

## TiO<sub>2</sub>/SiO<sub>2</sub> nano-catalysts for the photocatalytic abatement of inorganic pollutants

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### Introduction

Titanium dioxide is well known as a large band gap semiconductor that in recent years has attracted great attention mainly in expectation of being applied to environmental photocatalytic processes such as deodorization, prevention of stains, sterilization and removal of pollutants from air and water. Compared with traditional advanced oxidation processes the technology of photocatalysis is known to have some advantages, such as ease of setup and operation at room temperatures, no need for post-processes, low consumption of energy and consequently low costs, high degradation efficiency in removing organic pollutants even at ultra low concentrations. For the realization of these practical applications, development of highly active photocatalysts is keenly desired. TiO<sub>2</sub> nanoparticles in the anatase crystal form having both high crystallinity and large surface area [1] must exhibit higher photocatalytic activity. The control of the final features of the TiO<sub>2</sub> photocatalysts can be achieved by several approaches: sol-gel synthesis [2], employing surfactants [3] and introducing titanium oxides into high surface area support materials [4]. Particularly attractive at this end are ordered mesoporous silica materials as: MCM-41, SBA-15, MCM-48.

The twofold goal of this work is the synthesis of titania/silica systems characterized by high surface area and ordered pore structure for photocatalytic applications. Particular attention has to be paid to the influence of the TiO<sub>2</sub> amount on the chemical-physical properties of the final systems. In fact, different Ti loadings in the catalysts may induce changes not only in the textural characteristics but also in the surface chemical properties of the TiO<sub>2</sub>/SiO<sub>2</sub> composites. As a second goal, the catalytic behaviour of the investigated systems will be tested towards the photocatalytic abatement of NO<sub>x</sub> in gas phase.

### Experimental

The MCM-41 support was prepared as reported in a previous work [5]. The silica support was activated with TiO<sub>2</sub> by incipient wetness impregnation by using an alcoholic solution of Ti(iOPr)<sub>4</sub>. Five samples with increasing Ti/Si ratio (9 wt%, 17 wt%, 23 wt%, 28 wt%, 33 wt%) have been prepared. The calcined samples are labelled 'TM<sub>x</sub>' where 'T' stands for TiO<sub>2</sub>, 'M' for MCM-41 and x for the TiO<sub>2</sub> effective content of catalyst.

The samples have been characterized by: ICP, XPS, XRD, N<sub>2</sub> physisorption and the photocatalytic activity of

samples has been evaluated in the NO oxidation reaction [for the experimental setup see ref. 5]

### Results and Discussion

In order to evaluate the textural properties of the synthesized systems in terms of surface area, porosity and crystalline structure, physisorption, XRD and TEM analyses were carried out. As expected the TiO<sub>2</sub> introduction on the silica supports determines a contraction of the surface area and pore volume values that increases proportionally with the TiO<sub>2</sub> loading. The pore size distribution is bimodal for all the modified systems characterized by a second peak corresponding to a pore diameter centred at about 4 nm. This last feature can be plausibly related to a partial collapse of the porous structure after the introduction of the active phase, in particular as consequence of the second calcination treatment. On the other hand, the existence in all the catalysts of a substantial fraction of pores at about 2.5 nm, thus smaller than those in the silica support (2.8 nm) suggests, together with the decrease of total pore volume, the presence of a fraction of TiO<sub>2</sub> within the channels of MCM-41. Despite the variations of both surface area and pore size, the shape of the isotherm is retained after the introduction of TiO<sub>2</sub> nanoparticles, indicating that the mesoporous morphology of the support has been preserved. The structural informations (from XRD and TEM analyses), instead, can be summarized in the following points:

- (i) the introduction of TiO<sub>2</sub> on the silica support affected partially the structural integrity of the MCM-41 but the mesoporous order is retained to a certain degree in all the catalysts;
- (ii) only nanocrystalline TiO<sub>2</sub> in the anatase phase was detected in all the systems;
- (iii) the X-ray amorphous phase detected in all the composites decreases with the increasing crystalline anatase content.

The catalytic results obtained for all the samples are represented in Fig. 1. As expected, the pure silica MCM-41 support was catalytically inactive in the reaction while all the TiO<sub>2</sub>/MCM-41 catalysts were active in our experimental work conditions, and showed good conversion values.

Surprisingly, the conversion values were found to be not proportionally related with the amount of the active phase: the best performance was reached by the TM16 catalysts containing a 16 wt% TiO<sub>2</sub> content. The increase of TiO<sub>2</sub> loading over the former value did not improve the catalytic activity; on the contrary a progressive

decrease of the conversion rates was observed as the TiO<sub>2</sub> concentration increased from 16 to 32 wt%.

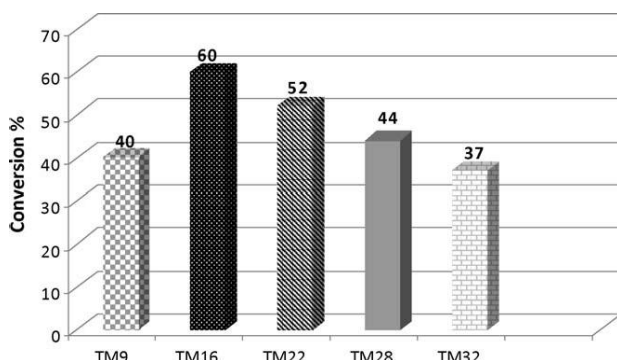


Fig. 1: Catalytic results for the NO oxidation reaction.

TM16 and TM22 samples are characterized by the best compromise between surface area, ordered structure and crystalline anatase content that justify partly their high catalytic activity; however, this is not sufficient to interpret the catalytic trend in particular the progressive decrease of the conversion rates observed as the TiO<sub>2</sub> concentration increased from 22 to 32 wt%.

In order to gain more information about the surface chemical properties of the systems and to investigate thoroughly their catalytic behaviour XPS was resorted on. XPS results are in good agreement with the catalytic performance of the samples being TM16 the most efficient photocatalyst followed by TM22. It is well known that the pure anatase form (TM22, one XPS species at 458.8 eV) is the most active in a photocatalytic reaction, but the presence of a small amount of substoichiometric TiO<sub>2</sub> (TM16) could slow down the electron-hole recombination, close of the photocatalytic processes, and improve the sample efficiency. In all other cases, the presence of a larger and larger content of the Ti<sup>(4+delta)+</sup> species brings about a progressive efficiency loss of the photocatalyst.

## Conclusions

In this work we optimized a reliable procedure for the synthesis of nanoporous silica/titania systems. The NO oxidation, employed as test reaction, was strongly influenced by the degree of TiO<sub>2</sub> loading and good performances could be achieved by an optimal compromise between surface area, crystalline form and the chemical environment around the active site. The obtained results showed that the application of these catalysts is well suitable in gas photocatalytic reactions (inorganic pollutants degradation).

## References

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## Biosketch

Valentina Trevisan graduated on Industrial Chemistry in 2003 and actually she is a PhD student on Chemistry at Cà Foscari University. She has collaborated for five years with Catalysis Group of the same University pointing her interesting on Heterogenous Catalysts for Industrial applications. Her scientific interests are in the field of Catalysis with a focus on the synthesis of new nanostructured photocatalysts and their use in environmental chemistry.

Michela Signoretto is currently assistant professor at the Chemistry Department of the University Cà Foscari of Venice. She has authored over 60 scientific publications on international journals in the field of heterogenous catalysis. Special areas of focus in Signoretto's work include nanomaterials for catalytic and pharmaceutical applications.

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