Effect of the carbon species equilibrium on the CO_2 photocatalytic reduction in a TiO_2 slurry

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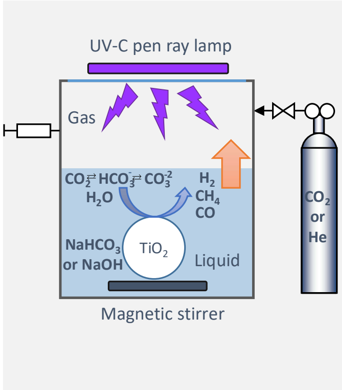

An experimental study was conducted to investigate the effect of dissolved inorganic carbon equilibrium, which is pH-dependent, on product yields during CO_2 photocatalytic reduction using a P25 TiO_2 suspension. Various solutions saturated with CO_2 and He were employed to carry out the photoreaction with the aim of evaluating optimal conditions to enhance product yields. On one hand, a 0.2 M solution of $NaHCO_3$ was saturated with either CO_2 or He for the photocatalytic reduction. On the other hand, product yields were compared when saturating a 0.2 M solution of NaOH with CO_2. Product yields significantly improved when the initial inorganic carbon in the TiO_2 suspension and the dissolved CO_2 concentration in the liquid phase were increased by employing the $NaHCO_3$ solution and saturating with CO_2.

Introduction

One of the most demanding issues in contemporary society is the energy production, coupled with the annual emission of 31.5 billion tons of carbon dioxide from fossil fuel combustion, a primary greenhouse gas [1]. Consequently, the photocatalytic reduction of carbon dioxide emerges as a promising solution to address these challenges [2]. Photocatalytic CO_2 conversion needs no additional energy input apart from solar radiation, rendering it the most appealing pathway for long-term CO_2 transformation.

Unfortunately, the photocatalytic conversion of carbon dioxide is still very low. This reaction is a very complicated combination of photophysical and photochemical processes. Formation of the desired products - methane or methanol - is more difficult than formation of other possible products like carbon monoxide, formaldehyde and formic acid from the reason of kinetic drawback because more electrons are required for the former reactions [3]. In addition, the water splitting reaction competes for the electrons in a reductive media producing hydrogen.

Moreover, according to the demonstration of Nakanishi et al. [4] the carbon species that takes place during the photocatalytic reduction is the dissolved CO_2 which is in equilibrium with other carbon species, such as bicarbonates and carbonates, and its concentration is a function of the solution pH.

This research is focused on the photocatalytic reduction of CO_2 in a liquid suspension of TiO_2 and the influence of the carbon species equilibrium on the yields of various products of this process (CO, CH_4, H_2). The objective of this work is to identify the optimal conditions to carry out the photocatalytic CO_2 reduction.

Material and Methods

A stirred batch photoreactor (173.9 ml) with 1 g L^{-1} P25 TiO_2 suspension was illuminated by an 8 W Hg lamp with a peak light intensity at 254 nm (Ultra-Violet Products Inc., USA, 11SC-1) situated on the quartz glass window (see Graphical Illustration). The photocatalyst powder was suspended in 40 ml of 0.2 M NaOH or $NaHCO_3$ solutions for typical batches. A magnetic stirrer at the bottom agitated the slurry to prevent sedimentation of the photocatalyst. The pressure of the gas phase was continuously monitored. Prior to the illumination, CO_2 or He was bubbled with a constant flow through the stirred suspension for at least 25 min to purge the air and to saturate the solution. The reactor was tightly closed and the pressure was maintained at 120 kPa. Then, the photocatalytic reaction was started by switching on the Hg lamp. Samples of gas phase were taken at various times during the irradiation using a gas-tight syringe (10 ml) through a septum and the samples were immediately analysed using a gas chromatograph equipped with a barrier discharge ionization detector (BID). The pH of the solutions was measured before to start CO_2 or He saturation and after the gas saturation. In addition, measurements with a Total Organic Carbon (TOC) analyser were performed to determine the Dissolved Inorganic Carbon (DIC) at the end of the saturation with CO_2 or He of the different solutions.

Results and Discussion

The equilibrium reactions for carbonate species dissolved in water are:

$$CO_2 + H_2O \rightleftarrows H_2CO_3 \rightleftarrows HCO_3^- + H^+ \rightleftarrows CO_3^{-2} + 2H^+$$

From calculations of these equilibrium reactions, the carbon species concentration in function of the pH can be plotted, the so called Bjerrum plot (Figure 1).

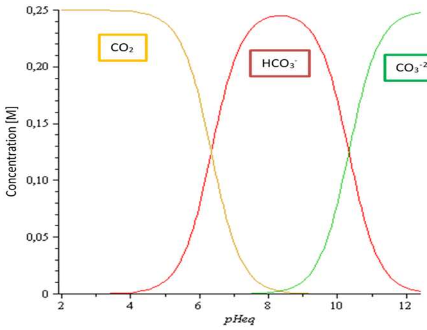

Figure 1. Bjerrum plot in equilibrium with a CO_2 atmosphere

In Table 1, the pH measurements of the different solutions before and after gas (CO_2 or He) saturation and the dissolved inorganic carbon (DIC) after the gas saturation are presented.
In Figure 2, the main product yields (CO, CH_4, and H_2) for the different tested systems are shown. The solution of $NaHCO_3$ saturated with CO_2 presented the highest products yields. This system, the same as the NaOH solution, presents at the pH of 6.7 after CO_2 saturation, 38% of dissolved CO_2, the reactant associated to the photocatalytic reduction [4], and 62% of $NaHCO_3$ specie in equilibrium. The higher yield can be related to the total DIC contributed by the $NaHCO_3$ solution plus the CO_2 capture. The measured DIC in the NaOH solution is slightly lower since only CO_2 contributes to DIC, although the amount of captured CO_2 is much higher since the change of pH is significantly greater than in the $NaHCO_3$ solution. On the other hand, for the $NaHCO_3$ solution saturated with He, the final pH is higher. So, the reaction is occurring with only about 2% of dissolved CO_2 and then the products yields for these conditions are lower.

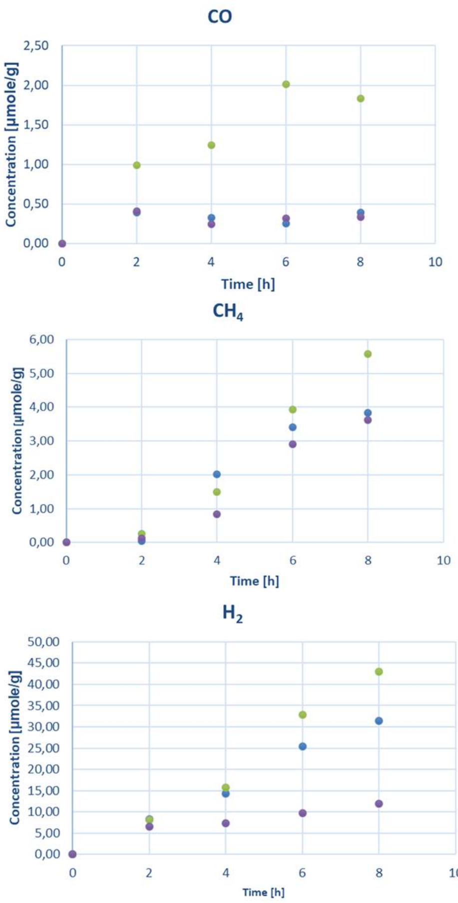

Figure 2. Products yields varying the carbon source dissolved in the photocatalyst suspension and the atmosphere: i) ● Saturation of CO_2 in a NaOH solution, ii) ● Saturation of CO_2 in a $NaHCO_3$ solution, and iii) ● Saturation of He in a $NaHCO_3$ solution

Table 1. pH before and after gas (CO_2 and He) saturation and DIC concentration after gas saturation

System	pH before CO_2 or He saturation	pH after CO_2 or He saturation	DIC after CO_2 or He saturation [M]
$NaHCO_3$ 0.2 M + He	7.9	7.9	0.22
NaOH 0.2 M + CO_2	12.4	6.7	0.25
$NaHCO_3$ 0.2 M + CO_2	7.9	6.7	0.26

Conclusions

The effect of the total dissolved carbon on the photocatalytic CO_2 reduction was experimentally studied saturating with CO_2 or with He a NaOH or $NaHCO_3$ solution. The products yields significantly improved when the inorganic carbon concentration in the TiO_2 suspension was increased by employing a $NaHCO_3$ solution and saturating with CO_2. In addition, this experimental condition results in a lower pH than saturating with He and the dissolved CO_2 in the liquid phase is favoured, that is the specie that is reduced on the irradiated TiO_2.

Acknowledgments

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