Short Communication

On the impact of Cu dispersion on CO₂ photoreduction over Cu/TiO₂

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A family of Cu/TiO₂ catalysts was prepared using a refined sol–gel method, and tested in the photocatalytic reduction of CO₂ by H₂O to CH₄ using a stirred batch, annular reactor. The resulting photoactivity was benchmarked against pure TiO₂ nanoparticles (synthesised by an identical sol–gel route). CO₂ photoreduction exhibited a strong volcano dependence on Cu loading, reflecting the transition from 2-dimensional CuOx nanostructures to 3-dimensional crystallites, with optimum CH₄ production observed for 0.03 wt.% Cu/TiO₂.

1. Introduction

The natural environment is well-versed in maintaining an equilibrium between carbon dioxide (CO₂) fixed through photosynthesis, and that released into the atmosphere via normal biochemical processes. However, this natural equilibrium has been strongly perturbed over the past few centuries through increased CO₂ emissions arising from fossil fuel combustion. The consequential dramatic rise in atmospheric CO₂ concentrations is well documented as the major contributor to ongoing climate change [1]. The most promising strategies proposed to slow, and eventually reverse, this rising CO₂ emissions are a switchover to renewable energy sources, or implementing carbon capture and storage technologies (CCS) alongside conventional chemical processes. Direct CO₂ utilisation as a chemical feedstock (notably for methane or methanol production) remains poorly exploited by current industrial processes, hence there exists great potential for new clean technologies for large-scale CO₂ fixation [3].

CO₂ photoreduction is one such promising method for ameliorating atmospheric CO₂ levels, while simultaneously providing energy-rich or chemically useful products such as CO, methane (CH₄), methanol (CH₃OH), formaldehyde (HCHO) or formic acid (HCOOH). A major challenge to such chemistry remains the development of efficient photocatalysts for direct CO₂ photoreduction offering high quantum yields, activity and selectivity. TiO₂ is widely used in photocatalysis due to its low cost and toxicity, thermal stability and photo-response under UV irradiation, and thus may be viewed as a potential candidate for CO₂. However, the highest CO₂ photoreduction rate achieved using unpromoted TiO₂ is only 25 μmol·g⁻¹·h⁻¹ [4,5], and consequently too low for industrial commercialisation. Methods to modify the titania band gap, such as N-doping, or the addition of metal or oxide promoters to promote separation of photo-excited charge carriers and increase their lifetime for re-action with adsorbrates, have both shown promise as routes to improve CO₂ photoreduction activity [6–8]. However, to date, there has been little effort to optimise promoter loadings or understand their impact upon TiO₂ catalysed CO₂ photoreduction. Here we systematically explore the influence of Cu promotion via incorporation during sol–gel synthesis, upon photocatalytic CH₄ production from CO₂, and demonstrate that the resulting CuO dispersion plays a critical role in regulating the photocatalytic performance of Cu/TiO₂, wherein highly-dispersed (likely 2-dimensional islands) CuO nanostructures maximise the CH₄ yield.

2. Experimental

2.1. Catalyst preparation

Pure and copper loaded TiO₂ were prepared by a modified sol–gel method adapted from Wu et al. [9] employing titanium (IV) n-butoxide (Ti(OC₄H₉)₂, Acros Organics, 99%) and copper (II) chloride (CuCl₂·2H₂O, Certified AR, 99%) precursors. To provide the stoichiometric amount of water for hydrolysis of the titanium precursor, 0.02 mol of Ti(OC₄H₉)₂ was mixed with 0.08 mol of n-butanol (C₄H₉OH, Certified AR, 99.5%) and 0.08 mol of acetic acid (CH₃COOH, Acros Organics, Glacial 99.8%).
Cu-loaded TiO₂ was synthesised by pre-dissolving the desired amount of copper precursor (to provide 0.01–0.3 wt.% Cu/TiO₂) in the 0.08 mol n-butanol in order to achieve uniform copper incorporation throughout the titania support. Upon mixing the Ti(OCH₂CH₃)₄ with n-butanol and acetic acid, esterification of the latter two chemicals resulted in slow water release and Ti(OCH₂CH₃)₄ hydrolysis [10] which was complete after 6 h. The resulting sol–gel was placed in a chamber furnace and heated at 3 °C min⁻¹ to 150 °C and held for 2 h to dry the precursor. The temperature was then ramped at 5 °C min⁻¹ to 500 °C and held for 1 h to remove residual hydrocarbons and crystallise the titania. Samples were then ground by mortar and pestle for 20 min into powder form prior to CO₂ photoreduction tests.

2.2. Catalyst characterization

The resulting titanias were analysed by powder X-ray diffraction (XRD, Hiltonbrooks) to identify the associated crystal phases. Analyses were conducted using Cu Kα radiation at 1.5406 Å over 20 = 5°–65° at 2°/min. Crystallite sizes were estimated from line broadening using the Scherrer equation [11]. Elemental analysis of the metal loaded TiO₂ catalysts was performed via ICP-MS (Thermo-Fisher Scientific X-series®). The surface composition [12] and chemical environment was evaluated by X-ray photoelectron spectroscopy (XPS) on a Kratos Axis HSi instrument using a Mg Kα excitation source and equipped with a charge neutraliser and magnetic focusing lens. Particle morphology was examined by transmission electron microscopy (TEM, JEOL 2100F, 200 kV) with analysis using a Gatan Orius camera and ImageJ 1.43u software.

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revealing significant Cu surface segregation with surface compositions of 1.2–8.7 wt.% versus bulk values spanning 0.47–1.76 wt.%, indicative of phase separated Cu$_2$O, rather than framework substituted Cu$^+$ ions.

Total surface areas of the commercial and sol–gel titanias are shown in Fig. S2 from which it is evident that Cu loading has little effect upon the textural properties of the sol–gel materials, with areas only decreasing by 10% from the parent TiO$_2$ across the series. It is interesting to note that the lowest (<=0.02 wt.% Cu) loadings actually induce a small, but systematic increase in total surface area, before the subsequent net fall. Changes of this small magnitude are not expected to influence titania-related contributions to the resultant photoactivity [16,17], however, we believe these low loading surface area changes are a genuine effect associated with the formation of 2-dimensional Cu$_2$O islands. In contrast to the total areas, specific copper surface areas and associated dispersions are strongly loading dependent (Fig. 3). At loadings below 0.03 wt.% Cu is essentially 100% dispersed, corresponding to either atomically isolated species, or 2-dimensional rafts (a partial encapsulating monolayer over the titania nanocrystallites). In the former scenario, the copper chemical environment should resemble that within a titanate, and not Cu$_2$O as observed by XPS, hence we can discount the presence of isolated Cu atoms. The initial plateau in dispersion for loadings up to 0.03 wt.%, followed by rapid fall towards zero for higher copper concentrations, strongly suggests the existence of two growth regimes: 2-dimensional Cu$_2$O island growth for loadings between 0.01 and 0.03 wt.%; and subsequent genesis and growth of 3-dimensional Cu$_2$O nanoparticles. This transition point occurs at very low effective Cu coverages, far below the nominal full monolayer, evidencing a Volmer–Weber growth mode, and poor wetting of titania by copper oxide as observed by STM [18] and XPS [19] over rutile TiO$_2$(110). Nucleation, growth and coalescence of oxide and metal nanoparticle on planar and porous substrates are complex processes [20–22], where we hope to utilise scanning probe microscopy and in-situ XAS to further investigate the atomic-scale structure of our Cu$_2$O nanostructures in the future.

3.2. Photocatalytic activity

CO$_2$ photoreduction was performed for 1.5 h during UVA irradiation and the resulting correspondence between methane yields and Cu dispersion/surface area is presented in Fig. 4. A strong volcano dependence of photoactivity for methane production with copper loading was observed for the sol–gel materials, wherein the CH$_4$ yield of the best-performing 0.03 wt.% Cu/TiO$_2$ catalyst was exhibited a 10-fold rate-enhancement over that of undoped titania. Since the mean TiO$_2$ crystallite sizes are all close to the optimal value (14 nm) for CO$_2$ photoreduction [23], and in common with their total surface areas, show little variance across the series, this pronounced effect cannot be attributed to geometric differences in the titania support. The extremely low copper concentrations necessary to achieve such promotion, with the maximum yield attained at only 400 ppm Cu, is especially striking, and also indicates a phenomenon arising from the promoter phase, rather than changes in the bulk properties of the titania parent. Fig. 4 demonstrates that CO$_2$ photoreduction is strongly associated with the exposed Cu$_2$O surface area; methane yield tailing off coincident with the switchover from 2-dimensional islands to 3-dimensional Cu$_2$O crystallites. It is interesting to note the different selectivity reported for higher loading Cu/TiO$_2$ photocatalysts prepared via a similar sol–gel route [6], wherein methanol and not methane was the primary product of CO$_2$ photoreduction. Although the origin of this copper loading dependence requires further investigation, it may reflect band gap broadening with Cu$_2$O crystallite size, affording more energetic photo-excited electrons necessary to drive the more thermodynamically difficult reduction of CO$_2$ to methanol ($E^\text{redox} = -0.38$ V vs. NHE, compared with -0.28 V for methane production) [4]. Peak methanol production reported in reference [6] (780 nmol/h/g) is also substantially higher than our best methane productivity (24 nmol/h/g), reflecting the widely disparate reaction conditions employed; specifically, the use of higher energy UVC in reference [6], which also utilised internal reactor illumination (resulting in a higher photon flux to the catalyst), and

![Fig. 2. Cu 2p XP spectra of: (A) Pure TiO$_2$; (B) 0.5 wt.% Cu/TiO$_2$; (C) 1 wt.% Cu/TiO$_2$; and (D) 2 wt.% Cu/TiO$_2$ sol–gel catalysts.](image-url)

![Fig. 3. Copper dispersion and specific surface area of Cu/TiO$_2$ sol–gel catalysts as a function of nominal bulk Cu loading.](image-url)

![Fig. 4. Correspondence between 1.5 h CH$_4$ yield from CO$_2$ photoreduction over Cu/TiO$_2$ sol–gel catalysts and Cu surface area and dispersion.](image-url)
crucially added NaOH to the reaction mixture to act as hole-scavengers suppressing recombination, all of which served to enhance methanol production.

3.3. Possible mechanism of copper promotion

It has been previously postulated that Cu$^+$ dopants (as free ions or the oxide) could serve as traps for photoexcited electrons or holes arising from TiO$_2$ [24,25]. Such electron–hole exchange could also occur between Cu$_2$O nanostructures and TiO$_2$ in this work, slowing slow e$^-$–h$^+$ recombination within the parent titania and thereby increasing the probability of electron transfer to adsorbed CO$_2$ and the genesis of reactive intermediates such as CO$_2$ and HC$O_2^-$ [26–28]. Such charge-trapping is expected to be heavily influenced by the nature of the heterojunction interface between Cu$_2$O and TiO$_2$, with 2-dimensional copper oxide islands facilitating rapid charge migration from the underlying titania substrate (for subsequent CO$_2$ and water activation), while minimising the potential for bulk e$^-$–h$^+$ recombination within 3-dimensional Cu$_2$O crystallites [29,30]. If surface Cu$_2$O species are indeed the active centre for CO$_2$ photoreduction, then one would anticipate a linear correlation between photoactivity and Cu dispersion, precisely as seen in Fig. 5. It is important to recall that the band gap of Cu$_2$O lies in the visible, and thus may itself undergo direct photoexcitation upon UVA or solar irradiation, contributing to methane production. However, at the extremely low Cu concentrations found to be optimal within this study, it seems more probably that Cu$_2$O acts as a intermediary in CO$_2$ photoreduction, trapping and stabilising a high flux of photoexcited electrons created on titania, for transport to adsorbed carbon dioxide.

A recent in-situ DRIFTS study utilising isotopically-labelled $^{13}$CO$_2$ showed that surface carbon impurities may act as a carbon source for the production of reactively-formed hydrocarbons from CO$_2$ photocatalysis over titania, via the reverse Boudouard reaction, and corresponding intermediate CO formation [31]. Although Yui and co-workers have since used isotopic labelling to unequivocally demonstrated that CO$_2$ can indeed be photoreduced to methane over TiO$_2$ and Pd/TiO$_2$ [32], the question remains as to what extent the reverse Boudouard reaction (4) competes with direct CO$_2$ photoreduction (3) as a source of methane, or indeed whether direct photo-oxidation of surface carbon may occur (5).

\[
\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CH}_4 + 2\text{O}_2 \quad \text{true photosynthesis via direct CO}_2 \text{ photoreduction} \quad (3)
\]

\[
\text{CO}_2 + \text{C}_2 \rightarrow 2\text{CO} \quad \text{reverse Boudouard reaction (surface C participation)} \quad (4)
\]

\[
\text{H}_2\text{O} + \text{C}_2 \rightarrow \text{CO} + \text{H}_2 \quad \text{photo – oxidation of surface carbon (no CO}_2 \text{ participation)} \quad (5)
\]

Fig. 5. Linear correlation between CH$_4$ yield and Cu dispersion over Cu/TiO$_2$ sol–gel catalysts.

The last scenario, namely whether methane arise from photo-oxidation of surface carbon by water (the only possible process by which it could form without direct participation of CO$_2$) can be easily discounted by a simple control experiment in which we exposed our catalysts to water and UV light in the absence of CO$_2$, resulting in negligible methane. This definitively proves that photo-activated CO$_2$ is an essential reactant in our methane production, as first postulated by Inoue and co-workers [33] and demonstrated by isotope-labelling experiments [31,34], enabling us to discount reaction (5). In order to assess the likely contribution of reaction (4), i.e. surface carbon assisted CO$_2$ photoreduction, to our observed methane yield, we examined the relationship between methane production and the initial surface carbon concentration of our as-prepared Cu/TiO$_2$ catalysts from XPS. Fig. 6 reveals a strong inverse correlation between carbon impurities on our as-prepared catalysts and methane production. While this does not conclusively prove that surface carbon plays no role in our observed photocatalysis, it offers strong evidence that the major route to reactively-formed methane is via direct CO$_2$ photoreduction and not carbon-assisted reverse disproportionation. It is important to note that the goal of this communication is not to elucidate the global reaction pathway in CO$_2$ photoreduction, but rather, to identify key structural aspects in Cu-doped TiO$_2$ photocatalysts to guide future materials design and thereby engineer improved methane production. Future isotope studies would be welcome to quantify the extent of any possible minor contributions from reaction (4).

4. Conclusions

Copper-loaded titania photocatalysts, prepared via a one-pot, sol–gel synthesis, comprise highly dispersed and surface localised Cu$_2$O nanostructures decorating 14 nm anatase crystallites. Cu$_2$O strongly promotes CO$_2$ photoreduction to methane under UVA light, with up to 10-fold rate-enhancements over the analogous unloaded anatase. This promotion is strongly linked to the nature of the dispersed copper oxide morphology, with 2-dimensional islands proposed both as trapping centres for anatase photoexcited charge carriers, and the primary active site responsible for CO$_2$ photoreduction. Formation of Cu$_2$O multilayers/nanoparticles at Cu loadings >0.03 wt.% limits the magnitude of this promotion, possible reflecting increased e$^-$–h$^+$ recombination within the bulk of 3-dimensional copper oxide crystallites. There is no evidence that reactively-formed methane arises from the reverse disproportionation reaction of CO$_2$ with surface carbon, although we cannot discount minor contributions from such a reverse Boudouard process.

Fig. 6. Inverse correlation between 1.5 h CH$_4$ yield from CO$_2$ photoreduction over Cu/TiO$_2$ sol–gel catalysts and surface carbon content.
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Appendix A. Supplementary data

Supplementary data to this article can be found online at doi:10.1016/j.catcom.2012.03.025.

References


