

# Synthesis and Characterization of Titanium Dioxide Supported on Hexagonal Mesoporous Silica and its Application as Photocatalyst for the Wastewater Treatment

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**Abstract:** Template synthesis of the porous materials is one of the most intensive research fields in the preparation of materials and catalysts. Many kinds of mesoporous materials such as hexagonal mesoporous silica (HMS), SBA-n and FSM-16 were synthesized by using various types of organic templating agents since M41S materials were successfully synthesized. These materials present a regular array of uniform one- or three-dimensional pores with diameters of 1.5–10 nm and high surface areas. Therefore, the mesoporous materials are suitable for use as a catalyst or support for the chemical reactions with larger molecules. Among these materials, the mesoporous molecular sieve with a wormhole framework structure denoted as HMS has many advantages. HMS is easily synthesized by the sol–gel reaction using a cheaper primary alkylamine as the structure direction agent at room temperature. Such HMS possesses thicker framework walls, small crystallite size of primary particles and complementary textural porosity to provide better transport channels for reactants and products. The transition metal cations can be incorporated into the HMS framework uniformly with high contents and the organic phase can be totally removed from the as-synthesized HMS samples by simple calcination. In the present work, we report the synthesis and characterization of such materials impregnated titanium dioxide (TiO<sub>2</sub>) supported on Hexagonal Mesoporous (HMS).

**Keywords:** Water treatment, hexagonal mesoporous silica, TiO<sub>2</sub>/HMS.

## 1. Introduction

Many pollutants in aqueous solution are decomposed in the presence of TiO<sub>2</sub> power illuminated with near-UV light and this process as a means of purifying water was paid much attention. Although phenols are often formed as intermediate compounds in the process, these and other organic compounds including chlorinated organic compounds have been shown to be completely mineralized to CO<sub>2</sub> and H<sub>2</sub>O. Solar illumination may also be used to drive the reaction. Recent studies show that the photocatalytic degradation of pollutants in aqueous solution is attracting considerable attention for application to environmental problems [1-2]. In order to apply this technology to the actual

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wastewater treatment, it is still necessary to develop the catalysts exhibiting higher photocatalytic activities. Because mesoporous molecular sieves have large and uniform pore size. They allow sterily hindered molecules facile diffusion to internal active sites and the nanopore properties are similar to nanoparticle properties, which have arisen attention in the area of catalysis. Recently, since the discovery of the new family of mesoporous silica molecular sieves with pore diameters in the 2.0-10 nm range, designated as M41S, is of considerable interest for heterogeneous catalysis and material science [3]. This family of materials is characterized by a regular array of pores with uniform diameter, high specific surface areas and pore volumes, which are advantageous for the adsorption and catalysis. Depending on the synthesis conditions, different phases could be obtained, like the hexagonal phase MCM-41, the cubic one MCM-48 as well as the lamellar compound MCM-50. Huo et al [4]. proposed four complementary synthesis pathways. The first pathway implicated the direct co condensation of cationic surfactant ( $S^+$ ) with anionic inorganic species ( $I^-$ ) to create assembled ion pairs ( $S^+I^-$ ). In the second pathway, an anionic template ( $S^-$ ) was used to direct the self-assembly of cationic species ( $I^+$ ) through ( $S^-I^+$ ) ion pairs. Pathways 3 and 4 involved counter ion-mediated assemblies of surfactants and inorganic species of similar charge. These counter ion-mediated pathways created assembled solution species of type  $S^+XI^-$  or  $SM^+I^-$ . Furthermore, another pathway was proposed by Tanev et al. [5] to prepare mesoporous silicas at room temperature by neutral templating route. In this case, the organic surfactant is not quaternary ammonium cation but a primary amine, and the assembly involves hydrogen-bonding interactions between neutral primary amines and neutral inorganic precursors. These materials denoted HMS, reveal excellent catalytic capacity for macro molecular reactions and suggest new opportunities for transition metal incorporation into silica frameworks. In the present work, we report the synthesis and characterization of such materials impregnated ( $TiO_2$ ) supported on hexagonal mesoporous silica (HMS), and their test as a photocatalyst for the wastewater treatment.

## 2. Catalysts Preparation

The HMS material was prepared following the pathway reported by Tanev and al. [5]. In a representative preparation, hexadecylamine (HDA) (0.3 mol) was added to a solution containing water (36 mol) and ethanol (EtOH) (7 mol) and the mixture was stirred until homogeneous. Then 1 mol of tetraethyl orthosilicate (TEOS) was added under vigorous stirring. This solution was then stirred at room temperature for 24 h to obtain the products. The solids were recovered by filtration, washed with distilled water, and air-dried at 393K. Organic molecules occluded in the mesopores were removed by solvent extraction. The dried precursor was dispersed in ethanol (5 g/100 ml) and the mixture was refluxed under vigorous stirring for 2 h. The solid was then filtered and washed with cold ethanol. The extraction procedure was repeated twice before drying the samples at 393 K in an oven. Finally the samples were calcined at 823 K in air for 6 h. Impregnated mesoporous materials titanium dioxide ( $TiO_2$ ) supported on hexagonal mesoporous silica ( $TiO_2$ /HMS) is prepared as follows: the amount of titanium dioxide are added to 5 g of pure silica mesoporous material (HMS) and 50 g of methanol. The mixture is agitated at ambient temperature during 2 h, the solvent is then rapidly evaporated under vacuum and the solid is calcined under air at 723K overnight at a heating rate of 1 K/min.

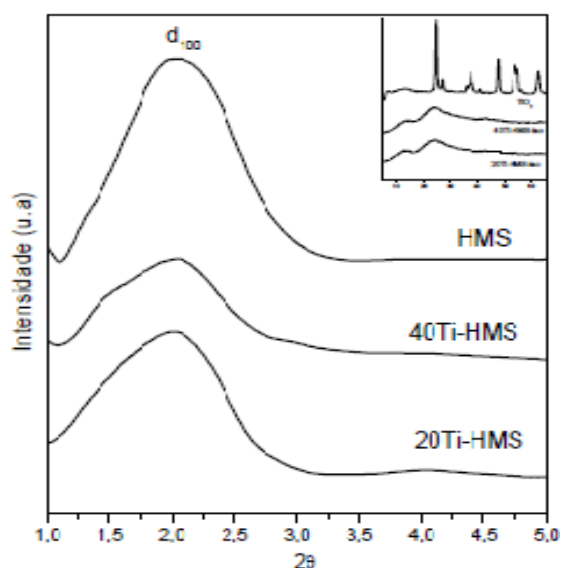
## 3. Catalysts Preparation

The powder XRD patterns of the calcined samples at figure 1 showed that all materials exhibited single  $d_{100}$  reflections that are characteristic of HMS materials [6]. In 20Ti-HMS and 40Ti-HMS samples, the  $d_{100}$  peak was shifted toward lower angles. The XRD patterns collected at high angles and presented inset of fig. 1 did not show peaks belonging to titania phase. The single intense reflection at  $2\theta \approx 2.25$  and the inflection point at  $P/P_0 \approx 0.30$  (isotherm fig. 2) in samples containing Ti indicated that the HMS material structure and mesoporosity were preserved upon

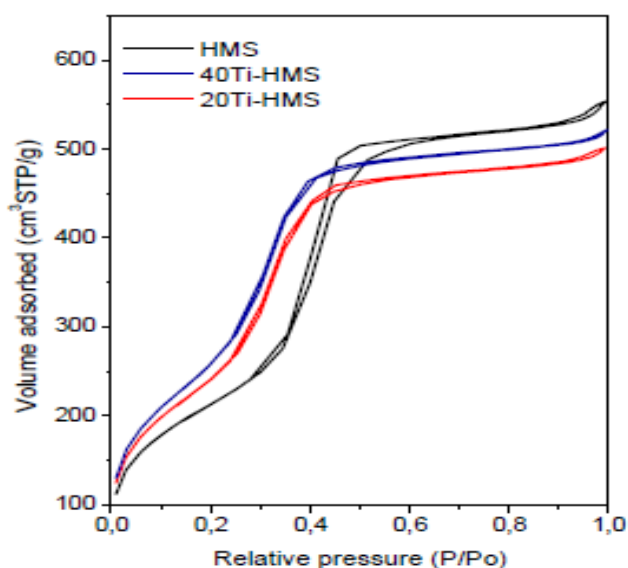
incorporation of Ti. The textural properties of samples based on Ti are listed in table 1. The chemical composition results showed that Ti was successfully introduced. The highest surface area was observed in sample with low Si/Ti ratio. High surface areas in mesoporous materials modified by Ti can be explained by the “mineralizing” effect that consists in the Si substitution for Ti which removes the defect sites in pure silica structure [7]. Conversely the average pore diameter was the same for both samples and the average pore volume did not show difference, demonstrating that the mesoporous structure was maintained, which is consistent with the XRD results. The FTIR spectra of the catalysts showed two absorption bands at 791, 897 and 2000–1400  $\text{cm}^{-1}$  corresponding respectively to the symmetrical Si–O–Si stretching vibration, the formation of Ti–O–Si bridges and the harmonic of  $\text{SiO}_2$  [8]. The intensity of this last band increased with the Ti content of the solids.

**Table 1.** Textural properties of  $\text{TiO}_2/\text{HMS}$  materials.

Sample	Ti (Wt%)	$S_{\text{BET}}(\text{m}^2\text{g}^{-1})$	pore diameter (nm)	Pore volume ( $\text{cm}^3\text{g}^{-1}$ )
HMS	-	1170	3.8	0.97
40Ti-HMS	1.2	954	2.72	0.89
20Ti-HMS	2.5	886	2.80	0.85



**Fig. 1** Powder XRD patterns.



**Fig. 2**  $\text{N}_2$  adsorption-desorption isotherms.

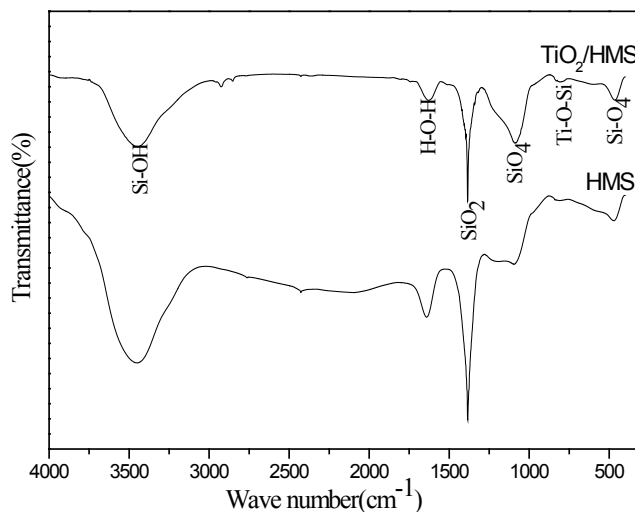


Fig. 3 FT-IR spectra of HMS and TiO<sub>2</sub>/HMS samples.

#### 4. Conclusions

In the present study, the titanium dioxide -containing mesoporous silica HMS materials has been synthesized at ambient temperature using hexadecylamine (HDA) as the template agent. The TiO<sub>2</sub>/HMS samples keep the hexagonal of the parent HMS and have many medium acid sites and small amount of strong acid sites. XRD and N<sub>2</sub> adsorption measurements of the obtained TiO<sub>2</sub>/HMS materials confirm that the structure of the materials is maintained even at low Ti content. The catalytic activity of the TiO<sub>2</sub>/HMS samples was tested for the wastewater treatment.

#### References

- [1]. U. Stafford, K.A. Gray, P.V. Kamat, *Hetero. Chem. Rev.* 3 (1996) 72.
- [2]. A.L. Linsebigler et al. *Chem. Rev.* 95 (1995) 735.
- [3]. C. T. Kresge, M. E. Leonowicz, W.J. Roth, J. C. Beck, *Nature*, 359 (1992) 710.
- [4]. Huo, D. I. Margolese, U. Ciesla, P. Feng, T. E. Gier, P. Sieger, V. Leon, P. M. Petroff, F. Schuth, G. D. Stucky, *Chem. Mater.* 6 (1994) 1176.
- [5]. P. T. Tanev, M. Chibwe, T. J. Pinnavaia, *Nature*, 368(1994) 317.
- [6]. L. Guo; X. Dong; X. Cui; F. Cui; J. Shi, *Mat. Lett.*, 63(2009) 1141.
- [7]. D. Zhao; S. Budhi; A. Rodriguez; R. T. Koodali, *Int. J. HydrogenEnergy*, 35(2010) 5276.
- [8]. K. Bachari, O. Cherifi, *J Porous Mater.* 15 (2008) 325.