Preparation of nanostructured TiO_2 photocatalysts based on the well-ordered hexagonal SBA-15 structure

R. Passalacqua[1], S. Perathoner[1], P. Lanzafame[1], G. Centi[1], G. Martra[2], and D. Su[3]

[1] *Dept. of Ind. Chemistry and Eng of Materials, Univ. of Messina, UdR INSTM and ELCASS*[1]
[2] *Dept. of Chemistry IFN, University of Torino, Via P. Giuria, 7, 10125, Torino - Italy*
[3] *Dept. Inorg. Chem., Fritz Haber Inst -Max Planck Soc., Faradayweg 4-6,D-14195 Berlin, Germany*

Abstract

The use of mesoporous hexagonal SBA-15 as structural matrix/template to prepare V_2O_5 nanowires and embed them in a ordered array into titania as well as to produce size confinement in titania particles is discussed, with the objective to produce novel nanostructured photocatalysts based on titania containing solid state sensitizers for enhancing visible light response.

Introduction and Objectives

Titania (TiO_2) is a widely used photocatalyst, with several applications ranging from water purification to health protection (indoor and outdoor air purification), H_2 production (by water photo-dissociation) and preparation of advanced materials (self-cleaning glasses and tissues, etc.). With respect to other semiconductors, the main advantage of titania is related to its low toxicity and good robustness, but the main drawback is the low activity with visible light. In fact, the band gap edge lies in the near UV region (close to 300 nm) and therefore only about 4% of the incoming solar energy can be used. Therefore, there is large current interest in the modification of titania to make it active with visible light.

There are several attempts in literature to reach this goal, either by using organic sensitizers (which suffer of low stability, however) or inorganic sensitizers. Large interest have received recently the possibility of improving visible light response with doping with transition metals such as Cr, V, but quite expensive methods (ion implantation and more recently magnetosputtering) are required (doping by conventional methods such as sol-gel is ineffective) and these materials find application only in some cases (for example, they are not effective in forming H_2 by water photo-oxidation). Large interest has been also stimulated by the possibility of modification of titania band-gap by doping with N, but there are again problems of effectiveness of these materials. Therefore, there is still need to

[1] Salita Sperone 31, 98166 Messina. Fax: 090-391518, ✉:*perathon@unime.it.* INSTM: Consorzio InterUniv. per la Scienza e Tecn. dei Materiali. ELCASS: Europ. Lab. of Catalysis and Surface Science.

search for alternative approaches in developing titania modified by solid-state sensitizers.

Finally, a further problem in using titania photocatalysts relies in its still too low activity which makes it applicable usually to the removal of pollutants in quite low concentrations. Increasing the surface area, it is possible in theory to increase the activity, but (i) smaller titania particles shift the band edge toward UV region (therefore, further depressing quantum efficiency) and (ii) surface defects are introduced which improve the rate of holes/electron recombination (thus depressing again photo-activity). For this reason, still P25 Degussa (a relatively low surface area titania) is one of the most effective photocatalysts, but there is large research activity in nanostructuring titania with inorganic fibers, zeolites and mesoporous materials.

We were interested in particular, to the possibility of nanostructuring titania using the well-ordered hexagonal SBA-15 structure. The idea was the possibility to use this mesoporous silica as matrix/template to prepare TiO_2 road-type nanoparticles. In fact, silica is transparent to solar light and road-type titania nanoparticles should have an anisotropic electron transfer favouring charge separation, but at the same time maintaining a high aspect ratio (ratio between surface/volume). A columnar-type titania thin film, in fact, shows an enhanced photoresponse. In addition, the stabilization of the titania particles by the silica matrix having relatively low channel diameter (around 5 nm) allows the annealing at relatively high temperature necessary to reduce surface defects.

The further idea was to use the SBA-15 as matrix to produce V_2O_5 nanowires which due again to their anisotropic characteristics and oxide-oxide heterojunctions could act as efficient solid state sensitizers of the titania. The silica matrix should prevent their sintering during annealing (typically, when TiO_2 particles doped with vanadium and produced by sol-gel are annealed, the formation of small V_2O_5 islands is observed, which introduce further energy states in the band gap reducing the photo-charge separation). Therefore, TiO_2/SBA-15 and TiO_2-$(V_2O_5)_{nw}$/SBA-15 (where *nw* indicates nanowires) are potentially quite interesting new photocatalytic materials, but very few indications are present in the literature on the synthesis and characteristics of these materials.

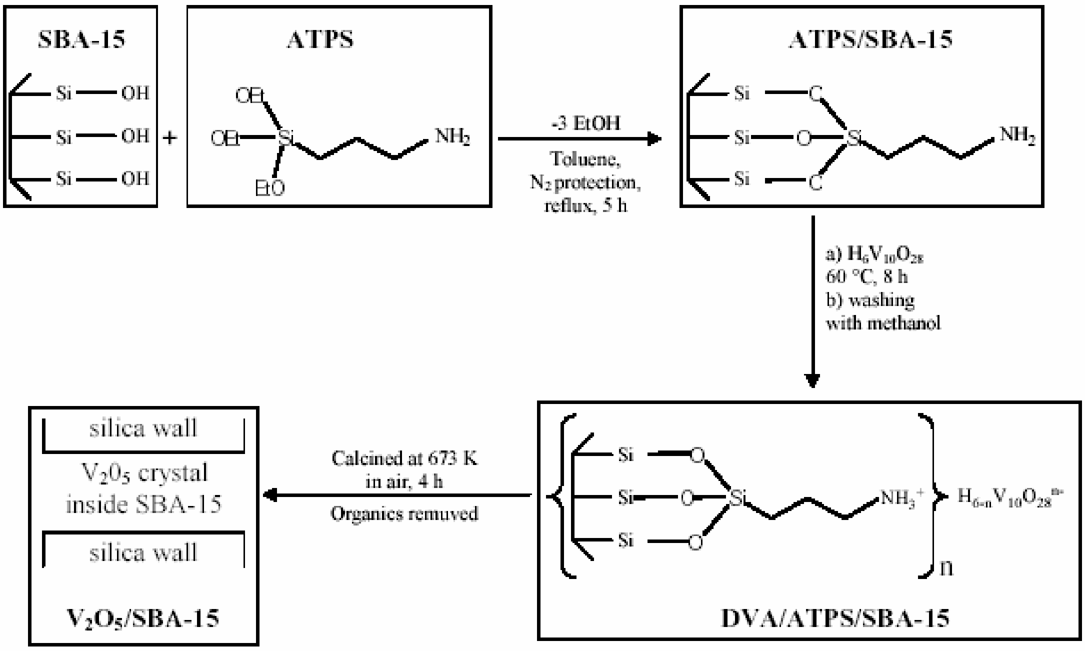
Preparation of catalysts

Two approaches are used for the introduction of vanadium on titania, both inside the hexagonal channels of the SBA-15 structure. The experimental procedure followed several steps:

Route A: for TiO_2/V_2O_5/SBA-15 catalyst

1. synthesis of SBA-15 according to literature procedure with minor modification;[1]
2. functionalization of SBA-15 channel surface by aminosilylation (see scheme 1);
3. immobilization of decavanadic acid inside ATPS/SBA-15;
4. formation of V_2O_5 nanowires inside SBA-15 channel
5. grafting of TiO_2 inside V_2O_5/SBA-15

Route B: to obtain the V_2O_5/TiO_2/SBA-15 catalyst. It involves a first step in which the TiO_2 was grafted on the SBA-15 support, the material was after modified according to steps 2, 3 and 4.



Scheme 1. Steps 2, 3 and 4 of the synthesis procedure.

Characterization of catalysts

XRD powder diffraction patterns of SBA-15, APTS/SBA-15 and V_2O_5/SBA-15 were performed in the ranges $10° < 2\theta < 70°$ and $0.5° < 2\theta < 10°$. At low angle all samples showed three peaks which are characteristic of the reflections of hexagonal mesoporous SBA-15, and indicate that the samples consist of well-ordered channels which are maintained during all the reaction procedures. The formation of V_2O_5 inside SBA-15 leads to a decrease in the intensity off all reflections.

The N_2 adsorption-desorption isotherm of SBA-15 is of IV Type, which exhibits typical hysteresis loop of mesoporous materials. The modified samples show the same shape of isotherm but the amount of nitrogen decreases and the onset of the capillary condensation step shift to relative lower pressures. The decrease of the amount of nitrogen in the modified samples can be attributed to the reduced pore volume.

UV-Vis diffuse reflectance spectra in the wavelength range 200-800 nm of the two samples which differ for the order of vanadium introduction, TiO_2/V_2O_5/SBA-15 (*Route A*) and V_2O_5/TiO_2/SBA-15 (*Route B*), are compared in Figure 1 with the spectra of V_2O_5, TiO_2 prepared by sol-gel, and the reference TiO_2 P25 from Degussa. SBA-15 do not show absorption bands in this spectral region. It is evident that the introduction of vanadium (about 10 % w/w) cause a red shift of the TiO_2 absorption edge, but that the method of preparation influences also the characteristics of absorption edge.

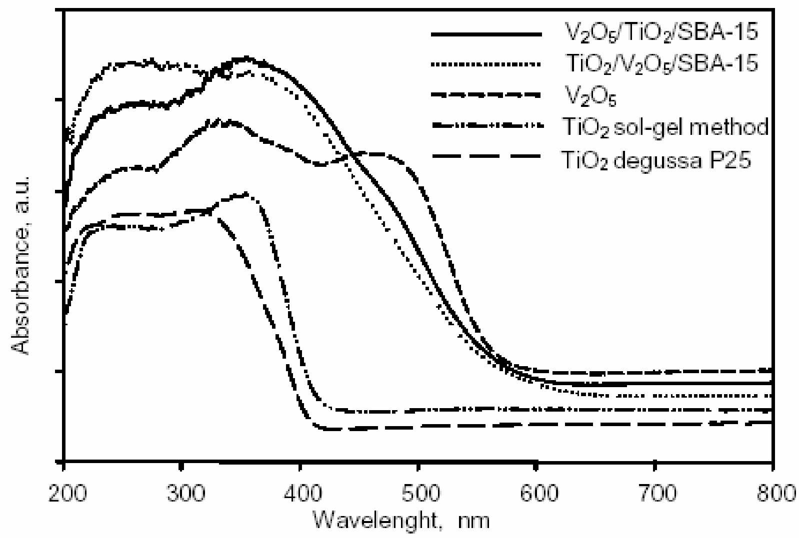


Figure 1. Absorption spectra of the prepared catalysts and reference species.

SEM and TEM studies confirm the presence of the V_2O_5 nanowires and give further indications about the microstructure of these materials and the matrix/template effect of SBA-15 to produce new oxide-type nanostructured materials. Experiments about photo-activity of these materials are also in progress.

Acknowledgements

Financial support of MIUR (PRIN 2003, Materiali multifunzionali nanostrutturati con attività fotocatalitica) is gratefully acknowledged. The authors thank also Mr. Daniele Cosio for technical support. This activity is realized in the frame of EU CONCORDE Coordination Action and EU IDECAT Network of Excellence.

References

1 D. Zhao, J. Sun, Q. Li, G.D. Stucky, Chem. Mat., 12 (2000) 275.