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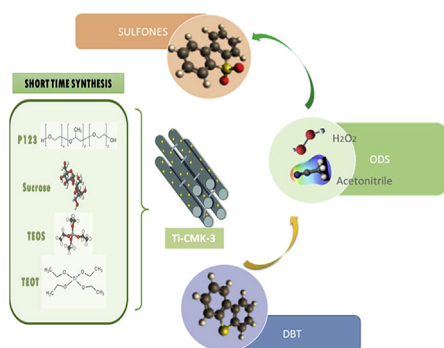
# Novel and simple one-pot method for the synthesis of TiO<sub>2</sub> modified-CMK-3 applied in oxidative desulfurization of refractory organosulfur compounds



Lorena P. Rivoira, Brenda C. Ledesma, Juliana M. Juárez, Andrea R. Beltramone\*

Centro de Investigación en Nanociencia y Nanotecnología (NANOTEC), Facultad Regional Córdoba, Universidad Tecnológica Nacional, Maestro López y Cruz Roja Argentina, 5016 Córdoba, Argentina

## GRAPHICAL ABSTRACT



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## ABSTRACT

Ti-CMK-3 carbon mesoporous was prepared using a novel synthesis method. This new method avoids the hard template synthesis used commonly. The precursors of silicon, carbon and titanium are incorporated together with the other components during the only step of the synthesis. The method developed here, allows reducing time and energy consumption by 60% and thus, the cost of the overall process of synthesis. Structural and textural characterization of the titanium modified-mesoporous carbon was performed by N<sub>2</sub> adsorption, XRD, UV-Vis-DRS, XPS, Raman spectroscopy and TEM. The characterization results indicated that the textural and structural properties of the material synthesized by the short time method are comparable with the properties of the material prepared by the hard template method. Ti modified-mesoporous carbon was synthesized by different methods in order to prepare catalysts to be tested in the oxidative desulfurization (ODS) of sulfur compounds. The catalyst prepared by the one-pot method is capable to oxidize high amount of sulfur (2000 ppm) in only 30 min of reaction time at 60–80 °C. The good performance and stability of the catalyst prepared using a novel synthesis method was attributed to well dispersed anatase nanospecies over the high area mesoporous carbon. Main advantage of the present study is the reduction of time and cost in the synthesis of the new material and the applicability for ODS reactions.

## 1. Introduction

Mesoporous carbons are versatile materials with enormous potential

applications such as adsorption, catalysis, electrochemistry and energy storage and drug delivery. Their controllable and excellent properties differentiate them from other mesoporous materials; notwithstanding,

\* Corresponding author.

E-mail address: [abeltramone@frc.utn.edu.ar](mailto:abeltramone@frc.utn.edu.ar) (A.R. Beltramone).

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the template carbonization method is an issue from the practical and economic point of view. Nanocasting was, until now the only one method for creating mesoporous carbons, using inorganic materials as hard template, such as, zeolite, alumina or mesoporous silica [1–4] to design a highly porous solid and functional carbonous material with miscellaneous properties and interesting application perspectives. By this traditional method, the inorganic template is eliminated from the preparation at the final step of the synthesis, becoming a complicated, long and high cost process [5–8]. The functionalization and modification of mesoporous carbons may increase the catalytic activity because of the interaction between the active catalytic phase and the high area support [9–13].

Literature demonstrates that  $\text{TiO}_2$  and  $\text{TiO}_2$  particles dispersed over high area mesoporous materials are very active in the oxidative desulfurization (ODS) of refractory dibenzothiophenes [14–22].

In our previous work [14] we incorporated Ti as dispersed  $\text{TiO}_2$  particles into the traditional synthesized carbonous support CMK-3 by the post synthesis method. The transition metal incorporation, with the formation of anatase nanoparticles changed the nature of the surface generating an active catalyst for oxidation reactions like oxidative desulfurization of sulfur compounds.

Recently, Ledesma et al. [23], looking for a shorter path to obtain titania-modified CMK-3, found improvements of the synthesis route. Titanium species were incorporated directly into the carbon mesoporous structure using Ti-SBA-15 as template instead of the traditional method, that use SBA-15 as template followed by the impregnation method with a titanium precursor. In this way, one of the steps is avoided diminishing time and cost. The obtained high specific surface area catalyst with narrow mesopore size distribution and with  $\text{TiOx}$  species highly dispersed was successfully applied in catalytic hydro-treating reactions (HDT) [23].

Since the high cost of the synthesis of templated mesoporous carbon is dependent of the nanostructured inorganic template and these templates are sacrificed in the final stage of the preparation. The reduction of time, energy and cost are factors related to the potential applications of mesoporous carbon in industrial processes. For that reason, in this work, we propose a short time synthesis route to incorporate titanium species into the framework of the CMK-3 mesoporous carbon without the use of the siliceous hard template. The novel pathway performed here, challenges and directs the future for the better development of mesoporous carbon materials.

The justification of ODS as chosen catalytic process is based on the importance of reduce the content of sulfur-compounds as measures aimed to obtain better quality of fuels. ODS is a simple and efficient method to eliminate sulfur from diesel fuel as an alternative to the traditional hydrodesulfurization (HDS) process in order to reduce emissions to the atmosphere [24–27]. ODS is the oxidation of the most refractory sulfur molecules in HDS, existent in diesel, by an oxidant agent in the presence of a catalyst [24,26,28–31]. In these conditions, in order that oxidation reaction occurs it is necessary the presence of a polar solvent capable to extract the S-molecules from diesel phase to be in contact with the oxidant agent (polar) and the catalyst. Thus ODS occurs in a three phase system (L(diesel)-L(solvent)-S(catalyst)) and it becomes a two steps extraction/oxidation process [32].

The major hurdles of ODS are oxidant cost, minimize equipment; minimize operating costs, catalyst cost and disposition of the sulfone extract. The best solution to this problem is to find the most effective oxidant, and develop catalysts that are active for the oxidation reaction and are completing the process development necessary for commercialization. The cost of the catalysts in ODS has more influence in the total cost of the process than in HDT, where hydrogen supply has the largest impact in cost [33]. For that reason, the reduction of the cost of the catalyst will have large impact in the cost of the process.

The choice of the oxidant agent is important from economical point of view; the most used are nitrogen oxides, nitric acid,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$  and organic peroxides. Wei et al. [34] used cyclohexanone peroxide

(CYHPO) as the oxidant in the ODS of DBT over cobalt supported on KIT-6 mesoporous silica. They found that the optimum values, applying the Box-Behnken design, were obtained using 5.7 (O/S molar ratio) at 93 °C. In contrasts, Yang et al. [35] found that the molar ratio (O/S) was 2.5 at 100 °C using  $\text{MoO}_3/4\text{A}$  molecular sieve as catalysts. This number is slightly superior that the theoretical stoichiometric molar ratio of 2 using CYHPO as oxidant. However, they found that the optimum CYHPO/DBT was the 3.8 at 67 °C and 38 min to achieve a conversion of 100%. Similar results were reported by Long et al. [36,37] using catalyst W/D152 and molybdenum supported on modified medicinal stone.

In consideration of the cost of CYHPO in the reaction system, the appropriate mass ratio found in the optimized processes described above, is a very important goal from the industrial point of view. However, in the systems that use hydrogen peroxide as oxidant, the O/S values reported in literature are higher [16,17,32,38,39]. Ding et al. [39] reached complete sulfur removal using O/S ratio of 10 over iron-modified mesoporous SBA-15. Cedeño Caero et al. [40] studied the effect of the variation of  $\text{H}_2\text{O}_2$  to substrate ratio by using synthetic diesel, with a  $\text{H}_2\text{O}_2/\text{S}$  ratio of 21.3 or 2.13. They reported that the conversion of sulfur compounds increased with increasing  $\text{H}_2\text{O}_2$  addition. They observed that the excess of oxidant increased the activity and the water produced (from ODS reaction and thermal decomposition) hindered the ODS reaction. Hence, it is very important to control  $\text{H}_2\text{O}_2$  concentration because the thermal decomposition of hydrogen peroxide is well known.

The results indicate that high activity is associated to the capability of the catalyst to decompose  $\text{H}_2\text{O}_2$  and form the appropriate Ti-peroxo intermediate that renders the reactive oxygen species for the oxidation of DBT to sulfone. The proposed oxidation mechanism of peroxyoxygen is according to Garcia Gutierrez et al. [41] in which the peroxide reacts with DBT to produce DBT sulfoxide, and further oxidation produces the corresponding sulfone in presence of the catalyst. According Bakar et al. [42,43] the mechanism is an oxidation by nucleophilic attack of the sulfur atom on the peroxo species of  $\text{TiOx}$  attached to the matrix.

Literature indicates that in the ODS of DBT, the kinetics follows the pseudo-first order equation. Wei et al. [34] evaluated the conversion of DBT using Co/KIT-6. The experiment under various temperatures presented activation energy of 25.26 kJ/mol. They also indicated that the kinetics followed the pseudo-first order equation. In a previous work, we obtained a value of 43 kJ/mol using  $\text{TiO}_2$ -SBA-16 catalyst [29]. The obtained value was in the range obtained for H/Na titanate nanotubes (45 kJ/mol) [44], Ti-based metal-organic frameworks (75 kJ/mol) [45], and phosphotungstic-doped  $\text{TiO}_2$  matrixes (55 kJ/mol) [46].

In our previous reports [29,14,47], vanadium and titanium oxides supported on SBA-15 and CMK-3 have been tested in the ODS of sulfur compounds obtaining high efficiency in removing sulfur at very short time, more than 80% at 10 min of reaction time by using hydrogen peroxide as oxidant and acetonitrile as solvent.

Our primary aim in this work is to evaluate the ODS activity of the titania-modified mesoporous carbon CMK-3, synthesized by the short time method, in order to achieve total removal of sulfur compounds from diesel fuel. In order to compare the performance of the catalyst developed here, we choose similar reaction conditions that the used in our previous work using titanium grafted into CMK-3 [14]. We use dibenzothiophene (DBT) as a model molecule,  $\text{H}_2\text{O}_2$  as oxidant and acetonitrile as solvent.

## 2. Experimental

### 2.1. Synthesis of titanium-modified CMK-3 by the short time method

By this new method of synthesis, we aim to avoid the use of the siliceous hard template attaining a shorter path to obtain mesoporous carbon. Siliceous source (tetraethyl orthosilicate, TEOS 99% Sigma-Aldrich) is incorporated together with the other components during the

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