity in Cu/TiO_2 Photocatalyst.

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Photoreduction of carbon dioxide (CO_2) on titanium dioxide (TiO_2) into fuels is an important topic in the area of solar fuels [1]. To increase performance, semiconducting photocatalysts such as TiO_2 may be modified by addition of a metal co-catalyst [2]. The metal particles act as traps for the photo-produced electrons and decrease the recombination of the electron-hole pairs [3]. We are interesting in understanding the relationship between catalyst nanostructure and photocatalytic activity. In the current work, we correlate transmission electron microscopy observations with photoreactor studies to investigate the structure-property relationship for Cu/TiO_2 photocatalysts for methane production from CO_2 and H_2.
Cu metal was finely dispersed on the surface of TiO_2 using an incipient wetness impregnation method at metal loadings of 5 and 10 % by weight. TiO_2 (aeroxide® TiO_2 P25) from Evonik was impregnated under controlled humidity and temperature conditions. The Cu precursor ($Cu(NO_3)_2$) was first dissolved into alcohol, and the desired volume of the copper solution was added to the TiO_2. The wet powder was mixed for 10 minutes, dried, calcined and reduced in H_2 to give a dispersion of metallic Cu particles. The Cu/TiO_2 samples were analyzed in a JEOL JEM-2010F TEM/STEM microscope. A probe size of 0.5 nm was used for acquiring the STEM images and the detector was a JEOL ADF. The photoreactions with reactant gases of CO_2 and H_2 were carried out for 12 hours in a quartz window photoreactor under ultraviolet light (wavelength of 306 nm) with intensity at the sample of 0.0175 W/cm^2. After the irradiation time, the product gases were analyzed and quantified by Varian gas chromatography system equipped with both a flame ionization and thermal conductivity detector.

Figure 1 shows a standard gas chromatogram obtained from the gas in the photoreactor after irradiation and clearly shows that methane (CH_4) has been produced on the photocatalyst (CH_4 elutes from the first column at 0.85 minutes and from the second column at 3.2 minutes). The yield (ppm) is obtained after integrating the area under the CH_4 peak as shown in Table 1. The best activity was obtained from the 5% Cu loaded catalyst. The yield from the 10 %Cu sample was significantly lower than the 5% sample and even the bare TiO_2. To investigate the difference in performance of these catalysts, we performed Z-contrast STEM imaging to examine the Cu metal dispersion. The image from the 5% samples (Figure 2a) showed a uniform dispersion of Cu particles with a few nanometers in size over almost all of the titania support. The 10% sample showed a much less uniform metal loading with areas of substrate with almost no metal dispersion (Figure 2b) and areas with reasonable metal dispersion (Figure 2c). Thus, we would expect the yield from high dispersion sample to be greater than the yield from the low dispersion sample. However, this does not explain the drop in yield that we observe on the 10%Cu sample compared to the bare TiO_2. However, we notice that the heavier loading sample is much darker than the sample with 5% loading. This may indicate that a significant fraction of UV radiation may get directly absorbed by the metal with heavier metal loading, thus reducing the total number of electron-hole pairs available for photocatalysis. This and other issues related to the oxidation state of the Cu will be discussed.

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Table 1: Yield of CH_4 produced by the catalysts.

Catalyst	**CH_4 yield (ppm)**
TiO_2	55.4
5% Cu/TiO_2	73.4
10 % Cu/TiO_2	8.7

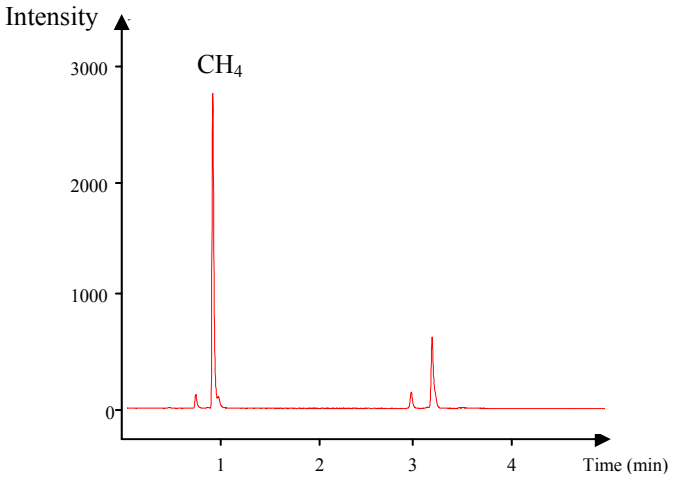

Figure 1: Gas chromatogram acquired from the flame ionization detector showing CH_4 peak for 5% Cu/TiO_2 catalyst.

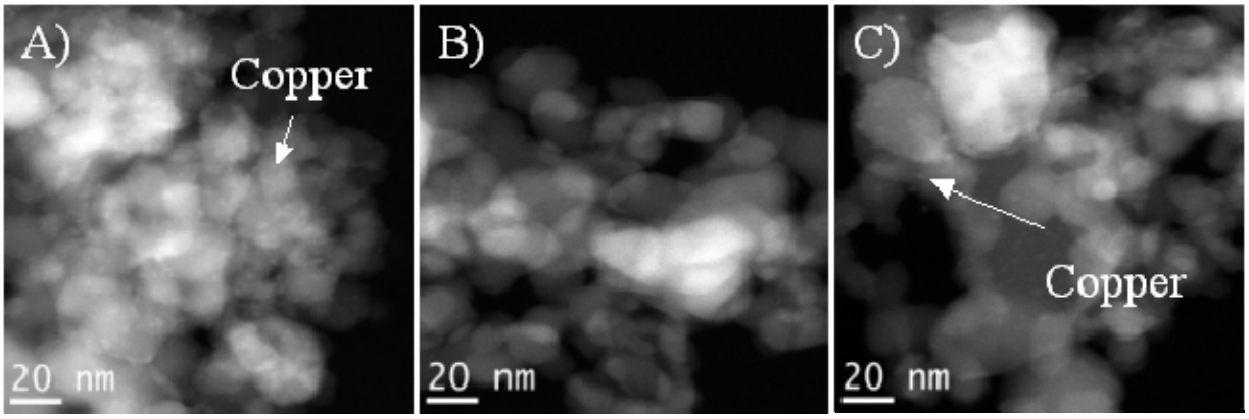

Figure 2: a) Z-contrast image of 5% Cu/TiO_2 showing good dispersion, b) and c) Z-contrast images of 10% Cu/TiO_2 showing variations in local metal loading.

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