PHOTO-CATALYTIC REDUCTION OF CARBON DIOXIDE OVER Fe-TiO$_2$ AND Fe-PILC: EFFECT OF THE SUPPORT

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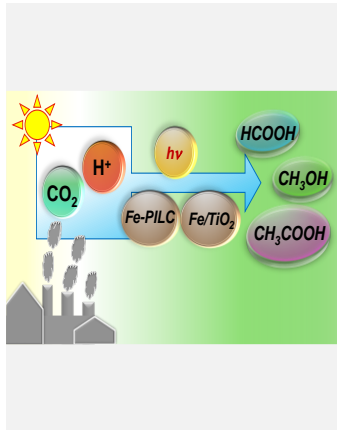
Most of the research on CO$_2$ photo-reduction is related to titanium dioxide (TiO$_2$) as catalyst due to its numerous advantages and distinctive properties. However, its practical use is limited due to its low photoactivity under Vis light. Pillared interlayer clay (PILC) has been reported as co-catalyst in environmental catalytic processes. In this work, bentonite was pillared with Fe (Fe-PILC) and TiO$_2$ was doped with Fe (Fe-TiO$_2$), in order to assess the effect of the support for CO$_2$ photo-reduction. Atomic absorption spectrometry (AAS), X-ray diffraction (XRD), N$_2$ adsorption–desorption, infrared spectroscopy (IR) and scanning electron microscopy (SEM) were the techniques used to characterize the materials. Formic acid was identified as the primary product using both catalysts, with a highest specific productivity of 214 μmol/g$_{cat}$ using Fe-TiO$_2$ at 293.15K, under basic conditions in STR. The presence of peroxide, and consequently hydroxyl radicals, was found to influence the production of formic acid.

Introduction

In recent years, the amount of anthropogenic CO$_2$ released into the atmosphere, primarily due to the widespread use of fossil fuels for energy, has become a matter of significant concern. This emission has risen from pre-industrial levels of 280 ppm to the current level of over 410 ppm. As a result, there have been significant disruptions in weather patterns and a global increase in temperature. Thus, there is a pressing need to develop methods for CO$_2$ reduction to convert and remove CO$_2$ from the atmosphere. Herein, CO$_2$ is the most abundant and cheapest source of carbon on the earth. From this point of view, research on photochemical, electrochemical, and photoelectrochemical CO$_2$ reduction has increased considerably in recent years, transforming it into molecules that are precursors or intermediates in the chemical reduction of CO$_2$, and with added value such as organic molecules, among them formic acid, (HCOOH), formaldehyde (HCHO) and methanol (CH$_3$OH), among others [1]. HCOOH has become attractive since it has been studied as a new generation fuel in direct formic acid fuel cells due to the advantages regarding the use of Hydrogen (H$_2$): a lower risk of explosion in storage and transportation, moderate operating temperatures and greater energy production. [2, 3]. Photo-reduction presents various challenges to be faced, one of them is the low catalytic yield in addition to the use of high-energy radiation to activate the catalysts. To overcome these issues, this work proposes the use of Fe-PILC and Fe-TiO$_2$ catalysts, since Fe has been used as effective catalyst in advanced oxidation processes (POA), and these processes are characterized by oxidant species such as the hydroxyl radical, which has been reported as important specie in the reduction of CO$_2$ [4]. On the other hand, TiO$_2$ has been the semiconductor more related to this kind of reaction, meanwhile PILCs are increasingly used as catalytic support for green chemical processes.

The objective of this study was to evaluate the effectiveness of iron as a catalyst over TiO$_2$ and pillared clays in the photo-reduction of CO$_2$ to produce energetically valuable compounds, namely formic acid and methanol, utilizing a stirred tank reactor. The variables under investigation included the type of support (TiO$_2$ versus clay) and the wavelength of light (UV versus visible light).

Material and Methods

Fe-TiO$_2$ synthesis was carried out using sol-gel method. Firstly, a solution of titanium butoxide and ethanol was prepared, after P-123 surfactant was added, and then the iron precursor was incorporated (required amount to obtain iron at about 4%). Finally, nitric acid was slowly dripped and the resulting solution was vigorously stirred for about 3 h and dried on a rotary evaporator. After that, it was calcined (1°C/ min) to 400°C for 3 hours.

Fe-PILC was prepared by ion exchange, dissolving FeCl$_3$·6H$_2$O in a 0.2M NaOH solution (pillaring solution), pH requires adjusting to 1.78-1.80 by adding HCl. Pillaring solution was added to a bentonite suspension at 2 wt% until complete dispersion. The intercalated clay was filtered off and the recovered solids were washed with deionized water until the conductivity value was 5µS. The material was dried at 70° C overnight and calcined at 400 °C for 2 h. The synthesized catalysts were characterized by XRD, SEM-EDS, FTIR and nitrogen physisorption techniques.

Catalytic evaluation in CO_2 photo-reduction reaction was carried out in a stirred batch reactor, employing a 0.5 M NaOH solution as the reducing agent at 25°C to enhance CO_2 absorption [5], with continuous stirring at 1400 rpm. Reaction products formation in liquid phase were analyzed and monitored by ultra high-performance liquid chromatography (UHPLC) and gas chromatography.

Results and Discussion
Catalyst characterization:
Fe-TiO_2 catalyst exhibited reflections attributed only to the anatase crystalline phase with a 0.35 nm interplanar distance (d_{101}), meanwhile 2.19 nm for Fe-PILC (d_{100}) as can be seen in Table 1. In the same table also Iron content is presented, it was obtained by SEM-EDS. SEM images show the morphology for both materials with a particle size not larger than 10 μm for Fe-PILC and about 20 μm for Fe-TiO_2 (Fig.1a and b).

Table 1. Basal space (by XRD) and iron content % (EDS).

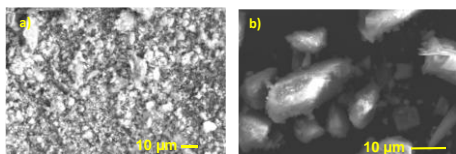| Catalyst	Basal space (nm)	Fe, %
Fe-PILC	2.19	1.9
Fe-TiO_2	0.35	1.4

Figure 1. SEM images for a) Fe-PILC (1000x) and b) Fe-TiO_2 (2000x).

FTIR revealed the characteristic appearance of clays such as 3567 cm^{-1} signal attributed to Al_2OH group of octahedral layer and also helped us to corroborate the pillarization process, (i.e., intensity of 523 cm^{-1} - Si-O-).

CO_2 photoreduction:

Fe-TiO_2 and Fe-PILC in suspension with 0.5M NaOH were used to carry out the CO_2 conversion, which was performed by irradiating UV light. It was observed that TiO_2 support leads to a higher specific productivity of formic acid compared to the clay support over the course of the reaction, the highest production is obtained at 1 hour of reaction with 214 μmol/g_{cat} for Fe-TiO_2 and 157 μmol/g_{cat} for Fe-PILC (Fig. 2a). The higher catalytic activity of Fe-TiO_2 is attributed to the photogenerated particles h^+/e^- since it is well-known TiO_2 as support favors them to start this reaction. The activity of the materials is also related to the production of hydrogen peroxide and then the presence of hydroxyl radicals during the reaction, as it is observed in Fig 2b and it is represented in Eq. 1.

$$H_2O_2 + e^-_{CB} \rightarrow \bullet OH + [OH]^- \qquad (1)$$
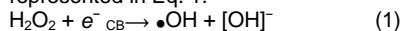
At the beginning of CO_2 photo-reduction, formic acid production has a maximum productivity at 1 h (Fig. 2a), and after that time it begins to decline. This decrease is related to the formation and accumulation of H_2O_2 and •OH. Fig. 2b shows this consumption after 4 hours of H_2O_2 monitoring. The highest catalytic yield for Fe-TiO_2 was obtained at short periods of reaction. On the other hand, activation of the catalysts was achieved at 254 nm. This wavelength is known for its high oxidizing power, which was confirmed with the decrease of the formic acid and the increase of peroxide amount produced.
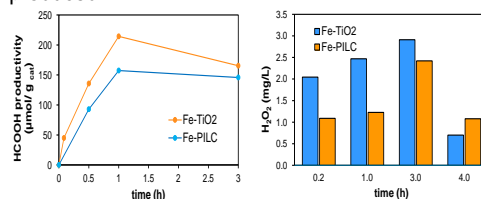
Figure 2. a) HCOOH specific productivity and, b) H_2O_2 production along reaction, using Fe-TiO_2 catalyst.

Conclusions
The photocatalytic activity of Fe-TiO_2 in suspension for CO_2 reduction is slightly higher than Fe-PILC which is related to the photogenerated particles (h^+/e^-) when TiO_2 is used as support. H_2O_2 produced in situ favors the beginning of the reaction, after that is consumed to oxidate reduced molecules.

References
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