Photocatalytic production of methanol from CO_2 at Cu/TiO$_2$ surfaces in a continuous optofluidic microreactor

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1. Introduction

The recycling of CO_2 by using sunlight (the photocatalytic reaction of CO_2 and H_2O, also known as artificial photosynthesis) is a promising alternative for the production of methanol (CH_3OH) at mild conditions, in contrast to the conventional thermocatalytic reforming of CH_4 through syngas. It is a "killing two birds with one stone" approach, since it allows closing the carbon loop and generate a valuable chemical from CO_2 in a circular economy [1]. The slow kinetics of CO_2 photoreduction and the low quantum efficiencies (which are directly related to the photocatalytic material used and cell configuration), however, limit the widespread use of this technology. Titanium dioxide (TiO_2) has been the most widely used semiconductor for solar-fuel production. This is because TiO_2 is a wide bandgap (3.0 eV), cheap and nontoxic semiconductor, also resistant to photocorrosion. Nevertheless, it is also well known that TiO_2 presents poor electron-hole pair separation. Doping TiO_2 with copper (Cu) has been proven a successful strategy for improving the ability to trap electrons, without affecting their mobility, and thus reducing recombination losses [2]. Cu is also able to enhance the photocatalytic production of CH_3OH [3], which can be probably ascribed to the preference of H to adsorb on Cu and react with O of the co-adsorbed O-CH_3 intermediate, thereby forming CH_3OH [4]. In any case, the photoreactor design is also key in the process. The recent research in the so-called optofluidics, a synergy of microfluidics and optics, has shown several advantages in photocatalytic processes, including large surface-area-to-volume ratio, uniform light distribution, enhanced mass transfer and fine flow control [5]. The use of optofluidic microreactors can also reduce the requirements for time, sample volume and equipment. In spite of that, their use has been scarcely explored for the photocatalytic reduction of CO_2 [3].

In light of this, the main objective of this work is to evaluate the continuous photocatalytic conversion of CO_2 into CH_3OH in an optofluidic microreactor using Cu-decorated TiO_2 surfaces. The analysis includes the effect of structural parameters of the photoactive layer such as Cu content and photocatalyst loading, as well as operating variables such as flow rate, irradiance and cell configuration (i.e. one or two compartments configuration). The results are then compared with current state of the art for CO_2 photoreduction to CH_3OH.

2. Methods

The Cu/TiO$_2$ photo-responsive surfaces with different loadings, L, ranging from 0.5 to 3 mg/cm^2 were manufactured by airbrushing a photocatalytic ink onto a teflonated porous carbon paper (TGP-H60, Toray Inc.). This ink was prepared by a mixture of commercial Cu (Cu and Cu_2O, Sigma Aldrich) and TiO_2 (P25, Sigma Aldrich), Cu nanoparticles synthesized in 3-methyl-n-butylimidazolium tetrafloroborate [bmim][BF$_4$] ionic liquid and decorated on TiO_2 (P25) [6] or bare TiO_2 photocatalysts, a Nafion® dispersion 5wt.% (Alfa Aesar) as binder, and isopropanol (Sigma Aldrich) as vehicle, with a 70/30 catalyst/Nafion mass ratio and a 3% solids (catalyst + Nafion) percentage. The Cu/TiO$_2$ carbon papers were then placed in the reaction microchamber with high surface-area-to-volume ratio (1 cm^2, 75 µL). The material was sandwiched with PTFE gaskets between two highly transparent PMMA plates. A CO_2 saturated 0.5 M KHCO$_3$ (Panreac >97%) aqueous solution was supplied with a peristaltic micropump (Miniplus 3 Gilson) with a flow rate, Q, ranging from 25 to 200 µL/min. 1200 mW LED lights (LED Engin) of 365 nm (UV) and 450 nm (Vis) lights illuminated the microchamber. The irradiance, E, varied from 2.5 to 10 mW/m^2, measured by a radiometer (Photoradiometer Delta OHM). CH_3OH concentration at the outlet of the microreactor was analyzed by duplicate in a headspace gas chromatograph (GCMS-QP2010 Ultra Shimadzu) equipped with a FID detector. The performance is evaluated in terms of formation rate, r (i.e., yield per gram of material and time) and the apparent quantum yield, AQY, defined as the rate of electrons transferred towards CH_3OH per rate of incident photons on the surface.

3. Results and discussion

The continuous photocatalytic reduction of CO_2 at the Cu/TiO_2-based carbon papers led predominantly to the formation of CH_3OH, with also C_2H_5OH and $HCOOH$, a potential intermediate in the CO_2-to-CH_3OH conversion pathway [7]. Figure 1a and 1b show the effect of Cu content and photocatalyst loading, respectively, on CH_3OH production with Cu/TiO_2 synthesized in [bmim][BF_4] (as representative case) after 2 hours of UV illumination. The material presents also activity under Vis light illumination, although the yields are far from those obtained with UV light.
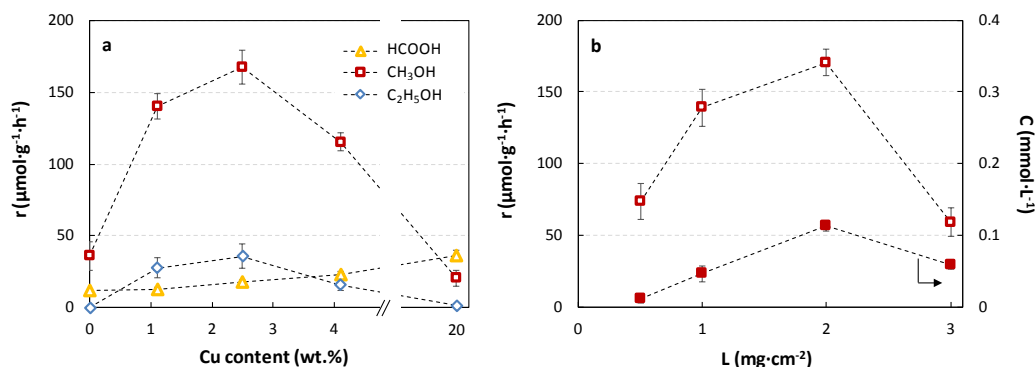

Figure 1. CH_3OH yields at different (a) Cu contents and (b) L under UV illumination.

As observed, CH_3OH yield increases with Cu content until 2.5 wt% ($r= 167.5$ µmol·g^{-1}·h^{-1}, $AQY= 3.7$ %), clearly enhancing the values obtained at bare TiO_2 ($r= 36.5$ µmol·g^{-1}·h^{-1}, $AQY= 0.79$ %). Cu can serve as an electron trapper, partially avoiding electron-hole recombination. Higher Cu contents, however, can shield the photoexciting capacity of TiO_2. Besides, Figure 1b shows that CH_3OH yield finds an optimum at $L= 2$ mg·cm^{-2}. Below this L, the number of generated electron-hole pairs is reduced due to a lower photoactive surface available. Higher loadings led to particle agglomeration, reducing the photoactive surface and limiting the access of CO_2 and OH^- due to a higher photocatalyst thickness layer. Moreover, formation rates can be still enhanced when increasing irradiance up to 10 mW·cm^{-2}, although AQY fell as the additional UV light supplied is consumed by side reaction, such as the probable production of H_2, and due to a higher electron-hole recombination rate. Besides, increases in Q produce a slight alteration in the conversion rate, which can indicate that the reduction products are not efficiently washed away from the photoactive surface, and reoxidation of CH_3OH in the microchamber occurs. In any case, using lower Q is preferred since a more concentrated product can be obtained without sacrificing the conversion rate. Finally, the microreactor configuration is able to vary product selectivity under identical conditions. Thus, when CO_2 is supplied as gas in a two-compartment configuration, CH_3OH and C_2H_5OH can be produced, with small amounts of $HCOOH$. This may be explained by the alteration provoked by CO_2 in the vicinity of the photocatalytic material and the enhanced diffusion of products at the reactor outlet.

4. Conclusions

All in all, the maximum r obtained with 2.5% wt. Cu/TiO_2 in the microreactor system for the continuous transformation of CO_2 to CH_3OH is $r= 208.2$ µmol·g^{-1}·h^{-1} at $L= 2$ mg/cm^2, $Q= 50$ µL/min and $E= 10$ mW·cm^{-2} (UV light). This value outperformed most of the values previously reported at Cu/TiO_2-based systems in common CO_2 photoreactor configurations (i.e. batch and slurry reactors), which can be partially ascribed to the enhanced mass transport, larger volume/active area ratio and uniform light distribution in this photoreactor design. The results are a step forward in the development of efficient processes for the photoreduction of CO_2, although the research efforts should continue in developing more active photocatalysts and optimizing reactor configuration in order to boost CH_3OH yields.

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