

CO₂ Photoreduction to Solar Fuels: Basis effect on TiO₂ Photocatalysts

A. Olivo, M. Signoretto, E. Ghedini

Dept. of Molecular Sciences and Nanosystems, Ca' Foscari University Venice and
Consortium INSTM, Venezia, Italy

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. CO₂ 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 CO₂, 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 CO₂ adsorption. Calcium oxide and magnesium oxide, in different amounts (0.5, 1.0 and 2.0 wt. %) were introduced in TiO₂ photocatalyst aimed at investigating which one provided the best results in CO₂ photoreduction tests and at correlating the catalytic results with materials physicochemical and surface properties.

CaO and MgO introduction on TiO₂ led to a total selectivity to methane, indicating that only CO₂ 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 CO₂ 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.