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Oxidative desulfurization of dibenzothiophene compounds with titania based catalysts

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ABSTRACT

Titanium oxide nanotubes (TiN) and a titanium-substituted mesoporous SBA-15 molecular sieve were synthesized, characterized and tested in oxidative desulfurization (ODS) of dibenzothiophene compounds prevailing in diesel fuel. Two commercial titanias were used as references. The structural and textural properties of the titania based catalysts were characterized by X-ray diffraction (XRD), transmission and scanning electron microscopy (TEM and SEM-EDX), and nitrogen adsorption–desorption measurements. The ODS tests were carried out in three-phase (L–L–S) system but also in a two-phase (L–S) system to evaluate the oxidation taking place in the liquid phase only. The reaction results indicate that the best catalytic performance is achieved with TiN and that for the most active catalysts the removal of sulfur could be limited by the mass transfer between the two liquid phases (solvent extraction and oil).

1. Introduction

Oxidative desulfurization (ODS) is a current process that has been discussed recently in several publications [1–3] as an alternative to reduce the sulfur content in transportation fuels. The process takes place in a three-phase (L–L–S) system and generally consists of two simultaneous steps of extraction and oxidation [4,5]. The sulfur compounds in the diesel are extracted to a solvent phase, where the sulfur compound contacts the solid catalyst in presence of an oxidant agent, producing the sulfone derivatives of the corresponding sulfur compound. The interesting elements in this process are the absence of hydrogen, and the fact that, in some cases, contrary to the conventional hydrodesulfurization (HDS) process, the ease to oxidize the S-bearing molecules increases as their desulfurization reactivity decreases [6] when peracids like formic or acetic acid are used as oxidizing agents. In contrast, the oxidation with organic hydroperoxides occurs in presence of a solid catalyst and the reactivity trend order is inverse [4,7]. Nevertheless, in both cases the ODS process is conducted under very mild conditions (atmospheric pressure and 60–90 °C), compared with the conventional HDS process, where pressures higher than 30 bar and temperatures from 300 to 380 °C are commonly used.

Dibenzothiophene derivatives (DBTs) are the most difficult sulfur species to eliminate from transport fuels due to its low reactivity [1]. Therefore, the ODS process wherein the DBTs are converted to its corresponding sulfones is an approach that is being actively pursued using a variety of different methodologies [2–4].

The oxidation of DBTs with organic hydroperoxides or H_2O_2 is known to occur over various catalytic heterogeneous systems, such as supported oxide metals [7,8] or titanium silicalites [9–11]. Titanium silicalites are active in the presence of diluted aqueous solutions of H_2O_2, whereas organic hydroperoxides are the oxidants of choice for the former catalysts. Typical catalytic supports, such as alumina, titania and silica, present low ODS activity of DBTs and their activity differences cannot be correlated to surface area [8]. In contrast, Otsuki et al. [12] evaluated similar materials as catalysts for ODS of a middle distillate using t-butyl hypochlorite as oxidant, and they obtained relatively high activities.

The use of new large surface area Ti-containing materials such as mesoporous Ti-modified SBA-15 (TiSBA15) and titanium oxide nanotubes (TiN) could be interesting alternatives as catalysts for the ODS process. TiN prepared by hydrothermal synthesis have attracted special attention because these materials can be potentially used in several catalytic applications due to three main advantages: high specific area, low cost, and feasibility to be produced in large quantities [13].

The aim of this study is to evaluate the ODS activity of TiN, TiSBA15, using as reference catalysts two commercial titanias with different surface area, Degussa P25 and Hombiteck TiO_2.

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2. Experimental

Titanium oxide nanotubes (TiN) and Ti-substituted SBA-15 (TiSBA15) were prepared and characterized by several techniques. The reference catalysts, TiO_2 Hombiteck (TiH) and Degussa (P25), were purchased and used as supplied.

2.1. Preparation

Titanium oxide nanotubes (TiN) were prepared following the method reported by Kasuga et al. [13]. Briefly, 2 g of TiO_2 (P25, Degussa) were mixed with 134 mL of an aqueous solution of NaOH (10 M). The mixture was kept under stirring in a Teflon autoclave at 110 °C for 24 h. Then, the autoclave was quickly cooled to room temperature and opened to recover a white precipitate, which was thoroughly washed with distilled water and with an aqueous solution of HCl (0.1 M) to eliminate the remaining sodium ions. The product was then filtered and dried in air at 120 °C for 12 h. The dried material (TiN) was calcined in static air at 300 °C for 4 h. After calcination the titanium nanotubes were labeled TiNC.

Ti-substituted SBA-15 (TiSBA15) was prepared by chemical grafting of Ti onto pure siliceous SBA-15, previously synthesized according to the procedure described elsewhere [14]. Titanium(IV) isopropoxide solution in 1-propanol (97%, Aldrich), was used as titania source and dry ethanol (EtOH, Aldrich, 99.999%) as the solvent. In the grafting procedure, calcined SBA-15 was slurried in dry EtOH containing the Ti source for 8 h at room temperature. To eliminate the excess Ti source the filtered material was washed with EtOH three times. The solid product was then dried in air at room temperature and calcined in static air at 550 °C for 5 h.

2.2. Characterization

SEM images and EDX microanalysis were obtained using a JEOL JSM-5900LV scanning electron microscope equipped with an Oxford-Isis energy dispersive X-ray analyzer. TEM images were obtained using a JEOL2010 transmission electron microscope at 200 kV. For TEM analysis the samples were dispersed by ultrasonication in ethyl alcohol for 20 min and a drop of the supernatant liquid was placed onto a holey carbon film supported on a copper grid. The structure of the materials was characterized by X-ray diffraction (XRD) using a Siemens D5000 diffractometer with a Cu Kα source (λ = 1.5406 Å). Textural properties were determined by nitrogen physisorption, using a Micromeritics TriStar apparatus. The specific area was calculated from the Brunauer–Emmett–Teller (BET) equation and the pore size distribution was analyzed with the Barrett–Joyner–Halenda (BJH) method.

2.3. Catalytic experiments

All reactants were purchased from Sigma/Aldrich and used without further treatment. Dibenzothiophene (DBT) and its alkyl derivatives (4-MDBT, 96% and 4,6-DMDBT, 97%), which represent sulfur species in diesel, were selected to evaluate the catalysts activity in the ODS reaction. The reaction results obtained in the typical extraction–oxidation ODS system consisting of two liquid phases, diesel and extraction solvent, and a solid catalyst in a three-phase system (L–L–S) were compared with those obtained in a two-phase ODS system (L–S), using DBTs in acetonitrile as model diesel. The two-phase experiments were performed to evaluate the liquid phase oxidation without the limitations imposed by the mass transfer from liquid to liquid. For both cases, model diesel (DBTs in decane) for the three phase system, and DBTs in acetonitrile for the intrinsic activity studies, the feedstock for the ODS reaction was prepared with 610 S ppm: 220 of DBT, 200 of 4-MDBT and 190 of 4,6-DMDBT. Hydrogen peroxide (H_2O_2, 30 wt.%) was used as oxidant (O/S = 6 initial ratio, mole/mole). In L–L–S system, acetonitrile (99.9%) was used as extraction solvent in a diesel/solvent ratio equal to one.

A batch reactor, fitted with condenser, mechanical stirrer and a thermocouple, was used to carry out the oxidation reaction. The reactor was immersed in a thermostatically controlled water bath to carry out the reactions at 60 °C. In a typical run, the water bath was first heated up and stabilized to the desired reaction temperature and the solution (50 mL) containing the reactants was added to the reactor. Then oxidant and catalyst (100 mg) were introduced into the reactor with vigorous stirring (~500 rpm). At 15, 30, 60, and 90 min, reaction samples were withdrawn and injected at room temperature to the GC-FID. GC-FID analyses were performed with an HP5890 Series II Gas Chromatograph equipped with a PONA capillary column (Methyl silicone Gum, 50 m × 0.2 mm × 0.5 μm film thickness). Reactant and product identifications were achieved by comparing retention times in the GC-FID, a GC-PFPD (Varian CP-3800), and from results obtained with a GC–MS (HP5890 Series II with MS detector). The H_2O_2 content was measured by standard iodometric titration.

3. Results and discussion

First we will present the characterization of the catalysts. After that, catalytic activity in ODS will be analyzed in terms of the sulfone yields of DBTs.

3.1. Characterization of catalysts

SEM observations of the as-prepared TiN material showed the presence of bundles of filaments of different widths, 40–100 nm, and lengths of several hundreds of nanometers (Fig. 1a). The presence of nanotubes was made evident by the observation of the samples by TEM. Fig. 1b and c shows some details of the tubular structure of the filaments. The nanotube walls seem to be formed by several layers separated by ca. 0.7 nm, in good agreement with previous reports of 0.78 and 0.71 nm in the separation of the layers forming the nanotube wall [15,16]. The inner diameter of the observed TiN ranged from 5 to 15 nm, and the outer diameter from 11 to 18 nm.

Fig. 2 shows the XRD diffractograms of TiN calcined at different temperatures. The diffractogram of the uncalcined sample (TiN) presents peaks at 2θ = 9.54, 24.40, 26.98, 32.28, 48.40 and 50.02°, which have been previously assigned to trititanate or trititanic acid ($H_2Ti_3O_7$) in tubular form [16,17]. These peaks diminish their intensity when the material is calcined at 300 °C (TiNC), while the main peak corresponding to titanium oxide-anatase at 2θ = 25.4° begins to appear. After calcination at 400 °C the trititanate peaks disappear and instead the peaks corresponding to TiO_2–anatase are clearly displayed. Calcination at 500 °C only increases the crystallization of the anatase phase. According to the TEM results, it is evident that as the calcination temperature is increased, the tubular structure of the TiN, which was well defined for the as-prepared material, becomes less defined at 300 °C and clearly deteriorated at 500 °C. In fact at 500 °C the formation of some round anatase particles of about 20 nm is clearly evident. For the ODS tests the uncalcined material (TiN) and that calcined at 300 °C (TiNC) were selected. Textural properties of these materials are presented in Table 1.

Titania was incorporated to the surface of SBA-15 by chemical grafting [18]. This method was chosen because of the advantages it has in comparison with the incorporation of Ti into the SBA-15 structure during the hydrothermal synthesis, or by incipient wetness impregnation. Thus, (i) chemical grafting allows deposition of highly dispersed Ti oxide species on the surface of the parent SBA without altering significantly its structure and texture and (ii)

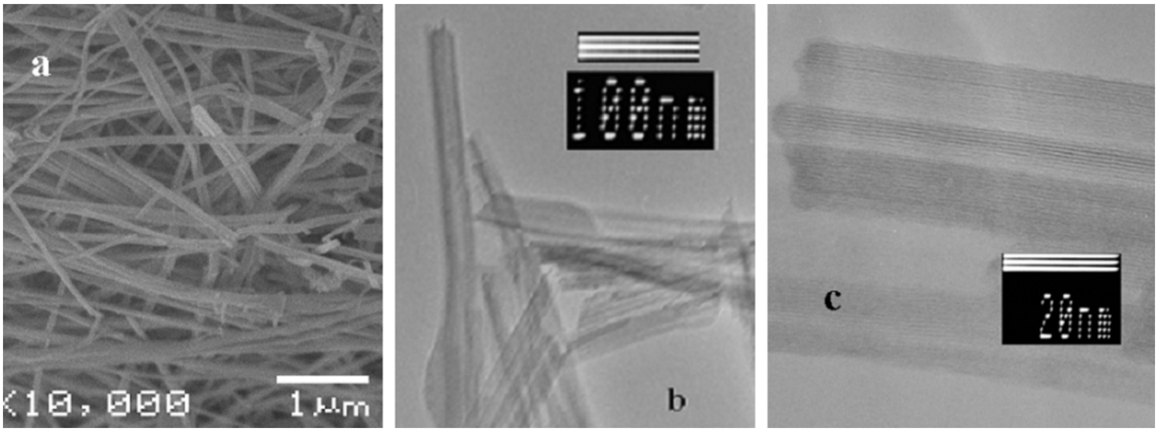

Fig. 1. (a) SEM image of TiN, (b) TEM image of TiN, and (c) magnified TEM image of a nanotube, where a central channel and wall details can be observed.

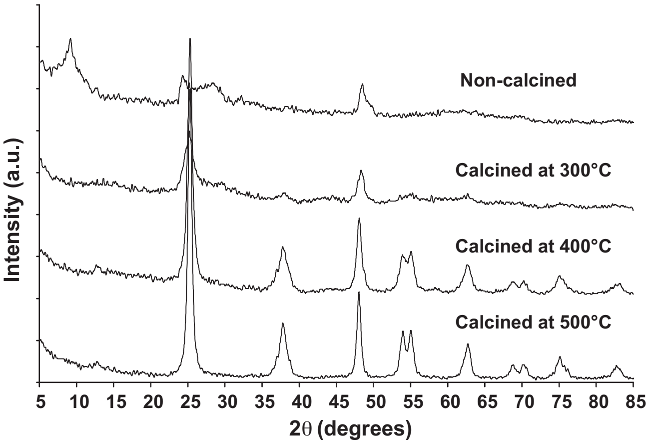

Fig. 2. XRD diffractogram of TiN as-prepared and calcined in static air at different temperatures.

grafted species are located on the support surface, and this makes them accessible for the interaction with other species.

Ti modified SBA-15 was prepared so that the theoretical metal oxide loading would be 19 wt.% of TiO_2. The results from chemical analysis show that TiSBA15 has a chemical composition similar to the expected one. Nitrogen adsorption–desorption isotherms of SBA-15 and TiSBA15 are shown in Fig. 3. The shape of the N_2 adsorption–desorption isotherms is characteristic of well-formed SBA-15 materials. Incorporation of Ti to SBA-15 by grafting does not produce changes in the characteristic shape of the isotherm, indicating that Ti incorporation does not affect the original pore structure of the parent SBA-15, although some decrease in the amount of adsorbed N_2 is observed. The uniform mesopore diameter of TiSBA15 sample is equal to 59 Å and 64 Å in the parent SBA-15. Taking into account the distance between pore centers (a_0) measured by small-angle XRD, the estimated pore wall thickness (d) for TiSBA15 is 46 Å and 40 Å for the parent SBA-15. Textural properties of these materials are presented in Table 1.

Table 1
Textural properties of the catalysts.

Sample	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (Å)
TiN	318	1.14	110
TiNC	296	1.16	118
TiSBA15	510	0.80	59
SBA-15	869	1.19	64
TiH	120	0.38	130
P25	53	0.25	172

The small-angle XRD pattern of the SBA-15 and TiSBA15 exhibits three well-resolved peaks characteristic of SBA-15, namely, a very intense peak at about 1.0° (2θ) and two distinct weak peaks between 1.58 and 2.08 (2θ) (Fig. 4). These XRD signals are related to the (1 0 0), (1 1 0) and (2 0 0) reflections associated with p6mm hexagonal symmetry of the pore structure. The high-intensity (1 0 0) peak reflects a d-spacing of 86.5 Å and the following peaks have d values of 51.6 Å for the (1 1 0) peak and 45.0 Å for the (2 0 0) peak, consistent with a bi-dimensional hexagonal arrangement of the pores with a unit-cell parameter $a_0 = 100$ Å. The structural parameters obtained from XRD and N_2 physisorption are well in line with the corresponding values measured directly from the TEM images. The above results point out a high dispersion of the grafted Ti species.

XRD patterns of TiO_2 Hombiteck (TiH) and Degussa (P25) (not shown) present the main diffraction peaks attributed to titania–anatase (JCPDS-ICDD File Card No. 21-1272) in $2\theta = 25.4°$ (1 0 1), 37.9° (0 0 4), 48.0° (2 0 0), 53.8° (1 0 5), and 55.2° (2 1 1).

The textural characteristics (surface area, total pore volume and pore diameter) of all the Ti-containing materials used in this work are given in Table 1.

3.2. Catalytic performance of the catalysts

The extraction–oxidation system consists of two liquid phases, model diesel and extraction solvent, and a solid catalyst in a three-

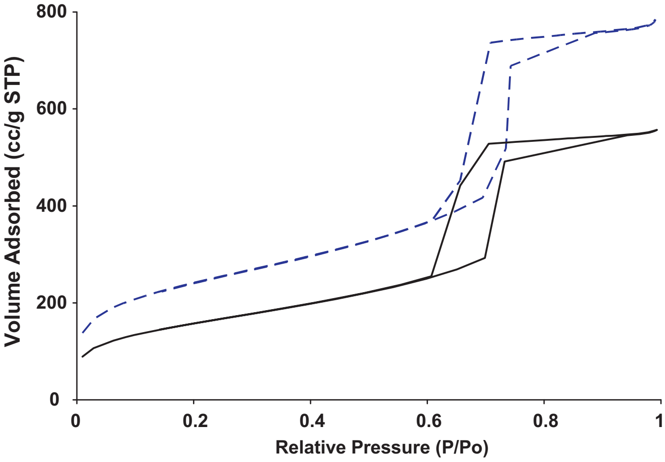

Fig. 3. Nitrogen adsorption–desorption isotherms of (- - -) SBA-15 and (—) TiSBA15.

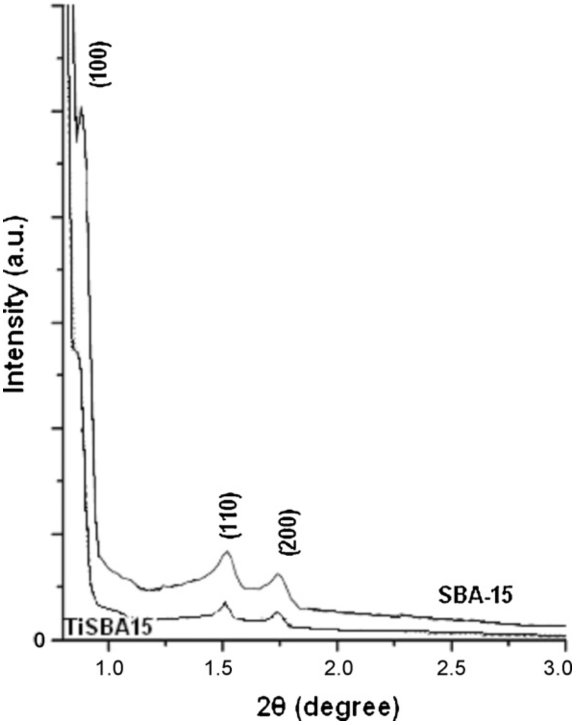

Fig. 4. Small-angle XRD patterns of SBA-15 and TiSBA15.

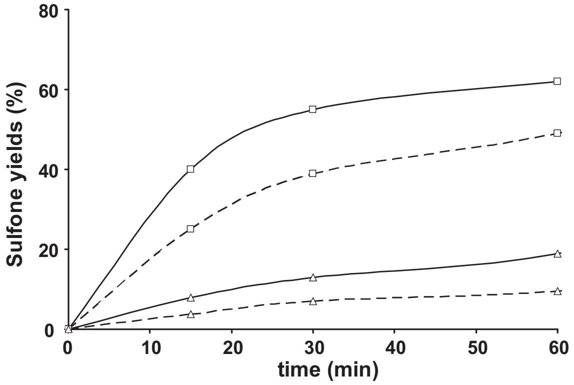

Fig. 5. Yield to (□) DBT-sulfone and (△) 4-MDBT-sulfone vs. reaction time for (—) L–S and (- - -) L–L–S phases systems, with TiH.

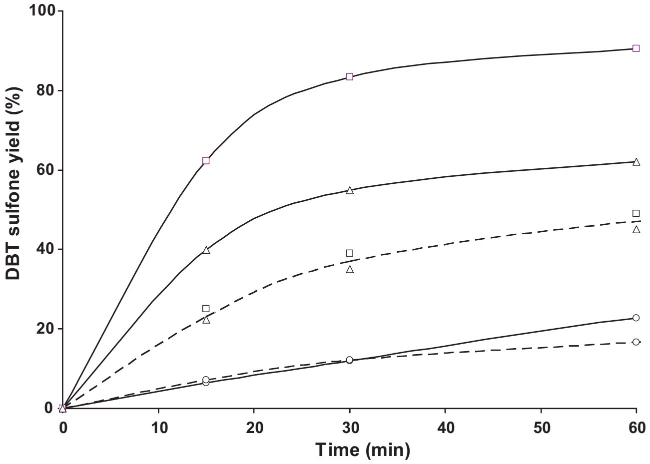

Fig. 6. Yield to DBT-sulfone vs. reaction time for (—) L–S and (- - -) L–L–S phase systems, using TiN (□), TiH (△) or P25 (○) as catalyst.

phase system (L–L–S). When these phases are mixed, DBTs present in the diesel phase are partially extracted to the solvent phase, where oxidant reagent is predominantly present, and the oxidation reaction takes place therein producing the corresponding sulfone [4,5,8]. As DBTs-sulfones are obtained only in the solvent phase, the process consists of extraction–reaction consecutive steps. If the liquid–liquid extraction step occurs rapidly the oxidation of the DBTs is the rate determining step of the ODS process. Otherwise the transfer of DBTs from the diesel phase to the solvent phase will impose some limitations to the rate of the global process. To demonstrate the effect of the extraction process over the global oxidation rate a comparison was made between the L–S and L–L–S phases systems. The two phase system uses the same solvent as the three phase system (acetonitrile), which contains the different DBTs used to model the sulfur compounds in diesel. In other words, the experiment with the two phase system avoids the mass transfer limitations imposed during the extraction step and will allow to estimate the intrinsic rate of the catalytic step. A comparison of the DBT and 4-MDBT sulfones yield for the L–S and L–L–S phase systems using TiH as catalyst is presented in Fig. 5. It can be observed that L–S system gives higher sulfone yields than the L–L–S system, indicating that the overall sulfur removal rate is affected by the mass transfer between the two liquid phases, and therefore, that a useful comparison of the activity of the various catalysts can only be made eliminating the L–L mass transfer effects. For all the other catalysts similar results were obtained. Fig. 6 presents the reaction results obtained during ODS of DBT using three different catalysts (TiN, TiH and P25) in L–S and L–L–S phases systems. For all catalysts the two phase system performs better supporting the conclusions drawn from Fig. 5. Additionally, the experiments show clear evidence that the nature of the Ti catalyst significantly affects the sulfone yield in both the two and three phase systems. In fact at 60 min reaction time in the two phase system TiN displays a sulfone yield 1.4 times that of TiH and 3.9 times that of P25. It is clear that when the rate of reaction is low, as for P25, the difference between the L–S and L–L–S systems is smaller. In contrast, for a highly active catalyst as TiN the difference is high. Therefore, to compare all the different catalysts a two phase system (L–S) should be used.

Fig. 7 shows DBT-sulfone yields in a L–S system for all catalysts during 60 min of reaction. TiNC reaches the highest activity of the series, with 99% of DBT-sulfone production. Whereas TiSBA15, with the highest specific area (Table 1), only achieves 78% of DBT-sulfone yield, indicating that the observed differences in activity are not

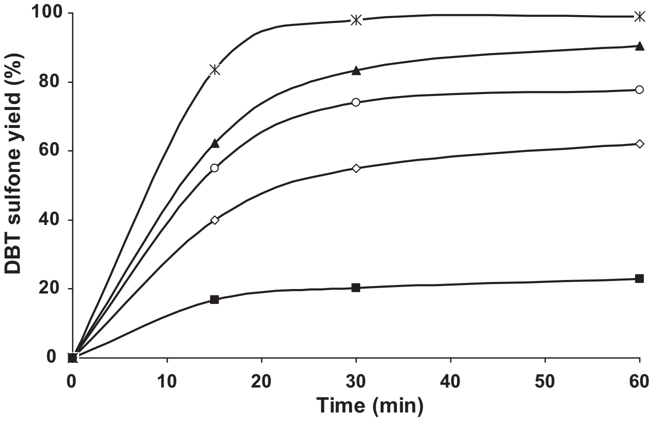

Fig. 7. DBT sulfone yields vs. reaction time with TiNC (X), TiN (▲), TiSBA15 (○), TiH (◊), and P25 (■).

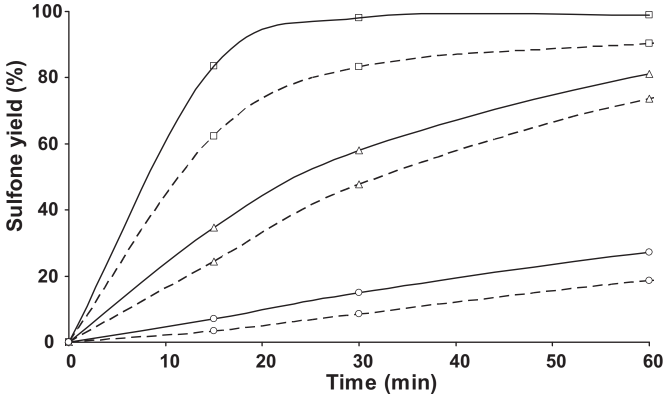

Fig. 8. Sulfone yields of (□) DBT, (△) 4-MDBT, and (○) 4,6-DMDBT vs. reaction time with TiN (- - -) and TiNC (—).

the result of differences in surface area. It must be considered that TiSBA15 only has 19 wt.% of TiO_2 whereas TiN, TiH and P25, which are titanium compounds (trititanate and TiO_2-anatase) achieved 90, 62, and 23% of DBT-sulfone yield, respectively. Although the Raman spectrum of TiSBA15 (not shown) presents clearly the main band of TiO_2-anatase at 144 cm^{-1} it is highly possible that on the catalyst surface exist isolated Ti species linked to Si atoms through oxygen bridges, the latter presenting lower activity than TiO_2 particles.

It is interesting to note that calcination of trititanate (TiN) leads to a catalyst TiNC with less surface area but higher activity. To enquire more on this difference, experiments with different DBTs were made with these two catalysts. The results are presented in Fig. 8. For these solid catalysts the usual reactivity order [4,7]: DBT > 4-MDBT > 4,6-DMDBT is maintained and TiNC displays higher sulfone yield in all cases. Since calcination of trititanate leads to TiO_2-anatase this result indicates that TiO_2 is the main active phase. In fact if one compares the catalysts containing only titania, TiNC, TiH and P25, the conversion obtained is closely proportional to the surface area of the catalyst (see Table 1). Fig. 9 presents the initial reaction rate values for all catalysts during the ODS of DBT, 4-MDBT, and 4,6-DMDBT, which confirm the previous findings.

H_2O_2 profiles were monitored in every reaction test and clear changes in the percentage of H_2O_2 remaining after reaction were observed (Fig. 10). The calcined titanium oxide nanotubes present the higher ODS activities, followed by the uncalcined titanium nanotubes (trititanate, TiN), which explains the low amounts of oxidant after reaction. H_2O_2 titrations with commercial titanias (TiH and P25) demonstrate that hydrogen peroxide is not fully decomposed, since more than 75% of the oxidant remains in the system after reaction time, according to the lowest ODS activities observed for these catalysts. 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 the sulfur compound (DBTs) to the corresponding sulfone.

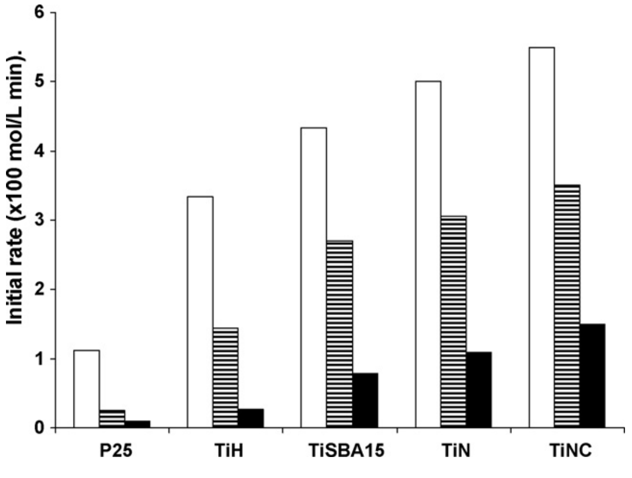

Fig. 9. Initial ODS rate of (□) DBT, (—) 4-MDBT, and (■) 4,6-DMDBT sulfones.

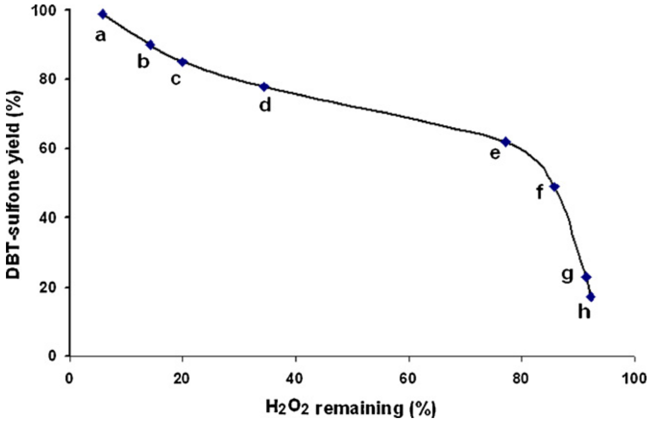

Fig. 10. DBT-sulfone yield vs. H_2O_2 remaining after ODS reaction, with TiNC (a), TiN (b), TiSBA15 (d), TiH (e) and P25 (g) in L–S phases system. Also, with TiN (c), TiH (f) and P25 (h) in L–L–S phases system.

Comparison of the surface area and activities of TiNC and TiN shows that TiNC with a surface area of 296 gives a conversion at 60 min of 99% while TiN with surface area 318 only gives 90.5% conversion. This indicates that the structure of TiO_2 in TiNC is more active than that of trititanate for the decomposition of H_2O_2 towards reactive oxygen. In line with this, the two commercial titanias that have also a surface consisting mainly of TiO_2 present an activity, compared to TiNC, closely proportional to the surface area exposed to the reactants (see Table 1).

TiSBA15 cannot be compared in the same terms because in spite of its high surface area, not all the surface exposed to the reactants consists of Ti oxide species. Since SBA-15 is not active for the ODS reaction [8] the high activity displayed by TiSBA15 is due to Ti and indicates a good dispersion of the titanium species on the surface of the support. The results suggest that higher loading of well dispersed Ti on SBA-15 may render a promising catalyst with an activity close to that of TiNC.

4. Conclusions

Different titanias and catalysts containing Ti have been evaluated in two (L–S) and three (L–L–S) phase systems for the ODS reaction of DBTs. The following conclusions can be extracted from the results:

In the L–L–S three phase system mass transfer between liquid phases limits sulfur removal for the high activity catalysts. The reaction rate for the lowest activity catalyst (P25) is not limited by L–L mass transfer.

Calcined and uncalcined Ti nanotubes are highly active catalysts for the ODS reaction.

The activity of the TiO_2-containing catalysts seems to be directly proportional to the exposed TiO_2 surface area.

The formation of reactive oxygen to produce the corresponding DBT-sulfone is not exclusive of TiO_2 structures since trititanate nanotubes also display high activity.

Ti-modified SBA-15 with 19 wt.% of TiO_2 presents an intermediate activity due to the presence on the surface of TiO_2 particles but possibly also Ti–O–Si isolated species with different activity.

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