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Photocatalytic CO_2 reduction to methanol: How can the dilemma be solved?

Alberto Garcia-Baldovi[1], Abdullah M. Asiri[2] and Hermenegildo Garcia[1,2]

Abstract

In the context of the upcoming hydrogen technology, methanol can play a crucial role as liquid hydrogen organic carrier and as energy vector. However, for this new role, methanol has to be obtained through a CO_2-neutral footprint process. One appealing possibility is the selective solar-light photocatalytic CO_2 reduction with H_2O. The present opinion highlights the contradiction of methanol being easily oxidized under photocatalytic conditions and its possible formation using photocatalysis. The opinion emphasizes the importance of control experiments, particularly the use of isotopic labeled $^{13}CO_2$, to firmly support the source of possibly detected methanol. A viable strategy to solve the conundrum is the use of heterojunctions in which the oxidizing component does not show preference for methanol adsorption.

Addresses

[1] Instituto Universitario de Tecnología Química, Consejo Superior de Investigaciones Científicas-Universitat Politecnica de Valencia, Universitat Politecnica de Valencia, Av. De Los Naranjos S/b, 46023, Valencia, Spain

[2] Center of Excellence in Advanced Materials Research, King Abdulaziz University, Jeddah, Saudi Arabia

Corresponding author: Garcia, Hermenegildo (hgarcia@qim.upv.es)

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Photocatalysis, Solar fuels, Methanol synthesis from CO_2, Isotopic labeling.

Introduction

The massive CO_2 emissions to the atmosphere is considered as one of the major anthropogenic contributions to the Earth global warming and associated climate change. Among the various complementary strategies to diminish these emissions, a longer term possibility is the shift from fossil fuels to CO_2-neutral energy sources [1]. While this revolutionary change in energy sources occurs, a valid approach for a temporary period could be CO_2 capture from large stationary sources and its subsequent utilization, implementing the first steps for a CO_2 circular economy [2]. CO_2 capture and utilization processes would still be viable at long term for renewable CO_2 sources as biogas and fermentation plants and even for the direct use of atmospheric CO_2.

Among the possible CO_2-derived products, the most appealing ones are those that currently have a high economic interest or large potential for market growth, as it is the case of C_{2+} hydrocarbons, aromatic compounds and alcohols. In this context, methanol is one of the most interesting CO_2-derived products, since its production volume is expected to double in the next few years and can be used either as bulk chemical in the preparation of resins and polymers or as a fuel [3]. Being a liquid at ambient conditions, methanol can be used directly as transportation fuel with a high heat volumetric capacity or it can be considered as a liquid hydrogen organic carrier, being possible to decompose methanol to provide on -board hydrogen with one of the highest H_2 storage capacity values up to 18 wt%. In this sense, CH_3OH can also play a certain role in the future H_2 economy, thus providing a smooth transition from CO_2-forming fuels to H_2 as energy vector.

While methanol can be obtained catalytically by CO_2 hydrogenation, the thermal process is very unsatisfactory and only a limited progress towards large scale implementation has been achieved [4]. Besides green H_2 availability, one of the major drawbacks of the thermal process is the contradictory constraints imposed by thermodynamics and kinetics, there being still a need for suitable catalysts [4]. On one hand, CO_2 hydrogenation to methanol is an exothermic process and heating at high temperatures disfavors the equilibrium, favoring alternative products, particularly CO and CH_4. On the other hand, the high thermodynamic stability of the CO_2 molecule makes necessary high temperatures to overcome the energy barriers of CO_2 activation. Due to the lack of catalysts that could promote the reaction at near ambient temperatures, the best compromise between thermodynamics and catalysis is reached at temperatures in the range from 250 to 300 °C, but the operating pressure should be high, above 50 bars. Even under these conditions, CO_2 conversion is typically low if a high methanol selectivity is going to be achieved.

Conventional catalysis uses heat as energy source to overcome kinetic barriers. In contrast to thermal catalysis, photocatalysis employs the energy of photons to reach electronically excited surfaces of the substrates in which reactions can occur at ambient or even below ambient temperatures [5]. The reaction mechanism in photocatalysis starts with absorption of a photon by a material or compound that becomes excited from the ground state to an upper electronic state. For solid semiconductors, this photon absorption of energy higher than the bandgap and the consequent electron excitation results in an almost universal state of charge separation with electrons being promoted to the semiconductor conduction band, leaving behind a positive charge (electron hole) in the material valence band. This transient state of charge separation generated in the subpicosecond timescale decays by geminate charge recombination or after migration of electrons and holes (charge carriers) to trapping sites, reaching the surface on which chemical reactions can occur. Photocatalysis developed in the eighties, mainly as an advanced oxidation technique for water and air purification using lamps as light sources [6].

In the context of substituting fossil fuels for alternative clean primary energy sources, there is an increasing interest in the use of sunlight as primary energy. Sunlight is a polychromatic radiation constituted by UV-A ($380<\lambda<420$ nm), visible ($420<\lambda<800$ nm) and IR ($800<\lambda>1500$ nm), with a typical energy distribution of 4%, 42%, and 54%, respectively, for these three regions. Accordingly, photocatalysis has refocused in the last decades towards conversion of solar or visible light into the generation of fuels using natural solar irradiation, although most of the studies are performed using simulated sunlight from a Xe lamp with adequate air mass filter. In this new research area termed "*Solar Fuels*" [7], photocatalytic CO_2 reduction has been, together with H_2 generation, two of the most widely studied photocatalytic reactions. Among the major differences between overall water splitting to generate H_2 and photocatalytic CO_2 reduction, one is that the latter processes can give rise to various products, such as CO, methane, formic acid, ethylene and methanol, depending on the number of electrons, protons and involved CO_2 molecules [8]. The present opinion discusses some reports dealing with methanol generation from photocatalytic CO_2 reduction. The purpose is to critically comment literature data on photocatalytic methanol formation from CO_2 reduction contrasted with results from our laboratory. For the sake of space, we will limit mostly to reports using modified graphitic carbon nitride (g-CN) forming heterojunctions with other materials, either carbon dots (CDs) or metal-organic frameworks (MOFs), since they have achieved recent remarkable results or data that need to be confirmed. Our aim is to pay attention to the issue of methanol stability under the photocatalytic conditions in which it should be formed, urging for a deep understanding of the reasons why methanol appears as product in photocatalytic g-CN systems.

Photocatalytic methanol formation from CO_2

Carbon dots as hole scavengers without promoting CH_3OH oxidation

Recently in 2020, Tang and coworkers disclosed that CDs obtained from citric acid and urea under hydrothermal conditions by microwave heating are excellent hole acceptors in heterojunctions constituted by these CDs (2−10 nm) supported on g-CN [9]. The resulting CD/g-CN heterojunction is able to generate stoichiometric amounts of methanol and oxygen from CO_2 and H_2O with a remarkable quantum efficiency over *2%* at 420 nm and nearly 100% product selectivity upon irradiation with visible light. CO_2 was confirmed as precursor of the observed MeOH by ^{13}C isotopic labeling experiments. The CD/g-CN heterojunction was used in three consecutive runs (12 h in total) reproducing in the three cases the temporal profile of MeOH evolution [9].

Certainly these results are remarkable for several reasons, including the high photon efficiency and almost complete methanol selectivity, but also for the visible light photoactivity of the system (up to 600 nm) and the use of H_2O as electron and proton donor. There are very few photocatalytic studies reporting methanol formation together with the simultaneous evolution of the corresponding 3:2 stoichiometric amounts of O_2 according to equation (1). In fact, it is the reverse reaction, i.e., photocatalytic methanol oxidation to CO_2, what should be in principle highly favored due to the fast hole and electron trapping by methanol and oxygen, respectively. This means that in the present case, after charge separation and migration of holes to CD, this component should somehow favor hole quenching by H_2O rather than by MeOH, in spite of the more favorable thermodynamic potential of the latter. In fact, MeOH is widely used in aqueous solutions to accelerate hole quenching due to the sluggish reactivity of holes with H_2O in most of the photocatalysts and the high oxidation potential needed. However, in contrast of this general behavior a control experiment using aqueous MeOH showed the formation of CO using g-CN as photocatalyst, but not in the case of CD/g-CN, meaning that the heterojunction does not oxidize MeOH [9].

$$2CO_2 + 4H_2O_{CD/g-CN} \xrightarrow{h\nu} 2CH_3OH + 3_O2 \qquad (1)$$

Understanding on the performance and selectivity of the CD/g-CN heterojunction was gained by combination of transient absorption spectroscopy (TAS) measurements and density functional theory (DFT) calculations. TAS measurements revealed a six-fold increase of the

electron lifetime on the CD/g-CN heterojunction in comparison with the single g-CN component. Since electron lifetime is determined by the electron/hole recombination rate, the longer electron lifetime in the CD/g-CN heterojunction proves indirectly that the holes have migrated preferentially to CDs, where they go undetected by the TAS measurement of the CD/g-CN heterojunction. The benefits of the CD/g-CN heterojunction from the point of view of charge separation were also confirmed by photocurrent measurements that show that under the same conditions illumination of CD/g-CN photoanodes produces double current intensity than g-CN photoelectrode [9].

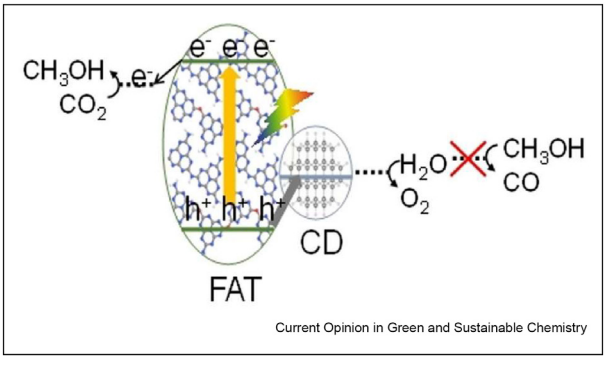
In the CD/g-CN system, one key point in the MeOH formation is the nature of CD. Other CD type prepared from different precursors, such as glucose, does not exhibit a similar behavior. In the case of glucose as precursor, the CDs obtained by alkali-assisted sonication synthesis were more amorphous as evidenced by XRD and transmission electron microscopy. The heterojunctions of these amorphous CDs with g-CN afford as photocatalysts CO under identical reaction conditions in which MeOH was formed for more crystalline CDs. Furthermore, evidence by TAS indicates that those amorphous CDs act as electron trapping component in junction with g-CN, behaving in the opposite direction as the more crystalline CDs [9].

In addition to CD, also the nature of g-CN plays a key role in the performance of the heterojunction as photocatalyst. By treating dicyandiamide with formic acid, a g-(FA)CN having similar structure as g-CN, but additional carbonyl groups at the periphery of the particles, is obtained [10]. The heterojunction of the crystalline CD formed by microwave treatment from citric acid and urea and g-(FA)CN exhibits even improved efficiency in the photocatalytic CO_2 reduction by H_2O to MeOH and O_2, reaching a remarkable 6% of quantum efficiency at 420 nm and evolving MeOH at a rate of 24.2 μmol g^{-1} h^{-1} upon irradiation in the range between 420 and 700 nm at a power of 100 mW cm^{-2} [10]. Formation of MeOH was also in this case confirmed by ^{13}C isotopic labeling experiments. Stability of the CD/g-(FA)CN heterojunction was studied by performing three consecutive runs, measuring similar rates of MeOH evolution of 1.7, 1.5 and 1.7 μmol h^{-1} for the first, second and third use, respectively. TAS measurements show that CD/g-CN and CD/g-(FA)CN exhibit similar trends, but CDs are able to extract about 75% of the photogenerated holes in g-(FA)CN as deduced by the decrease in the transient signal intensity monitored at 510 nm that is associated to holes on g-(FA)CN. As in the previous commented study for CD/g-CN, holes on CD go undetected. The efficient hole migration to CD results in a higher quantum yield in comparison to g-CN and in the commented stability of MeOH during the photocatalytic experiments since holes in CD do not oxidize MeOH. This reflects the benefits of the oxygen functional groups on CN acting as electron traps favoring charge separation. Again, the performance of the CD/g-(FA)CN depends on the nature of CD, the most efficient being the most crystalline CD sample of the series obtained at the highest employed microwave power of 300 W. Figure 1 illustrates the proposed mechanism leading to the selective photocatalytic CO_2 reduction to methanol by CD/g-CN.

Heterojunctions of graphitic carbon nitride and reduced graphene oxide with MOFs

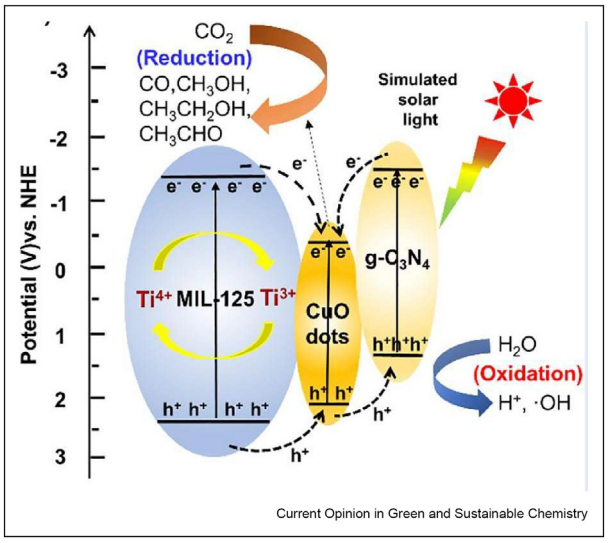
Heterojunction of g-CN with CuO dots encapsulated inside MIL-125(Ti) has also been reported to form MeOH, although in this case together with other products, including CO and C_2 products such as ethanol and acetaldehyde [11]. In comparison with CD, MIL-125(Ti) is a porous crystalline MOF having $Ti_8O_8(OH)_4^{12-}$ rings as nodes connected to twelve terephathalate linkers [12]. The network defines two types of cavities of 0.61 and 1.25 nm diameter, respectively. The presence of octameric Ti oxo-hydroxy clusters connected to the organic linkers acting as a quantum dot, together with the structural robustness, has made of MIL-125(Ti) one of the favorite MOF photocatalyst [13]. In addition, photo active guests, such as CuO, can be occluded within the lattice cavities of MIL-125(Ti) where they become stabilized against growth by spatial confinement. In the present case, the material was prepared by adsorbing $Cu(NO_3)_2$ in MeOH into preformed MIL-125(Ti) followed by calcination at 150 °C and hybridization of CuO/MIL-125(Ti) at 70 °C in MeOH with protonated g-CN obtained from urea polymerized at 500 °C [11]. With the material having the optimal CuO and g-CN composition [2.5% g-C_3N_4/1% CuO@MIL-125(Ti)], productions of 180.1, 997.2, 531.5 and 1505.7 μmol/g for CO, methanol, acetaldehyde and ethanol, respectively, were measured at 3 h under 300 W Xe lamp irradiation. The origin of the products as arising

Figure 1



Mechanism of selective methanol formation upon irradiation of CD/g-CN. Taken with permission from Ref. [10]. The key factor of methanol selectivity is that holes located on CD are quenched by H_2O as electron donor and not do not react with MeOH.

Figure 2



Band alignment of the various components of g-CN/CuO@MIL-125(Ti) photocatalyst leading to the formation of methanol and other photoproducts. Taken with permission from Ref. [11]. Note that due to band alignment photogenerated electrons become trapped on CuO rather than on g-CN.

from CO_2 was determined indirectly by performing a control experiment in the absence of CO_2 in which no products were observed. It would have been important to perform ^{13}C isotopic labeling experiments to confirm the source of MeOH, as it was proved for the case of CO. Typically, formation of C_2 products from CO_2 are observed only under conditions in which the transfer of many electrons and protons through multiple reaction intermediates is possible [14]. For this reason, generally C_1 products such as formate, CO or CH_4 prevail and formation of C_{2+} is normally not observed. It is also interesting to note that according to the proposed mechanism of the photocatalytic reaction based on band energy alignment of the three components of the system, photogenerated electrons remain on CuO performing CO_2 reduction, while g-CN acts as a hole scavenger in which H_2O oxidation must occur, something that contrasts with the prior detailed study on the CD/g-CN heterojunction. Figure 2 summarizes the band alignment of the various components of the photocatalytic g-C_3N_4/CuO@MIL-125(Ti) system.

In a related system, the heterojunctions of reduced graphene oxide (RGO) and MIL-125(Ti)−NH_2 and even MIL-125(Ti)−NH_2 were also reported to form MeOH from CO_2 upon irradiation [15]. In contrast to the use of terephthalate, aminoterephthalate as a linker forms an isostructural MIL-125 MOF, but exhibiting an absorption band in the visible region at λ_{max} 420 nm as consequence of the new electronic transition from the N lone electron pair to the lowest unoccupied crystal orbital. Although the study was supported by DFT calculations on CO_2 adsorption, no ^{13}C isotopic labeling experiments were performed. The present article calls out about the importance to confirm CO_2 as the source of detected MeOH by performing appropriate ^{13}C isotopic labeling experiments and monitoring of the products by mass spectrometry in which the spectrum of $^{13}CH_3OH$ should be recorded with the expected peak intensity values. Table 1 provides a summary of the lack of isotopic labeling to support CO_2 as the source of MeOH in the photocatalytic reaction in two of the references previously commented.

The performance of the 2.5% g-C_3N_4/1% CuO@MIL-125(Ti) and RGO/MIL-125(Ti)−NH_2 affording methanol as product of the photocatalytic reaction is opposite to that reported in other articles for MIL-125(Ti)−NH_2 [16,17] and even CuO@MIL-125(Ti) [18,19] in which MeOH is decomposed by the photogenerated holes. Although the conditions of the irradiation are not the same, serious attempts to justify why MeOH does not become oxidized by the holes should have been made.

Checking CO_2 as methanol source by ^{13}C isotopic labeling experiments

Given the apparent contradiction between MeOH formation as product in photocatalytic systems based on MOFs, on one hand, and the reported use of MeOH as sacrificial agent becoming oxidized by photogenerated

Table 1

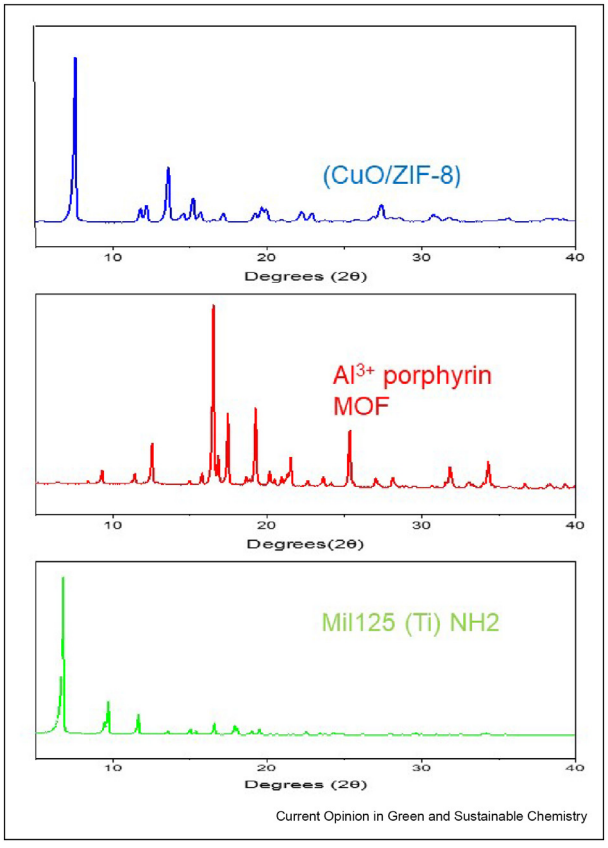
Summary of the reported MeOH production using MOF composite photocatalysts.

Photocatalyst	Conditions	MeOH production (μmol/g)	Isotopic labeling experiments	Reference
2.5% g-C_3N_4/1% CuO@MIL-125(Ti)	300 W Xe lamp. 3 h	997.2[a]	No mass spectrum of methanol is provided	11
MIL-125(Ti)−NH_2	Visible light CH_3CN/H_2O/TEOA 16/2/2. 24 h	39,600	No mass spectrum of methanol is provided	15
RGO/MIL-125(Ti)−NH_2	Visible light CH_3CN/H_2O/TEOA 16/2/2. 24 h	47,200	No mass spectrum of methanol is provided	15

[a] Formation of ethanol (1505.7 μmol/g) was also reported without isotopic labeling data.

holes, on the other, we were interested in repeating some of the reported data, particularly in those in which no ^{13}C labeling experiments were performed, by using $^{13}CO_2$ as precursor. Note that reproducing reported photocatalytic data from a different lab may not be an easy task due to the difficulty in precise sample preparation and differences in irradiation conditions. Thus, using $^{13}CO_2$ as precursor, we have been able to detect $^{12}CH_3OH$, but no $^{13}CH_3OH$ in three common MOFs in which photocatalytic MeOH formation has been reported. Figure 3 shows the XRD patterns of the three MOF materials used by us in the study of ^{13}C isotopic labeling of CO_2 photoproducts. One of these cases was Cu oxide incorporated within ZIF-8 (CuO/ZIF-8) [20]. CuO/ZIF-8 was prepared by hydrothermal treatment at 110 °C for 2 days of preformed ZIF-8 with a solution of $CuSO_4$ and NH_4OH [20]. The photocatalytic reduction was carried out with CO_2 dissolved in NaOH and Na_2SO_3 as sacrificial agent. The blank controls reported in the literature to confirm MeOH formation were suspended Cu/ZIF-8 in the dark and irradiation in the absence of Cu/ZIF-8 [20].

Figure 3



XRD patterns of the three MOFs reported as photocatalysts leading to the formation of methanol from CO_2 reduction that were checked herein using $^{13}CO_2$ without observing the corresponding $^{13}CH_3OH$ photoproduct.

In a second example, an Al^{3+} porphyrin MOF obtained from 5,10,15,20-tetrakis (4-carboxyphenyl)porphyrin as linker without or with Cu^{2+} complexed at the porphyrin macroring was reported to form MeOH from CO_2 at a rate of 37.5 and 262.6 ppm g^{-1} h^{-1} for the MOF without or with Cu^{2+}, respectively [21]. Irradiations were carried out in water with visible light using UV-filtered light from a 300 W Xe lamp ($\lambda > 420$ nm) using triethylamine as sacrificial agent [21].

No controls were reported to confirm the origin of detected methanol, something particularly relevant when using an organic amine as whole scavenger and also considering the organic composition of the MOF. In our hands, no evidence of the formation of $^{13}CH_3OH$ could be obtained for the Cu^{2+}-MOF using isotopically labelled $^{13}CO_2$.

In a third case, MIL-125(Ti)$-NH_2$ was used as photocatalyst to promote reduction of $^{13}CO_2$ in CH_3CN/H_2O using triethanolamine as sacrificial agent as reported. However, in our hands, no evidence of the formation of $^{13}CH_3OH$ in the liquid phase could be again obtained, suggesting that the remarkable methanol production rate of 36 $mmol_{CH3OH}$ g^{-1} in 24 h should be revisited [15].

Conclusions

In view of the current interest in methanol as hydrogen carrier and energy vector, it would be very appealing to develop efficient photocatalytic procedures for the selective CO_2 reduction to methanol using solar light. Photocatalytic processes have to overcome the dilemma of how to form a product such as methanol that is highly reactive with photogenerated holes. One possibility recently reported is the use of heterojunctions in which the hole scavenger has preferential adsorption for H_2O vs. CH_3OH and it is also able to oxidize H_2O with high efficiency. This exquisite selectivity has recently been reported for certain, but not all, carbon dots, making them important components of photocatalytic systems worth to be further explored. As shown in this opinion the source of detected methanol has always to be carefully checked by ^{13}C isotopic labeling experiments to confirm on firm ground that methanol derives from CO_2. To support this opinion we have revisited three reports on the photocatalytic CO_2 reduction to methanol, being unable to observe the corresponding isotopically labeled methanol in any of the three cases, although unlabeled methanol was detected. It is, therefore, proposed that the most efficient photocatalytic systems reported so far for methanol generation should be confirmed by different labs.

Author contribution

A.G.-B. perform the photocatalytic $^{13}CO_2$ labeled reactions. HG conceived the Opinion and write the

article. The two authors revised and approved the manuscript.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this article.

Data availability

Data will be made available on request.

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