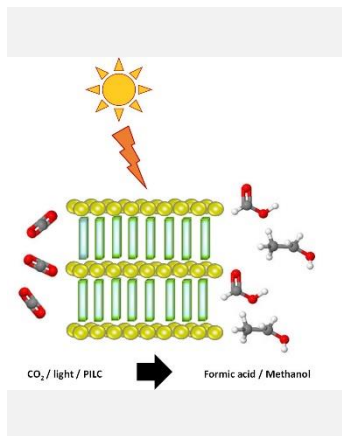


## CO<sub>2</sub> Photo-reduction over (Al, Cu and Fe) – Pillared interlayer clay catalysts

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Pillared interlayer clay (PILC) is a low-cost material that has spectacular properties that make it effective in catalytic reactions. In this work, bentonite, a natural silicate clay, was pillared with Al, Cu and Fe by ion exchange and then characterized. The characterization results confirmed that the pillaring process was successful and the pillars increased the basal space and specific surface area of the bentonite. The catalysts showed activity for CO<sub>2</sub> photo-reduction. The reaction products were identified by gas and liquid chromatography, and formic acid (FA) was identified as the major product. The studied variables were the effect of cation, catalyst loading (0, 0.05 and 0.5 g/L) and wavelength (UV light vs visible light). The highest catalytic yield corresponded to 0.05 g L<sup>-1</sup> (3926  $\mu\text{mol}\cdot\text{gcat}^{-1}\text{h}^{-1}$ ) for Al/Cu-PILC. Isopropanol and methanol were used as scavengers and they efficiently extract the photoinduced holes ( $h^{\cdot}$ ). The results of this research provide an alternative to develop highly effective materials for CO<sub>2</sub> photo-reduction.

### Introduction

The high energy demand for fossil fuels and their respective combustion has led to an increasingly high concentration of CO<sub>2</sub> in the environment, causing an irreversible change in the climate and a shortage of energy sources [1]. In this sense, it is essential to search for alternatives to minimize its emissions or its revaluation, since CO<sub>2</sub> represents a source of carbon for obtaining other chemical products with an inherent value [2]. The semiconductor most related to CO<sub>2</sub> photo-reduction is TiO<sub>2</sub> due to its numerous advantages, but its application is limited (low quantum yield and its energy bandwidth). Recently, natural silicate clay is increasingly used as catalytic support for green chemical processes, due to their low cost, accessibility, nontoxicity, durability and plentifulness [3]; and they can be recovered for using in other reactions. The intercalation of inorganic compounds through the exchange of ions between Na<sup>+</sup> and/or Ca<sup>2+</sup> of a clay, results in an increased basal spacing, enlarged interlayer spaces, larger pore volume, higher surface specific area and thermal stability [4]. Metal oxides, known as “pillars”, produced between the clay layers can provide Lewis or Brønsted acid sites of strong nature. The objective of this work was to assess the performance of pillared clays to carry out the photo-reduction of CO<sub>2</sub>, which are not tested before in this reaction, to produce compounds of interest mainly useful in the energy industry, such as: formic acid, using a stirred tank reactor. Type of cation exchanged (Al, Fe and Cu), amount of catalyst (0, 0.05, and 0.5 g/L), and wavelength (UV vs visible light) were the studied variables.

### Material and Methods

Pillaring solutions were prepared by dissolving the cation precursor ( AlCl<sub>3</sub>·6H<sub>2</sub>O, CuCl<sub>2</sub>·2H<sub>2</sub>O and/or FeCl<sub>3</sub>·6H<sub>2</sub>O) in a 0.2M NaOH solution. These solutions were added to a bentonite suspension at 2 wt% until complete dispersion. The intercalated clays were filtered off and the supernatants were washed until the conductivity was reduced. The solid products were dried at 70° C and calcined at 400 °C for 2 h. The materials were characterized by XRD, AA, nitrogen physisorption, XPS, IR and SEM techniques.

The CO<sub>2</sub> photo-reduction reaction was carried out in a stirred batch reactor, using 0.1 L of 0.5 M NaOH solution at 25°C, conditions that favor the absorption of CO<sub>2</sub> [5], and constant stirring (1400 rpm). After photo-reduction reaction, to measure the reaction products formation, several aliquots were taken from the reaction system and analyzed by high-performance liquid chromatography (HPLC) and gas chromatography.

### Results and Discussion

#### Catalyst characterization:

X-ray diffraction patterns confirm the successful modification of the initial material due to the pillaring process, through the d<sub>001</sub> reflection shift at 7° (2 $\theta$ ) to lower values and the opening in interlaminar space (basal space), which harmonize with other studies [6]. The results are shown in Table 1 and it can be observed that the ion exchange in the pillared clay increases the basal space of bentonite and it causes changes on textural properties, as the increase in

specific area. This was expected because of the clay swelling and the introduction of different polyhydroxycations (Table 1).

**Table 1.** XRD results (basal space) and textural/ chemical properties (SSA, metal content).

Material	Basal space (Å)	Specific Surface Area (m <sup>2</sup> /g)	Fe, Cu, Al, %	%	%
Bentonite	12.7	34.7	3.0	-	8.1
Cu/Fe-PILC	21.4	137.1	24.3	3.8	6.6
Fe-PILC	21.9	245.9	5.0	-	9.1
Al-PILC	18.0	319.4	-	-	10.8
Al/Cu-PILC	17.1	145.3	-	0.2	11.5

FTIR revealed the characteristic appearance of clays such as 3567 cm<sup>-1</sup> signal attributed to Al<sub>2</sub>OH group of octahedral layer and corroborated the pillarization, (i.e., intensity of 523 cm<sup>-1</sup> -Si-O-). The morphology observed by SEM was a flake-shaped structure and EDS confirmed the presence of Fe and Cu, the increase of Al content, and decrease of Na content. By XPS the presence of Al<sub>2</sub>O<sub>3</sub> and Al in the pillars was evident.

#### CO<sub>2</sub> photo-reduction:

Fig. 1 presents the FA production during CO<sub>2</sub> photo-reduction using different cations to exchange the starting bentonite. The highest FA production was obtained with Al/Cu-PILC even though it possess a low SSA and the lowest copper content, it seems there is a sinergetic effect between the higher Al content in this material to form Al<sub>2</sub>O<sub>3</sub> (as XPS showed) and the Cu content which is considered active for this reaction; and has been previously observed that when a greater amount of Cu is

#### Conclusions

Al/Cu-PILC provides the best results in terms of formic acid production. Scavengers test indicated that charge carriers (*h*<sup>+</sup>) are active species during the reaction. Tested PILCs showed higher catalytic activity for FA production during CO<sub>2</sub> reduction than starting material, indicating that bentonite modification is a good option for this kind of reaction.

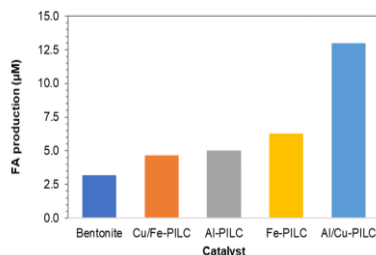
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loaded, the catalytic activity is lower [7]. This behaviour is probably due to the decrease of the active sites for an excessive deposition of Cu clusters. By increasing catalytic loading by 10-fold, productivity decreases in the same ratio. This is attributed to the light scattering effect caused when a high catalyst amount inhibits the light. The effect of the wavelength in the CO<sub>2</sub> photo-reduction was studied. The highest FA yield (3926 μmol g<sub>cat</sub><sup>-1</sup> h<sup>-1</sup>) was achieved at 254 nm.



**Figure 1.** Cation effect on the formic acid production (μM).

By other side, FTIR-ATR spectra of liquid samples provided evidence for the formation of protonated O=C=O--H<sup>+</sup> species along reaction. Additionally, isopropanol and methanol, were selected as hole scavengers to demonstrate that if the consumption of conduction band electrons is not efficiently accompanied by holes reduction through electron (e<sup>-</sup>) donating species, the reaction is depressed. Results suggest, scavengers initially inhibit the production of FA. Therefore, these alcohols efficiently extract the photoinduced holes (*h*<sup>+</sup>) and suggest the importance of hydroxyl radical in the production of FA.