

# Photocatalytic CO<sub>2</sub> Reduction in Gas-Solid Regime in the Presence of Bare, SiO<sub>2</sub> Supported or Cu-Loaded TiO<sub>2</sub> Samples

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**Abstract:** Both commercial and home prepared (HP) TiO<sub>2</sub> samples have been tested for the photocatalytic reduction of CO<sub>2</sub>. (HP) TiO<sub>2</sub> powders were prepared by using TiCl<sub>4</sub> or Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> as the precursors to obtain HP1 and HP2 samples, respectively. Also HP Cu-loaded and SiO<sub>2</sub> supported TiO<sub>2</sub> powders were prepared. The HP samples were more active than the commercial ones for the photoreduction of CO<sub>2</sub> with and without water vapour. HP1 produced mainly formaldehyde, HP2 principally methane. Acetaldehyde was found to be the primary product obtained when HP1 was supported on SiO<sub>2</sub>. The addition of Cu increased the photocatalytic reactivity either of bulk and SiO<sub>2</sub>-supported HP1. In particular, 1 wt % of Cu improved the formaldehyde yield obtained with the bare HP1 by one order of magnitude. Differently, the presence of Cu or SiO<sub>2</sub> in the HP2 samples markedly reduced the production of methane.

**Keywords:** CO<sub>2</sub> reduction, Photocatalysis, TiO<sub>2</sub>, Cu-loaded-TiO<sub>2</sub>, TiO<sub>2</sub>/SiO<sub>2</sub>, Cu-loaded-TiO<sub>2</sub>/SiO<sub>2</sub>.

## 1. INTRODUCTION

The increasing levels of CO<sub>2</sub> in the atmosphere have become a global environmental problem so that, during the last twenty years, a strong research effort has been aimed not only to abate this greenhouse gas, but also to form, at the same time, organic molecules suitable to be used as fuels or for industrial applications [1]. CO<sub>2</sub> is an inexpensive, non-flammable and non-toxic carbon source so it should be desirable to convert it into useful carbon products [2, 3]. In this context CO<sub>2</sub> valorization to obtain fuel feedstocks by using a cheap and abundant energy source such solar irradiation appears to be a desirable technology to explore. Heterogeneous photocatalysis is an attractive, inexpensive and environmental friendly tool for this purpose because this process not only allows to remove CO<sub>2</sub>, but it can also convert CO<sub>2</sub> into other organic compounds that can be used as fuels or as starting materials for the synthesis of valuable products [2, 3].

Photocatalytic reduction of CO<sub>2</sub> has received much attention since 1979, when Fujishima *et al.* [4] firstly reported that HCOOH, HCHO, CH<sub>3</sub>OH and CH<sub>4</sub> were obtained from CO<sub>2</sub> and H<sub>2</sub>O by irradiation of aqueous suspensions of a series of semiconductors (TiO<sub>2</sub>, ZnO, CdS, GaP and SiC). Albeit several semiconductors have an adequate position of their conduction band to reduce CO<sub>2</sub>, TiO<sub>2</sub> has been the most frequently used photocatalyst since it is chemically and biologically stable, effective in different operative conditions, inert, resistant to corrosion and cheap. In a typical photocatalytic process, electron-hole pairs are produced and, in the absence of O<sub>2</sub>, the photoproducted electrons can in principle reduce adsorbed CO<sub>2</sub>, while the holes can interact with hole scavengers like H<sub>2</sub>O, both in aqueous and in gas-solid systems, to achieve small organic molecules. Nowadays the main aspects of the mechanism of the surface reactions over UV illuminated TiO<sub>2</sub> for the degradation of organic pollutants are known [5], however the

photo-reduction of CO<sub>2</sub> is quite obscure, and in particular the intermediate species involved in the formation of products are often only hypothesized, due to the very low amounts of product obtained.

The photocatalytic reduction of CO<sub>2</sub> on TiO<sub>2</sub> has been studied in aqueous solutions [4,6-13], in liquid CO<sub>2</sub> [14] and in solid-gas systems [15-18]. The efficiency of the conversion of CO<sub>2</sub> to fuels in aqueous suspension systems was very low when H<sub>2</sub>O was used as the reductant but higher yields of products were obtained in the presence of molecules acting as hole sacrificial scavengers. The formation rate of methane was much enhanced in the presence of 2-propanol [8,14] but the presence of organic molecules can interfere with the detection of the CO<sub>2</sub> reduction products so that the reaction of CO<sub>2</sub> with H<sub>2</sub>O vapour is a more desirable system.

Saladin *et al.* [16] obtained CO, H<sub>2</sub> and CH<sub>4</sub> by UV irradiation of microcrystalline TiO<sub>2</sub> powder in the presence of CO<sub>2</sub> and H<sub>2</sub>O in gas phase. Anpo *et al.* [15] found CH<sub>4</sub> as the major product produced on anatase TiO<sub>2</sub> powders. Irradiation of rutile (100) single crystals led to the evolution of CH<sub>4</sub> and CH<sub>3</sub>OH and only CH<sub>3</sub>OH was detected with the (110) surface [15].

The efficiency of the photoreduction of CO<sub>2</sub> can be increased by loading TiO<sub>2</sub> with metals and, in particular, Cu was found to be particularly effective. Hirano *et al.* [19] firstly observed the beneficial effect of copper on the formation of methanol and formaldehyde by mixing a TiO<sub>2</sub> powder suspension with copper powder: Cu worked not only as catalyst but also as sacrificial electron donor. Adachi *et al.* [20] obtained CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>2</sub>H<sub>4</sub> using copper loaded TiO<sub>2</sub> prepared by suspending TiO<sub>2</sub> powders in a CuCl<sub>2</sub> solution. The formation of CH<sub>3</sub>OH was more efficient than that of CH<sub>4</sub> in the presence of Cu/TiO<sub>2</sub> catalysts prepared by impregnation of a TiO<sub>2</sub> powder with CuCl<sub>2</sub>·2H<sub>2</sub>O [21]. An increased methanol yield was also obtained loading silica supported TiO<sub>2</sub> powders with copper [9,13] or by impregnating Degussa P25 with copper nitrate [12]. The addition of Cu species, markedly increased the overall CO<sub>2</sub> conversion efficiency as well as the selectivity to CH<sub>4</sub> [13].

The function of copper and the real active Cu species have been not yet clarified. Anpo *et al.* [21] suggested that Cu<sup>+</sup> played a sig-

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nificant role in the formation of CH<sub>3</sub>OH. XPS analysis revealed that the copper species in Cu-loaded TiO<sub>2</sub> were predominantly Cu<sub>2</sub>O and only a minor amount of Cu<sup>0</sup> [10,22]. Tseng *et al.* [10] suggested that Cu(I) was the active species for the CO<sub>2</sub> photoreduction since the photocatalytic performance of the sample decreased after additional reduction with H<sub>2</sub>. Slamet *et al.* [12] prepared photocatalysts with various copper species (Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>0</sup>) and demonstrated that CuO is the most active dopant in improving the CO<sub>2</sub> photoreduction over TiO<sub>2</sub>. Li *et al.* [13] hypothesized that Cu(I) species may be reduced to Cu(0) during the photoreduction, and the Cu(0) species can be re-oxidized back to Cu(I) in air environment.

TiO<sub>2</sub> has been also incorporated in micro or macroporous materials to increase the reactivity and selectivity of the catalyst. Anpo and coworkers observed the predominant formation of CH<sub>3</sub>OH as well as CH<sub>4</sub> on highly dispersed TiO<sub>2</sub> anchored on porous Vycor glass [15,23], or within zeolites or mesoporous silica materials [24-29]. In situ spectroscopic studies indicated that the CH<sub>3</sub>OH formation was linked to the high activity of the charge transfer excited complexes [Ti<sup>3+</sup>-O] of the tetrahedrally-coordinated titanium oxide species within the silica frameworks [30].

Li *et al.* [13] studied Cu-doped TiO<sub>2</sub> catalysts supported on mesoporous silica. The synergistic combination of Cu deposition and high surface area of the SiO<sub>2</sub> support enhanced the CO<sub>2</sub> photoreduction rate to CO and CH<sub>4</sub>.

Recently, Yang *et al.* [31] demonstrated, by the combined use of DRIFT spectroscopy and <sup>13</sup>C labelled CO<sub>2</sub>, that carbon residues formed during the catalyst synthesis procedures involving the use of Ti-alkoxides and organic solvents significantly contribute to the formation of CO over Cu-promoted crystalline TiO<sub>2</sub> catalysts.

In the present study, commercial and home prepared TiO<sub>2</sub> samples were used in gas-solid regime to reduce carbon dioxide in the presence of water under UV irradiation. The catalysts were synthesized by thermohydrolysis of TiCl<sub>4</sub> to avoid the presence of carbon containing precursors. Some samples were loaded with copper species and/or supported on SiO<sub>2</sub>. The activity of these photocatalysts was compared with that of TiO<sub>2</sub> and Cu-loaded TiO<sub>2</sub> prepared according to a sol-gel process reported in the literature [9, 22].

## 2. EXPERIMENTAL

### 2.1. Catalyst Preparation

Four commercial TiO<sub>2</sub> powders were used: Merck, Evonik P25, Mirkat M211 and Hombikat PC500. Home prepared (HP) TiO<sub>2</sub> samples were obtained by using titanium(IV) chloride (TiCl<sub>4</sub>, Fluka 98%) and titanium(IV) butoxide (Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, Sigma Aldrich 97%) as the starting materials.

TiCl<sub>4</sub> was slowly added to distilled water (molar ratio Ti/H<sub>2</sub>O 1:60; volume ratio 1:10) at room temperature. After ca. 12 h of continuous stirring, a clear solution was obtained. The solution was boiled for 2 h under agitation. This treatment produced a milky white TiO<sub>2</sub> dispersion that was dried under vacuum at 323 K. This sample was labeled as HP1.

A composite TiO<sub>2</sub>/SiO<sub>2</sub> material was prepared in order to study the role of SiO<sub>2</sub> as support. 10 g of commercial SiO<sub>2</sub> (Cabot) were added to 110 mL of the solution obtained by adding 10 ml of TiCl<sub>4</sub> to 100 ml of H<sub>2</sub>O. The stirred suspension was boiled for 2 h, cooled to room temperature and dried in a rotary evaporator. The sample was labeled as HP1/SiO<sub>2</sub>.

Copper-loaded samples were prepared by adding the desired amount of CuCl<sub>2</sub>·2H<sub>2</sub>O (Sigma Aldrich 99%) to the aqueous TiCl<sub>4</sub> solution. Two samples were prepared with Cu percentage amounts

of 1 and 2 wt % with respect to TiO<sub>2</sub>. The codices used for these samples were 1%Cu-HP1 and 2%Cu-HP1, respectively. Copper-loaded samples supported on SiO<sub>2</sub> by a procedure analogous to that described for the bare TiO<sub>2</sub>/SiO<sub>2</sub> were labeled as 1% and 2%Cu-HP1/SiO<sub>2</sub>.

10 mL of TiCl<sub>4</sub> were slowly added to 50 ml of distilled water at room temperature. After ca. 15 min of continuous stirring, the clear obtained solution was sealed in a bottle and kept in an oven at 373 K for 48 h. The bottle was allowed to cool to room temperature and the resultant solid was recovered using a vacuum pump at 323 K. The sample was labeled HP-rutile.

15 mL of TiCl<sub>4</sub> were added dropwise to a solution containing 630 mL of demineralized water and 240 mL of concentrated hydrochloric acid. The solution obtained after continuous stirring was heated in a tightly closed glass bottle and aged at 373 K in an oven for 48 h. The resultant precipitate contained a mixture of brookite and rutile. Pure brookite nanoparticles were separated by peptization by removing many times the supernatant and adding water to restore the initial solution volume. After a few washings, a dispersion of brookite particles was obtained whilst the rutile phase remained as a precipitate. The dispersions containing the brookite particles were collected and dried under vacuum at 673 K. The sample was identified as HP-brookite.

6.8 mL of Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> were added to a solution of 7.3 mL of anhydrous n-butanol (Sigma Aldrich 99.8%) and 4.6 mL of acetic acid. The mixture was vigorously stirred for 1 h and the resultant solution was dried in an oven at 423 K. The recovered solid was calcined at 773 K for 0.5 h. The sample was labeled as HP2.

A Cu-loaded sample, identified as 2%Cu-HP2, was prepared by adding the desired amount of CuCl<sub>2</sub>·2H<sub>2</sub>O to the solution containing anhydrous n-butanol, acetic acid and Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>.

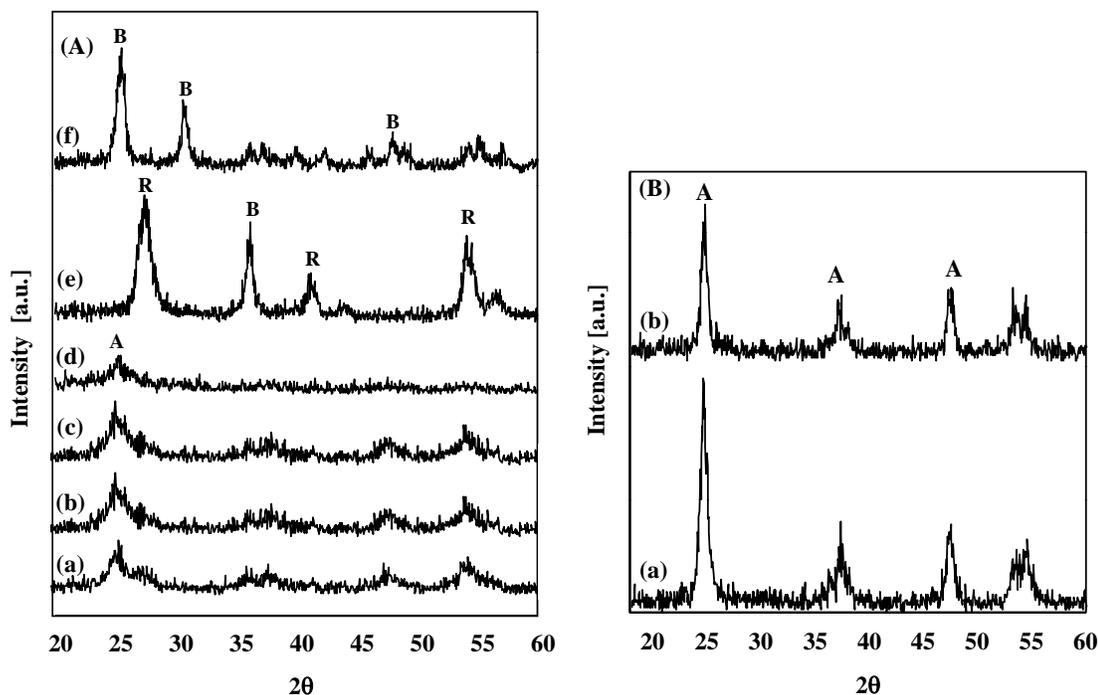
A supported TiO<sub>2</sub>/SiO<sub>2</sub> sample was prepared following the same procedure of the sample HP2 by adding Santa Barbara amorphous silica-15 (SBA) [32] to the solution containing Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>, n-butanol, acetic acid and CuCl<sub>2</sub>·2H<sub>2</sub>O. This sample was labeled as HP2/SiO<sub>2</sub>-SBA.

### 2.2. Characterization of the Samples

X-ray diffraction patterns of the powders were recorded at room temperature by an Ital Structures APD 2000 powder diffractometer using the Cu K<sub>α</sub> radiation and a 2θ scan rate of 2°/min. The specific surface area (SSA) of the powders were determined in a Flow Sorb 2300 apparatus (Micromeritics) by using the single-point BET method. The samples were degassed for 0.5 h at 250 °C prior to the measurement. SEM observations were obtained using a Philips XL30 ESEM microscope, operating at 25 kV on specimens upon which a thin layer of gold had been evaporated. An electron microprobe used in an energy dispersive mode (EDX) was employed to obtain information on the content of Cu loaded on the samples. UV-Vis spectra of the solid photocatalysts were obtained by diffuse reflectance spectroscopy using a Shimadzu UV-2401 PC instrument. BaSO<sub>4</sub> was used as a reference sample and the spectra were recorded in the range 200-800 nm.

### 2.3. Photocatalytic Experiments

The photocatalytic runs were carried out in a Pyrex batch gas-solid reactor (V = 100 mL) irradiated from the top by a 400 W medium pressure Hg lamp. A water filter was positioned between the lamp and the photoreactor in order to cut the infrared radiation. 0.5 g of catalyst powder were placed inside the photoreactor, and be-



**Fig. 1.** XRD patterns of (A): (a) HP1; (b) 1%Cu-HP1; (c) 2%Cu-HP1; (d) HP1/SiO<sub>2</sub>; (e) HP-rutile; (f) HP-brookite and (B): (a) HP2; (b) 2%Cu-HP2. A: Anatase; R: Rutile; B: Brookite.

fore beginning any run, N<sub>2</sub> was flushed for some hours inside the system under UV irradiation in order to phorodesorb possible impurities or carbon residues from the catalyst surface. Afterwards, the photoreactor was saturated with CO<sub>2</sub> and then a certain amount of water was injected in the reactor with a microsyringe. 0.5 ml of the gaseous mixture were withdrawn at fixed irradiation times by using a gas-tight microsyringe. The evolution of the formed products was followed by a GC-2010 Shimadzu gas chromatograph equipped with a Phenomenex Zebtron Wax-plus (30 m×0.32 μm×0.53 μm) column and a flame ionization detector, using He as the carrier gas.

### 3. RESULTS AND DISCUSSION

#### 3.1. Characterization of the Photocatalysts

(Fig. 1) shows the diffraction patterns of the home prepared samples. (Fig. 1A) reports the diffractograms of the samples prepared from TiCl<sub>4</sub>, (Fig. 1B) those prepared from Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>.

All the HP1 samples presented peaks of anatase and rutile. The peaks were very broad, characteristic of partially crystalline powders. Single sharp peaks of rutile or brookite were instead obtained for the HP-rutile and HP-brookite samples, respectively.

The X-ray diffraction peaks of the HP2 samples (Fig. 1B) were consistent with those of anatase. HP2 samples were more crystalline than the HP1 ones due to the high temperature reached during their preparation. In any case, no peaks related to Cu were observed in the Cu-loaded samples, probably due to the low amount and/or to the high degree of dispersion of the metal species on the support.

As reported in (Table 1), the specific surface areas of the various home-prepared samples ranged between 31 and 87 m<sup>2</sup>·g<sup>-1</sup>. A noticeable increase of SSA ranging between 114 and 217 m<sup>2</sup>·g<sup>-1</sup> was obtained when TiO<sub>2</sub> was supported on silica.

(Fig. 2) shows SEM images of some home-prepared samples. The morphology of the powders synthesized from TiCl<sub>4</sub> in mild conditions was very different from that of the catalysts obtained

from Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub> and calcined at 773 K. HP-rutile (Fig. 2a) consisted of particles of spheroidal shapes with average sizes of 1-2 μm which were aggregates of smaller particles with diameters ranging between 40 and 70 nm. The micrographs of HP1 (Fig. 2b) revealed more regular aggregates of small particles with diameters ranging between 60 and 70 nm. As shown in (Fig. 2c), the samples supported on SiO<sub>2</sub> exhibited similar morphology by indicating that the silica particles worked as nucleation centres for the precipitation of TiO<sub>2</sub>. Differently, HP2 samples (Fig. 2d) consisted of very fine close-packed particles with diameters of 10–20 nm. No significant differences could be seen from the micrographs of the Cu loaded samples compared to those of bare HP1 or HP2 samples.

EDX mapping analysis of Cu on the catalysts indicated that Cu was uniformly dispersed on the TiO<sub>2</sub> surface. (Table 1) reports the atomic percentages of Cu with respect to the (Cu + Ti) atomic content.

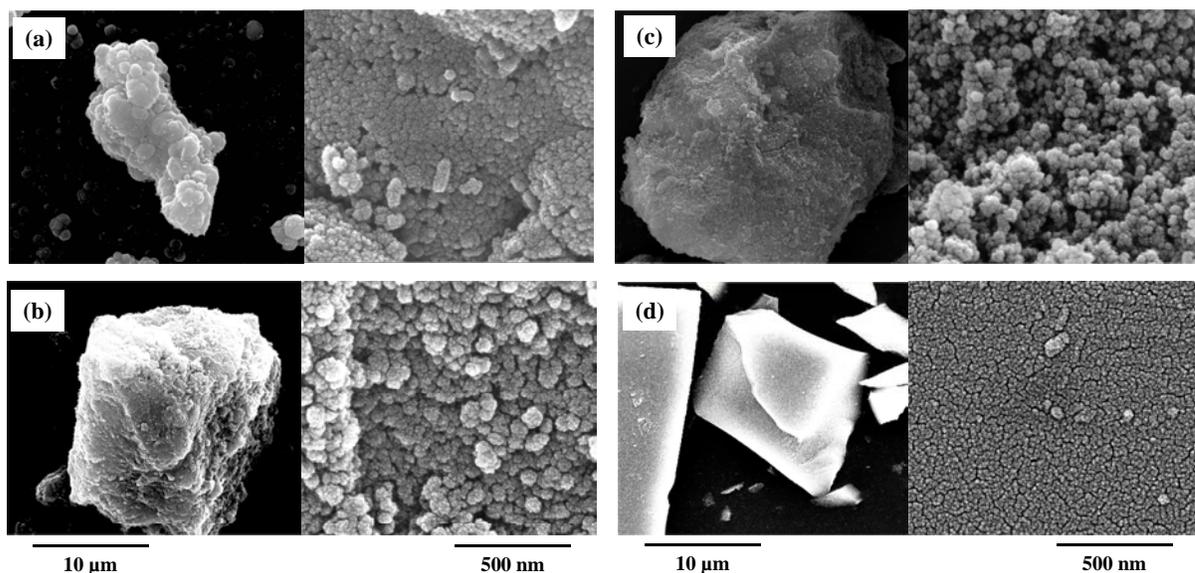
(Fig. 3) shows diffuse reflectance spectra of various samples. The spectra of the powders supported on SiO<sub>2</sub> were similar to those of the unsupported samples. All the spectra of the copper-loaded samples showed a maximum value of reflectance at about 500 nm. The presence of copper caused the shift of the absorption edge toward higher wavelengths with respect to the bare TiO<sub>2</sub> powders. The band gap energy, E<sub>g</sub>, of each sample was estimated from the tangent line in the plots of the modified Kubelka-Munk function [F(R'<sub>∞</sub>)hv]<sup>1/2</sup> versus the energy of the exciting light [33]. As shown in (Table 1), the E<sub>g</sub> values of the Cu-loaded HP1 samples were lower than those of the bare HP1 powders and decreased with increasing the copper content.

#### 3.2. Photocatalytic Results

Blank tests carried out in the same experimental conditions ensured that no organic compounds were produced in the absence of catalyst as well as in the dark.

**Table 1. Properties of the Catalysts**

Photocatalyst	Phases <sup>1</sup>	SSA <sup>2</sup> [m <sup>2</sup> g <sup>-1</sup> ]	Band-gap [eV]	Cu/(Ti + Cu) at.% calculated	Cu/(Ti + Cu) at.% EDX
TiO <sub>2</sub> Merck	A	10	3.24	-	-
TiO <sub>2</sub> Evonik P25	A, R	50	3.13	-	-
TiO <sub>2</sub> Mirkat M211	A	180	3.24	-	-
TiO <sub>2</sub> Hombikat PC500	A	350	3.25	-	-
HP-rutile	R	87	3.02	-	-
HP-brookite	B	82	3.26	-	-
HP1	A, R	54	3.00	-	-
1%Cu-HP1	A, R	76	2.98	1.2	1.4
2%Cu-HP1	A, R	62	2.92	2.4	3.7
HP1/SiO <sub>2</sub>	A, R	177	3.02	-	-
1%Cu-HP1/SiO <sub>2</sub>	A, R	114	2.97	1.2	2.9
2%Cu-HP1/SiO <sub>2</sub>	A, R	121	2.92	2.4	4.1
HP2	A	31	-	-	-
2%Cu-HP2	A	35	-	2.4	2.2
HP2/SiO <sub>2</sub> SBA	A	217	3.12	-	-

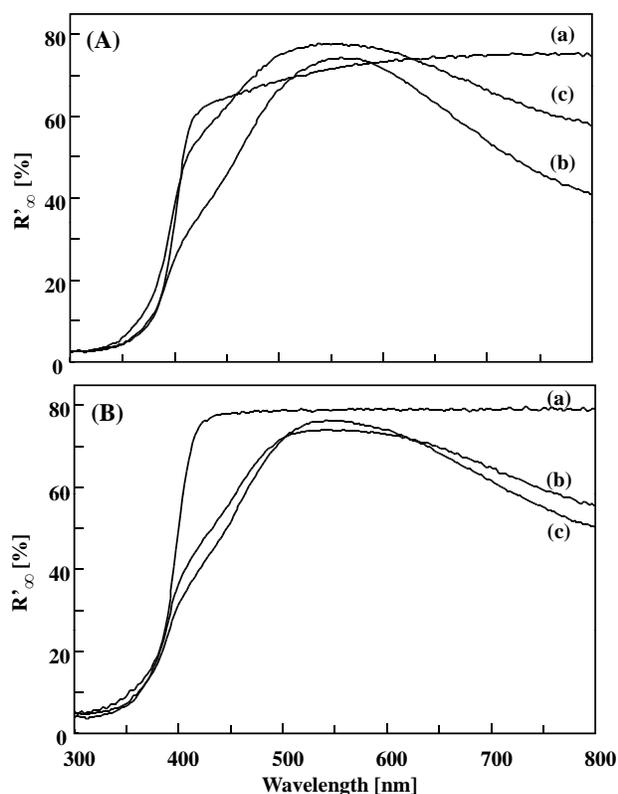
<sup>1</sup> A: anatase; R: rutile; B: brookite.<sup>2</sup> BET specific surface area.**Fig. (2).** SEM micrographs of (a) HP-rutile; (b) HP1; (c) HP1/SiO<sub>2</sub>; (d) HP2.

Preliminary photocatalytic tests were carried out in the presence of only CO<sub>2</sub> without H<sub>2</sub>O. (Fig. 4) shows a comparison among the peak amounts of the main conversion products obtained with commercial and home-prepared samples. TiO<sub>2</sub> Evonik P25 and TiO<sub>2</sub> Hombikat PC500 were inactive whereas some reactivity was observed in the presence of TiO<sub>2</sub> Merck or TiO<sub>2</sub> Mirkat M211. By using TiO<sub>2</sub> Merck, mainly acetaldehyde was obtained with a maximum amount of 0.27 μmol/g-cat after 4 h of UV irradiation, that decreased until 0.08 μmol/g-cat after 8 h. Very low amounts of methane, methanol and propanone (0.04, 0.02 and 0.02 μmol/g-cat, respectively) that remained almost constant during the run were also detected. Differently, TiO<sub>2</sub> Mirkat M211 yielded formaldehyde

(0.17 μmol/g-cat) and methane (0.1 μmol/g-cat) as the primary reduction products after 5 h of irradiation.

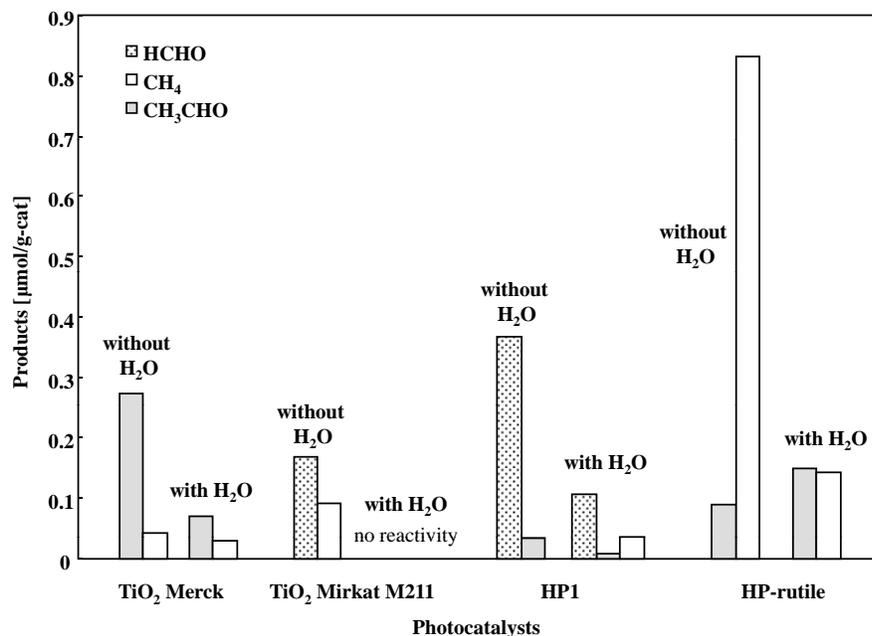
The home-prepared HP1 and HP-rutile samples were more efficient than the commercial TiO<sub>2</sub> powders. HP1 produced a maximum amount of 0.37 μmol/g-cat of formaldehyde in 1 h whereas ca. 0.83 μmol/g-cat of methane and 0.09 μmol/g-cat of acetaldehyde were obtained after 6 hours of irradiation in the presence of HP-rutile. It is worth noting that HP1-brookite was practically inactive.

The formation of hydrogenated compounds without any apparent proton source is justified by the presence of surface physically



**Fig. (3).** Diffuse reflectance spectra of (A): (a) HP1; (b) 1%Cu-HP1; (c) 2%Cu-HP1 and (B): (a) HP1/SiO<sub>2</sub>; (b) 1%Cu-HP1/SiO<sub>2</sub>; (c) 2%Cu-HP1/SiO<sub>2</sub>.

adsorbed water, already previously determined by thermogravimetric analysis [34], which is activated upon illumination [31]. When the photocatalytic runs were carried out in the presence of water vapour, CH<sub>4</sub> yield generally decreased and, in the case of HP-rutile, a six fold diminution was observed. This result can be explained by considering the competition of water molecules with CO<sub>2</sub> for the adsorption on the catalyst surface.



**Fig. (4).** Peak amounts of the main compounds obtained by photocatalytic reduction of CO<sub>2</sub> with and without H<sub>2</sub>O on commercial and home-prepared samples.

Formaldehyde was the major product detected when the photocatalytic runs were carried out in the presence of CO<sub>2</sub> and water vapour using bare and copper-loaded HP1 catalysts. (Fig. 5) shows the time dependence of the formaldehyde yields obtained with the three catalysts. Formaldehyde continuously increased and reached the amount of 0.11 μmol/g-cat after 6 hours of irradiation of HP1. When the samples were loaded with 1 or 2% of Cu, the amount of formaldehyde increased to ca. 1.14 or 0.8 μmol/g-cat, respectively. The production of formaldehyde stopped when the light was turned off confirming that HCHO was photocatalytically formed. As shown in (Fig. 5), a volcano dependence of the formaldehyde yield with the copper loading was observed. 1%Cu-HP1 was more active than 2%Cu-HP1 and exhibited a ca. 10-fold enhancement of formaldehyde production with respect to that of bare HP1. These results are in agreement with literature works reporting an optimum copper loading of various TiO<sub>2</sub> photocatalysts active for the photo-reduction of CO<sub>2</sub> to methanol [9,12,22,35,36] or methane [37]. Copper probably serves as an electron trapper that inhibits the recombination of holes and electrons but excess Cu loading can mask the TiO<sub>2</sub> surface, reducing the light exposure of the catalyst. Moreover, the incorporation of copper generates basic sites relatively stronger than those of TiO<sub>2</sub> [38] so that a larger amount of CO<sub>2</sub> can be adsorbed by the catalyst.

(Fig. 6) shows a comparison among the peak amounts of the main conversion products obtained with various catalysts. Differently from the results obtained with the unsupported samples, acetaldehyde and not formaldehyde was the main compound produced in the presence of HP1/SiO<sub>2</sub> and 1%Cu-HP1/SiO<sub>2</sub>. The amount of acetaldehyde increased with the irradiation time and reached 0.35 and 0.5 μmol/g-cat, respectively, after 6 hours of irradiation. Methane (ca. 0.04 μmol/g-cat), methanol and propanone (0.02 μmol/g-cat) were also obtained, but their amounts remained almost constant throughout the runs. The presence of 1 wt % of copper enhanced the yield of acetaldehyde but 2%Cu-HP1/SiO<sub>2</sub> was much less active, producing only a small amount of methane.

The formation of acetaldehyde is probably favoured by the high dispersion state of TiO<sub>2</sub> and the largest specific surface area of the

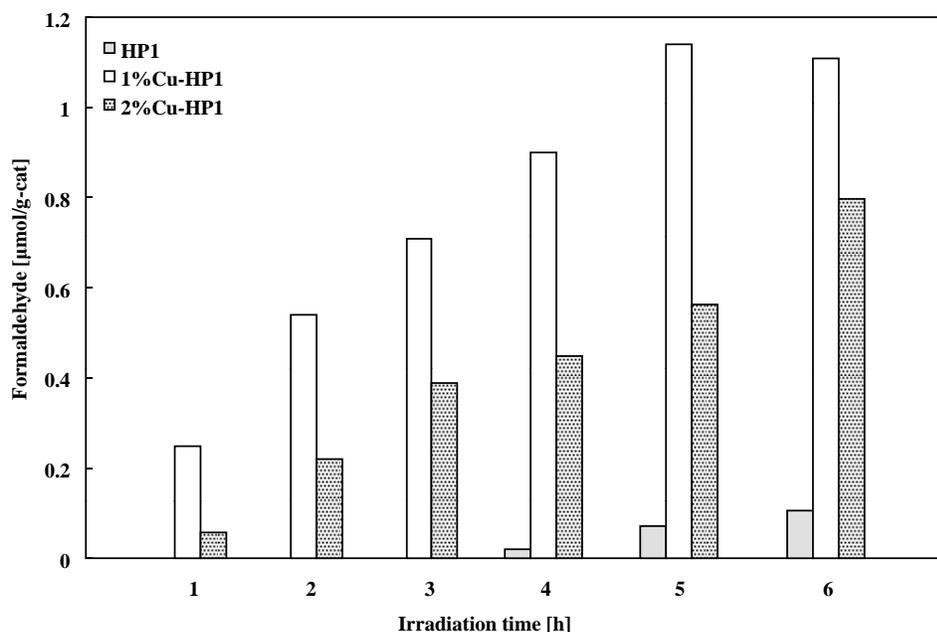


Fig. (5). Time dependence of the formaldehyde production on bare and Cu-loaded HP1 samples.

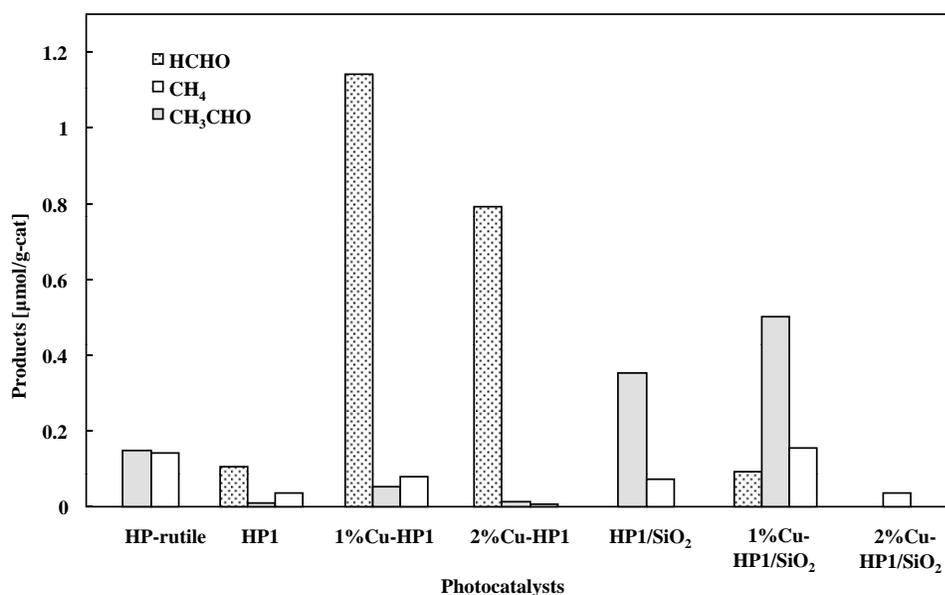


Fig. (6). Peak amounts of the main compounds obtained by photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on various catalysts prepared from TiCl<sub>4</sub>.

TiO<sub>2</sub>/SiO<sub>2</sub> samples while formaldehyde is prevalently obtained with the bulk TiO<sub>2</sub> catalysts.

Acetaldehyde was also obtained in the presence of HP-rutile along with methane as main products of the reaction. Anyway, the maximum amount of acetaldehyde obtained with HP1/SiO<sub>2</sub> was about 3.3 times higher than that detected with HP-rutile whereas the methane yield was practically the same.

Thermodynamically, the reduction of CO<sub>2</sub> requires that the bottom energy level of the conduction band of the semiconductor is more negative than the reduction potential of the various processes that lead to the reduced products. (Fig. 7) shows the alignment of the conduction bands of anatase [39] and rutile [40] with the reduction potentials of the possible reactions that can occur in the reduction of CO<sub>2</sub> [41]. All potentials are referred to the normal hydrogen electrode at pH 7. Only the formation of methane is energetically

possible in the presence of rutile and this justifies the absence of formaldehyde that is instead the main compound obtained with the HP1 samples that prevalently consist of anatase.

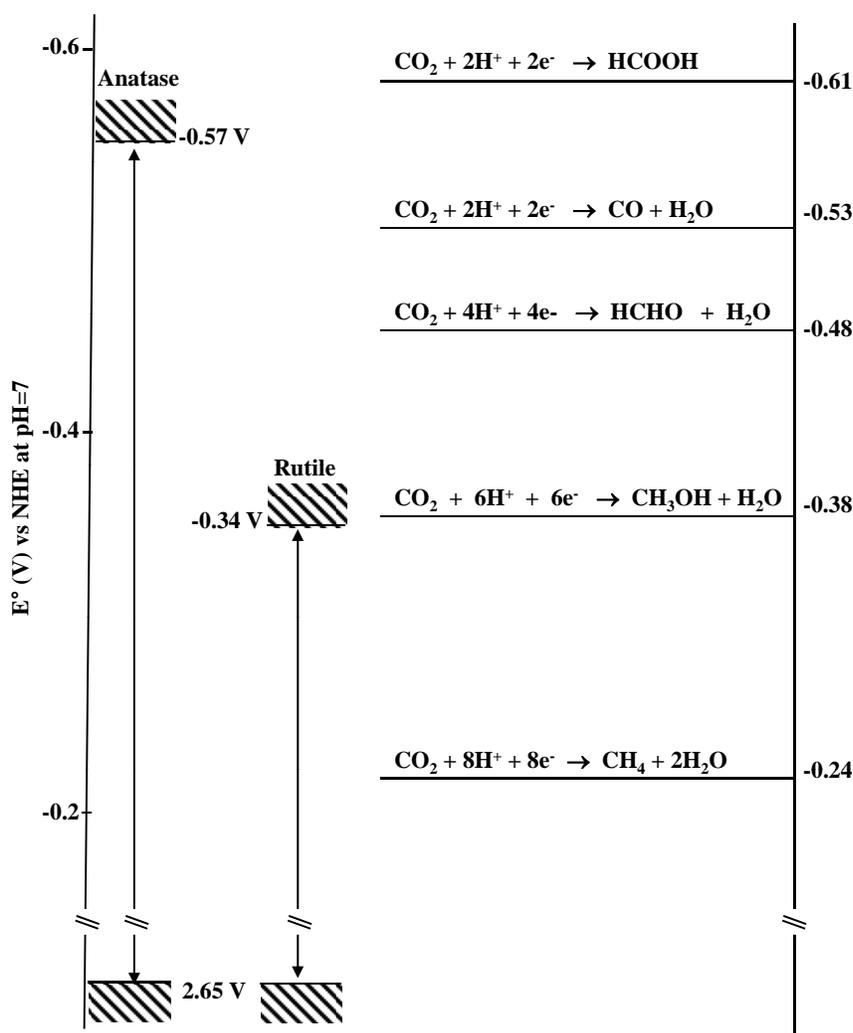
The photocatalytic conversion of CO<sub>2</sub> to organic compounds is quite complex and most of the researchers have hypothesized multi-electron transfer processes to obtain the final hydrogenated products [4,8,17,42-44].

The formation of formaldehyde and/or methane can be justified by a mechanism proposed by Subrahmanyam *et al.* [42]. UV irradiation of TiO<sub>2</sub> generates electron-hole pairs according to Eq. (1):



In the absence of molecular oxygen, H<sup>+</sup> can be reduced to H<sup>•</sup>:





**Fig. (7).** Relationship between the band structures of anatase and rutile and the thermodynamic potentials for the reduction of  $\text{CO}_2$  to various products versus NHE at  $\text{pH} = 7$ .

Hydrogen atoms can combine to give hydrogen molecules or react with  $\text{CO}_2$  to give formic acid:



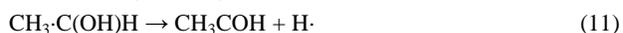
Formic acid can react with  $\text{H} \cdot$  giving formaldehyde that can be reduced to methanol:



Finally, methanol can be reduced to methane:



Acetaldehyde could be formed by reaction between  $\text{CH}_3 \cdot$  and formaldehyde:



The kind of obtained products depends on the nature of the catalyst and on the experimental conditions such as  $\text{H}_2\text{O}/\text{CO}_2$  ratio, UV wavelength, light intensity, reaction medium and reactor configuration.

The experimental results seem to suggest that the reaction (10), involving the formation of a C-C bond and leading to acetaldehyde through the reaction (11), occurs preferentially on photocatalysts with relatively high specific surface areas (HP-rutile, HP1/SiO<sub>2</sub> samples) since the interactions among the adsorbed precursor species should be statistically favoured on a larger surface.

(Fig. 8) shows the peak amounts of the main conversion products obtained in the presence of the HP2 samples and water vapour. Methane was the main compound detected by using bare HP2. Its concentration increased during the run reaching ca. 3.1  $\mu\text{mol/g-cat}$  after 6 h of irradiation. Also formaldehyde and acetaldehyde were formed, albeit their concentration increased to ca. 0.85 and 0.3  $\mu\text{mol/g-cat}$  respectively after 1.5 hours and then decreased to ca. 0.2  $\mu\text{mol/g-cat}$  after 6 hours of irradiation. The yields of formaldehyde and methane dramatically decreased if HP2 was loaded with 2% of copper or supported on mesoporous SBA silica. These results apparently disagree with those reported by Wu and coworkers who prevalently obtained methanol with samples prepared in a similar way. Anyway, it is worth noting that the reaction system was often completely different (photoreactor with TiO<sub>2</sub> coated optical fibers [35, 36], UVC light as irradiation source [10,22]) or  $\text{CO}_2$  photoreduction occurred in an aqueous solution [9] rather than in vapour phase.

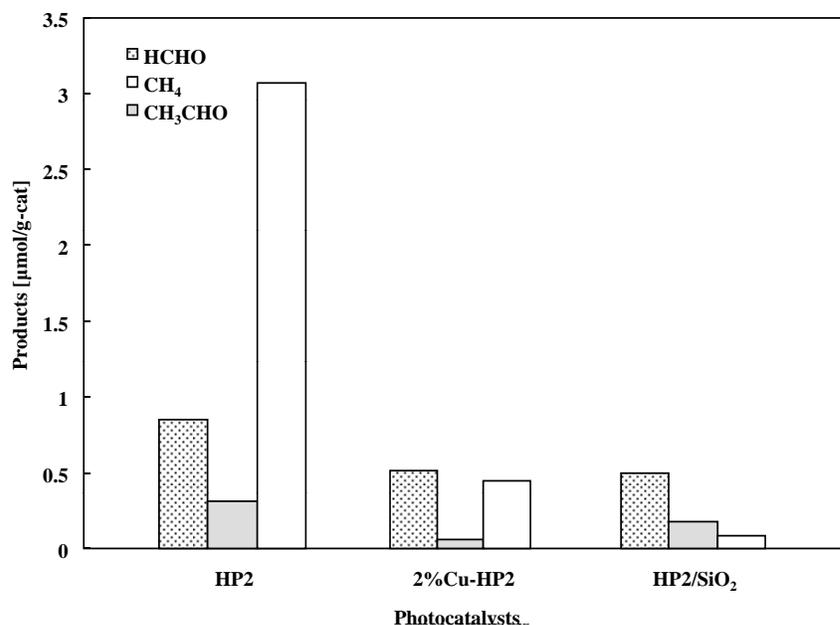


Fig. (8). Peak amounts of the main compounds obtained by photocatalytic reduction of CO<sub>2</sub> with H<sub>2</sub>O on various catalysts prepared from Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>.

#### 4. CONCLUSION

The photocatalytic reduction of CO<sub>2</sub> has been performed with various TiO<sub>2</sub> catalysts prepared by hydrolysis of TiCl<sub>4</sub> or Ti(OC<sub>4</sub>H<sub>9</sub>)<sub>4</sub>. Depending on the type of catalyst, different photocatalytic reactions and different compound selectivities were observed. Formaldehyde or acetaldehyde were the major products obtained with the HP1 samples prepared from TiCl<sub>4</sub> whilst methane was mainly produced in the presence of the HP2 samples synthesized from Ti butoxide. The presence of 1% wt of Cu increased the formation of the products obtained with bare or silica-supported HP1 samples whereas it was detrimental when the photoreduction of CO<sub>2</sub> occurred with the HP2 samples. Although the obtained yields are not high, the samples prepared by simple thermohydrolysis of TiCl<sub>4</sub> are promising candidates as new and applicable photocatalysts for the reduction of CO<sub>2</sub> with H<sub>2</sub>O to form formaldehyde or acetaldehyde selectively.

#### CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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