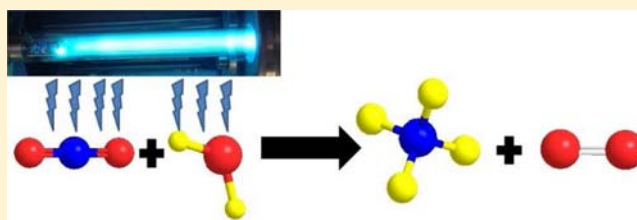


185 nm Photoreduction of CO₂ to Methane by Water. Influence of the Presence of a Basic Catalyst

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ABSTRACT: Photolysis of CO₂ at 185 nm using a Hg lamp in the presence of H₂ or H₂O leads to the formation of CH₄ (after an induction period) and a lesser amount of CO. Using H₂ gas as reducing agent, up to 40% conversion was achieved with almost complete selectivity to methane and energy consumption of 1.55 Gcal/mol. When CO₂ irradiation is carried out in the gas phase in the presence of H₂O, both reagents can undergo photolysis, and H₂ generation from water is a competing process accompanying the formation of CO and CH₄ (CO₂ conversion 0.67% at 14 h). For the irradiation of CO₂ using H₂O as reducing agent, basic solids (K⁺-exchanged Y zeolite or hydrotalcites) can increase CO₂ conversion up to 2.21% with total selectivity toward CH₄ and an energy consumption of 4.5 Gcal/mol. This result opens a door in the quest for efficient photocatalysts that could further increase the apparent quantum yield of the process, particularly at longer wavelengths.



■ INTRODUCTION

Activation of carbon dioxide is one of the present challenges in chemistry.^{1–3} One current line of research that is related with renewable energies is the replacement of fossil fuels by sustainable energy resources that do not exert a negative influence on the environment.^{4–6} In this context, one possibility is the photochemical reduction of CO₂ to form methanol, methane, and CO among other possible products.^{4,6,7} Most of the current approaches to achieve this transformation are based on the use of UV or visible light in combination with a photocatalyst.^{8,9}

The present report deals with an innovative methodology in which photochemical irradiation is performed in the “deep” UV region (radiation wavelength shorter than 200 nm). Photons in the deep UV zone can be directly absorbed by H₂O or CO₂ and have enough energy to effect the monophotonic direct photolysis of these two highly stable molecules. Deep UV photolysis of CO₂ to split into CO and oxygen atoms has been reported in the literature to occur with high quantum efficiency.^{10–12} In addition, it is known that the photolysis of CO and H₂O with deep UV can form alcohols and aldehydes among other compounds.¹³

The reaction of CO₂ and H₂O promoted by light mimics in a certain way natural photosynthesis in which these two molecules are the substrates for the formation of carbohydrates and oxygen.^{14–16} We have also recently shown that, similar to the direct photolysis of water in the gas phase, deep UV photons can also effect surface photochemistry via O–H bond cleavage of surface hydroxyl groups in solids that are otherwise photochemically inert to UV and visible radiation.^{17,18} UV photochemistry has been generally ignored as a means to promote organic transformation due to the fact that most solvents and gases absorb in this region, while some organic

chromophores can be selectively excited by irradiation at wavelengths longer than 250 nm. Deep UV photochemistry can be extremely useful and widely applicable for the activation of simple molecules, particularly H₂O, CO₂, and CH₄ in the gas phase or on solid surfaces. In this context, it is worth commenting that there are commercially available simple light sources for deep UV irradiation based on the emission of mercury vapor (185 nm) or deuterium gas (165 nm). Metal halides, and particularly calcium fluoride, are convenient optically transparent materials in this region for chambers and cells.

Herein, we have taken advantage of direct 185 nm irradiation of CO₂ and H₂O to develop a simple and efficient methodology for the photochemical reduction of CO₂ to methane with an energy consumption in the range of large industrial processes such as steam re-forming or water–gas shift. Although the strategy reported here cannot serve for direct solar light conversion, it has in common the use of light and photocatalysts to effect CO₂ reduction by hydrogen or water. In the context of solar fuels production, our method, requiring the prior conversion of sunlight into electricity, can be competitive with direct visible light photocatalytic conversion due to the higher efficiency inherent to monophotonic processes based on deep UV compared to multistep photon absorption mechanisms.

■ RESULTS AND DISCUSSION

185 nm Reduction of CO₂ by H₂. H₂ and N₂ gases do not absorb at 185 nm, while CO₂ absorbs from 165 to 205 nm.¹⁹

Received: May 21, 2012

Published: August 6, 2012

When a mixture of CO₂ and H₂ diluted in N₂ is photolyzed at 185 nm, the highly selective formation of methane with very minor amounts of CO is observed. The presence of methanol or other products is not detected at any time during the reaction. Figure 1 shows the temporal profile of CO₂

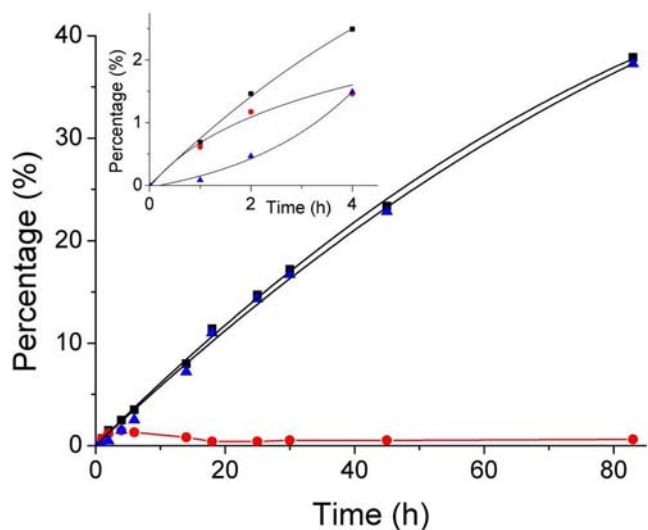
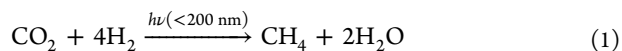


Figure 1. Temporal profile of the CO₂ (■) conversion and CH₄ (▲) and CO (●) yields. Photolysis conditions: 185 nm at 65 °C; mixture of H₂ (44%), CO₂ (9.5%), and N₂ (45%).

conversion, as well as the yields of methane and CO vs the irradiation time. As can be seen in this figure, under our irradiation conditions, conversion of CO₂ increases almost linearly with the irradiation time in the time interval up to 3 h. High conversions, about 40%, were obtained at 80 h under our photolysis conditions. These conversions are without precedent for a photochemical CO₂ activation.⁶ Interestingly, the formation of CO develops faster than that of methane (see inset in Figure 1) but reaches a quasi stationary low level that reaches a steady state at longer irradiation times. In contrast, the formation of methane exhibits an induction period, but after this initial time its concentration grows over time, parallel to the CO₂ conversion.

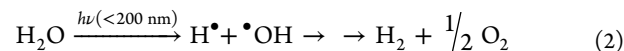
In order to gain information on the reaction stoichiometry and particularly on the products arising from oxygen removed from CO₂, we performed an analogous experiment using isotopically labeled ¹³C¹⁸O₂ and followed the reaction by mass spectrometry. Although the presence of lesser amounts of ¹⁸O₂ was detected, the predominant oxygen-containing product accompanying ¹³CH₄ was H₂¹⁸O. Accordingly, eq 1 summarizes the stoichiometry of the photochemical CO₂ splitting.



Most of the present study has been carried out using a mercury lamp that emits at two wavelengths, namely 185 nm with lower intensity and 254 nm with higher intensity (see Experimental Section for the lamp emission). Control experiments using quasi monochromatic 254 nm light from a low vapor pressure mercury lamp indicate that the photons causing the chemical transformation are those at 185 nm and not those at 254 nm.

CO₂ Reduction at 185 nm Promoted by H₂O. Considering that the direct photolysis of H₂O with deep UV

was one of the first processes studied in this wavelength range,²⁰ and that it leads to homolytic OH bond cleavage with a quantum efficiency approaching unity (eq 2), we envisioned the



possibility of coupling direct H₂O splitting and H₂ generation with CO₂ reduction. To address this possibility, we performed 185 nm irradiation of CO₂ diluted in moisture-saturated N₂ at room temperature; the molar ratio of the CO₂ and H₂O feed was 1:20. Under these conditions, a gradual generation of hydrogen was observed, indicating that eq 2 is operating. It should be commented that although deep UV photons can effect homolytic water splitting as indicated in eq 2 to generate hydrogen atoms and hydroxyl radicals, controls by colorimetric titration have not been able to detect the formation of measurable amounts of hydroxyl peroxide.

The concentration of hydrogen coming from water increases steadily with time. In addition of H₂, formation of CH₄ after some induction period is also observed. Figures 2 and 3 show

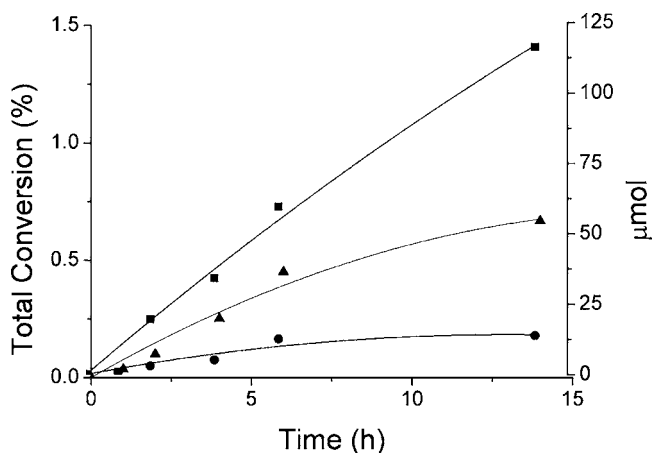


Figure 2. Temporal profile of the CO₂ conversion (■, left vertical axis) and H₂ (▲, right vertical axis) and CH₄ (●, right vertical axis) production upon irradiation of CO₂ and H₂O with deep UV light. Photolysis conditions: mixture of CO₂ (9.5%) and N₂ (90.5%) with saturated water; no catalyst; Hg lamp as irradiation source, 185 nm; 60 °C.

the temporal evolution of CO₂ conversion and formation of H₂ and CH₄ over time when a mixture of CO₂ and H₂O (1:20) is photolyzed in the gas phase in the absence or in the presence of Zn/Ti LDH solid. Neither methanol nor CO was detected under any conditions during the reaction time. The absence of CO previously observed in the photolysis of CO₂ in the presence of H₂ indicates that reduction of CO in the photolysis where H₂O is present has to be considerably faster than its formation.

To determine the stoichiometry of the CO₂ reduction by H₂O and the possible evolution of oxygen in the photolysis, we studied the reaction using isotopically labeled ¹³C¹⁸O₂ and followed the reaction by mass spectrometry. Under these conditions, in which there is an excess of H₂O with respect to ¹³C¹⁸O₂, we observed a scrambling of ¹⁸O atoms from ¹³C¹⁸O₂ to H₂O as well as the formation of ¹⁶O₂, ¹⁶O¹⁸O, and ¹⁸O₂ in relative proportions of 100, 0.1, and 0.08%. These results indicate that a fast equilibrium through the formation of carbonic acid with oxygen scrambling between C¹⁸O₂ and

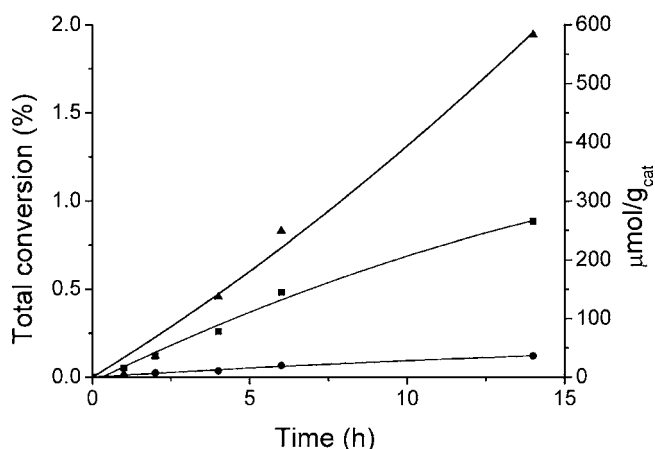
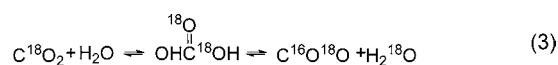


Figure 3. Temporal profile of the CO₂ conversion (■, left vertical axis) and H₂ (▲, right vertical axis) and CH₄ (●, right vertical axis) production upon irradiation of CO₂ and H₂O with deep UV light. Photolysis conditions: mixture of CO₂ (9.5%) and N₂ (90.5%) with saturated water; Zn/Ti LDH, 0.5 g; Hg lamp as irradiation source, 185 nm; 60 °C.

H₂¹⁶O takes place before the photochemical reaction (eq 3), and depending on the initial proportion of ¹⁶O /¹⁸O, a statistical distribution of isotopically labeled molecular oxygen evolves.



It is noticeable that the CO₂ conversion in the presence of an excess of H₂O is about 15-fold smaller than for the irradiation in H₂. This is due to the fact that H₂ does not absorb 185 nm light, while H₂O has a strong absorption at this wavelength.²⁰ Moreover, being in large excess, H₂O prevents the photolysis of CO₂. To increase CO₂ conversion, we performed photolysis with a much smaller H₂O excess. Upon photolysis of a CO₂/H₂O 1:1 mixture, up to 420 μmol of H₂, 60 μmol of CO, and 15 μmol of methane was achieved with an energy consumption of 20 Gcal/mol.

Although CH₄ is a common final product of deep UV photolysis using H₂ or H₂O as reducing agent, we notice that, at least in part, the reaction mechanism must be different for the two substrates. The difference must arise from the fact that H₂ does not absorb 185 nm photons, and, therefore, in this case, the CO₂ conversion must come exclusively from the CO₂ irradiation, probably leading to CO. However, in the case of

H₂O that also absorbs in the deep UV, two alternative pathways could be available, depending on which substrate is photolyzed, either CO₂ or H₂O. The fact that CO₂ conversions using water as reducing agent are lower than those using H₂ while the product distribution is the same suggests that water photolysis is the exclusive hydrogen source and the hydroxyl radical and other intermediates derived from water photolysis are not involved in the formation of CH₄.

Influence of the Presence of a Basic Solid. We recently reported that deep UV photolysis for methane activation can be carried out more efficiently on a solid surface.^{17,18} Thus, we have shown that deep UV photolysis of silanol groups on the surface of silicates can serve to activate methane toward the formation of C1 oxygenates.^{17,18} In the present case, the situation is somewhat different since, in contrast to methane activation, direct photolysis at 185 nm of CO₂ can take place in the gas phase regardless the presence or not of any solid surface. However the presence of a surface could lead to an increase on the photochemical yield by adsorbing and confining CO₂ and the reaction on a 2D or 3D space. In addition, the presence of a solid can open new pathways for the reaction.

Aimed at addressing the influence of a solid surface on the 185 nm photolysis of CO₂ we screened a series of materials including [Ti]Beta, Beta(OH), and HY zeolites and TiO₂, CeO₂, and MgO metal oxides. In all these cases, we observed that the conversion of CO₂ either using H₂ or H₂O as reductant, decreased considerably, thus showing the negative influence of the solid on the photoreaction. We also tested the performance of a basic large pore zeolite (KY) and two hydrotalcites (Zn/Ti LDH and Zn/Ce LDH) as promoters of the photochemical CO₂ reduction by water.

The case of TiO₂ is interesting considering that the experiments were carried out with a light source that contains also 254 nm (see Figure 5 in the Experimental Section for the emission spectrum of the lamp) and that TiO₂ has been reported to have some photocatalytic activity for CO₂ reduction.^{21–24} Thus, in principle the possibility of a synergy between the direct deep UV photolysis (185 nm) and photocatalytic CO₂ reduction promoted by TiO₂ (254 nm) could be expected. The fact that the conversion decreased in the presence of TiO₂ clearly indicates that the contribution of the direct gas phase photolysis of CO₂ is much larger than any possible photocatalytic conversion occurring on the TiO₂ surface. This prevalence of the deep UV pathway can be simply understood considering that the accepted mechanism for the photocatalytic TiO₂ reduction of CO₂ involves several

Table 1. CO₂ Conversion Mass Balance, Selectivity and Energy consumption for the 185 nm Photolysis of CO₂ in the Presence of Basic Solids^a

catalyst	CO ₂ conversion (%)	molar balance	selectivity		energy consumption (Gcal/mol)	μmol H ₂ /(g _{cat} -h)	μmol CH ₄ /(g _{cat} -h)
			CO	CH ₄			
none	0.67	96.8	0	100	14.9	9.9 ^d	2.1 ^d
KY	0.85	98.6	0	100	11.7	63.2	3.1
Zn/Ce LDH	1.14	99.9	0	100	8.7	33.1	4.3
Zn/Ti LDH	0.88	99.9	0	100	11.2	41.4	3.3
Zn/Ti LDH ^b	2.21	95.3	0	100	4.5	740	77
Zn/Ti LDH ^c	1.75	99.9	0	100	5.4	31.2	3.77
MgO	0.23	98.9	0	100	42.8	14	0.63

^aPhotolysis conditions: feed, water-saturated mixture of 90.5% N₂ and 9.5% CO₂; irradiation time, 14 h; solid, 500 mg unless indicated otherwise; catalyst distributed in a 4 × 13 cm² shallow bed and illuminated with 86 W/m². ^b100 mg of catalyst. ^c50 mg of catalyst. ^dμmol of CH₄/h.

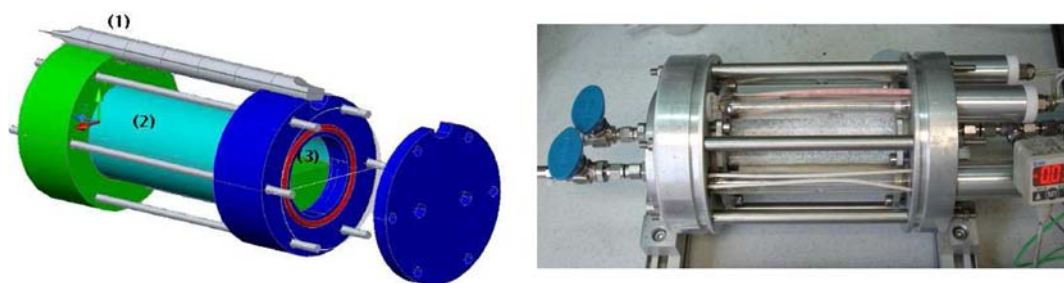


Figure 4. Left: 185 photoreactor composed by In Hg lamp (1), synthetic quartz windows (2), gas chamber (3). Right: Upper view showing the shallow bed of the material placed in the photoreactor.

steps requiring light absorption and is a totally different process than the direct bond splitting occurring in deep UV.

It is known that CO_2 can be adsorbed on basic solids, this being the key point for developing efficient CO_2 adsorbents.^{25–27} In the case of microporous zeolites it has been shown that basicity can be introduced by exchanging Na^+ by other alkali metal cation with larger ionic radius.^{28,29} Zeolite Y is a microporous crystalline aluminosilicate having quasi spherical cavities (about 1.3 nm diameter) tetrahedrally interconnected by windows of about 0.72 nm.³⁰ LDHs are layered materials that contain a divalent metal cation together with a proportion up to 30% of a tri- or tetravalent cation that is isomorphically replacing some of the positions of the divalent cation in the layer.^{31,32} The presence of the tri- or tetravalent cation introduces some positive charges in the framework that requires the presence of charge compensating anions in the intergallery space.^{31,32} Carbonate is one of the most common ions and even if other ion is initially present in the solid, it can subsequently be replaced by carbonates due to the high affinity for these dinegative anions.^{31,32} LDHs have also been used as basic catalysts to promote condensations and nucleophilic substitutions, among other reactions.^{33,34}

In this context the positive influence of the presence of KY zeolite or LDHs as catalysts on the photoreduction of CO_2 can be rationalized considering that due to their basicity these solids are good CO_2 adsorbents. Thus, due to the adsorption of CO_2 on the surface of these solids, the 185 nm photoreduction of CO_2 by H_2O would occur preferentially on the solid surface, where it should be a high concentration of these two molecules and the species derived from there.

In support of this proposal experiments was carried out using H_2 gas instead of H_2O as reducing agent. Under these conditions and considering that H_2 adsorption on the solid surface at 60 °C should be negligible in contrast to the strong adsorption of CO_2 , it was observed that the presence of any of these three solids plays an adverse effect reducing CO_2 conversion with respect to the conversions in the gas phase photolysis. Therefore, comparison of the conversions in the presence of solids using H_2 or H_2O as reducing agent clearly revealed notable differences in the reaction mechanism and opens the door for implementing the use of solid surfaces as photocatalyst to enhance CO_2 conversion in the deep UV photolysis.

Concerning the possibility that Zn/Ti or Zn/Ce LDHs were acting merely as CO_2 adsorbent or if in addition to their adsorption capacity these Zn-containing LDHs promote CO_2 reduction also photocatalytically, absorbing light and injecting electrons into CO_2 , it is worth commenting the difference in behavior of these Zn LDHs with other basic LDHs or MgO. In principle all LDHs as well as MgO should adsorb significant

amounts of CO_2 and if this were the only operating factor, i.e. no photocatalysis is taking place, all of them should behave similarly promoting the reaction. This is apparently not the case and the composition of the LDH and the nature of the solid play a role in the promotional effect of CO_2 reduction. This influence of the metals present in the LDH and, particularly the fact that Zn-containing LDH have been found to be photocatalysts for water splitting, suggest that also in this case there is some contribution of photocatalysis when certain LDHs solid are present in the photolysis. Therefore it seems that in order to develop materials for the photocatalytic CO_2 reduction, solids that combine CO_2 absorption capacity together with photoresponse at the appropriate wavelength appear as promising materials. Considering the diversity of metal combinations that can be present in their composition, hydroxalicates appear as highly promising materials for this photocatalytic reduction.

CONCLUSIONS

In the present study we have shown that 185 nm photolysis of CO_2 in the presence of either hydrogen or water leads to the formation of CH_4 . When using water as reagent there is a possibility to increase the yield of the process by performing the reaction on the surface of solids with adequate basic strength. The energy consumption per mole of converted CO_2 varies depending the conditions, but when water is used as reductant it is only about 4.5 Gcal/mol of CO_2 converted, a value in the same range as large-scale industrial processes such as steam reforming.^{17,18} Our results open the way to further implementation of solids as catalysts that can promote more efficiently the photoreduction of CO_2 by water.

EXPERIMENTAL SECTION

Materials. The Zn–Ti LDH was prepared by coprecipitation of zinc and titanium salts from homogeneous solution. A solution of zinc chloride (6×10^{-2} mol) and titanium tetraethoxide (9.5×10^{-3} mol) was mixed with a 1 M urea solution under magnetic stirring at 100 °C, for 48 h under inert atmosphere. After filtration and washing several times in distilled water at pH 7, the product was dried at 60 °C for 13 h.

Zn/Ce LDH was prepared also by the same method for comparison. TiO_2 P25 was a commercial sample from Degussa.

Basic zeolites were prepared starting from NaY (PQ, CBV100) by submitting the solids to ion exchange using 1 M aqueous solution of KAcO in a liquid/solid ratio of 10. The suspensions were magnetically stirred at 80 °C for 4 h and then the solids were filtered, washed with bidistilled water and dried at 200 °C under ambient atmosphere.

Description of the Photoreactor. Figure 4 provides a schematic of the photoreactor used in this study. Photolyses in the presence of solids were carried out by spreading uniformly a bed of powdered samples on the photoreactor covering a surface of $4 \times 13 \text{ cm}^2$. CO_2 gas

was introduced into the reactor diluted with hydrogen or nitrogen saturated with water. 185 nm Irradiation of the solid acting as photocatalyst was carried out using three Hg lamps emitting at 185 nm (4 W) and 254 nm (8 W) (see Figure 5). Due to the heating by the action of the light the temperature of the reaction chamber reached a stationary value of 60–65 °C.

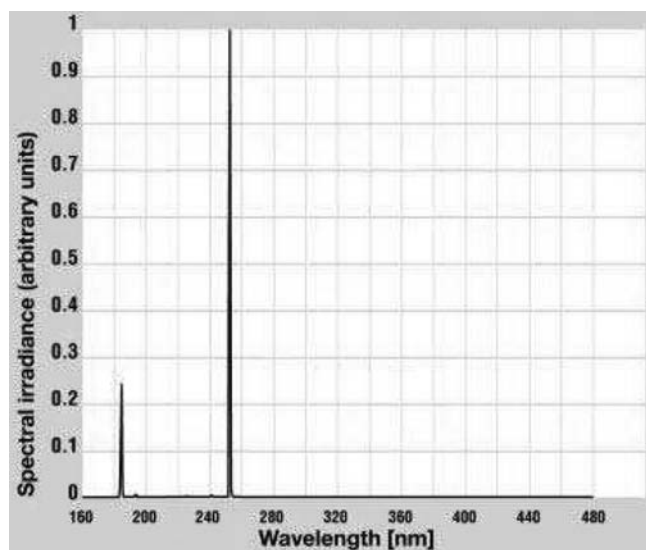


Figure 5. Emission spectrum for the mercury lamp.

The course of the reaction was followed by analyzing the gas phase and the organic compounds adsorbed on the solid, when a photocatalyst was present. Reproducibility of the data was checked by performing independent experiments in quadruplicate, whereby consistent results with significant variations were obtained.

The gas products were analyzed using a Rapid Refinery Gas Analyser from Bruker that consists in a three channel GC. The first channel analyses H₂ using a micro packet HayeSep Q and Molsieve 5A column with Ar as carrier gas and TC detector. The second channel analyses CO, CO₂, N₂, and O₂ with a combination of micropacket Haysep Q, H–N and Molsieve 13X columns using He as carrier gas and a TC detector. The third channel analyses hydrocarbons from C₁ to C₅ in an Al₂O₃ plot column with He as carrier gas and a FI detector. The mass balance of each experiment was determined by adding the moles of the products in the gas phase to the moles of CO₂ converted on the solid. Quantification of the moles of the products in the gas phase was carried out considering that N₂ remains constant during the experiment and using this gas as standard. The response factor of the products with respect to N₂ was determined by independent calibrations.

Controls to determine the possibility of H₂O₂ formation were performed by photolyzing for 60 min moisture saturated N₂ and then injecting 50 mL of the gas into an aqueous solution of K₂(TiO)-(C₂O₄)₂ (Aldrich) in H₂SO₄/HNO₃ as colorimetric titrator. After 5 min the solution was monitored at 420 nm for the formation of the peroxytitanyl according to the standard method to titrate H₂O₂.³⁵

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support by the Spanish Ministry of Economy and Competitiveness (CTQ-2009-11586) is gratefully acknowledged.

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