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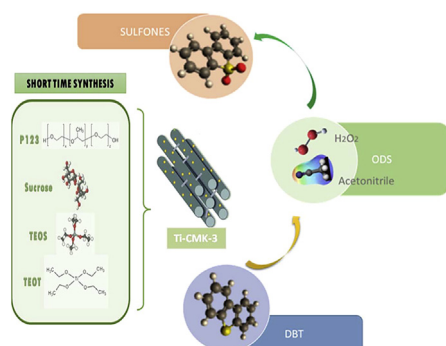
Novel and simple one-pot method for the synthesis of TiO₂ modified-CMK-3 applied in oxidative desulfurization of refractory organosulfur compounds



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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 N₂ 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,

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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 TiO_2 and 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 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 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, O_2 , H_2O_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 H_2O_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 H_2O_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 H_2O_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 H_2O_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 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 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 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, H_2O_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

only step of the synthesis. Tetraethyl orthotitanate (TEOT, 98% Sigma-Aldrich) was the titanium source and sucrose the carbon source. The synthesis must be done under acid conditions by dissolving 4 g of triblock copolymer P123 and 1 g of sucrose in a 2 M HCl solution at 40 °C. TEOS (8.6 mL) was added to the mixture after 2 h of vigorous stirring. After 15 min more of stirring, TEOT (0.6 mL) was added too, and kept stirring another 15 min. After 24 h of being retained static in a polypropylene bottle at 100 °C, the liquid mixture became solid and was filtered and washed with deionized water to handle the pH until 6. The sample was left 48 h at 50 °C. After that, the mixture was added into a solution containing 1 mL of H₂SO₄ (98 wt%) and 10 mL of deionized water. Next, the sample was stirred at room temperature for 18 h and it was subsequently dried at 160 °C for 6 h. To reach total carbonization of sucrose the dark brown powder was calcinated under 20 mL/min of N₂ flow. The temperature was raised to 900 °C. The composite was treated with HF (5 wt%) twice so as to ensure the complete elimination of the silica. The material was filtered out, washed with ethanol and dried at 50 °C. The resulting sample was denoted Ti-CMK-3-ST with nominal content of Si/Ti = 20 M ratio.

2.2. Synthesis of titanium-modified CMK-3 by nanocasting strategy

For comparative study, titania-modified CMK-3 was also synthesized by nanocasting strategy by two different ways. In the first way, titanium was grafted over CMK-3 by the wet impregnation method. In the second way, titanium was incorporated directly in the mesoporous structure using Ti-SBA-15 as hard template. We previously reported both methods [14,23]. Briefly, CMK-3 mesoporous carbon was carried out using siliceous SBA-15 as the hard template and sucrose as the carbon precursor, following the traditional synthesis procedure described in our previous work [14]. In order to incorporate titanium species by the wet impregnation method, the ordered mesoporous carbon CMK-3 was used as support and tetrabutyl orthotitanate (TBOT) was used as source of titanium. To have a nominal content of 5 wt% of Ti in the final powder, 10 mL of a solution of tetrabutyl orthotitanate in ethanol was mixed with pure CMK-3 solid. The mixture was placed in a rotary evaporator to remove excess of ethanol at about 40 °C and 60 rpm. Finally, the resulting material was dried at 100 °C and then heated in nitrogen flow of 20 mL/min from 25 to 200 °C with a slope of 4 °C/min. After that, the temperature was increased to 470 °C with a slope of 10 °C/min and kept at this temperature during 5 h. The sample was named TiO₂-CMK-3.

In the other hand, titanium was incorporated directly during the synthesis of the mesoporous carbon using Ti-modified SBA-15 as the hard template. The procedure was developed by us and reported in our previous work [23]. Ti-SBA-15, with Si/Ti = 20 M ratio, was used as hard template and sucrose was used as source of carbon. The obtained material was denoted by Ti-CMK-3. For comparative analysis of the time employed in the direct synthesis of Ti-CMK-3 and the novel short time synthesis method of Ti-CMK-3-ST, the following paragraph describes the procedure in detail. The typical synthesis of Ti-CMK-3 was carried out by nanocasting strategy using Ti-SBA-15 as a template. The procedure was the following: The surfactant used in the synthesis, Pluronic 123 was dissolved in acidic medium (9 g of P123 in 288 mL of HCl (2 M)). The temperature of the P123 solution was controlled at 35 °C and stirred until complete dissolution. Afterwards, 20.1 mL of TEOS (silica source) were added to the acid solution stirring continuously for 20 min, and then 2.1 mL of TEOT were added and maintained at static condition for 24 h. The mixture was transferred into a Teflon bottle and kept at 80 °C for 72 h under static conditions. To extract the template, the material was first immersed in ethanol reflux for 6 h. The product was filtered, washed, and dried in air at 50 °C. To ensure the elimination of the structure-directing agent, it was heated under N₂ flow, at 20 mL/min at 550 °C for 6 h and then a calcined at the same temperature in air for 6 h. This sample denoted Ti-SBA-15 was used as template in order to obtain the mesoporous carbon CMK-3

modified with titania by nanocasting strategy using sucrose as source of carbon. Typically, 1.1 g of sucrose was immersing in an acid solution of H₂SO₄ and water (0.14 g in 5 g). To this solution the template Ti-SBA-15 was added, and then dried at 100 °C and afterwards heated at 110 °C for 6 h to complete carbonization of sucrose. In order to ensure the complete filling of the pores of the template, a second impregnation was carried out, using another H₂SO₄ solution with 0.75 g of sucrose. The heating procedure was repeated after this second impregnation step. The dark brown powder obtained is then heated at 900 °C under N₂ flow during 4 h. The template removal was performed using a HF solution (5%wt.) at room temperature. To ensure the complete removal of the silica, this procedure was performed twice. The carbon sample was filtered, washed with ethanol solution and dried at 50 °C.

Comparing the times necessary in the different synthesis methods, using the novel method of synthesis there is a reduction of approximately 60% (120 h vs. 50 h).

2.3. Catalytic activity

The catalytic oxidation of the sulfur compound with hydrogen peroxide was carried out in a glass batch reactor, equipped with a magnetic stirrer, a thermometer and a condenser. In a typical run, the solid catalyst (60 mg) was suspended under stirring (750 rpm) in 20 mL of a solution of 500 ppm of S as DBT (or other) in acetonitrile. Then, appropriate amount of 30% aqueous H₂O₂ was added at constant temperature. The experiments were performed in a three-phase liquid-liquid-solid (L (oil)-L (solvent)-S (catalyst)) system, acetonitrile was used as solvent and dodecane as oil phase. Solution samples were recovered at various times. The products were analyzed by GC HP 5890 Series II with a HP-5 column and connected to FID and PFPD detectors, after filtration and eventually decantation step. The products were confirmed using a Shimadzu GCMS-QP5000 with a GC-17A gas chromatograph and AOC-20i autoinjector and HP-5 column 30-m length, 25-mm inner diameter, and 25-µm film thickness.

2.4. Characterization

X-ray diffraction patterns were obtained with a PANANALITYCAL Phillips X'pert XDS diffractometer with a diffractometer beam monochromator and CuK α radiation source. Elemental analysis was performed by inductively coupled plasma-atomic emission spectroscopy (VISTA-MPX) operated with high frequency emission power of 1.5 kW and plasma air flow of 12.0 L/min. N₂ adsorption/desorption isotherms at -196 °C were measured on ASAP 2020 equipment after degassing the samples at 400 °C. The pore size distribution of SBA-15 samples was determined by the Nonlocal Density Functional Theory (NLDFT) applied for cylindrical pores of siliceous adsorbents at -196 °C, using the adsorption branch. The pore size distribution of the mesoporous carbon samples was determined by the QSDFT (Quenched Solid Density Functional Theory) using kernel N₂ at -196 °C on carbon (slit-cylindrical pores, adsorption branch). The same models were applied to calculate mesopore volumes; the specific surface area was determined by Brunauer-Emmett-Teller (BET) method. Ultraviolet-visible diffuse reflectance spectroscopy (UV-Vis-DRS) was recorded with a Perkin Elmer Lambda 650 spectrophotometer equipped with a diffuse reflectance accessory. X-ray Photoelectron Spectra (XPS) were obtained on a MicrotechMultilb 3000 spectrometer, equipped with a hemispherical electron analyzer and MgK α ($h\nu = 1253.6$ eV) photon source. An estimated error of ± 0.1 eV can be assumed for all measurements. TEM micrographs were obtained on a JEOL model JEM-1200 EX II microscope. Raman spectrum was obtained from an InVia Reflex Raman microscope and spectrometer using a 532 nm diodelaser excitation.

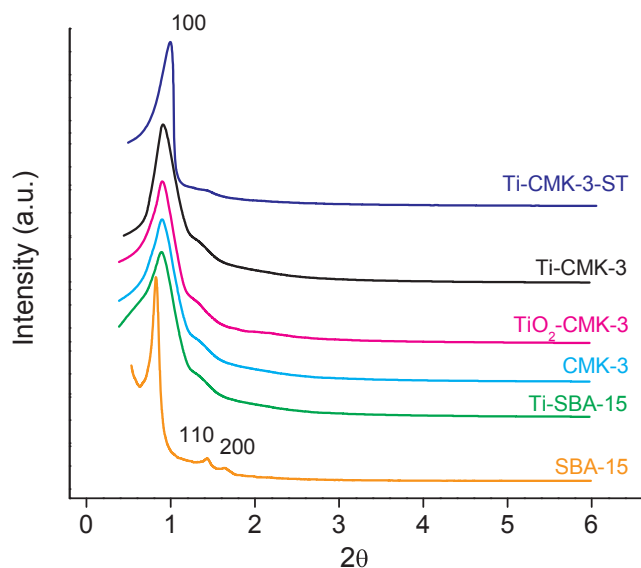


Fig. 1. Low angle XRD patterns of the samples synthesized.

3. Results and discussion

3.1. XRD

Fig. 1 presents the XRD patterns of the mesoporous carbon catalysts as well as the siliceous materials, Ti-SBA-15 and SBA-15, used as hard template for the synthesis of Ti-CMK-3 and CMK-3, respectively. CMK-3 pattern is shown as Refs. [48–53]. As expected, characteristic signals are observed for 2D-hexagonal $p6m$ symmetry in CMK-3, TiO_2 -CMK-3 and Ti-CMK-3 patterns. The ordered structures are exactly negative replicas of the hard template SBA-15 [51,52]. The ordered mesoporous carbon structure of the novel material Ti-CMK-3-ST (synthesized without hard template) was confirmed because of the similarity with the CMK-3 pattern.

Fig. 2 shows the wide-angle XRD patterns of the mesoporous carbon modified with titanium. The Figure presents wide diffraction peaks characteristics of the graphite carbons [54]. Comparing with the anatase pattern added as reference, anatase phase peaks were found in each of the samples corresponding to the [1 0 1] plane. According to the

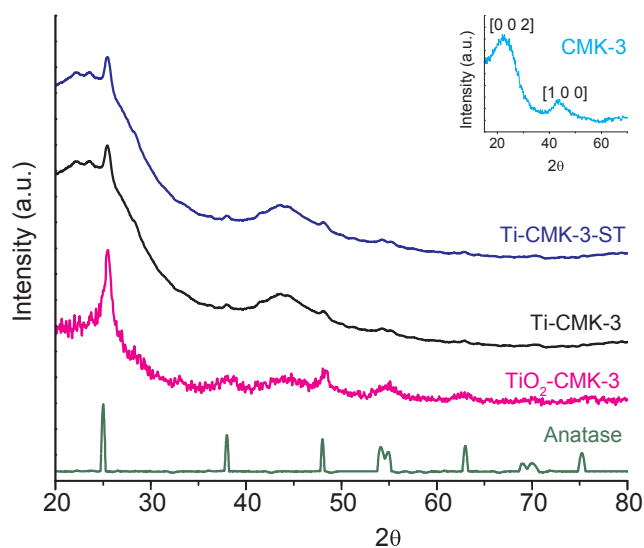


Fig. 2. Wide-angle XRD patterns of the samples synthesized and anatase pattern as reference.

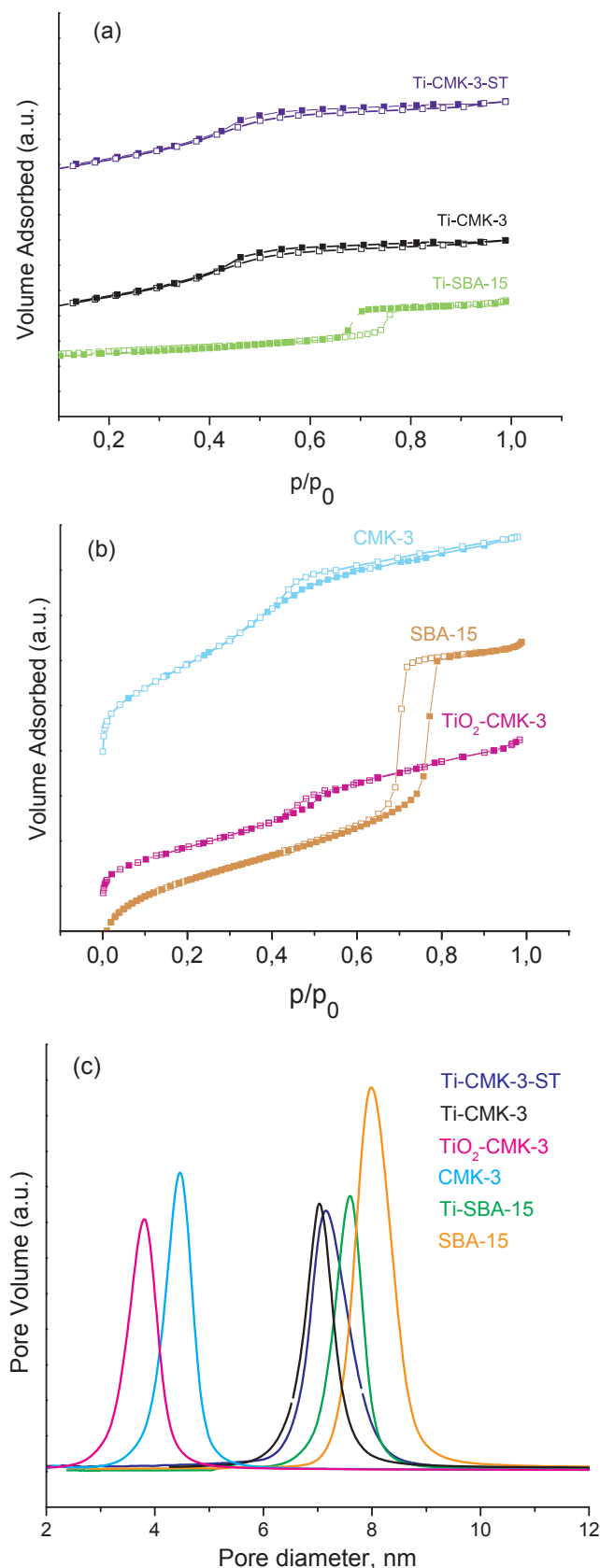


Fig. 3. a) Nitrogen adsorption (solid symbols)-desorption isotherm (open symbols) of Ti-CMK-3-ST, Ti-CMK-3 and Ti-SBA-15. b) Nitrogen adsorption (solid symbols)-desorption isotherm (open symbols) of CMK-3, SBA-15 and TiO_2 -CMK-3. c) Pore size distribution of all the samples.

Table 1
Textural and structural properties of the samples synthesized.

Samples	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_p ($\text{cm}^3 \text{g}^{-1}$)	D_p (nm)	Ti wt.% by ICP
SBA-15 (template for CMK-3)	1030	1.28	7.8	–
CMK-3 (support for TiO_2 -CMK-3)	1325	1.01	4.5	–
Ti-SBA-15 (template for Ti-CMK-3)	880	1.30	8.0	5.2
TiO_2 -CMK-3	805	0.80	3.9	5.3
Ti-CMK-3	1044	0.80	7.0	4.3
Ti-CMK-3-ST	1052	0.88	7.2	5.0

Figure, the anatase species are highly dispersed and present small size in Ti-CMK-3 and Ti-CMK-3-ST particularly. TiO_2 -CMK-3 pattern presents more intense signals, then it is feasible the presence of larger crystalline anatase particles. By means of Scherrer's formula [55] average anatase cluster size was estimated at about 8 nm of diameter for TiO_2 -CMK-3, 3.3 nm for Ti-CMK-3 and 3 nm for Ti-CMK-3-ST. These estimated values lead us to conclude that it was achieved a good dispersion of titanium species and Ti-CMK-3-ST presents the smaller particle size.

3.2. Analysis of adsorption/desorption isotherms

Surface area (SBET) and mean pore diameter (D_p) of the mesoporous carbons modified with Ti were studied by nitrogen sorption desorption method. Type IV isotherms were observed for all the samples (Fig. 3 (a) and (b)), characteristic of mesoporous materials according to the IUPAC classification. That mesoporous structure consists mainly in hexagonal cylindrical pores (channels) randomly interconnected to each other with microporosity in their walls. Fig. 3 (c) shows the mesopore size distribution and Table 1 presents structural and textural properties of the materials. Ti-SBA-15 isotherm was added as reference. With regard to diameter of the mesopore it was observed a similar behavior for both samples prepared by direct synthesis but different methods, pore diameter resulted to be 7 nm in Ti-CMK-3 and 7.2 nm in Ti-CMK-3-ST. For the titanium-modified sample obtained by wet impregnation (TiO_2 -CMK-3) the pore size decreased dramatically to 3.9 nm. Possibly due to the presence of larger anatase particle blocking partially the pores. All the samples obtained showed high surface area and ordered mesoporous structure. The catalyst obtained by short time method (Ti-CMK-3ST) showed the highest area comparing with TiO_2 -CMK-3 and Ti-CMK-3. These results indicate the success of the new synthesis by the short time method. We obtained an ordered mesoporous material with the most desired characteristics for catalytic applications, like high surface area, high pore volume and narrow mesopore size distribution. Titanium contents listed in Table 1 were determined by ICP-AES.

3.3. TEM

Fig. 4 shows the pore channels distribution of the titanium-modified synthesized samples. All the samples present hexagonal symmetries and ordered pore channels. Is important to note, that the sample prepared by the short time method, without the use of hard template, presents well-ordered channels with a calculated pore diameter of about 7 nm. The structure is very similar to Ti-SBA-15 as can be seen in Fig. 4 (a) and (b). This is in agreement with N_2 isotherms analysis. The mean size of the anatase species was difficult to determine with this technique for Ti-CMK-3 and Ti-CMK-3-ST, probably due to the small particle size and high dispersion. In the case of TiO_2 -CMK-3 in Fig. 4 (c), the higher size of the particles allows us to calculate the particle size distribution. We can observe that the TiO_2 mean particle size is close to 8 nm and

ranging from 7 to 9 nm.

3.4. UV-Vis-DRS

UV-Vis diffuse reflectance spectroscopy was applied to determine the chemical environment of the titanium moieties. According literature, the band at 200–210 nm is characteristic of tetrahedral coordinated titanium species. The broadening of this band indicates the presence of both tetrahedral and octahedral titanium species as well dispersed anatase nanospecies [56,57]. Fig. 5 shows the spectra for the three titanium-modified mesoporous carbons. Ti-CMK-3 and Ti-CMK-3-ST present a band close to 205 nm indicating that tetrahedral titanium is well dispersed. In the case of TiO_2 -CMK-3, the broadening of this band to higher wavenumbers indicates the presence of anatase species of higher size, corroborating the previous analysis.

3.5. Raman spectroscopy

Raman Spectroscopy analysis of the titanium-modified mesoporous carbons are shown in Fig. 6. Anatase spectrum was added as reference. All samples present the bands characteristic of TiO_2 in anatase phase, this confirms XRD and UV-Vis-DRS studies. The higher intensity of these bands is observed for TiO_2 -CMK-3 sample, indicating the presence of crystalline anatase particles. The other samples synthesized by novel methods present signals with similar widths and intensity giving account of the similar dispersion and nanometric size of the active species. Moreover, the characteristic peaks of E2g mode of graphite and vibrations of C–C bond at 1355 and 1579 cm^{-1} , respectively are present in all the samples [58–62].

3.6. XPS

XPS analysis of Ti-CMK-3 and TiO_2 -CMK-3 was reported in our previous works [14,23]. According literature, the characteristic binding energy of CMK-3 as graphitic and disordered carbon appears at 284 and 286 eV and are attributed to C–C sp³ and C=C sp², respectively [63–68]. Ti signals of Ti 2p_{3/2} at 458 eV corresponds to Ti as anatase phase [67,68]. Fig. 7 shows the XPS spectra for the three catalysts. The results confirm that TiO_2 species are in the anatase phase. The low values of Ti/C shown in Table 2, demonstrates that Ti species are well dispersed in the mesopores of CMK-3. This indicates the success of the short time method. The higher Ti/C ratio for TiO_2 -CMK-3 is in agreement with the higher size of the anatase particles, probably placed outside the pores and mainly in the external surface of the framework.

3.7. Catalytic activity

ODS of sulfur compound usually occurs in a three-phase liquid-liquid-solid [L (oil)-L (solvent)-S (catalyst)] system. When these phases are mixed DBT is easily extracted to the polar phase (solvent), where the oxidant agent is predominantly present and the oxidation of the sulfur compound occurs, becoming into the rate-determining step. A short reaction pathway to understand the formation of sulfoxide and/or sulfone products is $\text{R-S-H} + \text{oxidant} \rightarrow \text{R-SO-H} \rightarrow \text{R-SO}_2\text{-H}$.

In our previous work [14] we demonstrate that the sulfur removal was due mainly because of the presence of the active species on the supported catalysts. In that case, we tested the adsorption capacity of bare mesoporous CMK-3. CMK-3 (60 mg) was in contact with different DBT initial concentrations at 25 °C for 60 min. The adsorption amount was between 6 and 17 wt% depending on the initial concentration of DBT. When temperature was increased, the equilibrium adsorption amount of DBT decreased. The adsorbed amount of sulfur at the temperatures of the reaction (60 °C) was negligible. No conversion of DBT in presence of H_2O_2 ($\text{H}_2\text{O}_2/\text{S} = 6$) was obtained at 60 °C in the absence of the catalyst. The blank experiment probed that titania-species present in CMK-3 play the main role in the catalytic activity as can be

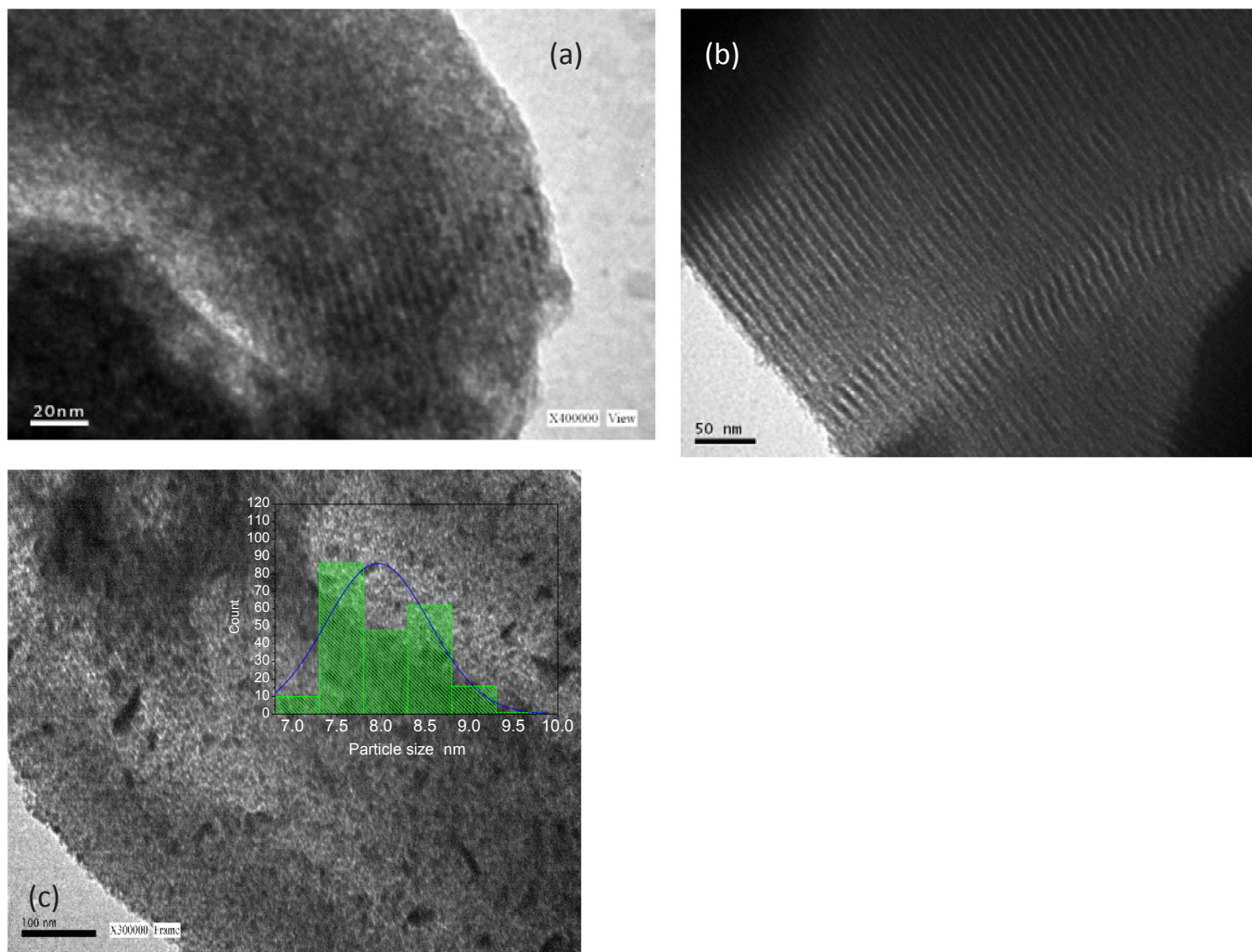


Fig. 4. TEM of the samples synthesized: a) Ti-CMK-3, b) Ti-CMK-3-ST, c) TiO₂-CMK-3.

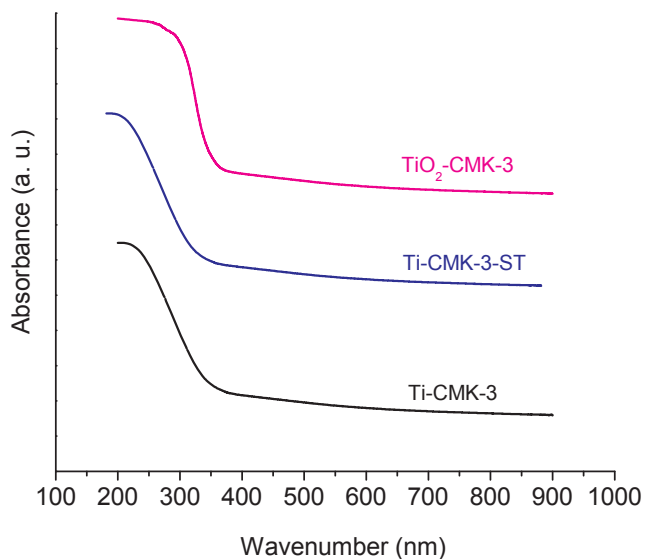


Fig. 5. UV-Vis-DRS of the catalysts synthesized.

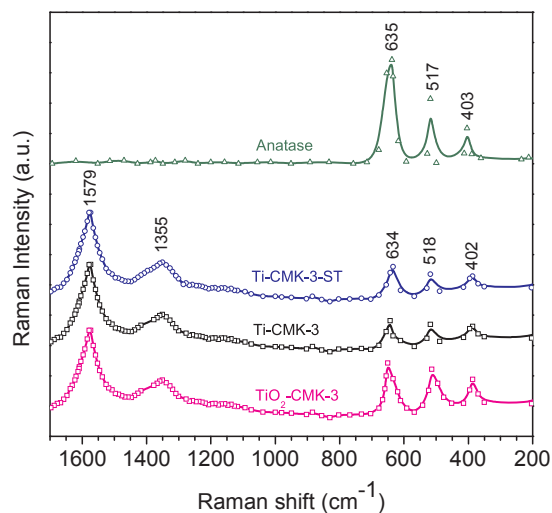


Fig. 6. Raman spectroscopy of the catalysts synthesized.

observed in Fig. 8.

The catalytic activity of the catalysts is shown in Fig. 8. Fig. 8(a), shows the conversion of dibenzothiophene in function of time in a three-phase liquid-liquid-solid [L (oil)-L (solvent)-S (catalyst)] system,

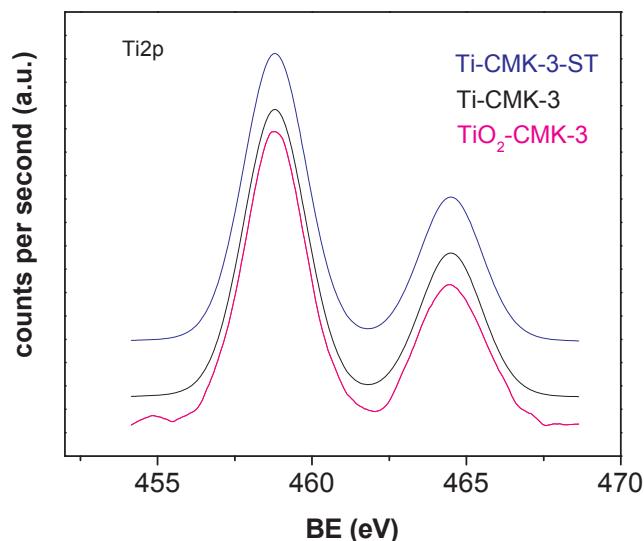


Fig. 7. XPS of the catalysts synthesized.

Table 2

Core levels and atomic surface composition of the synthesized samples obtained by XPS.

Sample	C1s	O1s	Ti2P _{3/2}	Ti/C	O/C
Ti-CMK-3-ST	284.4(91)	531.7(74)	458.5	0.020	0.0152
	286.2(9)	533.6(26)			
Ti-CMK-3	284.7 (88)	531.7(67)	458.6	0.022	0.0163
	286.5 (12)	533.7(33)			
TiO ₂ -CMK-3	284.7 (86)	531.7(62)	458.0	0.035	0.0195
	286.5 (14)	533.7(38)			

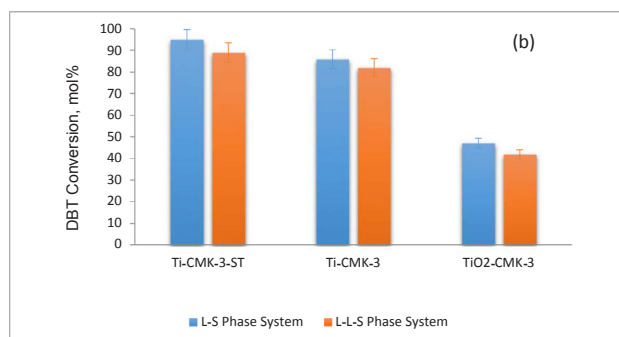
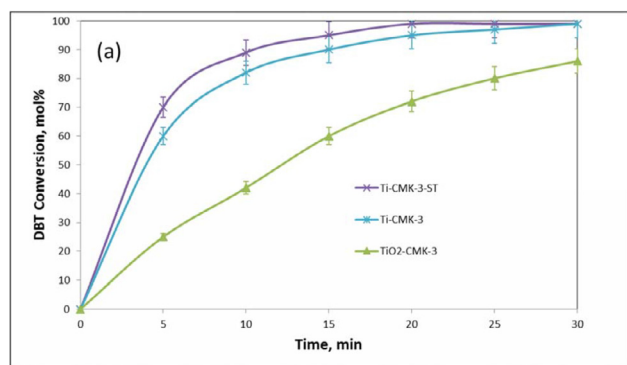


Fig. 8. (a) Catalytic activity in the ODS of DBT. Molar ratio O/S = 12, T = 60 °C. g DBT/g cat = 1.2 (500 ppm) in L(dodecane)-L(acetonitrile)-S(catalyst) phase system and (b) Effect of mass transfer limitation. Molar ratio O/S = 12, T = 60 °C. g DBT/g cat = 1.2 (500 ppm), time = 10 min.

using dodecane as the oil phase and acetonitrile as the solvent (polar) phase.

The sulfur atom presents in the S-containing compound possesses electronic d-orbitals easier to oxidize [69,70] in consequence, under the studied conditions, the oxidation reaction led directly to the dibenzothiophene sulfone. It seems clear that the catalyst synthesized by the short time method showed better performance than the others did.

In order to prove the performance of the catalyst avoiding the mass transfer limitations, the reaction were carried out in a two phase liquid-solid [L (solvent)-S (catalyst)] system, using acetonitrile as the solvent. The results are shown in Fig. 8(b). It is clear that a slight mass transfer limitation exists since all the catalysts presented lower activity in the L-L-S system than in the L-S system. This finding means that the liquid-liquid extraction step is not fast enough and that the transfer of DBT from the oil phase to the solvent phase limits the global rate of the ODS process. Ti-CMK-3-ST was the most active catalysts in both systems.

Previous works demonstrated that the nature of the catalyst is a determining factor that affects directly the success of the oxidation reaction. The hydrophilic character of the catalyst [71] as well as the particle size is two main factors. Zanella et al. [70] demonstrated that when H₂O₂ is the oxidant reagent, total sulfur removal is possible only when the catalyst satisfies those two requirements mentioned above. Smaller non-crystalline particles offer major imperfections on the solid surface and therefore much more active sites with low coordination number. The catalysts prepared by direct incorporation of titanium in this work were much more active than the grafted catalyst. That point could be explained, not only in terms of the nanometrical particle sizes achieved in our materials, but also in terms of the high porosity distinctive of mesoporous carbons, conferring them high surface area (1052 m²/g for Ti-CMK-3-ST) and hence a large number of vacant active sites. The use of large surface area Ti-containing materials has already been studied in previous works [14,15,23] indicating good performance for ODS of the most refractory sulfur-containing molecules in fuels. Ti-CMK-3-ST was the most active catalyst reaching total conversion at very short time. Based on the above comments, this fact can be understood in terms of the small tetrahedral titanium species highly dispersed into the matrix of the CMK-3 structure. The above-mentioned characterization studies give account of this fact. UV-Vis-DRS spectroscopy and Raman concluded that the dispersion of the titanium species for Ti-CMK-3-ST and Ti-CMK-3 catalyst was higher than in TiO₂-CMK-3.

For the titanium-modified sample obtained by wet impregnation, (TiO₂-CMK-3) the pore size decreased from 4.5 to 3.9 nm after impregnation. This was possibly due to the presence of larger anatase particles blocking the pores. This large particles made this catalyst less active because of the poor dispersion of the active site, despite of its higher loading (5.3 wt% of Ti). In addition, the small size of the pores could difficult the diffusion of DBT or the sulfone through the channels of the mesoporous carbon. These are the possibly reasons of the low activity of this catalyst.

Applying the wet impregnation method was possible to incorporate higher loading of Ti, but the formed TiO₂ species were large and placed mainly on the external surface of the framework, as it was determined by the characterization techniques. The one-pot method allows the incorporation of higher amount of Ti in Ti-CMK-3-ST than the direct method in the case of Ti-CMK-3. In addition, of the higher loading, this method favored the dispersion of the anatase particles giving more active sites available for the reaction. XPS indicated that these particles are mainly inside the pores of the mesoporous carbon. Higher surface area and pore size, in the case of the catalysts obtained via direct synthesis made suitable catalysts for large molecules as DBTs.

In resume, the results showed here, demonstrated that the short time synthesis was appropriate to confer good catalytic properties. Therefore, the oxidation activity increases because of an increase in the content of the isolated tetra-coordinated Ti (IV) in anatase phase, which are mainly present in Ti-CMK-3-ST.

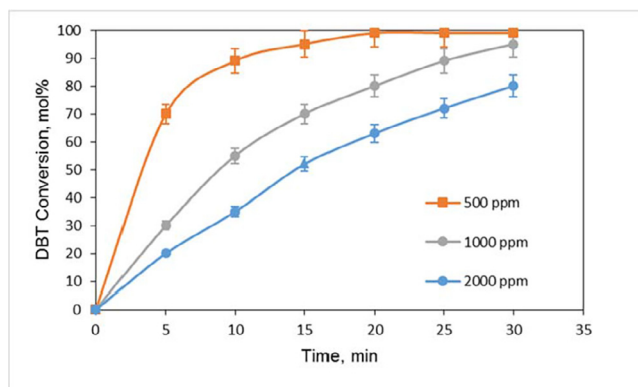


Fig. 9. Effect of the initial concentration of DBT over Ti-CMK-3-ST in L(dodecane)-L(acetonitrile)-S(catalyst) phase system. Molar ratio O/S = 12, T = 60 °C. Cat = 60 mg.

In order to improve conversion rates for this catalyst, and to outline how the catalyst performs under different conditions, we proceeded to change some operating variables. Fig. 9 shows the catalytic performance after increasing the amount of sulfur compound (from 500 to 2000 ppm) fixing the other conditions. Clearly, increasing the content of S leads to a decrease in conversion, the same as observed in our previous work [14]. However, the catalyst is capable to process high loaded feed (80% of 2000 ppm S) in 30 min.

Huang et al. [16] reported the decrease in conversion when the content of S increases. They explained that more polar sulfones, adsorb onto the surface of the catalyst, competing for the active sites, leaving a fewer sites available for DBT oxidation. Moreover, Jia et al. [26] confirmed that the decrease of the DBT oxidation, under relative high sulfur concentration, is due to adsorption competition between DBT and the sulfones.

Fig. 10 shows the catalytic performance for different H₂O₂ contents (expressed as O/S molar ratios). It seems clear that increasing the H₂O₂ content leads to an increase in conversion. There have been previous studies that showed that an increase in H₂O₂ content led to an improvement in conversion [38,71,72]. The reason for the increase in conversion can be due to the presence of more oxygen active sites availability, competing with peroxide decomposition. The high activity of our catalysts indicate that they have the capability to decompose hydrogen peroxide and form the reactive species Ti-peroxo intermediates that react with the sulfur compound to give the corresponding sulfone.

The effect of temperature of the reaction is shown in Fig. 11. Better conversion is obtained at higher temperature. More than 20% increase in value of DBT conversion within the temperature range indicates that

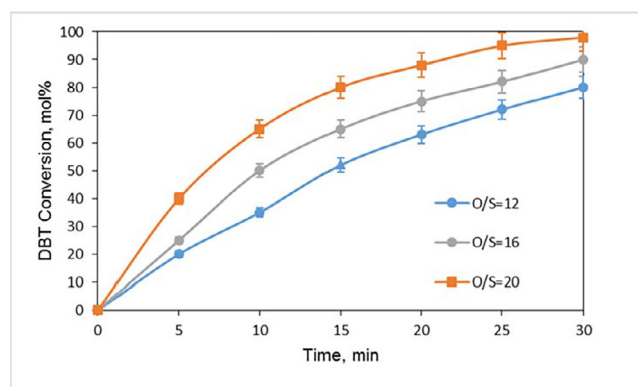


Fig. 10. Effect of the initial concentration of H₂O₂ over Ti-CMK-3-ST in L(dodecane)-L(acetonitrile)-S(catalyst) phase system. T = 60 °C. g DBT/g cat = 4.8 (2000 ppm).

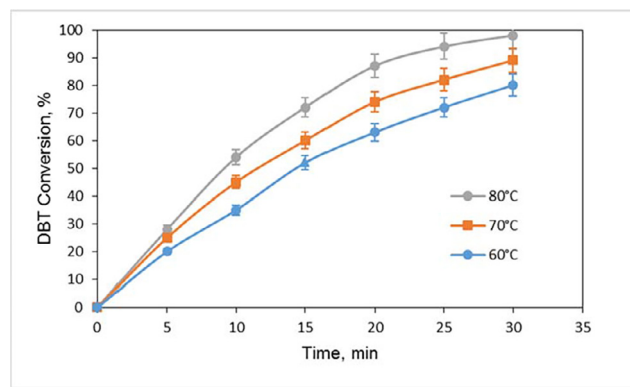


Fig. 11. Effect of the temperature over Ti-CMK-3-ST in L(dodecane)-L(acetonitrile)-S(catalyst) phase system. O/S = 12, g DBT/g cat = 4.8 (2000 ppm).

temperature was an important parameter. Experimental results indicate that even at lower temperature high efficiency can be achieved, making this process energy efficient. Total sulfur elimination is obtained at 80 °C using Ti-CMK-3-ST, this result is promissory since the catalyst is capable to oxidize high amount of sulfur (2000 ppm) in only 30 min of reaction time.

Main sulfur compound present in petroleum are mercaptans (R-SH), sulfurs (R-S-R), di sulfurs (R-S-S-R), some thiols and their thiophenes derivate. HDS process is highly efficiently for the elimination of thiols, sulfurs and disulfurs. However, thiophenes derivatives are very hard to eliminate and most abundant in diesel. In order to make the process as close to reality as possible, the experiments were performed using a mix of the most representative sulfur compounds. Reactor feed consisted in 2000 ppm of S conformed by dibenzothiophene (DBT), 4,6-dimethyl dibenzothiophene (4,6-DMDBT), benzothiophene (BT) and thiophene (TH) in dodecane. Sulfones were obtained only for DBT and 4,6-DMDBT meanwhile BT and TH resulted in the corresponding oxide. In concordance with previous studies, thiophene and benzothiophene are harder to oxidize than DBTs [73–76]. Fig. 12 shows conversion of the different sulfur compounds. The conversion of DBT and 4,6-DMDBT to their corresponding sulfones over Ti-CMK-3-ST was about 80% at 30 min. The most easy to oxidize was 4,6-DMDBT. It could be because of the higher electron density over the sulfur atoms present on it. Otsuki et al. [63] determined the electron densities of the sulfur compounds as follows: 4,6-DM-DBT (5.760) > DBT (5.758) > BT (5.739) > TH (6.042). According to literature, BT and TH display quite good results in ODS over Ti-containing mesoporous materials using different oxidants [73–75], even H₂O₂ [19]. In agreement with references, BT and TH conversion to sulfoxide using Ti-CMK-3-ST was close to 60 mol% at

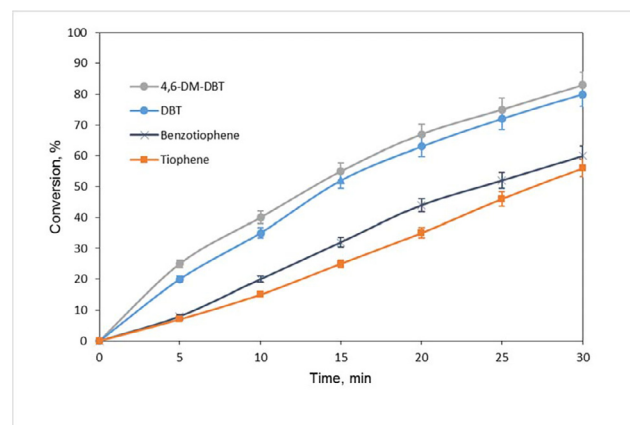


Fig. 12. ODS of different sulfur compounds over Ti-CMK-3-ST in L(dodecane)-L(acetonitrile)-S(catalyst) phase system. O/S = 12, T = 60 °C, (2000 ppm).

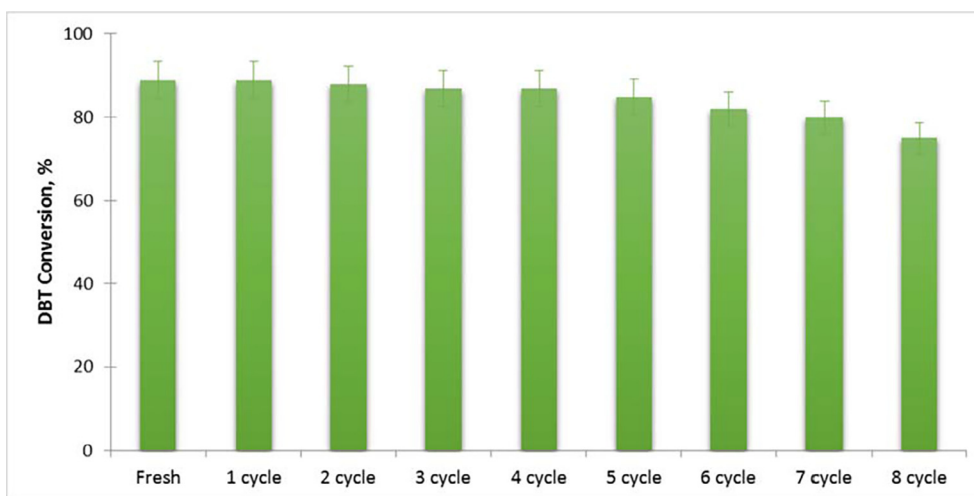


Fig. 13. Reuse study of Ti-CMK-3-ST at 10 min of reaction time in L(dodecane)-L(acetonitrile)-S(catalyst) phase system. Molar ratio $H_2O_2/DBT = 6$ (O/S = 12), $T = 60^\circ C$, g DBT/g cat = 1.2 (500 ppm).

30 min of reaction time, although it is a lower value than DBTs% conversion, this is a good performance taken into account their minor electron density.

3.8. Reusability

Reusability is an important parameter from the industrial point of view. In order to evaluate the stability of Ti-CMK-3-ST catalyst obtained by the short time method, the spent material was washed several times in excess of methanol and water, and finally filtered. The solid was dried and then desorbed in nitrogen flow of 20 mL/min from $25^\circ C$ to $470^\circ C$ following the same procedure as described in the experimental section. Fig. 13 shows that the catalyst retains its activity after several catalytic cycles.

The loss of activity found in ODS of DBT using vanadium-modified CMK-3 in our previous work [14] was about 13% after the third recycle compared to the fresh catalyst. The performance and reusability of Ti-CMK-3-ST synthesized by the short time method widely overcame the behavior of the vanadium or titanium-mesoporous carbons previously synthesized. In this work, only after the fifth recycle a slight decrease in conversion is observed, but is not more than 10% after 8 recycles. The good stability and reusability makes this catalyst suitable for industrial purposes.

4. Conclusion

The method of synthesis developed in this work allowed us to obtain the ordered titanium-mesoporous carbon reducing time and cost by avoiding the use of the expensive hard template. The precursors of silicon, carbon and titanium were incorporated together with the other components during the only step of the synthesis. The reduction of time and energy consumption is about 60% reducing the overall cost of the process of synthesis. The new material obtained had high specific surface area, pore volume and narrow mesopore size distribution, with highly dispersed Ti species.

Thus, in this paper we demonstrate that Ti-CMK-3 synthesized by the short time method is active for ODS of several sulfur compounds at mild conditions. Different parameters were studied in order to find the best performance of this catalyst.

Ti-CMK-3 synthesized by one-pot method was capable to process high loaded feed (80% of 2000 ppm S) in 30 min at 60° and O/S molar ratio of 16. When H_2O_2 content and temperature were increased, sulfur was completely removed. This catalyst was also very active in the removal of more refractory sulfur compounds as thiophene and

benzothiophene.

The higher catalytic activity of Ti-CMK-3 obtained by the short time method can be explained by considering that more dispersed titanium sites are obtained when this direct method of synthesis was applied.

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