

Photocatalytic CO₂ Reduction in Gas-Solid Regime in the Presence of Bare, SiO₂ Supported or Cu-Loaded TiO₂ Samples

Marianna Bellardita*, Agatino Di Paola, Elisa García-López, Vittorio Loddo, Giuseppe Marci and Leonardo Palmisano

"Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy

Abstract: Both commercial and home prepared (HP) TiO₂ samples have been tested for the photocatalytic reduction of CO₂. (HP) TiO₂ powders were prepared by using TiCl₄ or Ti(OC₄H₉)₄ as the precursors to obtain HP1 and HP2 samples, respectively. Also HP Cu-loaded and SiO₂ supported TiO₂ powders were prepared. The HP samples were more active than the commercial ones for the photoreduction of CO₂ 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 SiO₂. The addition of Cu increased the photocatalytic reactivity either of bulk and SiO₂-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 SiO₂ in the HP2 samples markedly reduced the production of methane.

Keywords: CO₂ reduction, Photocatalysis, TiO₂, Cu-loaded-TiO₂, TiO₂/SiO₂, Cu-loaded-TiO₂/SiO₂.

1. INTRODUCTION

The increasing levels of CO₂ 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]. CO₂ 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 CO₂ 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 CO₂, but it can also convert CO₂ 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 CO₂ has received much attention since 1979, when Fujishima *et al.* [4] firstly reported that HCOOH, HCHO, CH₃OH and CH₄ were obtained from CO₂ and H₂O by irradiation of aqueous suspensions of a series of semiconductors (TiO₂, ZnO, CdS, GaP and SiC). Albeit several semiconductors have an adequate position of their conduction band to reduce CO₂, TiO₂ 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 O₂, the photoproducted electrons can in principle reduce adsorbed CO₂, while the holes can interact with hole scavengers like H₂O, 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 TiO₂ for the degradation of organic pollutants are known [5], however the

photo-reduction of CO₂ 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 CO₂ on TiO₂ has been studied in aqueous solutions [4,6-13], in liquid CO₂ [14] and in solid-gas systems [15-18]. The efficiency of the conversion of CO₂ to fuels in aqueous suspension systems was very low when H₂O 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 CO₂ reduction products so that the reaction of CO₂ with H₂O vapour is a more desirable system.

Saladin *et al.* [16] obtained CO, H₂ and CH₄ by UV irradiation of microcrystalline TiO₂ powder in the presence of CO₂ and H₂O in gas phase. Anpo *et al.* [15] found CH₄ as the major product produced on anatase TiO₂ powders. Irradiation of rutile (100) single crystals led to the evolution of CH₄ and CH₃OH and only CH₃OH was detected with the (110) surface [15].

The efficiency of the photoreduction of CO₂ can be increased by loading TiO₂ 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 TiO₂ powder suspension with copper powder: Cu worked not only as catalyst but also as sacrificial electron donor. Adachi *et al.* [20] obtained CH₄, C₂H₆ and C₂H₄ using copper loaded TiO₂ prepared by suspending TiO₂ powders in a CuCl₂ solution. The formation of CH₃OH was more efficient than that of CH₄ in the presence of Cu/TiO₂ catalysts prepared by impregnation of a TiO₂ powder with CuCl₂·2H₂O [21]. An increased methanol yield was also obtained loading silica supported TiO₂ powders with copper [9,13] or by impregnating Degussa P25 with copper nitrate [12]. The addition of Cu species, markedly increased the overall CO₂ conversion efficiency as well as the selectivity to CH₄ [13].

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

*Address correspondence to this author at the "Schiavello-Grillone" Photocatalysis Group, Dipartimento di Energia, Ingegneria dell'Informazione e Modelli Matematici (DEIM), Università di Palermo, Viale delle Scienze, 90128 Palermo, Italy; Tel: 0039-091-238-63721; Fax: 0039-091-23860841; E-mail: marianna.bellardita@unipa.it

nificant role in the formation of CH₃OH. XPS analysis revealed that the copper species in Cu-loaded TiO₂ were predominantly Cu₂O and only a minor amount of Cu⁰ [10,22]. Tseng *et al.* [10] suggested that Cu(I) was the active species for the CO₂ photoreduction since the photocatalytic performance of the sample decreased after additional reduction with H₂. Slamet *et al.* [12] prepared photocatalysts with various copper species (Cu²⁺, Cu⁺, Cu⁰) and demonstrated that CuO is the most active dopant in improving the CO₂ photoreduction over TiO₂. 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.

TiO₂ 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 CH₃OH as well as CH₄ on highly dispersed TiO₂ anchored on porous Vycor glass [15,23], or within zeolites or mesoporous silica materials [24-29]. In situ spectroscopic studies indicated that the CH₃OH formation was linked to the high activity of the charge transfer excited complexes [Ti³⁺-O] of the tetrahedrally-coordinated titanium oxide species within the silica frameworks [30].

Li *et al.* [13] studied Cu-doped TiO₂ catalysts supported on mesoporous silica. The synergistic combination of Cu deposition and high surface area of the SiO₂ support enhanced the CO₂ photoreduction rate to CO and CH₄.

Recently, Yang *et al.* [31] demonstrated, by the combined use of DRIFT spectroscopy and ¹³C labelled CO₂, 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 TiO₂ catalysts.

In the present study, commercial and home prepared TiO₂ 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 TiCl₄ to avoid the presence of carbon containing precursors. Some samples were loaded with copper species and/or supported on SiO₂. The activity of these photocatalysts was compared with that of TiO₂ and Cu-loaded TiO₂ prepared according to a sol-gel process reported in the literature [9, 22].

2. EXPERIMENTAL

2.1. Catalyst Preparation

Four commercial TiO₂ powders were used: Merck, Evonik P25, Mirkat M211 and Hombikat PC500. Home prepared (HP) TiO₂ samples were obtained by using titanium(IV) chloride (TiCl₄, Fluka 98%) and titanium(IV) butoxide (Ti(OC₄H₉)₄, Sigma Aldrich 97%) as the starting materials.

TiCl₄ was slowly added to distilled water (molar ratio Ti/H₂O 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 TiO₂ dispersion that was dried under vacuum at 323 K. This sample was labeled as HP1.

A composite TiO₂/SiO₂ material was prepared in order to study the role of SiO₂ as support. 10 g of commercial SiO₂ (Cabot) were added to 110 mL of the solution obtained by adding 10 ml of TiCl₄ to 100 ml of H₂O. The stirred suspension was boiled for 2 h, cooled to room temperature and dried in a rotary evaporator. The sample was labeled as HP1/SiO₂.

Copper-loaded samples were prepared by adding the desired amount of CuCl₂·2H₂O (Sigma Aldrich 99%) to the aqueous TiCl₄ solution. Two samples were prepared with Cu percentage amounts

of 1 and 2 wt % with respect to TiO₂. The codices used for these samples were 1%Cu-HP1 and 2%Cu-HP1, respectively. Copper-loaded samples supported on SiO₂ by a procedure analogous to that described for the bare TiO₂/SiO₂ were labeled as 1% and 2%Cu-HP1/SiO₂.

10 mL of TiCl₄ 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 TiCl₄ 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(OC₄H₉)₄ 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 CuCl₂·2H₂O to the solution containing anhydrous n-butanol, acetic acid and Ti(OC₄H₉)₄.

A supported TiO₂/SiO₂ 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(OC₄H₉)₄, n-butanol, acetic acid and CuCl₂·2H₂O. This sample was labeled as HP2/SiO₂-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_α 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. BaSO₄ 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-

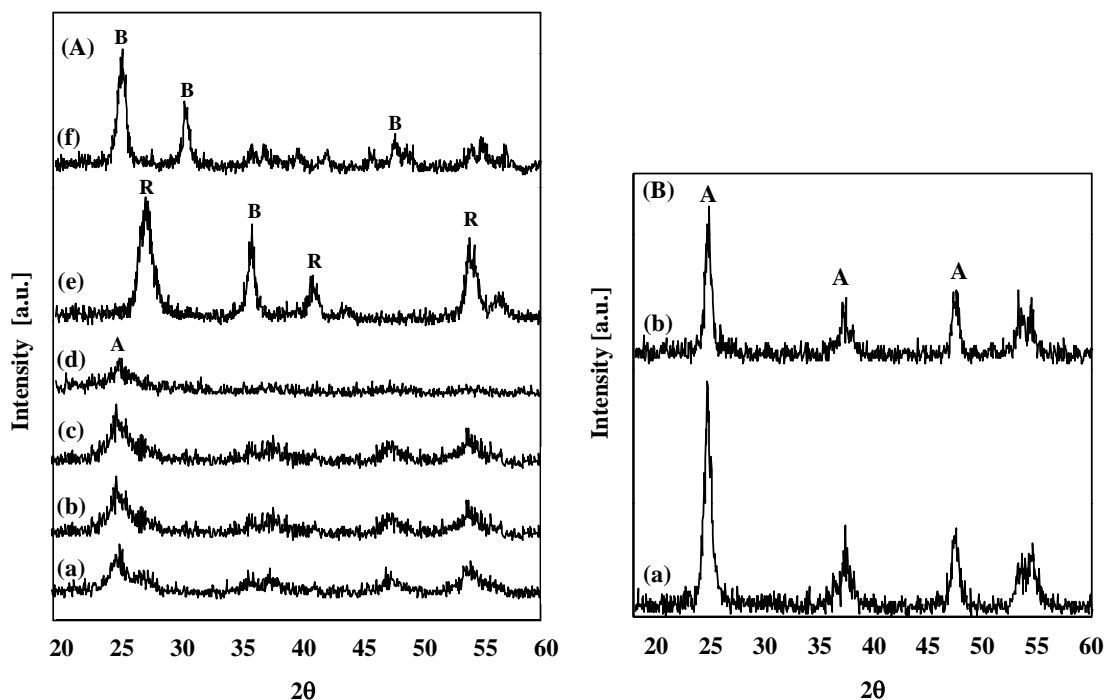


Fig. (1). XRD patterns of (A): (a) HP1; (b) 1%Cu-HP1; (c) 2%Cu-HP1; (d) HP1/SiO₂; (e) HP-rutile; (f) HP-brookite and (B): (a) HP2; (b) 2%Cu-HP2. A: Anatase; R: Rutile; B: Brookite.

fore beginning any run, N₂ was flushed for some hours inside the system under UV irradiation in order to phodesorb possible impurities or carbon residues from the catalyst surface. Afterwards, the photoreactor was saturated with CO₂ 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 TiCl₄, (Fig. 1B) those prepared from Ti(OC₄H₉)₄.

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 m²·g⁻¹. A noticeable increase of SSA ranging between 114 and 217 m²·g⁻¹ was obtained when TiO₂ was supported on silica.

(Fig. 2) shows SEM images of some home-prepared samples. The morphology of the powders synthesized from TiCl₄ in mild conditions was very different from that of the catalysts obtained

from Ti(OC₄H₉)₄ 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 SiO₂ exhibited similar morphology by indicating that the silica particles worked as nucleation centres for the precipitation of TiO₂. 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 TiO₂ surface. (Table 1) reports the atomic percentages of Cu with respect to the (Cu + Ti) atomic content.

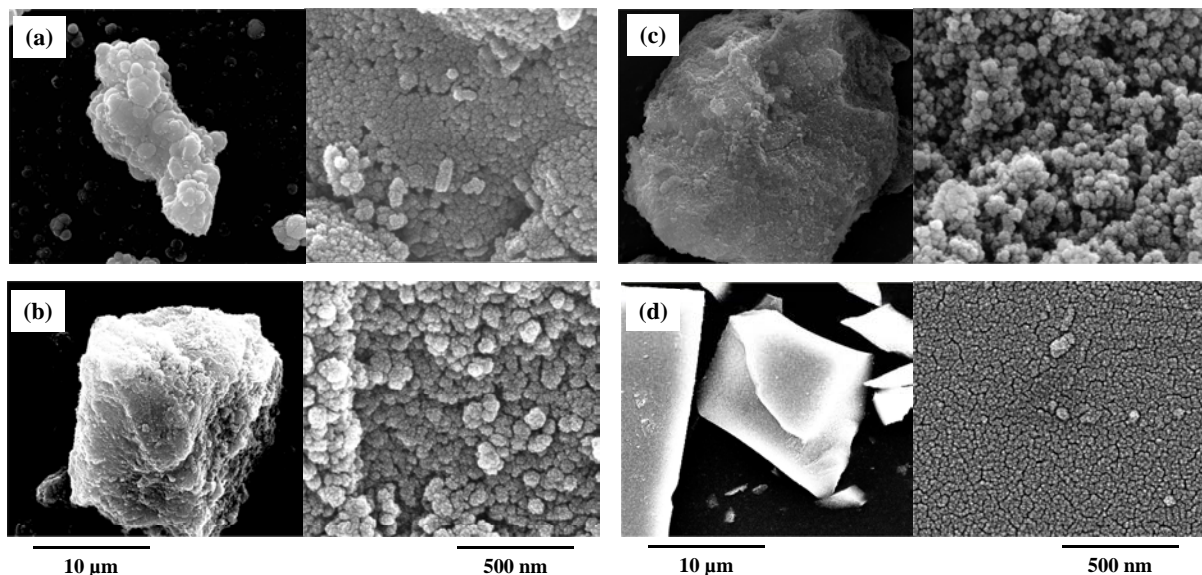
(Fig. 3) shows diffuse reflectance spectra of various samples. The spectra of the powders supported on SiO₂ were similar to those of the unsupported samples. All the spectra of the copper-loaded samples showed a maximum value of reflectance at about 500 nm. The presence of copper caused the shift of the absorption edge toward higher wavelengths with respect to the bare TiO₂ powders. The band gap energy, E_g, of each sample was estimated from the tangent line in the plots of the modified Kubelka-Munk function [F(R'_∞)hv]^{1/2} versus the energy of the exciting light [33]. As shown in (Table 1), the E_g 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 ¹	SSA ² [m ² g ⁻¹]	Band-gap [eV]	Cu/(Ti + Cu) at.% calculated	Cu/(Ti + Cu) at.% EDX
TiO ₂ Merck	A	10	3.24	-	-
TiO ₂ Evonik P25	A, R	50	3.13	-	-
TiO ₂ Mirkat M211	A	180	3.24	-	-
TiO ₂ 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 ₂	A, R	177	3.02	-	-
1%Cu-HP1/SiO ₂	A, R	114	2.97	1.2	2.9
2%Cu-HP1/SiO ₂	A, R	121	2.92	2.4	4.1
HP2	A	31	-	-	-
2%Cu-HP2	A	35	-	2.4	2.2
HP2/SiO ₂ SBA	A	217	3.12	-	-

¹ A: anatase; R: rutile; B: brookite.² BET specific surface area.**Fig. (2).** SEM micrographs of (a) HP-rutile; (b) HP1; (c) HP1/SiO₂; (d) HP2.

Preliminary photocatalytic tests were carried out in the presence of only CO₂ without H₂O. (Fig. 4) shows a comparison among the peak amounts of the main conversion products obtained with commercial and home-prepared samples. TiO₂ Evonik P25 and TiO₂ Hombikat PC500 were inactive whereas some reactivity was observed in the presence of TiO₂ Merck or TiO₂ Mirkat M211. By using TiO₂ 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, TiO₂ 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 TiO₂ 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

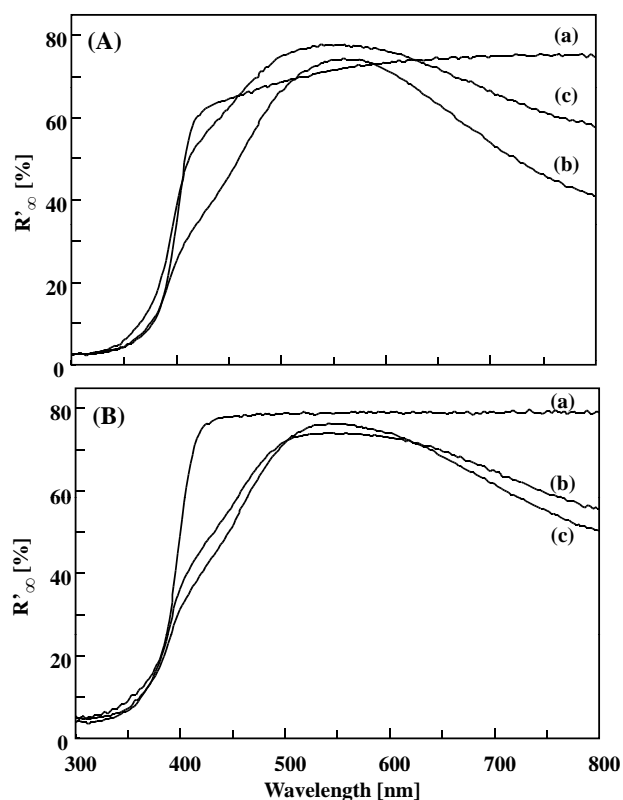


Fig. (3). Diffuse reflectance spectra of (A): (a) HP1; (b) 1%Cu-HP1; (c) 2%Cu-HP1 and (B): (a) HP1/SiO₂; (b) 1%Cu-HP1/SiO₂; (c) 2%Cu-HP1/SiO₂.

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, CH₄ 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 CO₂ for the adsorption on the catalyst surface.

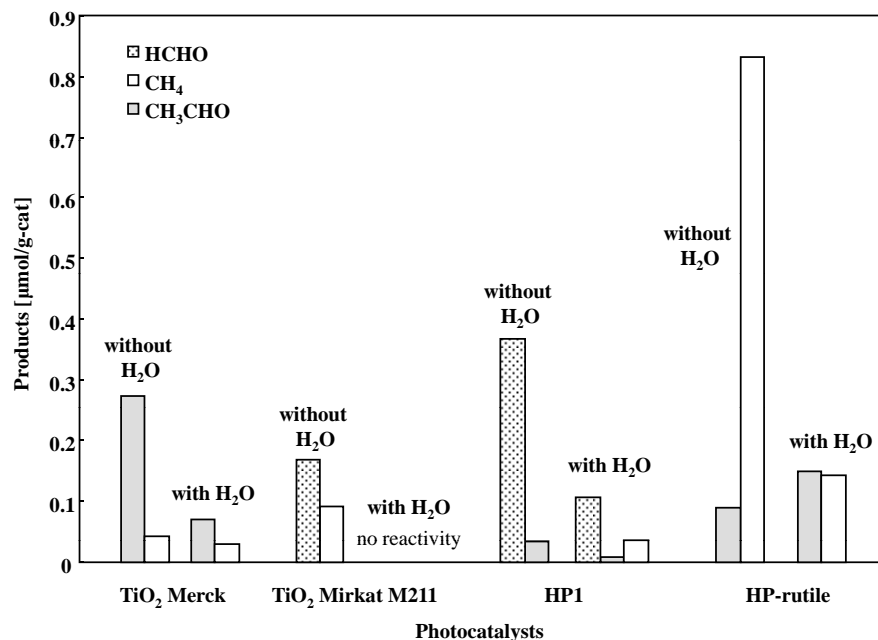


Fig. (4). Peak amounts of the main compounds obtained by photocatalytic reduction of CO₂ with and without H₂O on commercial and home-prepared samples.

Formaldehyde was the major product detected when the photocatalytic runs were carried out in the presence of CO₂ 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 TiO₂ photocatalysts active for the photo-reduction of CO₂ 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 TiO₂ surface, reducing the light exposure of the catalyst. Moreover, the incorporation of copper generates basic sites relatively stronger than those of TiO₂ [38] so that a larger amount of CO₂ 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/SiO₂ and 1%Cu-HP1/SiO₂. 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/SiO₂ was much less active, producing only a small amount of methane.

The formation of acetaldehyde is probably favoured by the high dispersion state of TiO₂ and the largest specific surface area of the

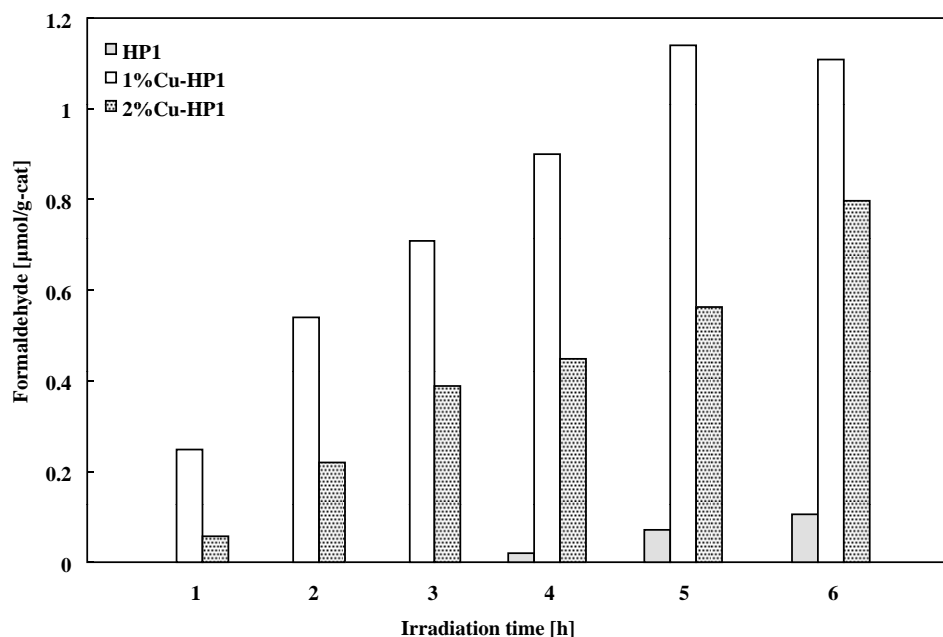


Fig. (5). Time dependence of the formaldehyde production on bare and Cu-loaded HP1 samples.

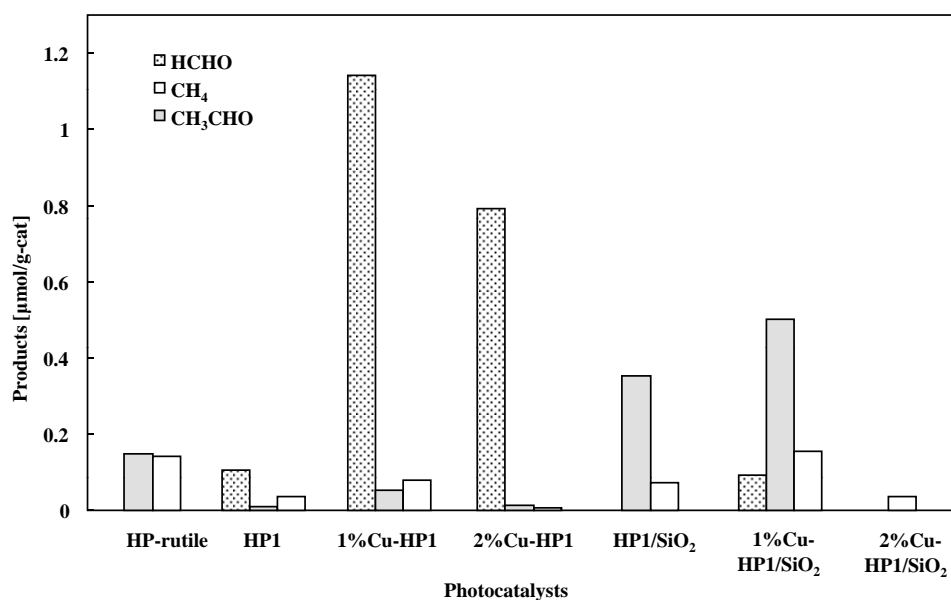


Fig. (6). Peak amounts of the main compounds obtained by photocatalytic reduction of CO₂ with H₂O on various catalysts prepared from TiCl₄.

TiO₂/SiO₂ samples while formaldehyde is prevalently obtained with the bulk TiO₂ catalysts.

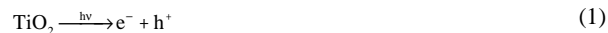
Acetaldehyde was also obtained in the presence of HP-rutile along with methane as main products of the reaction. Anyway, the maximum amount of acetaldehyde obtained with HP1/SiO₂ was about 3.3 times higher than that detected with HP-rutile whereas the methane yield was practically the same.

Thermodynamically, the reduction of CO₂ 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 CO₂ [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 CO₂ 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 TiO₂ generates electron-hole pairs according to Eq. (1):



In the absence of molecular oxygen, H⁺ can be reduced to H[·]:



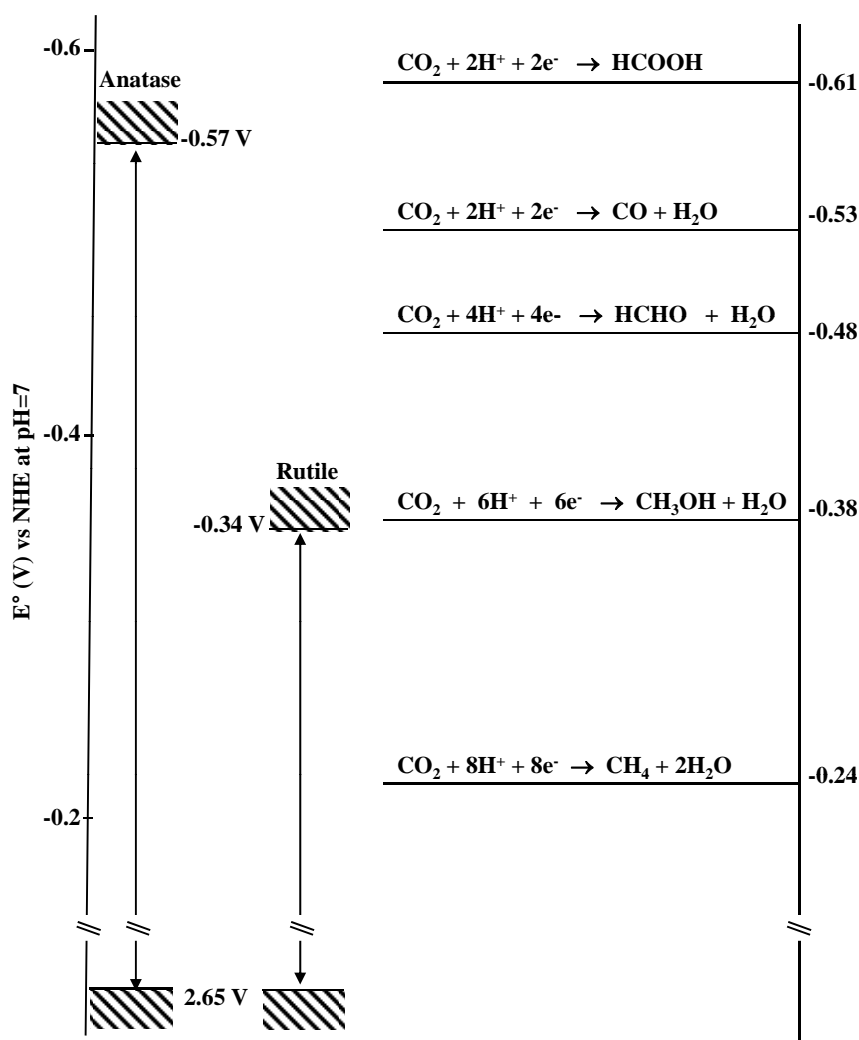
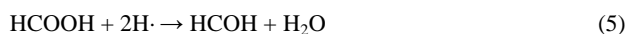


Fig. (7). Relationship between the band structures of anatase and rutile and the thermodynamic potentials for the reduction of CO_2 to various products versus NHE at $\text{pH} = 7$.

Hydrogen atoms can combine to give hydrogen molecules or react with CO_2 to give formic acid:



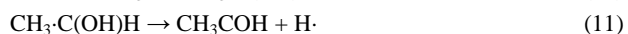
Formic acid can react with $\text{H} \cdot$ giving formaldehyde that can be reduced to methanol:



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/SiO₂ 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 TiO₂ coated optical fibers [35, 36], UVC light as irradiation source [10,22]) or CO_2 photoreduction occurred in an aqueous solution [9] rather than in vapour phase.

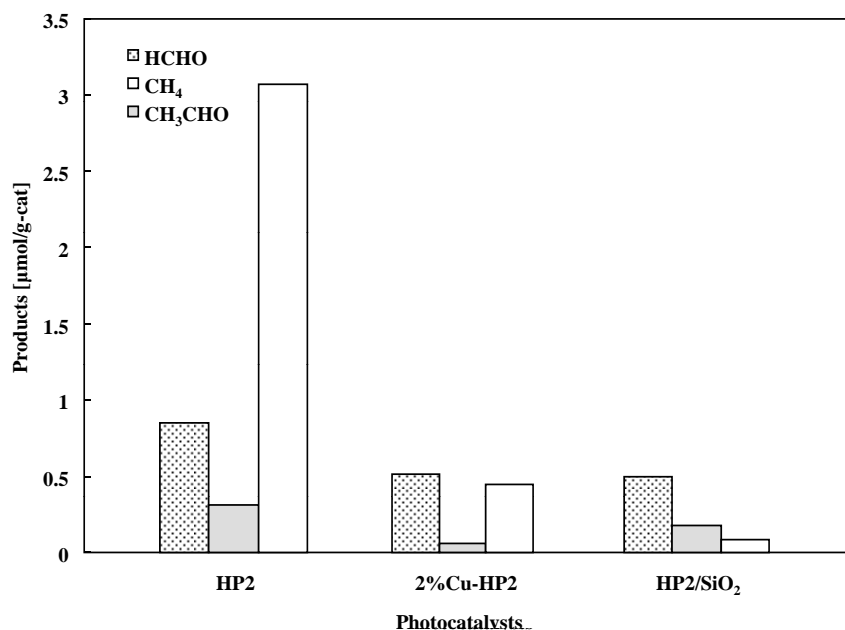


Fig. (8). Peak amounts of the main compounds obtained by photocatalytic reduction of CO₂ with H₂O on various catalysts prepared from Ti(OC₄H₉)₄.

4. CONCLUSION

The photocatalytic reduction of CO₂ has been performed with various TiO₂ catalysts prepared by hydrolysis of TiCl₄ or Ti(OC₄H₉)₄. 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 TiCl₄ 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 CO₂ occurred with the HP2 samples. Although the obtained yields are not high, the samples prepared by simple thermohydrolysis of TiCl₄ are promising candidates as new and applicable photocatalysts for the reduction of CO₂ with H₂O to form formaldehyde or acetaldehyde selectively.

CONFLICT OF INTEREST

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

ACKNOWLEDGEMENTS

The authors wish to acknowledge MIUR for economical support (PON01_02257).

REFERENCES

- Halmann, M.M. Chemical Fixation of Carbon Dioxide: Methods of Recycling CO₂ into Useful Products, CRC Press: Boca Raton, 1993.
- Shi, M.; Shen, Y.M. Recent progresses on the fixation of carbon dioxide. *Curr. Org. Chem.*, **2003**, *7*, 737-745.
- Dey, G.R.; Chemical reduction of CO₂ to different products during photocatalytic reaction on TiO₂ under diverse conditions: an overview. *J. Nat. Gas Chem.*, **2007**, *16*, 217-226.
- Inoue, T.; Fujishima, A.; Konishi S.; Honda, K. Photoelectrocatalytic reduction of carbon dioxide in aqueous suspensions of semiconductor powders. *Nature*, **1979**, *277*, 637-638.
- Augugliaro, V.; Bellardita, M.; Loddò, V.; Palmisano, G.; Palmisano, L.; Yurdakal, S. Overview on oxidation mechanisms of organic compounds by TiO₂ in heterogeneous photocatalysis. *J. Photochem. Photobiol. C*, **2012**, *13*, 224-245.
- G.R. Dey, A.D. Belapurkar, K. Kisshore, Photo-catalytic reduction of carbon dioxide to methane using TiO₂ as suspension in water. *J. Photochem. Photobiol. A: Chem.*, **2004**, *163*, 503-508.
- Mizuno, T.; Adachi, K.; Ohta, K.; Saji, A.; Effect of CO₂ pressure on photocatalytic reduction of CO₂ using TiO₂ in aqueous solution. *J. Photochem. Photobiol. A: Chem.*, **1996**, *98*, 87-90.
- Kaneko, S.; Shimizu, Y.; Ohta, K.; Mizuno, T. Photocatalytic reduction of high pressure carbon dioxide using TiO₂ powders with a positive hole scavenger. *J. Photochem. Photobiol. A: Chem.*, **1998**, *115*, 223-226.
- Yang, H.C.; Lin, H.Y.; Chien, Y.S.; Wu, J.C.S.; Wu, H.H. Mesoporous TiO₂/SBA-15, and Cu/TiO₂/SBA-15 composite photocatalysts for photoreduction of CO₂ to methanol. *Catal. Lett.*, **2009**, *131*, 381-387.
- Tseng, I.H.; Wu, J.C.S.; Chou, H.Y. Effects of sol-gel procedures on the photocatalysis of Cu/TiO₂ in CO₂ photoreduction. *J. Catal.*, **2004**, *221*, 432-440.
- Yahaya, A.H.; Gondal, M.A.; Hameed, A. Selective laser enhanced photocatalytic conversion of CO₂ into methanol. *Chem. Phys. Lett.*, **2004**, *400*, 206-212.
- Slamet; Nasution, H.W.; Purnama, E.; Kosela, S.; Gunlazuardi, J. Photocatalytic reduction of CO₂ on copper-doped titania catalysts prepared by improved-impregnation method. *Catal. Commun.*, **2005**, *6*, 313-319.
- Li, Y.; Wang, W.-N.; Zhan, Z.; Woo, M.-H.; Wu, C.-Y.; Biswas, P. Photocatalytic reduction of CO₂ with H₂O on mesoporous silica supported Cu/TiO₂ catalysts. *Appl. Catal. B: Environ.*, **2010**, *100*, 386-392.
- Kaneko, S.; Kurimoto, H.; Ohta, K.; Mizuno T.; Saji, A. Photocatalytic reduction of CO₂ using TiO₂ powders in liquid CO₂ medium. *J. Photochem. Photobiol. A: Chem.*, **1997**, *109*, 59-63.
- Anpo, M.; Yamashita, H.; Ichihashi, Y.; Ehara, S. Photocatalytic reduction of CO₂ with H₂O on various titanium oxide catalysts. *J. Electroanal. Chem.*, **1995**, *396*, 21-26.
- Saladin, F.; Forss, L.; Kamber, I. Photosynthesis of CH₄ at a TiO₂ surface from gaseous H₂O and CO₂. *J. Chem. Soc. Chem. Commun.*, **1995**, 533-534.
- Tan, S.S.; Zou, L.; Hu, E. Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO₂ pellets. *Catal. Today*, **2006**, *115*, 269-273.
- Varghese, O. K.; Paulose, M.; La Tempa, T. J.; Grimes, C.A. High-rate solar photocatalytic conversion of CO₂ and water vapor to hydrocarbon fuels. *Nano Lett.*, **2009**, *9*, 731-737.
- Hirano, K.; Inoue, K.; Yatsu, T. Photocatalytic reduction of CO₂ in aqueous TiO₂ suspension mixed with copper powder. *J. Photochem. Photobiol. A: Chem.*, **1992**, *64*, 255-258.
- Adachi, K.; Ohta, K.; Mizuno, T. Photocatalytic reduction of carbon dioxide to hydrocarbon using copper-loaded titanium dioxide. *Solar Energy*, **1994**, *53*, 187-190.
- Yamashita, H.; Nishiguchi, H.; Kamada, N.; Anpo, M.; Teraoka, Y.; Hatano, H.; Ehara, S.; Kikui, K.; Palmisano, L.; Sclafani, A.; Schiavello, M.; Fox, M.A. Photocatalytic reduction of CO₂ with H₂O on TiO₂ and Cu/TiO₂ catalysts. *Res. Chem. Intern.*, **1994**, *20*, 815-823.
- Tseng, I-H.; Chang, W.-C.; Wu, J.C.S. Photoreduction of CO₂ using sol-gel derived titania and titania-supported copper catalysts. *Appl. Catal. B: Environ.*, **2002**, *37*, 37-48.
- Anpo, M.; Chiba, K. Photocatalytic reduction of CO₂ on anchored titanium oxide catalysts. *J. Mol. Catal.*, **1992**, *74*, 207-212.

- [24] Anpo, M.; Yamashita, H.; Ichihashi, Y.; Fujii, Y.; Honda, H. Photocatalytic reduction of CO₂ with H₂O on titanium oxides anchored within micropores of zeolites: effects of the structure of the active sites and the addition of Pt. *J. Phys. Chem. B*, **1997**, *101*, 2632-2636.
- [25] Anpo, M.; Yamashita, H.; Ikeue, K.; Fujii, Y.; Zhang, S.G.; Ichihashi, Y.; Park, D.R.; Suzuki, Y.; Koyano, K.; Tatsumi, T. Photocatalytic reduction of CO₂ with H₂O on Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts. *Catal. Today*, **1998**, *44*, 327-332.
- [26] Ikeue, K.; Yamashita, H.; Anpo, M. Photocatalytic reduction of CO₂ with H₂O on titanium oxides prepared within the FSM-16 mesoporous zeolite. *Chem. Lett.*, **1999**, 1135-1136.
- [27] Shioya, Y.; Ikeue, K.; Ogawa, M.; Anpo, M. Synthesis of transparent Ti-containing mesoporous silica thin film materials and their unique photocatalytic activity for the reduction of CO₂ with H₂O. *Appl. Catal. A: Gen.*, **2003**, *254*, 251-259.
- [28] Ikeue, K.; Yamashita, H.; Anpo, M.; Takewaki, T. Photocatalytic reduction of CO₂ with H₂O on Ti-β zeolite photocatalysts: effect of the hydrophobic and hydrophilic properties. *J. Phys. Chem. B*, **2001**, *105*, 8350-8355.
- [29] Ikeue, K.; Nozaki, S.; Ogawa, M.; Anpo, M. Characterization of self-standing Ti-containing porous silica thin films and their reactivity for the photocatalytic reduction of CO₂ with H₂O. *Catal. Today*, **2002**, *74*, 241-248.
- [30] Mori, K.; Yamashita, H.; Anpo, M. Photocatalytic reduction of CO₂ with H₂O on various titanium oxide photocatalysts. *RSC Adv.*, **2012**, *2*, 3165-3172.
- [31] Yang, C.-C.; Yu, Y.-H.; van der Linden, B.; Wu, J.C.S.; Mul, G. Artificial photosynthesis over crystalline TiO₂-based catalysts: fact or fiction? *J. Am. Chem. Soc.*, **2010**, *132*, 8398-8406.
- [32] Zhao, D.; Huo, Q.; Feng, J.; Chmelka, B.F.; Stucky, G.D. Nonionic triblock and star diblock copolymer and oligomeric surfactant syntheses of highly ordered, hydrothermally stable, mesoporous silica structures. *J. Am. Chem. Soc.*, **1998**, *120*, 6024-6036.
- [33] Kim, Y.I.; Atherton, S.J.; Brigham, E.S.; Mallouk, T.E. Sensitized layered metal oxide semiconductor particles for photochemical hydrogen evolution from nonsacrificial electron donors. *J. Phys. Chem.*, **1993**, *97*, 11802-11810.
- [34] Bellardita, M.; Augugliaro, V.; Loddo, V.; Megna, B.; Palmisano, G.; Palmisano, L.; Puma, M.A. Selective oxidation of phenol and benzoic acid in water via home-prepared TiO₂ photocatalysts: distribution of hydroxylation products. *Appl. Catal. A: Gen.*, **2012**, *441-442*, 79-89.
- [35] Wu, J.C.S.; Lin, H.-M. Photoreduction of CO₂ to methanol via TiO₂ photocatalyst. *Int. J. Photoenergy*, **2005**, *7*, 115-119.
- [36] Wu, J.C.S.; Lin, H.-M.; Lai, C.-L. Photo reduction of CO₂ to methanol using optical-fiber photoreactor. *Appl. Catal. A: Gen.*, **2005**, *296*, 194-200.
- [37] Liu, D.; Fernández, Y.; Ola, O.; Mackintosh, S.; Maroto-Valer, M.; Parlett, C.M.A.; Lee, A.F.; Wu, J.C.S. On the impact of Cu dispersion on CO₂ photoreduction over Cu/TiO₂. *Catal. Commun.*, **2012**, *25*, 78-82.
- [38] Di Paola, A.; Garcia-López, E.; Marci, G.; Martin, C.; Palmisano, L.; Rives, V.; Venezia, A.M. Surface characterisation of metal ions loaded TiO₂ photocatalysts: structure-activity relationship. *Appl. Catal. B: Environ.*, **2004**, *48*, 223-233.
- [39] Kavan, L.; Grätzel, M.; Gilbert, S. E.; Klemenz, C.; Scheel, H.J. Electrochemical and photoelectrochemical investigation of single-crystal anatase. *J. Am. Chem. Soc.*, **1996**, *118*, 6716-6723.
- [40] Kalyanasundaram, K.; Grätzel, M. Applications of functionalized transition metal complexes in photonic and optoelectronic devices. *Coord. Chem. Rev.*, **1998**, *177*, 347-414.
- [41] Bard, A.J. *Encyclopedia of Electrochemistry of the Elements*, Dekker, New York, **1976**, Vol. 7.
- [42] Subrahmanyam, M.; Kaneco, S.; Alonso-Vante, N. A screening for the photo reduction of carbon dioxide supported on metal oxide catalysts for C1-C3 selectivity. *Appl. Catal., B: Environ.*, **1999**, *23*, 169-174.
- [43] Sasirekha, N.; Basha, S.J.S.; Shanthi, K. Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide. *Appl. Catal., B: Environ.*, **2006**, *62*, 169-180.
- [44] Dimitrijevic, N.M.; Vijayan, B.K.; Poluektov, O.G.; Rajh, T.; Gray, K.A.; He, H.; Zapol, P. Role of water and carbonates in photocatalytic transformation of CO₂ to CH₄ on titania. *J. Am. Chem. Soc.*, **2011**, *133*, 3964-3971.