Doctoral Dissertation Abstract
Doctoral Program in Material Engineering (32th Cycle)

Transition metals doped TiO_2 nanoparticles obtained by sol-gel templated assisted synthesis. Physico-chemical properties and catalytic applications

By

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Dissertation abstract

The discover made by Fujishima and Honda in 1972 on the photocatalytic water spitting catalysed by TiO_2 photosensitization effect [1] started a new increasing interest in the research of this material that was anyway long studied before (first report on TiO_2 photocatalysis was done by Renz et al. on 1921 [2]), which led to development of many new applications, especially in catalysis and photocatalysis, environmental field (anti-bacteria, deodorization, water treatment, dirtiness prevention by wettability control..), as well as in the energy harvesting and storage (e.g Grätzel cells and Lithium Ion Batteries) [3].
In the last decades many aspects of TiO_2 have been explored and countless efforts have been dedicated to characterize the properties of titanium dioxide, but due to the multitude of variables, much can still be explored and understood in order to have a better knowledge of the material properties and subsequently engineer the final product. For instance, final product properties strongly depends from synthetic conditions, methods and process parameters, used precursor materials, dopants, morphology and surface texture. Moreover, TiO_2 may occur as different polymorphs (mainly as anatase, rutile and brookite) as well as amorphous TiO_2, with up to 12 reported bulk and/or nanocrystalline phases, which compositions depends on these factors too as by adjusting the synthetic conditions and post treatments, the final combination of different amounts of each phase can be tuned.
Alongside the chemical and crystal properties, morphology and surface texture play an important role in the final material properties. Nanoparticles morphology, as an example, can enhance the adsorption coefficients of organic molecules adsorbed on their surfaces, the rate of adsorption of molecules and the rate of electron transfer at the particle surface. All important factors for catalytic processes. Therefore, tailoring particles shape, size and surface morphology is necessary for a variety of applications.
As can be easily understood, these mentioned "*variables*" are just for the starting material (TiO_2), but the problem (the final material properties-parameters relationship) become more and more complex as external variables are added. For example, in photocatalytic applications one of the key parameters of a catalyst is the band gap, which is easily tuneable by the presence of a doping element, which in turn may strongly modify all the other physio-chemical and textural properties, so increasing the complexity of the material characterization.

In this thesis, the TiO_2 system will be briefly introduced, with major stress on the last trends and applications of nanostructured titania systems. Whereas in the following chapters, the synthetic methodology adopted to produce metal oxides will be explored and lastly will be reported the characterization of the TiO_2 system that has been performed during this PhD work, having special consideration for high surface area nanoparticles synthetized by templated assisted sol-gel (TASG) synthesis, which is extremely flexible in terms of composition, precursors and

doping materials that can be used. Likewise, in terms of real cases usage, the synthetized materials have been tested for modern-day important applications by exploiting the tailored material properties.
High surface area NPs, possibly characterized by hierarchical inter-and/or intra-particle porosity, where obtained by using soft templates in order to improve the material catalytic activity and to facilitate the diffusion of reagents/products, as well as modify the surface physio-chemical characteristics of acidity, charge and phase composition. Moreover, the contribution of doping with heteroatoms, has been explored, and modification of physio-chemical properties as well as the changes in optical responses and the textural modifications due respect the bare titania has been studied.

In order to investigate and have an idea of the catalytic real cases performances, photocatalytic tests of Mo-doped TiO_2 samples have been carried out for photodegradation of Rhodamine B dye, a model molecule used as water "*pollutant*". Nonetheless manganese oxides, interesting due to various types of labile oxygen and oxidation states (Mn^{2+}, Mn^{3+} and Mn^{4+}), has been used at low doping concentration supported on the strong acidic surface of TiO_2 and tested as catalytic promoter for the low-temperature NOx removal by using the Selective Catalitic Reduction (SCR) with ammonia, exploiting the surface acidity/basicity characteristics as well as peculiar composition of the produced catalyst by the TASG method.