CO$_2$ Photoreduction to Solar Fuels: Basis Effect on TiO$_2$ Photocatalysts

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Abstract

The use of carbon dioxide, the most concerning environmental issue of XXI century, as a feedstock for fuels productions still represents an innovative yet challenging task for the scientific community. CO$_2$ photoreduction processes have the potential to transform this hazardous pollutant in important products for energy industry (e.g. methane and methanol) employing a photocatalyst and light as only energy input. Despite the great efforts to transform this technology into a real process, it is still far from a real application on a large scale.

Crucial issues to be dealt with are the complex network of physical phenomena and all possible chemical side-reactions: one of the most crucial is water splitting reaction, which, in this case, leads to reducing agent consumption and decrease in process selectivity. The affinity of titanium dioxide, the common photocatalyst toward CO$_2$, represents a physicochemical feature to be tuned to obtain a selective process. To this purpose, in this work carbon dioxide acidity was exploited: it was chosen to add abundant, inexpensive and easy-to-introduce basic oxides in order to favour CO$_2$ adsorption. Calcium oxide and magnesium oxide, in different amounts (0.5, 1.0 and 2.0 wt. %) were introduced in TiO$_2$ photocatalyst aimed at investigating which one provided the best results in CO$_2$ photoreduction tests and at correlating the catalytic results with materials physicochemical and surface properties.

CaO and MgO introduction on TiO$_2$ led to a total selectivity to methane, indicating that only CO$_2$ occurs. This means that water splitting reaction is completely suppressed. Unfortunately, the desired enhancement of selectivity conveyed a decrease in materials activity, especially for the sample featuring magnesium oxide. In particular, it was observed that activity loss was proportional to basic oxide amount. This peculiar behaviour was correlated to the different interaction these materials could have with carbon dioxide. This assertion was possible to a deep physicochemical characterization, which proved that the CaO and MgO introduction modifies CO$_2$ adsorption on the photocatalytic surface leading to different carboxyl species on the surface, which are characterised by a different reducibility, leading to a different effectiveness in carbon dioxide photoreduction.

Introduction

Carbon dioxide increasing concentration in atmosphere represent the most critical environmental issue of the XXI century: scientific community has unequivocally established that emissions from fossil fuels utilisation is the primary cause of this phenomenon, which leads to the increase of average world temperature and global environmental changes [1].

Several strategies have been studied and pursued to overcome this problem, such as: increase of effectiveness in traditional fuels utilisation, development of carbon capture and storage (CCS) technologies, enhanced oil recovery (EOR) processes [2-3]. In all these cases, carbon dioxide is dealt with like an environmentally hazardous pollutant: recently the attention has been focused on using this molecule as a substrate for chemical reactions [4].

Despite CO$_2$ is chemically and thermodynamically stable molecule, its conversion to useful chemicals (e.g. urea, carbonates, polycarbonates and fine chemicals [5]) might have a

benign effect on CO_2 emission, but, unfortunately, CO_2 uptake is too low to satisfy required goals. Thus, environmental changes mitigation by CO_2 conversion requires an efficient and inexpensive technology to convert this molecule in chemical compounds characterised by a worldwide huge market, i.e. fuels [6]. Among all possible products, methane is the most required, since it is considered as a green fuel, due to extremely low C-related emissions compared to coal and oil [7].

Photocatalytic conversion of carbon dioxide into methane or methanol or other hydrocarbons represents an appealing yet challenging process to reach this purposes. CO_2 conversion is driven by a light irradiation, which, in a foreseeable future, might be provided by sustainable and almost infinite solar light [8]. Among the possible reductants, focus was centred on water due to abundance and inexpensiveness. The presence of a photocatalyst is fundamental for light harvesting and electrons transfer from water to carbon dioxide. Among semiconductive photocatalysts, titanium dioxide is the most commonly used since valence band is sufficiently oxidising for H_2O oxidation to oxygen while valence band potential is negative enough for CO_2 reduction to happen [9].

Several reaction pathways using a TiO_2 photocatalyst have been proposed in literature [10-11] but it has not been unanimously accepted. However, in all cases the first step of the reaction is substrate adsorption on the surface. In particular, Ti^{4+} centres act as Lewis acid for oxygen atoms adsorption, while O^{2-} atoms are Lewis bases for electrophilic C from CO_2 and H from H_2O adsorption [12].

Langmuir-Hinshelwood mechanism suitably describes substrates adsorption mechanism: carbon dioxide and water competitively adsorb on adjacent surface sites and then react to form solar fuels. It was calculated that carbon dioxide adsorption on titanium dioxide surface is 400 times weaker than water [13]. This TiO_2 physicochemical property affects process selectivity: preferential water adsorption might lead to hydrogen production from water splitting into molecular hydrogen and oxygen [14]. This side-reaction, for the purposes of the work, is detrimental and undesired because decreases process selectivity and, at the same time, lead to reductant consumption.

Two strategies can be pursued to overcome this drawback. On one side, performing CO_2 photoreduction under high CO_2 excess hinders water adsorption. To do so, this reaction must be performed in gas phase using water vapour instead of liquid water. In this way it is possible to tune CO_2/H_2O ratio boosting carbon dioxide adsorption and hindering water one [15]. On the other side, catalyst modification might be used at the same purpose, exploiting CO_2 acidity. The introduction of inexpensive and stable basic metal oxides, such as calcium and magnesium oxides, increase materials compatibility to carbon dioxide.

Therefore, the goal of the work is the development of a selective process using TiO_2-based catalyst for CO_2 photoreduction. On one side, a bench scale photocatalytic rig is developed for this purpose, using a high CO_2/H_2O ratio. Both activity and selectivity are taken into account for these considerations. Reaction condition are extremely mild (i.e. room temperature, atmospheric pressure and low irradiance) in order to maximise process sustainability and design an effective process at the same time. On the other side, materials modification by calcium and magnesium oxides is investigated. Physicochemical properties effect on photoactivity is evaluated by an in-depth characterisation.

Experimental

Synthesis

Precipitation method was used to synthesise titania samples. In a typical synthesis, a 1.2 M titanyl sulphate ($TiOSO_4 \cdot xH_2O \cdot yH_2SO_4$, Ti assay > 29 % Sigma Aldrich) solution and a 9.0 M NaOH (assay > 97% Carlo Erba) solution was added drop wise and simultaneously to 200 mL of distilled water under vigorous stirring, in order to keep pH neutral. $Ti(OH)_4$ suspension was aged at 60 °C for 20 h. Afterwards, the precipitated was filtered and washed with distilled water to remove sulphate ions. The absence of sulphates has been verified by means of barium chloride test. Wet $Ti(OH)_4$ has been dried overnight at 110 °C. Calcium and magnesium oxides were introduced by incipient wetness impregnation using nitrate salts as

precursors ($Ca(NO_3)_2 \cdot 4H_2O$ Sigma Aldrich, assay > 99 % and $Mg(NO_3)_2 \cdot 6H_2O$ Sigma Aldrich, assay > 98 %). Three different alkaline earth metal amount were chosen, i.e. 0.5, 1.0 and 2.0 metal wt %. Finally samples were calcined at 400 °C for 4 h in air flow to obtain final materials. Samples were labelled as xMT, where x represents metal amount, M the alkali earth metal oxide (either Ca or Mg) and T stand for titanium dioxide. An unpromoted sample was prepared as well as a reference.

Two benchmark materials were used, namely P25 purchased from EVONIK gmbh and MIRKAT 211 from EUROSUPPORT sro.

Characterisations

X-Ray Diffraction (XRD) patterns were collected on a Bruker D8 Advance powder diffractometer with a sealed X-ray tube (copper anode; operating conditions, 40 kV and 40 mA) and a Si(Li) solid state detector (Sol-X) set to discriminate the Cu Kα radiation. Apertures of divergence, receiving and detector slits were 2.0 mm, 2.0 mm, and 0.2 mm, respectively. Data scans were performed in the 2θ range 5°–75° with 0.02° step size and counting times of 3 s/step. Quantitative phase analysis and crystallite size determination was performed using the Rietveld method as implemented in the TOPAS v.4 program (Bruker AXS) using the fundamental parameters approach for line-profile fitting. The determination of the crystallite size was accomplished by the Double-Voigt approach and calculated as volume-weighted mean column heights based on integral breadths of peaks.

N_2 adsorption–desorption isotherms at -196 °C were performed using a MICROMERITICS ASAP 2000 analyser to obtain information on the surface properties. All samples were previously outgassed at 200 °C for 2 h in vacuum. The mesopores volume was measured as the adsorbed amount of N_2 after capillary condensation. The surface area was evaluated using the standard BET equation [15] and the pore size distribution was obtained using the BJH method [16] applied to the isotherm desorption branch.

CO_2 temperature programmed desorption (CO_2-TPD) were performed to evaluate catalyst interaction with carbon dioxide. CO_2-TPD experiments were carried out in a lab-made equipment: samples (50 mg) were pre-treated at 110 °C for 30 minutes to clean materials' surface, then CO_2 was sent to the sample using 0.5 mL loop until surface saturation. Finally, materials were heated at 10 °C/min from 40 °C to 800 °C under helium flow (40 mL/min STP). The effluent gases were analyzed by a Gow-Mac TCD detector using a magnesium perchlorate trap to stop H_2O.

Reactivity Tests

The catalytic apparatus was reported in a previous work [17]. CO_2 photoreduction was performed using a borate glass thin film reactor (length 33 mm, height 18 mm, thickness 2 mm). The catalyst (10 mg) was inserted by depositing the catalyst suspended in 2-propanol on the light-exposed side of the reactor. Dried film was then dried at 110 °C for 1 h in order to eliminate the dispersing agent.

The samples were illuminated using a 125 W mercury UVA lamp (purchased from Helios Italquartz s.r.l. with emission range 315–400 shielded by a special tubular quartz, to select the 366 nm wavelength), with an average irradiance of 50 W·m^{-2}. Afterwards, a gaseous mixture of carbon dioxide and water has flown through the reactor. Compressed CO_2 (99.99%) regulated by a mass flow controller was carried through a water bubbler kept at 40 °C to generate CO_2 and H_2O vapour mixture (13.3 CO_2/H_2O molar ratio). The reactor was closed when the system reached the equilibrium state and this point was taken as the beginning of the reaction. Therefore, the reaction was not performed under a continuous gas flow, but it took place in static conditions. A total of 9.2 μmol of CO_2 and 0.7 μmol of H_2O were present within the sealed reactor. In all catalytic tests, the reaction time was 6 h.

The reaction products were analyzed by a gas chromatograph (HP G1540A) equipped with a Porapak Q column and a TCD detector. Activity results are expressed in turn over frequencies (TONs) in μmol·gcat^{-1}, as commonly used in literature.

Results and discussion

First unpromoted sample morphological properties were investigated to assess its suitability as a catalyst for CO_2 photoreduction. To do so, two benchmark titanium dioxide materials, namely P25 and MIRKAT 211, were used as reference materials.

From XRD analysis, reported in Figure 1a, T sample shows only anatase diffraction peaks (JCPDS card 00-002-0387). Sharpness of peaks indicates that high material's crystallinity, which was confirmed by Rietveld analysis (T is 98 % crystalline). Anatase is the most suitable phase for photocatalytic applications due to slower electron-hole recombination process compared to rutile and brookite [16].

Also in MIRKAT 211, anatase is the observed only crystal phase, but in this case, the width of the peaks indicates that in this material a large fraction of amorphous titanium dioxide. In fact, the manufacturer states that only 40 wt. % of the sample is anatase, while the rest is amorphous. Conversely, in P25, despite its high crystallinity, there is a co-presence of rutile and anatase (20:80 ratio).
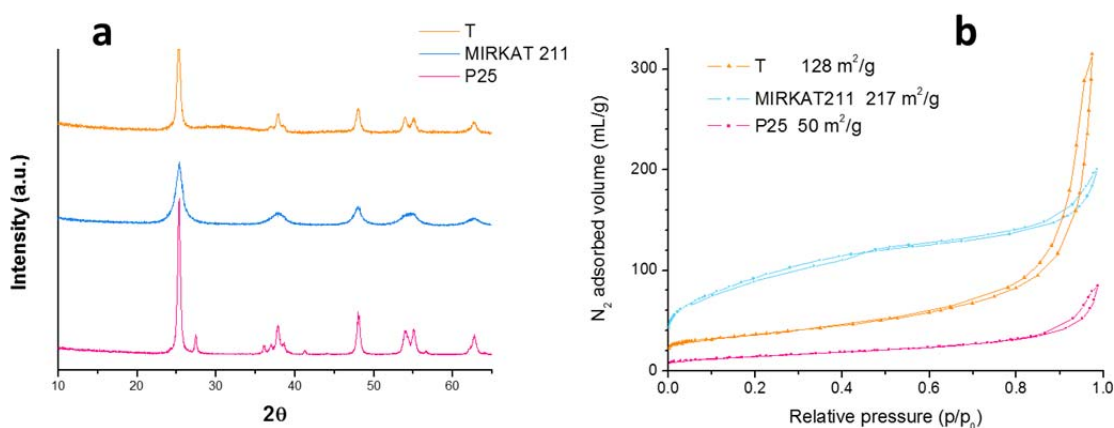

Figure 1 XRD analysis (a) and N_2 physisorption (b) of T sample compared to commercial P25 and MIRKAT 211.

Considering surface properties, all three samples are mesoporous materials, as confirmed by type 4 isotherm pattern in N_2 physisorption isotherms, but the different shapes indicate substantial differences in surface area and pore size distribution. P25 provides the lowest surface area (50 $m^2 \cdot g^{-1}$) and its hysteresis loop at high relative pressure indicates the presence of wide mesopores. Differently, MIRKAT 211 is characterised by a high surface area (217 $m^2 \cdot g^{-1}$) and an extremely wide pore size distribution. T sample provides an in-between surface area (128 $m^2 \cdot g^{-1}$) and a wide pore size distribution, ranging between 4 and 25 nm

Considering both crystallinity and surface area, P25 has high crystallinity (despite the presence of rutile) but low surface area, MIRKAT 211 high surface area but low crystallinity in anatase phase, whereas T represents the best compromise between high anatase crystallinity and relatively high surface area.

These morphological properties are reflected in the results from CO_2 photoreduction tests, reported in Figure 2. The use of a high CO_2/H_2O ratio, an exclusive feature of gas phase systems, allowed to maximise C-based products. In particular, in these extremely mild conditions (room temperature, atmospheric pressure and low irradiance), methane, the least kinetically favoured but thermodynamically stable product, is the only observed product from CO_2 photoreduction. P25 provides a considerably lower methane production compared to the other two samples, indicating the surface area, and the number of available photocatalytic sites as a consequence, have a great influence on the process. Comparing the two samples

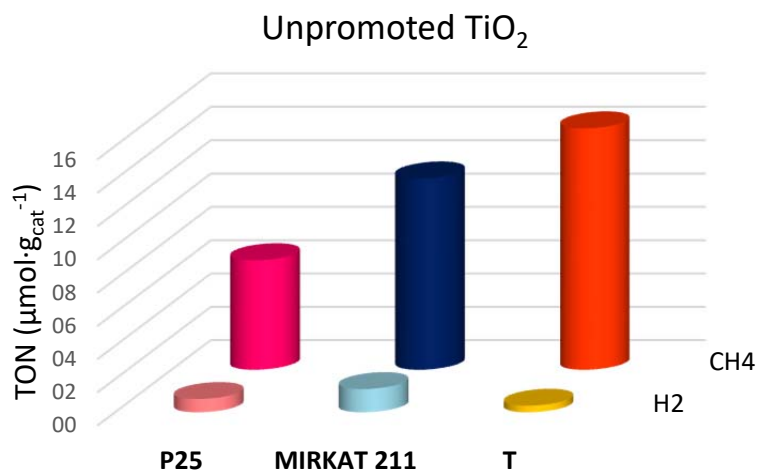with high surface area, T, the most crystalline in anatase phase, provides the highest methane production.

Figure 2 T sample photocatalytic activity compared to commercial P25 and MIRKAT 211.

Unfortunately, tuning reagents ratio was not sufficient to avoid water splitting: in fact all samples show hydrogen production. In this case, the lowest activity toward water splitting is provided by T sample. The co-presence of methane and hydrogen and their separation, considering the application of this technology on large scale, might be an unneglectable additional cost. To overcome this drawback and increase selectivity to CO_2 photoreduction even more, either CaO or MgO were introduced on T sample, aiming at a more efficient CO_2 adsorption on material's surface.
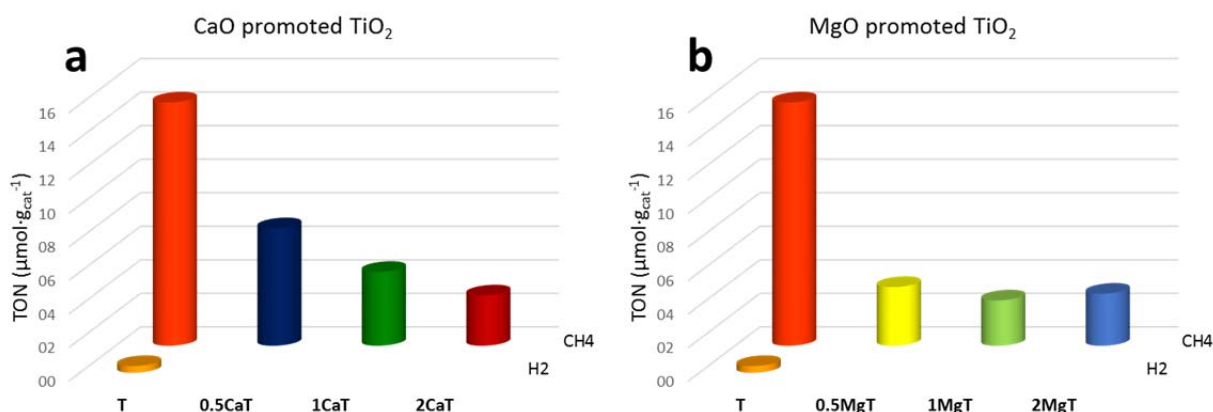Photocatalytic results are reported in Figure 3.

Figure 3 Photocatalytic tests results using CaO promoted sample (a) and MgO promoted ones (b).

All promoted samples provided a total selectivity to methane and no trace of hydrogen formation was observed regardless the dopant and its loading amount. Unfortunately, photoactivity was decreased by the introduction of either CaO or MgO. This effect is more noticeable for MgO promotion compared to CaO. In this latter case, there is a correlation

between CaO loading and photoactivity loss is observable. To understand these unexpected results, CO_2-TPD analysis, reported in figure 4, allowed to understand the interactions between carbon dioxide and the different photocatalytic surfaces.
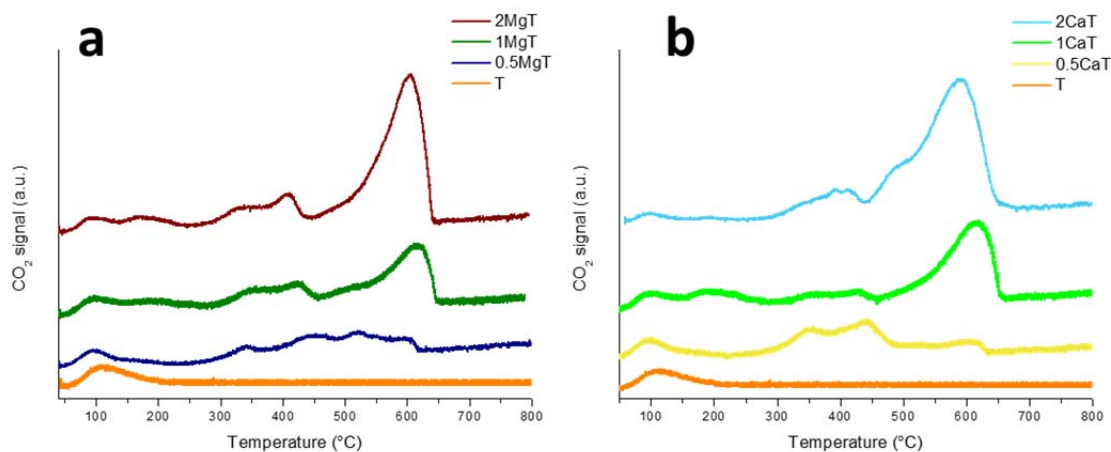

Figure 4 CaO promoted sample (a) and MgO promoted ones (b) CO_2-TPD patterns.

T's CO_2-TPD pattern shows only a small peak between 80 °C and 120 °C ascribable to CO_2 weakly adsorbed on the surface, and this signal is observable also for all promoted samples. Whereas, all promoted samples show also multiple peaks from 150°C to 650 °C in which, in the case of samples with the 1 and 2 wt.%, there is a clear CO_2 desorption peak from 450 °C and 650 °C. All these peaks are ascribable to the formation of different carbonate species whose adsorption is stronger than carbon dioxide [19]. In particular, it can be observed that, increasing basic dopant loading, there is an increase of strongly adsorbed and thus stable carbonates. Carbonate species are characterised by more negative reduction potentials than carbon dioxide and they are similar in value to titanium dioxide conduction band potentials. This means that their reduction on TiO_2 is thermodynamically less favoured, explaining photoactivity loss in promoted samples [20]. CO_2-TPD analyses are thus able to give an explanation for CaO promoted samples, where activity loss is evident in the samples containing the highest CaO amount, which provided the highest CO_2 adsorption. However, this cannot be considered satisfactory for MgO promoted samples: in fact, in this case, it does not seem to be a correlation between MgO adsorptive properties and activity loss.

However, according to DFT adsorption studies by Kwon and co-workers [21], due to lower ionic radius, electron transfer from MgO to adsorbed CO_2 (to form stable carbonates) is more efficient compared to CaO. This means that, even if CaO and MgO adsorb the same amount of CO_2 in TPD experiments the chemical nature of this bond is different. In fact, even a small amount of MgO is enough to almost completely suppress photoactivity, while milder CaO-CO_2 interaction leads to a gradual decrease in efficiency in CO_2 reduction.

Conclusion

CO_2 photoreduction is potentially able to use water as a reductant and light as a primary source of energy to obtain solar fuels even in mild conditions in terms of temperature, pressure and irradiance. Not only process efficiency, but also selectivity are strictly connected to photocatalyst interaction with substrates. In particular, the most delicate phenomenon to control is carbon dioxide adsorption on photocatalyst in order to avoid water splitting side reaction, especially in presence of TiO_2 based materials.

Performing reaction in gas phase conditions allows to increase selectivity using a high CO_2/H_2O ratio, but it is not sufficient to obtain a total selectivity to solar fuels. TiO_2 basis modification proved to be effective in yielding a total selectivity to methane, which

suppresses reductant consumption by water splitting and, in a possible application, might avoid separation processes.

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