

THE ROLE OF THE MESOPOROUS SILICA STRUCTURE ON THE NANODESIGN OF TITANIA/SILICA PHOTOCATALYSTS

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The world now faces tremendous challenge in various environmental problems. As a result, extensive research is done on advanced methods for elimination of hazardous chemical compounds from air and water. Photocatalytic oxidation of organic compounds in water and air has received much attention as a potential technology for pollution abatement. Titania has proved to be the most active photocatalytic semiconductor because it allows complete degradation of pollutants under ultraviolet irradiation [1-3]. To improve TiO₂ photoactivity, particles should be small enough to offer a high number of active centres by unit mass. Unfortunately, a small particle size leads to high filtration costs to remove the catalyst, hindering its industrial application. For this reason, a major focus of current photocatalysis research is the achievement of titania-based materials with suitable properties to present simultaneously high photoactivity and effective separation properties. Titania nanoparticles supported on silica might be materials capable of accomplishing both requests since they do not only take the advantage of high surface areas but of improved recovery properties as compared to pure titania, which may facilitate the separation.

In this work, we report the synthesis and photocatalytic behaviour of TiO₂/SiO₂ materials prepared by acid catalysed sol-gel method. As silica support, we have used hexagonally packed MCM-41 and SBA-15 mesostructures. Titania sol was obtained by controlled hydrolysis of titanium isopropoxide in nitric acid. The main objective of this work was to study the effect of the support's structure on the growth and properties of titania nanoparticles. The obtained materials were characterized by X-ray diffraction (XRD), N₂-sorption measurements, chemical analysis, Raman, UV-Vis diffuse reflectance spectroscopy. Based on the combined data from the structural characterization and chemical analysis, a mechanism for the growth of TiO₂ nanocrystals within the channels of MCM-41 and SBA-15 is proposed. In figure 1, the growth and localisation of the titania nanoparticles governed by mesoporous structure of the silica supports is presented schematically.

Throughout this study it is shown that the mesoporous structure of the support influences significantly the growth of titania nanoparticles. Moreover, deposition of different amounts TiO₂ leads to important modifications of the silica support structural characteristics and properties. This has a great impact on the overall adsorption capacity and photocatalytic activity of the TiO₂/SiO₂ catalyst towards the removal of organic dyes in aqueous solutions. The photodecomposition of rhodamine 6G (R6G) in aqueous medium was selected as probe reaction to test the photoactivity of the prepared materials and to verify the potential use of these materials for wastewater treatment. In table 1 are summarized the properties and photocatalytic performances of titania/silica prepared catalysts in R6G photo-oxidation process. For a better understanding of the tremendous role that the silica mesostructure plays on the nanostructuring and photocatalytic behaviour of titania, in table 1 are presented the catalytic performances of the pure TiO₂ prepared by ACSG-method. Prior to irradiation, the suspension was magnetically stirred for 30 minutes in order to establish the adsorption – desorption equilibrium between the catalyst surface and the dye. During this time, the dye could not be decomposed, because anatase needs UV-light for its catalytic activity. Because of the absence of UV-light, the decrease of the R6G concentration is due to the

adsorption of the dye on the surface of the catalyst (*adsorbed dye*). At time 0, the solution was irradiated with UV-light and during 1h the photocatalytic decomposition of R6G was followed (*degraded dye*). As it can be seen from table 1, all supported catalysts show lower catalytic activities than P25 in this reaction. However, important differences are obtained, depending on the titania loading, titania nanoparticles size and on the location of these nanoparticles within the mesopores of the support. The catalysts prepared using MCM-41 as support show higher adsorption capacity towards bulky molecules of R6G, due to the fact that the mesopores are not blocked by titania nanoparticles. In contrast, the channels of SBA-15 are choked by titania nanoparticles, limiting the access of R6G molecules inside the pores. Moreover, these catalyst show lower photocatalytic activity, in comparison with the TiO₂/MCM-41 materials. Since the titania nanoparticles are too big to enter inside the pores of MCM-41, they locate on the outer surface of the silica support. Thus a better accessibility of R6G molecules to the active sites is provided, resulting in a significantly increased photocatalytic activity.

References:

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Figures:

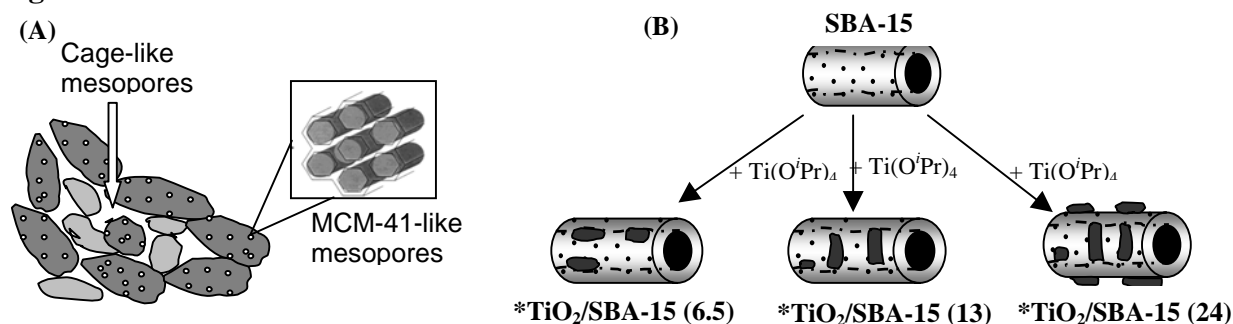


Figure 1. Nanostructuring of titania particles using (A) MCM-41 and (B) SBA-15 mesoporous silica as supports; * the numbers between brackets represent the initial titania concentration (in mmols Ti⁴⁺) used for deposition.

Tables 1: Properties and photocatalytic performances of TiO₂/SiO₂ prepared catalysts

Catalyst	Final loading (mmols Ti ⁴⁺)	TiO ₂ particles size (nm)	Adsorbed dye (%)	Degradated dye (%)	Removed dye (%)
TiO ₂ /MCM-41 (1.95)	1.69	2.46	98	41	999
TiO ₂ /MCM-41 (6.5)	0.39	3.87	89	73	97
TiO ₂ /MCM-41 (13)	0.32	4.61	61	52	81
TiO ₂ /MCM-41 (19.5)	0.43	4.85	64	32	75
TiO ₂ /MCM-41 (24)	0.44	4.61	70	56	87
TiO ₂ /SBA-15 (1.95)	-	0.74	88	14	90
TiO ₂ /SBA-15 (6.5)	-	3.86	43	28	59
TiO ₂ /SBA-15 (13)	-	4.48	30	15	41
TiO ₂ /SBA-15 (19.5)	-	4.83	40	34	60
TiO ₂ /SBA-15 (24)	-	5.03	32	21	46
TiO ₂ (24)	-	15.26	13	14	25
P25	-	-	16	88	90