

Heterogeneous oxidative desulfurization catalysed by titanium grafted mesoporous silica nanoparticles containing tethered hydrophobic ionic liquid: A dual activation mechanism

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Abstract

In this study, heterogeneous catalysts containing ionic liquid and/or titanium have been prepared and used for oxidative desulfurization. For the synthesis of hybrid mesoporous silica nanoparticles (ILBF₄-MSN), a grafting method has been employed with the ionic liquid 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (ILBF₄) which contains a long alkyl chain. Titanium hybrid mesoporous silica nanoparticles (ILBF₄-x%TiCp₂-MSN) and mesoporous silica nanoparticles containing titanium (TiCp₂-MSN) have also been prepared using titanocene dichloride. The catalyst containing ionic liquid and titanium, ILBF₄-3%TiCp₂-MSN exhibited the highest desulfurization efficiency (99.1%) in model oil with high concentration of DBT and using H₂O₂ as oxidant. In addition, the effect of immobilization of the ionic liquid on titanium materials has been investigated by solid-state ¹³C, ^{47/49}Ti and ¹⁹F NMR spectroscopy and solid state electrochemical techniques. The titanium species and ionic liquid play an important role in the oxidative desulfurization reaction since they might activate synergistically sulfur derivatives and enhance the process.

Keywords: hydrophobic ionic liquid, mesoporous silica nanoparticles, heterogeneous oxidative desulfurization, H₂O₂, dual activation

1. Introduction

One of the major concerns about environmental global pollution is the emission of nitrogen and sulfur oxides due to the presence and burning of sulfur and nitrogen low to medium molecular weight organic compounds in fuel. Moreover, sulfur species act as an efficient poison for the catalysts used in vehicles to reduce CO and NO_x emissions. Strict regulations have been imposed on the sulfur content of fuels to reduce the emissions and ultra-low sulfur diesel fuel is today required. Japan has limited the sulfur content of gasoline fuel to less than 10 ppm since 2007 and in Europe the maximum level has been fixed at 10 ppm since 2009 [1]. In the U.S., the limit of sulfur content of highway diesel have been restricted to less than 10 ppm since 2017 and China have reduced sulfur content of gasoline and diesel fuels from 50 ppm to less than 10 ppm [2].

The conventional technology to remove sulfur species is hydrodesulfurization which requires high temperature and hydrogen pressure to obtain ultra-low sulfur diesel (ULSD). Thus, several processes have been developed using mild conditions such as adsorptive desulfurization (ADS) [3], extractive desulfurization (EDS) [4], biodesulfurization [5], photo-oxidative desulfurization [6] and oxidative desulfurization (ODS) [7], which will be the focus of this study. ODS methodology involves the oxidation of sulfur derivatives to the corresponding sulfones which can be removed from fuel by extraction or absorption [8]. In this regard, titanium containing materials, such as Ti-HMS [9], TS-1 [10], Ti-SBA-15 [11] and more recently, TiO₂ [12], TiO₂/SBA-16 [13], nano-TiO₂ [14] and Ti-based MOFs [15], have demonstrated to be efficient catalysts for the ODS process. For example, hierarchical TS-1 zeolite with an average diameter of 30 nm exhibits higher catalytic activity in ODS of dibenzothiophene (DBT) than that of traditional TS-1 because of enhanced accessibility owing to the existence of intercrystal mesopores [16]. Chica et al. [17] studied the ODS of sulfur containing compounds with tertbutyl hydroperoxide as oxidant, on different metal containing molecular sieves. They concluded that Ti-MCM-41 showed better catalytic activity than MoO_x/Al₂O₃ and Ti-beta catalysts. Thus, the deactivation of MoO_x/Al₂O₃ due to metal leaching and sulfone adsorption can be inhibited in Ti-MCM-41 system by silylation of surface silanol groups affording a more hydrophobic and stable catalyst. Managing a similar strategy Kim et al. [11] synthesized titanium-containing organosilylated mesoporous silica (Ti-SBA-15) by

immobilization of titanium chelates on SBA-15 and subsequent functionalization with tetramethyldisilazane. These silica materials exhibited high efficiency for ODS using cumene hydroperoxide (CHP) as oxidant at 80 °C. The replacement of organic oxidants such as TBHP or CHP by H₂O₂, as alternative green and environmentally friendly oxidant, adds additional drawbacks in ODS processes since the system becomes biphasic; thiophene derivatives (thiophene, 2-methylthiophene, dibenzothiophene, 2-methylbenzothiophene, etc...) are present in oil phase and H₂O₂ in aqueous phase. To improve the oxidative desulfurization activity in the presence of heterogeneous catalyst and subsequent extraction of produced sulfone, polar solvents such as acetonitrile [13], methanol [15], ionic liquids [18] or eutectic solvents [19] are commonly used rendering liquid-liquid-solid systems (L-L-S). In this case, the sulfur compound is oxidized to the corresponding sulfone in the polar or ionic liquid phase and hence the use of large amounts of solvents, such as acetonitrile or methanol; or ionic liquids, less toxic but available at relatively high cost, is required. As an example, Llanos and co-workers [20] carried out the ODS of DBT in an organic biphasic system (n-hexadecane/acetonitrile) in the presence of Fe-TiO₂ as catalysts using H₂O₂ as oxidant and acetic acid as promoter. Recently, Fraile et al. [21] have published a different approach in order to avoid the use of a co-solvent. They have prepared an active catalyst for ODS of DBT in isooctane with H₂O₂ by immobilization of titanium tetraisopropoxide on silylated commercial amorphous silica highly hydrophobic. An alternative, that brings together some of these interesting approaches, is that published by Ding and coworkers [22] who designed a heterogeneous catalyst by immobilization of active species iron-based redox ionic liquid on SBA-15 for extractive catalytic oxidative desulfurization (ECODS) with conventional ionic liquid as extractant. Sharing this approach, other groups have prepared phosphotungstate-coupled polyionic liquids [23] or phosphomolibdate-coupled silica immobilized ionic liquids [24] highly active for heterogeneous ODS under mild conditions. PW-coupled polyionic liquids system's catalytic activity presents at first an increase and then a decrease trend with increasing alkyl chain length for PW-coupled polyionic liquids with carbon chains of different lengths (increase from 2 to 4 and decrease from 8 to 12) [25].

Based on these reports, we have developed a new strategy to approach this issue. A heterogeneous catalyst has been synthesized by simultaneous immobilization of

titanocene dichloride and a long alkyl chain ionic liquid on mesoporous silica nanoparticles. We expect that the incorporation of 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate, with a cationic 4,5-dihydroimidazolium group and an octyl chain substituent, will enhance the titanium based material activity as catalyst, for the oxidative desulfurization of DBT in model oil using H₂O₂ as oxidant and without the presence of a co-solvent.

2. Methodology

2.1. Materials

The catalysts were prepared using standard Schlenk tube techniques under an atmosphere of dry nitrogen or argon. Tetraethylortosilicate (TEOS) 98%, sodium hydroxide 97%, hydrogen peroxide 30%, triethoxy-3-(2-imidazolin-1-yl)propylsilane $\geq 97\%$, 1-chlorooctane 99%, dibenzothiophene 98%, dodecane $\geq 99.8\%$ and n-octane were purchased from Sigma Aldrich and used as received. Hexadecyltrimethylammonium bromide (CTAB) 99.7% was purchased from Acros and titanocene dichloride $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ 97% was purchased from Alfa Aesar and used as received. Organic solvents (toluene, hexane, tetrahydrofuran, acetone, dichloromethane and chloroform) were purchased from VWR International, distilled and dried before use according to conventional literature methods. Water was obtained from a Millipore Milli-Q system (Waters, USA). The mesoporous silica nanoparticles (MSN) were synthesized according to previously published procedures [26]. The synthesis and characterization of 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride or tetrafluoroborate (ILCl or ILBF₄) are included in the Supplementary material (see Scheme S1, Fig. S1 and Fig. S2).

2.2. Preparation of heterogeneous catalysts

2.2.1. Synthesis of MSN functionalized with ionic liquid (ILBF₄-MSN)

A solution of liquid ionic 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (ILBF₄) (0.94 g, 2 mmol) in chloroform was added to 1 g of MSN, previously dehydrated. The suspension was refluxed for 24 h and then the solid was obtained by filtration and washed with chloroform (3 x 20 mL). The solid obtained was dried under vacuum and labelled as ILBF₄-MSN.

2.2.2. Synthesis of titanium catalyst (TiCp₂-MSN)

In a typical experiment, 1.0 g of dehydrated MSN was suspended in 20 mL of THF and a solution of $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ (0.5 g, 2 mmol) in 20 mL of THF was added. The suspension was refluxed at 70 °C for 24 h. The solid was isolated by filtration and washed

with THF (3 x 20 mL). The resulting material was dried under vacuum and designated as TiCp₂-MSN.

2.2.3. Synthesis of titanium catalyst containing ionic liquid (ILBF₄-x%TiCp₂-MSN)

In a typical experiment 1.5 g of x%TiCp₂-MSN was suspended in 30 mL in chloroform and a solution of ILBF₄ (0.5 g, 2 mmol) in 20 mL of chloroform was added. The mixture was heated at 70 °C for 24 h. The solid was isolated by filtration and washed with chloroform (3 × 20 mL). The material obtained was dried under vacuum and designated as ILBF₄-x%TiCp₂-MSN.

2.3. Characterization

X-ray diffraction (XRD) patterns of the silicas were obtained on a Phillips Diffractometer model PW3040/00 X'Pert MPD/MRD at 45 kV and 40 mA, using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$). The titanium content was determined by XRF. N₂ gas adsorption-desorption isotherms were obtained using a Micromeritics TriStar 3000 analyzer, and pore size distributions were calculated using the Barret-Joyner-Halenda (BJH) model on the adsorption branch. Infrared spectra were recorded on a Nicolet-550 FT-IR spectrophotometer (in the region 4000 to 400 cm⁻¹) as KBr disks. ¹H NMR and ¹³C NMR spectra were recorded on a Varian Mercury FT-400 spectrometer. Transmission electron microscope (TEM) images were obtained using Philips Tecnai 20 operating at 200 kV. The samples for TEM characterization were prepared by placing and evaporating a drop of the sample in ethanol on carbon-coated copper grid. Cross Polarization ¹³C CP/MAS NMR spectra were recorded on a Varian-Infinity Plus 400 MHz Spectrometer operating at 100.52 MHz proton frequency (4 μ s 90° pulse, 4000 transients, spinning speed of 6 MHz, contact time 3 ms, pulse delay 1.5 s). The DR UV-Vis spectroscopic measurements were carried out on a Varian Cary-500 spectrophotometer equipped with an integrating sphere and polytetrafluoroethylene (PTFE) as reference, with $d = 1 \text{ g cm}^{-3}$ and thickness of 6 mm. Elemental analyses were carried out by the Microanalytical Service of the Universidad Complutense de Madrid. The C, H and N analysis was accomplished by combustion analysis with elemental microanalyzers LECO CHNS-932. The voltammograms were recorded with a potentiostat/galvanostat Autolab

PGSTAT302 Metrohm. A conventional three electrode system was used throughout the electrochemical experiments at the room temperature with a modified carbon paste electrode (CPE) as working electrode, a platinum wire as auxiliary electrode, and a saturated Ag/AgCl/KCl (3 M) electrode (Metrohm) as reference electrode against which all potentials were measured in this paper. The carbon paste electrodes (CPE) were prepared by mixing with a pestle in an agate mortar the studied titanium silica based materials with graphite (Metrohm) (6-10% (w,w) ratio) and mineral oil as agglutinant (Aldrich) until a uniform paste was obtained. The resulting material was packed into the end of a Teflon cylindrical tube equipped with a screwing stainless steel piston providing an inner electrical contact. All the initial electrode activity could always be restored by simply removing the outer layer of paste by treatment with polishing paper. The phosphate buffer used as aqueous electrolyte solution in the cell was purged with highly purified nitrogen gas for at least 5 min to remove dissolved oxygen and then a nitrogen atmosphere was kept over the solution during measurements. The CV voltammograms of titanocene dichloride in organic media was performed with a THF/ NBu_4PF_6 0.2M solution under inert atmosphere and a glassy carbon as working electrode.

2.4. Oxidative desulfurization

In a typical experiment: catalyst (0.5-5 mol%), 18 mL of model oil obtained by dissolving 0.8 mmoles of DBT in n-octane (S-concentration of 1420 ppm) and 30% H_2O_2 (0.41 mL, 4 mmol) were incorporated in a reactor of a completely automated and monitored MultiMax™ parallel reactor system from Mettler Toledo. The reaction was stirred at 500 rpm and maintained at 60 °C. After the reaction time, the catalyst was separated by centrifugation and the sulfur content in model oil analysed by gas chromatograph with a flame ionization detector (Agilent 6890N, DB-Wax capillary column 25 m, 0.53 mm). Dodecane was used as an external standard to quantify the DBT in the samples. The sulfone product was also identified by liquid ^1H NMR spectroscopy. The catalysts were separated after the oxidative desulfurization, washed with dichloromethane and dried at 60 °C for 2 h. The catalyst $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$ was reused three times under identical experimental conditions to those previously used.

3. Results and discussion

3.1. Synthesis and characterization of heterogeneous catalysts

Titanium heterogeneous catalysts have been synthesized by the immobilization of titanocene dichloride, $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$, as metallic precursor on mesoporous silica nanoparticles followed by the reaction with the ionic liquid 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (ILBF_4). The choice of the support, in this case, mesoporous nanoparticles with spherical morphology, and the additional functionalization with a long ionic liquid, octyl-chain 4,5-dihydro-imidazolium aims to ensure the efficient dispersion of the heterogeneous titanium catalyst. The catalyst denoted hereafter as $\text{ILBF}_4\text{-}x\%\text{TiCp}_2\text{-MSN}$ is easily dispersed in water, as well as, in organic non polar solvents. The immobilized ionic liquid with long side alkyl chains exhibit amphiphilic-like features due to the combination of a non-polar alkyl chain part and a polar cation head group. These types of ionic liquids have demonstrated to be very useful in the extractive desulfurization of fuels based on the high affinity among the sulfur containing hydrophobic molecules and the pendant group of the cations. We want to take advantage of these versatile properties of the ionic liquids attached to the silica surface to improve the diffusion process of reactants to the titanium active sites and facilitate the desorption and extraction processes of sulfone derivatives formed to the bulk of the reaction without the requirement of an organic co-solvent. Previous studies have demonstrated the effectiveness of imidazolium type ionic liquids as extractant in ODS heterogeneous catalyzed process and the influence of the anion in the desulfurization rate, concluding that BF_4^- anion showed higher desulfurization capacity than PF_6^- or Cl^- anions [22]. Taking into account these results we have synthesized, in a straightforward reaction, the ionic liquid 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium chloride (ILCl) by reaction of 3-(2-imidazolin-1-yl)propyltriethoxysilane and 1-chlorooctane, and 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate (ILBF_4) and subsequent anion interchange in the presence of NaBF_4 . (see Scheme S1, Fig. S1 and S2). For comparison purposes, $\text{ILBF}_4\text{-MSN}$ and $\text{TiCp}_2\text{-MSN}$ materials have also been synthesized and tested in the catalytic reaction under study.

Firstly, the catalysts were fully characterized. The low angle X-ray diffraction patterns of $\text{TiCp}_2\text{-MSN}$, $\text{ILBF}_4\text{-MSN}$ and $\text{ILBF}_4\text{-}0.6\%\text{TiCp}_2\text{-MSN}$ samples (see Fig. S3) show

an intense peak at low 2θ values at $2\theta = 2.3^\circ$ and two additional weaker peaks at $2\theta = 4.0^\circ$ and 4.7° , assigned to (100), (110) and (200) reflections, respectively. The patterns correspond to an ordered hexagonal lattice (p6mm) and demonstrate that the ordered mesoporous structure of pristine MSN is well retained after the immobilization inside the mesoporous of both, titanium precursor and ionic liquid. Nitrogen adsorption-desorption isotherms of materials show that all the materials exhibit a type IV BET isotherms characteristic of mesoporous materials (Fig. 1). Three different sections are distinguished, below 0.30, between 0.30 and 0.90 and above 0.90. Small and narrow hysteresis loops are observed associated with the existence of capillary condensation into the mesopores at $P/P_0 \cong 0.30$. In addition, the samples have a secondary adsorption above $P/P_0 \cong 0.90$, which is attributed to the textural porosity formed by the aggregation of the silica nanospheres of small particle size after drying. The textural properties of the materials are shown in Table 1. The parent MSN material shows a surface area of $1040.28 \text{ m}^2 \text{ g}^{-1}$, a pore volume of $0.79 \text{ cm}^3 \text{ g}^{-1}$ and a pore diameter of 30.21 \AA . After the incorporation of the ionic liquid on the MSN surface (ILBF₄-MSN) a slight decrease in the S_{BET} , pore volume and average BJH pore diameter is detected, due to the presence of ionic liquid grafted onto the channels partially blocking the adsorption of nitrogen molecules. The highest decrease in the surface area and pore volume is observed, as expected, in ILBF₄-3%TiCp₂-MSN. In addition, TEM micrograph of pristine MSN confirms the hexagonal symmetry of mesoporous silica nanospheres and their aggregates. The nanoparticles are approximately $(78 \pm 6) \text{ nm}$ in diameter (see Fig. S4). The titanium and ionic liquid loadings were calculated by X-ray fluorescence (XRF) and elemental analysis, respectively. As can be seen in Table 1, TiCp₂-MSN material shows 0.75 % (0.16 mmol/g) of Ti and a negligible amount of Cl, this suggests that the major species is that in which the two Ti-Cl bonds of the titanocene dichloride complex $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2\text{Cl}_2]$ react with silanol groups on the silica surface to form pseudotetrahedral species $[\text{TiCp}_2(\text{OSi})_2]$. The material containing titanium and ionic liquid, ILBF₄-3%TiCp₂-MSN, shows lower loading of ionic liquid than ILBF₄-MSN and ILBF₄-0.6%TiCp₂-MSN materials, as expected. Since this bulky ligand is immobilized in a second step a lower amount of silanol groups are available; besides steric requirements imposed by both the ionic liquid and the previously grafted titanocene complex must be considered.

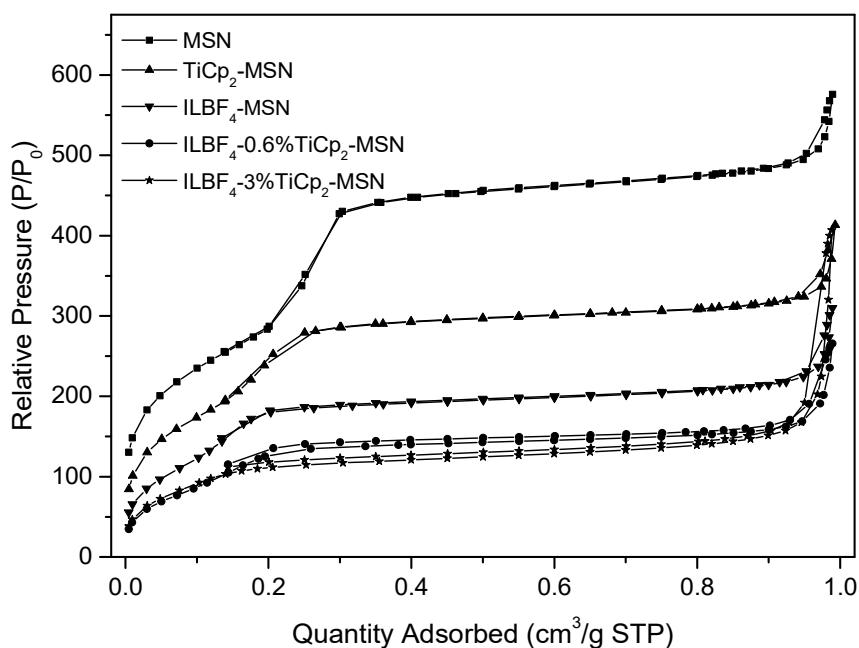


Fig. 1. Nitrogen adsorption-desorption isotherms of MSN materials. Type IV isotherms typical of mesoporous silica are exhibited.

Table 1. Textural properties and titanium and ionic liquid loading

Material	S_{BET} (m^2g^{-1})	Pore Volume (cm^3g^{-1})	Pore size (\AA)	Ti (%) ^a	Ti (mmol g^{-1})	ILBF ₄ (mmol g^{-1}) ^b
MSN	1040.28	0.79	30.21	-	-	-
ILBF ₄ -MSN	760.18	0.36	20.19	-	-	0.93
TiCp ₂ -MSN	836.32	0.52	22.75	0.75	0.16	-
ILBF ₄ -0.6%TiCp ₂ -MSN	529.14	0.30	22.34	0.56	0.12	1.20
ILBF ₄ -3%TiCp ₂ -MSN	423.72	0.31	21.54	3.02	0.63	0.84

^aThe titanium content was measured by X-ray fluorescence analysis (XRF).

^bThe ionic liquid loading was calculated based on elemental analysis measurements.

The FT-IR spectra of MSN materials are depicted in Fig. 2. All spectra show the characteristic bands of mesoporous silica nanoparticles. Two bands are observed at

3440 cm^{-1} and at 1634 cm^{-1} , attributed to O-H stretching and deformation vibrations of the physisorbed water molecules. The characteristic bands assigned to the Si-O-Si stretching vibrations appear at 1079, 960 and 801 cm^{-1} . After ILBF_4 immobilization new bands are observed at 2921 and 2850 cm^{-1} due to the $\nu(\text{C-H})$ stretching vibrations of the alkyl chain and at 1651 and 1450 cm^{-1} due to $\nu(\text{C=N})$ and $\delta(\text{C-H})$ vibrations of the 4,5-dihydro-imidazolium cation and alkyl chain, respectively (see Fig. S2). After titanium immobilization the most significant band should appear around 1400 cm^{-1} due to $\nu(\text{C=C})$ stretching vibrations of the cyclopentadienyl ligand bonded to titanium; nevertheless, this band overlaps with those previously discussed for the ionic liquid in the spectrum of those doubly functionalized materials.

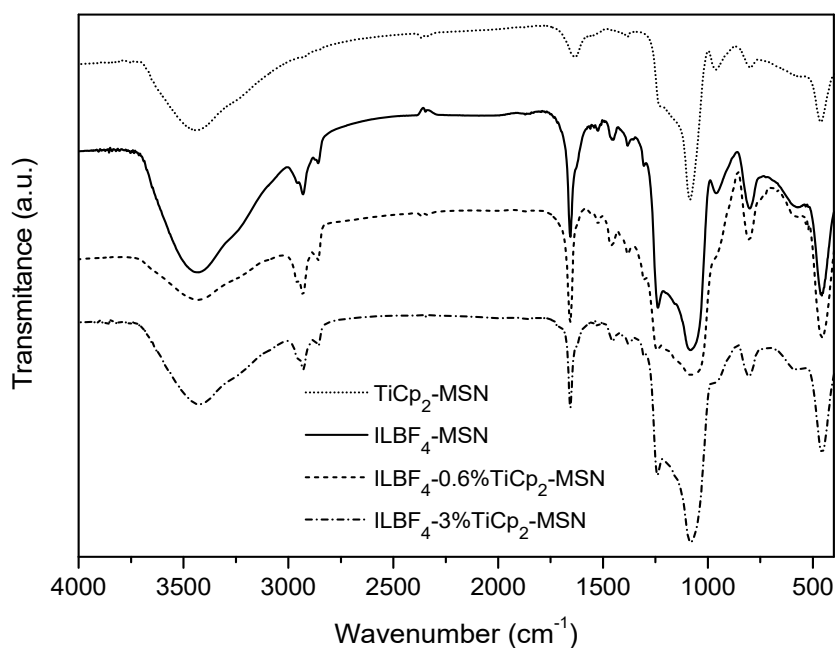


Fig. 2. FTIR spectra of heterogeneous catalysts

The ^{13}C CP MAS NMR spectra of titanium materials containing ionic liquid (Fig. 3), $\text{ILBF}_4\text{-0.6\%TiCp}_2\text{-MSN}$ and $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$ sustains the immobilization of, both, titanocene dichloride precursor and ionic liquid on the surface of mesoporous silica nanoparticles. The spectra show signals at 8 and 47 ppm due to the carbon atoms of the propyl chain $-\text{SiCH}_2-$ and $-\text{CH}_2\text{N}$, respectively. The peaks assigned to the methylene groups $(-\text{CH}_2-)_n$ of the propyl chain and octyl substituent appear between δ 11 and 31

ppm. The reaction of the silylated ionic liquid with the surface silanol groups is proposed to take place by reaction of two pendant $\text{CH}_3\text{-CH}_2\text{-O-Si-}$ groups since there is a signal at δ 16 ppm which can be attributed to the methyl group ($\text{CH}_3\text{-CH}_2\text{-O-Si-}$) of the third unreacted ethoxy groups attached to the Si atom. The expected signal for the methylene group ($\text{CH}_3\text{-CH}_2\text{-O-Si-}$) should appear around 50 ppm, which is overlapped with the peak at 47 ppm as previously described. The signals around δ 56 and 58 ppm and that observed at δ 156 ppm are due to the methylene $\text{-(CH}_2\text{)}_2\text{-}$ and -(NCHN)- carbon atoms of the 4,5-dihydro-imidazolium ring. Finally, the signal at 118 ppm confirms the presence of cyclopentadienyl ligands bonded to titanium.

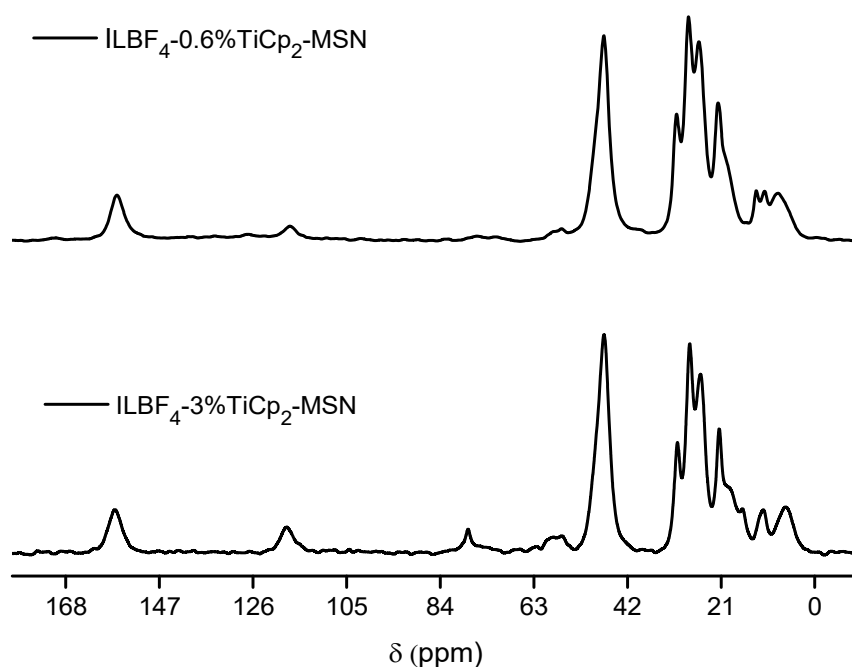


Fig. 3. ^{13}C CP-MAS NMR spectra of titanium materials containing ILBF_4 .

DRUV-vis spectroscopy was performed to obtain extra information about the environment of the titanium sites after immobilization (Fig. 4). For comparison purposes, the spectrum of $\text{ILBF}_4\text{-MSN}$ was first recorded. It shows an intense absorption band at 243 nm corresponding to the 4,5-dihydro-imidazolium group. The titanocene functionalized material $\text{TiCp}_2\text{-MSN}$ displays a diffuse reflectance spectrum composed of three different signals located at 214 and shoulders at 250 and 330 nm. The first signal has been assigned to the electronic transitions caused by the Ti-O bonds, while the other

two have been attributed to the coordination of the cyclopentadienyl rings to the metal. When the material was treated with the ionic liquid ILBF_4 , the DRUV spectrum changed significantly. As an example, the spectrum of ILBF_4 -x% TiCp_2 -MSN shows a band at 350 nm attributed to the absorption of cyclopentadienyl ligands, blue shifted in comparison to TiCp_2 -MSN. The signal associated with the Ti-O bond overlaps with the stronger band of the ionic liquid making it impossible to determine the influence of the ionic liquid on the environment of the titanium atom bonded to the silica surface.

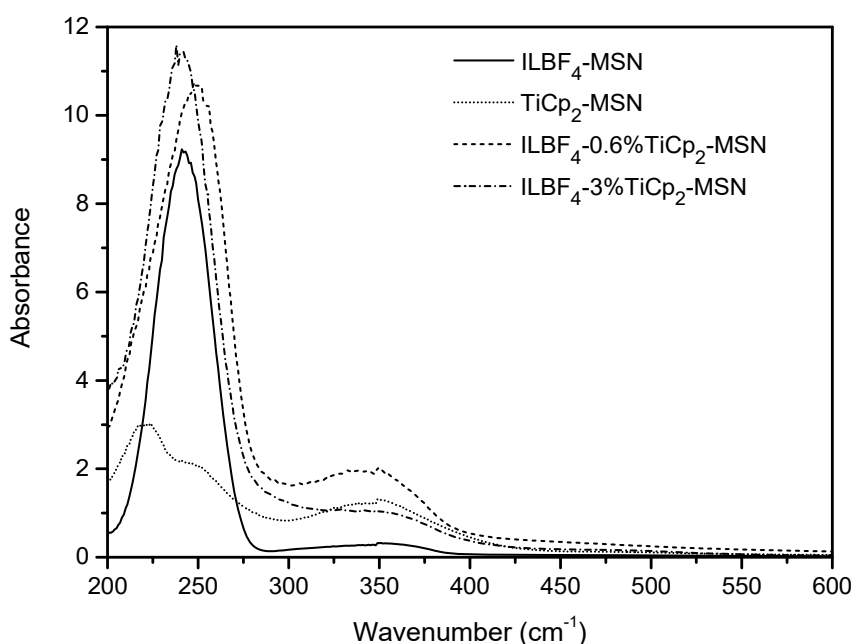


Fig. 4. DRUV-vis spectra of titanium-ionic liquid heterogeneous catalysts based on MSN.

3.2. Heterogeneous oxidative desulfurization of DBT

The titanium catalysts supported on mesoporous silica materials were tested in the oxidative desulfurization (ODS) of dibenzothiophene (DBT) by using H_2O_2 as oxidant. The reaction was performed in a MultiMax™ parallel reactor system at 60 °C, using high concentration of DBT in *n*-octane (1420 ppm) as a simulated solution of fuel oil. Blank experiment was carried out without catalyst (Entry 1, Table 2) and the conversion of DBT was only 0.2% after 8 h, which corroborates that the titanium species are the active sites in the catalytic process.

Table 2. Heterogeneous oxidative desulfurization (ODS) catalyzed by different materials^a

Entry	Catalyst	Ratio Ti/DBT (mol%)	Conversion of DBT (%) ^b	Sulfone Selectivity (%)
1	-	-	0.2	100
2	ILBF ₄ -MSN	-	37.6	100
3		0.5	1.2	100
4	TiCp ₂ -MSN	2	8.1	100
5		5	33.5	100
6		0.5	42.2	100
7	ILBF ₄ -0.6%TiCp ₂ -MSN	2	74.5	100
8		5	89.3	100
9		0.5	72.5	100
10	ILBF ₄ -3%TiCp ₂ MSN	2	86.8	100
11		5	99.1	100
12		0.5	4.3	100
13	ILCl-0.5%TiCp ₂ -MSN	2	14.8	100
14	ILBF ₄ -3%TiCp ₂ MSN ^c	5	89.9	100
15	MIL-125(Ti) ^d	-	26	-
16	HTS-1-a ^e	-	73	-
17	HTS-1-b ^e	-	51	-

^aReaction conditions: catalyst: 0.5-5 mol%, model oil: S-concentration of 1420 ppm in n-octane, temperature: 60 °C, time: 8 h.

^bRemoval of DBT was determined by GC analysis with the external standard method

^cReaction conditions: catalyst: 5 mol%, model oil: S-concentration of 1420 ppm in n-octane, temperature: 60 °C, time: 2 h.

^dRef. [15] Reaction conditions: catalyst: 0.1 g, model oil: S-concentration of 240 µg/g in

n-octane, temperature: 60 °C, time: 30 min.

^oRef. [16] Reaction conditions: catalyst: 50 mg, model oil: S-concentration of 1000 ppm in n-octane, temperature: 60 °C, time: 1 h, oxidant: TBHP.

3.2.1. Influence of different catalysts on oxidative desulfurization of DBT

The results achieved from the ODS of DBT with the different MSN catalysts in a liquid-solid phases system (L(oil)-S(catalyst)) are shown in Table 2. The results clearly showed different catalytic activity between the prepared heterogeneous catalysts obtaining in all cases sulfone as the only product. The catalysts containing titanium and 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate ionic liquid exhibited better activity (89.3% conversion for ILBF₄-0.6%TiCp₂-MSN and 99.1% conversion for ILBF₄-3%TiCp₂MSN) than the titanium catalyst (33.5% conversion) and the ionic liquid immobilized catalyst (37.6% conversion). From these results it can be proposed that there is a strong synergic effect between the immobilized metal and ionic liquid to enhanced the ODS reaction.

3.2.2. Influence of catalyst loading and metal content.

The reaction was carried out using different catalyst loading between 0.5-5 mol% with H₂O₂ molar ratio of 5. As can be seen in Fig. S5, the efficiency of desulfurization enhanced with the increase of catalyst using the different catalysts. For TiCp₂-MSN catalyst, 33.5% of conversion value is obtained with 5 mol%, while the conversion is only 8.1% with 2 mol% (Entries 4 and 5). The ILBF₄-0.6%TiCp₂-MSN catalyst exhibited low activity (42.2% conversion) using 0.5 mol% (Entry 6). When the amount of ILBF₄-0.6%TiCp₂-MSN catalyst was increased from 0.5 mol% to 5 mol% of activity was reached to 89.3% conversion (Entry 8). The influence of the amount of catalyst for ILBF₄-3%TiCp₂-MSN catalyst is less marked, using 2 mol% of conversion value was 86.8% and 99.1% when 5 mol% was used (Entries 10 and 11). The optimal amount of catalyst is 5 mol%.

The effect of metal content was also studied in the desulfurization oxidative of DBT using ILBF₄-functionalized catalysts with 0.6% and 3% titanium content. Increasing of the titanium content from 0.6% to 3% enhanced activity from 89.3 to 99.1% conversion (Entries 8 and 11). Then, ILBF₄-3%TiCp₂-MSN catalyst with the highest

amount of titanium immobilized led to the highest catalytic activity. To determine the influence of the anion of the ionic liquid in the oxidative desulfurization, ILCl-0.5%TiCp₂-MSN was also used, and the results were compared with ILBF₄-0.6%TiCp₂-MSN catalyst. The catalytic activity decreases significantly, when the BF₄⁻ anion of the ionic liquid was exchanged by the Cl⁻ anion (Entries 7 and 13).

Comparing our system with others previously published based on titanium heterogeneous materials, it should be mentioned that Ti-based metal-organic frameworks prepared recently by Zhang et al. [15] showed only 26% conversion in the oxidative desulfurization of DBT, without extractan, with H₂O₂ as oxidant and after 30 min in liquid-solid phase system (Entry 15). They used model oil, which contains 240 µg/g of sulfur content in *n*-octane. For ILBF₄-3%TiCp₂-MSN we achieved high efficiency of sulfur removal, 89.9 % conversion of DBT in 2 h (Entry 14) and 98.1% in 6 h, under similar conditions, but using model oil with high concentration of sulfur in *n*-octane (1420 ppm). Du et al. [16] also used high concentration of DBT in the model oil (1000 ppm) for the ODS reaction using TBHP as oxidant and hierarchical TS-1 zeolite as efficient catalyst. For HTS-1-a, 73% conversion of DBT was obtained after 1 h (Entry 16) and for HTS-1-b, 51% conversion of DBT in 1 h (Entry 17).

3.2.3. Reusability

The heterogeneous catalysts were separated by filtration, washed with dichloromethane and dried at 60 °C before reutilization. The DRUV-vis spectra of recovered titanium catalysts TiCp₂-MSN-R and ILBF₄-3%TiCp₂-MSN-R catalysts (Fig. 5) do not show the band at 350 nm corresponding to the cyclopentadienyl ligand, which indicates that the hydrolysis of the ligand has taken place as the oxidation reaction progress, as expected. The spectrum for the recovered TiCp₂-MSN-R catalyst displays a predominant band at 215 nm and a shoulder at higher wavelength >250 nm. These results suggest first the formation and second the maintenance of monomeric tetrahedral molecular species [Ti(OH)₂(OSi)₂] anchored to the silica surface, as predominant species, after catalytic reaction in the presence of moderate amount of oxidant. Nevertheless, the proportion of dimeric titanium species with higher coordination environments [Ti(OH)(OSi)]₂(µ-O)₂ becomes more important. The spectra

of catalysts containing ionic liquid, exhibit the band at around 243 nm attributed to 4,5-dihydro-imidazolium cation, being indicative of the presence of immobilized ionic liquid in the catalysts after oxidation reaction. In agreement with the DRUV-vis spectra, in the FT-IR spectra of the recovered catalysts containing ionic liquid (see Fig. S6), the characteristic peak at around 1650 cm^{-1} attributed to C=N of imidazole group is detected. The reusability of ILBF₄-3%TiCp₂-MSN-R catalyst was studied for three consecutive cycles and the results are summarized in Fig. 6. The catalytic activity is maintained for the two first runs, and only dropped slightly in the third run. As can be seen in Fig. S6b, the FT-IR spectrum of ILBF₄-3%TiCp₂-MSN-R catalyst shows a slight peak at 1160 cm^{-1} which can be assigned to the S=O stretching vibration of sulfone group [27]. This suggests that some sulfone product can be adsorbed on the recovered catalyst interacting with the ionic liquid and causing decreases of catalytic activity.

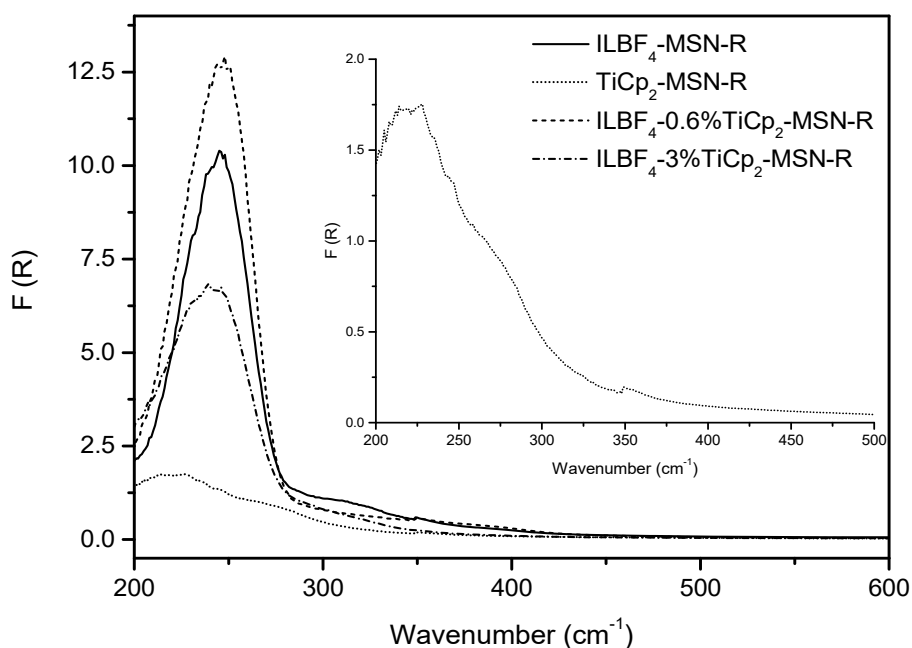


Fig. 5. DRUV-vis spectra of recovered heterogeneous catalysts. Inset DRUV-vis spectrum of TiCp₂-MSN-R.

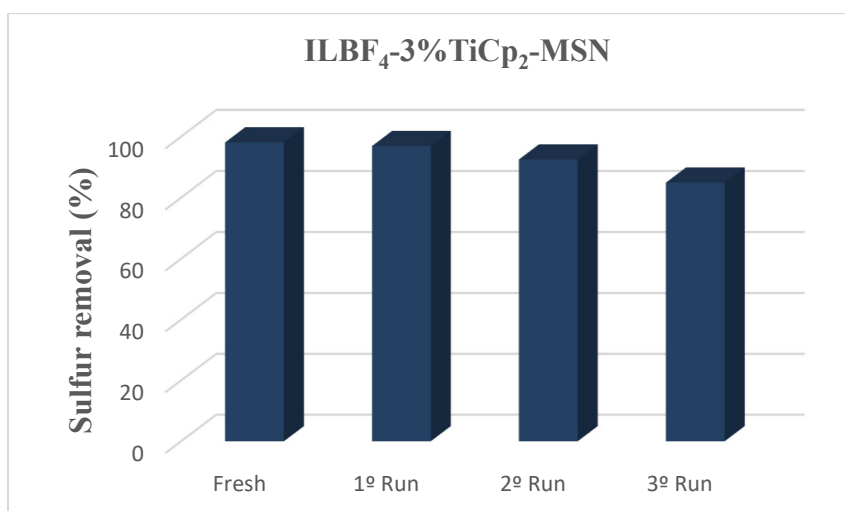


Fig. 6. Catalytic activity of ILBF₄-3%TiCp₂-MSN in consecutive reaction cycles of oxidative desulfurization of DBT. Reaction conditions: Ratio Ti/DBT: 5 mol%, model oil: sulfur-concentration of 1420 ppm in n-octane, H₂O₂ 30% (molar ratio O/S = 5), temperature: 60 °C, time: 6 h.

3.2.4. Study of oxidative desulfurization mechanism

Several studies have been carried out in order to investigate the relationship between the ionic liquid structure and its desulfurization efficiency in L-L-S systems [28]. In this present study, we have designed different strategies to determine the nature of the interaction between the ionic liquid, the substrate and the titanium catalyst in the synthesized titanium heterogeneous catalysts. First, and for comparison purposes, we studied the behaviour in solution of mixtures of titanocene dichloride, DBT and the ionic liquid ILBF₄ by using ¹H and ¹⁹F-NMR spectroscopy, since the changes in chemical shifts provide direct information on the environment, both, the cation and the anion of the ionic liquid, as well as, DBT.

As can be seen, in ¹H-NMR spectra in Fig. 7, the resonances assigned to the proton bonded to C₂ of the 4,5-dihydro-imidazolium cation in ILBF₄ at around δ 8 ppm, in free ionic liquid shifted slightly upfield in the presence of DBT (Δδ ≈ 0.01 ppm), as well as, the signal due to the methylene groups, at δ 3.93 ppm, attached to C₄ and C₅ (Δδ ≈ 0.02 ppm) and DBT signals (see Fig. 7 insets A, B and C); although appear just slightly shielded. This behaviour indicates that the environment of the ionic liquid, as well as DBT, have

changed, especially the electronic environment of ILBF₄ and justify the existence of some type of interactions between both compounds.

DFT studies performed by Lin and co-workers [29] have demonstrated the existence of strong hydrogen bond donor acceptor interactions between the fluorine atoms of tetrafluoroborate anion and the cation in N-butyl-N-methylimidazolium and N-butyl-N-methylpyrrolidinium tetrafluoroborate ionic liquids. To verify the presence of hydrogen bond interactions between [BF₄]⁻ anion and cation 4,5-dihydro-imidazolium we have studied carefully the FTIR spectra of the ionic liquids ILCl and ILBF₄ synthesized in this research work. The FTIR of ILBF₄ shows a weak peak around 3095 cm⁻¹, which can be attributed to the formation of this type of hydrogen bond interactions (Fig. S2) [30]. In addition, the important upfield displacement observed in the chemical shift of the proton bonded to C₂ of the 4,5-dihydro-imidazolium ring in ILBF₄, which appears shielded nearly 2.0 ppm in comparison to ILCl, supports this interaction.

The theoretical studies demonstrate also the great effect of cation structure on its interaction with DBT. When the cation has an aromatic ring, such as N-methylimidazolium, π^+ - π interactions are established and the π^+ cation adopts a displaced-stacked structure in which the π -rings are almost parallel, and the anion is over the imidazolium plane. With N-methylpyrrolidinium cation π^+ - π interactions are non-existent and hence the anion is positioned between cation and DBT. Considering these studies and the changes observed in ¹H-NMR spectra, we propose the existence of hydrogen bonding in the free ionic liquid between proton bonded to C₂ of the 4,5-dihydro-imidazolium ring and fluorine atom of the tetrafluoroborate anion, C₂-H \cdots F-BF₃, due to the larger positive charges on the C₂-H_{imidazolium} atom. Upon addition of DBT to a chloroform solution of ionic liquid, it can be deduced from the chemical shift change that the electron density of hydrogen atom bonded to C₂ of the 4,5-dihydro-imidazolium ring increases, as well as, those of methylene groups. We propose that the hydrogen bonding interaction between cation and anion in the ionic liquid is maintained in the presence of DBT and additional π^+ - π interaction between the 4,5-dihydro-imidazolium cation and DBT is established.

In our model system, when ILBF₄ was added to a CDCl₃ solution of titanocene, an

important downfield shift ($\Delta\delta \approx 0.05$ ppm) was observed for the signal attributed to the proton bonded to C₂. A much less pronounced downfield shift for the signal attributed to the protons bonded to C₄ and C₅ of 4,5-dihydro-imidazolium cation (see Fig. 7 insets A and C) was observed. Nevertheless, the singlet signal due to the cyclopentadienyl ligands remained unchanged at δ 6.59 ppm. This fact can be explained due the existence of an interaction between the imidazolium cation and the Lewis acid titanium atom (possibly through the nitrogen donor atom). Finally, when the ¹H NMR spectrum of ILBF₄ is recorded in the presence of both, titanocene and DBT a downfield shift of the signals attributed to 4,5-dihydro-imidazolium cation takes place, but less pronounced than that previously observed in the presence of titanocene. This fact can be interpreted as the existence of a counter balanced effect between titanocene and DBT in their interaction with the ILBF₄.

In the presence of ionic liquids based on metals, different situations have been found in bibliography depending on the metal [31,32]. In our model system and due to the Lewis acid properties of transition d titanium metal we propose that titanocene dichloride interacts with both, 4,5-dihydro-imidazolium cation and DBT. Titanium is a hard metal and has strong affinity for nitrogen donor atom of the 4,5-dihydro-imidazolium cation in ILBF₄. This affinity can also be extended to sulfur donor atom in DBT, which is not establishing any covalent interaction with the cation in the ionic liquid, as supported by previous theoretical studies [29]. This interaction between titanocene, DBT and ionic liquid is also sustained by the chemical shift observed for DBT in the presence of ionic liquid, and in the presence of both titanocene and ionic liquid. Finally, as can be seen, in the spectrum of the mixture of the three compounds, the singlet signal attributed to cyclopentadienyl ligands of titanocene dichloride remains unchanged which suggest, unexpectedly, that the chemical and electronic environment on titanium atom has not been significantly modified despite its interaction with DBT and ILBF₄.

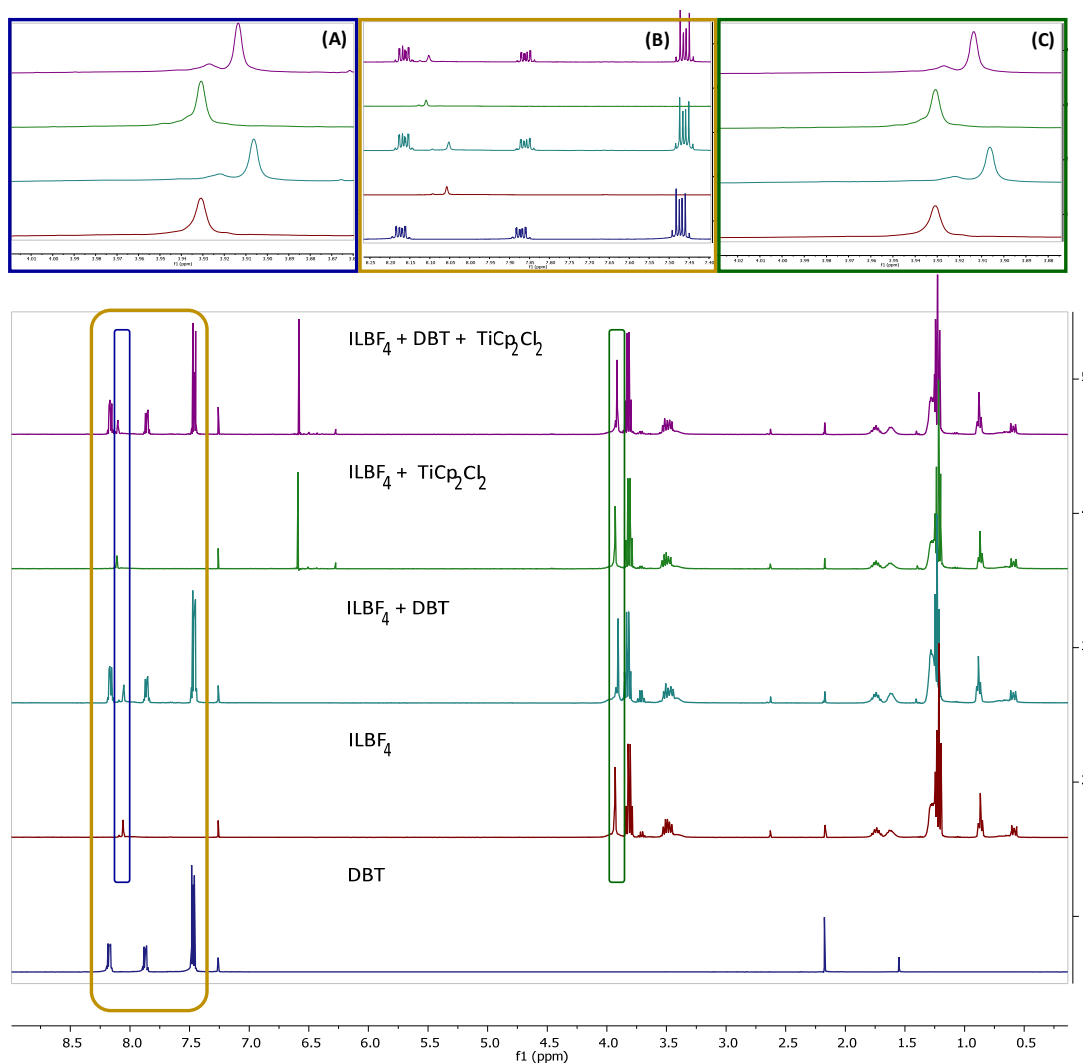


Fig. 7. ^1H -NMR spectra of ILBF_4 , $\text{DBT} + \text{ILBF}_4$, $\text{ILBF}_4 + \text{TiCp}_2\text{Cl}_2$ and $\text{ILBF}_4 + \text{DBT} + \text{TiCp}_2\text{Cl}_2$ in CDCl_3 .

When studying the ^{19}F -NMR spectra (Fig. 8) a similar behaviour is observed for the fluorine signals of the BF_4^- anion. In the ^{19}F -NMR spectrum of tetrafluoroborate 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium the signal attributed to tetrafluoroborate counter ion appears at δ -152.63 ppm splitted in two by the isotope effect of boron reflecting the 1 to 4 distribution of ^{10}B and ^{11}B . In the presence of DBT, this signal shifted slightly (δ -152.53 ppm) which suggests the establishment of additional hydrogen bond donor acceptor interactions between the fluorine atoms of BF_4^- anion and DBT, as supported by the theoretical studies of Lin and coworkers. They proposed that the $[\text{BF}_4]^-$ anion forms, besides the hydrogen bond interaction with 4,5-dihydro-imidazolium, stable lone pair \rightarrow π interactions with DBT [29]. In the presence of

titanocene dichloride, the signal attributed to tetrafluoroborate counter ion appears also down shielded at δ -152.55 ppm which highlights the existence of some type of interaction between the organometallic complex and the counter anion. In fact, metallocene Ti(IV) fluoride complexes can be prepared from the corresponding chloride or alkyl congeners by halogen exchange reaction with AgBF_4 or BF_3 [33] Finally, when the ^{19}F -NMR spectrum of the mixture titanocene-DBT-ILBF₄ is recorded the signal appears downfield shifted at δ -152.52 ppm. These results reflect the existence of a synergic effect in the interaction of DBT and titanocene dichloride with the tetrafluoroborate anion in the ionic liquid and allow us to propose the establishment of a three compounds interaction system (see Fig. 9).

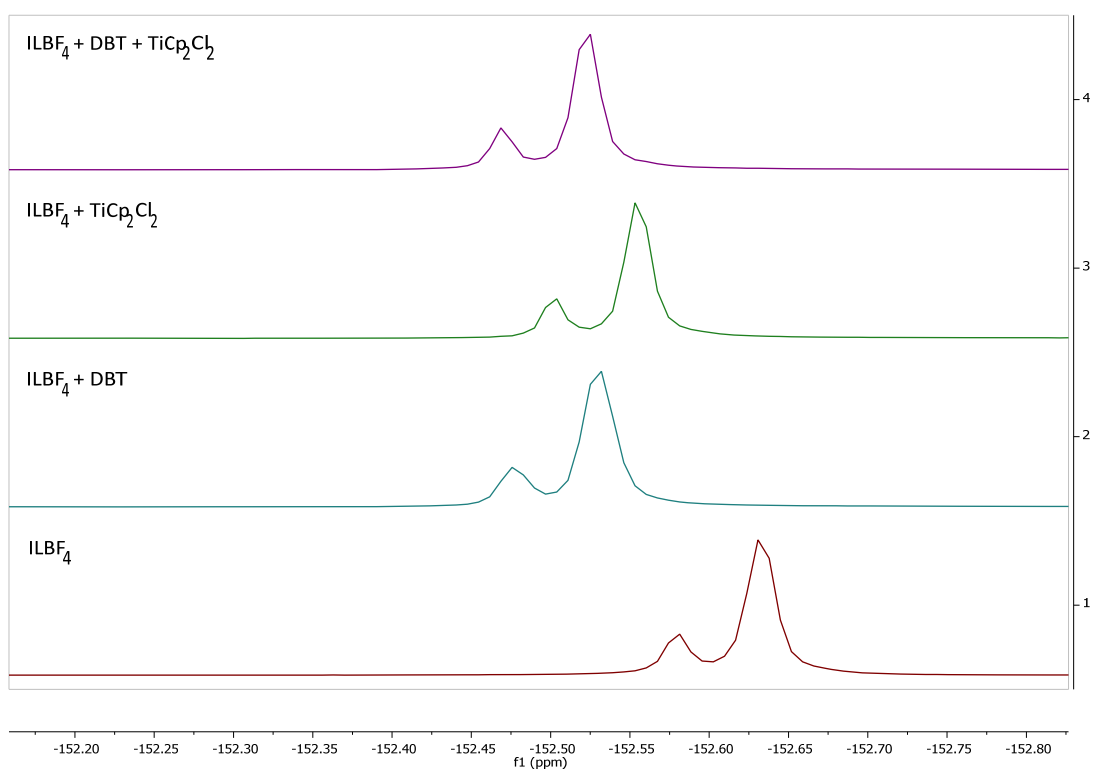


Fig. 8. ^{19}F -NMR spectra of ILBF₄, ILBF₄ + DBT, ILBF₄ + TiCp₂Cl₂ and ILBF₄ + DBT + TiCp₂Cl₂ in CDCl₃.

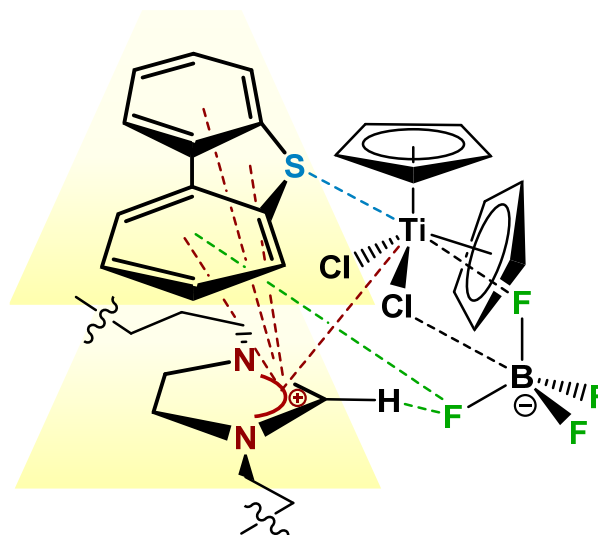


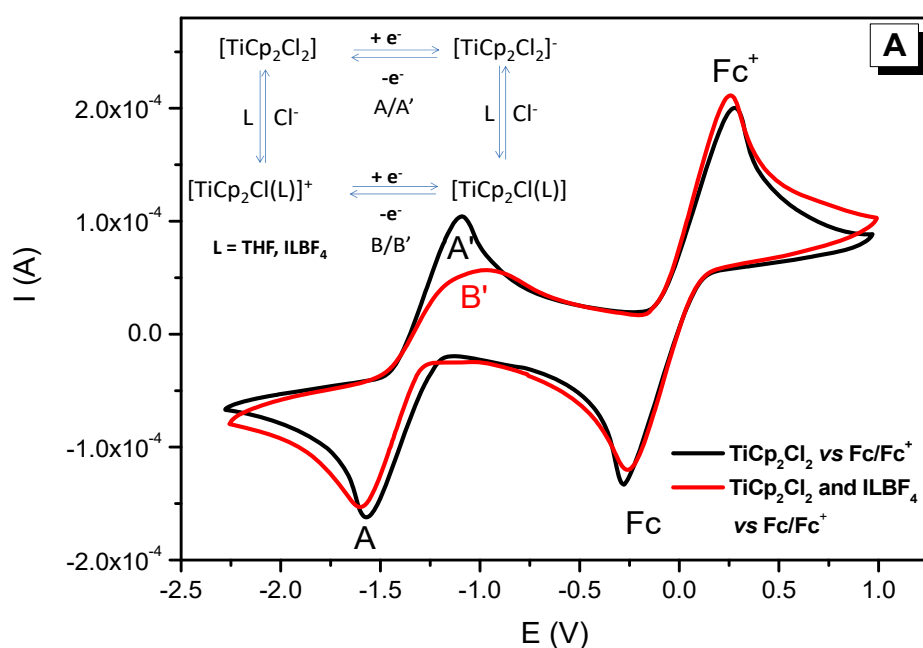
Fig. 9. A three compounds interaction system is proposed for titanocene, DBT and tetrafluoroborate ionic liquid in chloroform solution.

A similar study was conducted for ILCl (Fig. S7). The resonances assigned to the proton bonded to C₂ of the 4,5-dihydro-imidazolium cation in ILCl at δ 10.15 ppm shifted upfield ($\Delta\delta = 0.04$ ppm) in the presence of DBT due to the $\pi^+ - \pi$ interactions between the “4,5-dihydro-imidazolium” cation of the ionic liquid and DBT. When ILCl was added to a CDCl₃ solution of titanocene, the behaviour observed is opposite to that of ILBF₄, an important upfield shift in comparison to free ILCl ($\Delta\delta = 0.08$ ppm) is observed for the proton signals attributed to the imidazolium cation. When the ¹H NMR spectrum of ILCl is recorded in the presence of both, titanocene and DBT, the signals of the 4,5-dihydro-imidazolium cation showed also an upfield shift ($\Delta\delta = 0.05$ ppm), in between from that originated by titanocene and DBT by themselves. As previously mentioned, a three-component interaction system is established. Nevertheless, the different changes observed in the chemical shifts of the signal under study suggest that the anion plays an important role in these systems.

As previously discussed by ¹H-NMR studies, in solution, the electronic environment of titanium seems to be preserved in the presence of DBT or ionic liquid (ILBF₄ and ILCl). In order to further study this, we recorded the cyclic voltammogram of the metallic complex upon addition of the ionic liquids as co-solvent. In a THF solution, the most characteristic feature of the cyclic voltammogram of titanocene dichloride is the wave

of the redox couple $[\text{TiCp}_2\text{Cl}_2]/[\text{TiCp}_2\text{Cl}_2]^-$. The original proposal of Laviron was the existence of an E_{qC_i} mechanism where the *quasi*-reversible electrochemical reduction of $[\text{TiCp}_2\text{Cl}_2]$ is followed by the fast and chemically reversible cleavage of the anion $[\text{TiCp}_2\text{Cl}_2]^-$ [34]. In Fig. 10(A) a *quasi*-reversible wave at $E_{1/2}(\text{A}/\text{A}') = -1.36$ V was observed (vs Ferrocene/Ferrocenium couple) for the first electron uptake by $[\text{TiCp}_2\text{Cl}_2]$. A slight decrease in the peak current ratio $I_{\text{ox}}(\text{A}')/I_{\text{red}}(\text{A})$ with increasing sweep rate agrees with the dichloride anion formation and a rapid and reversibly dissociation to give a neutral, solvated monochloride complex. Its oxidation occurs after uptake of Cl^- (i.e. regeneration of the dichloride anion), at peak A' or at peak B' (peak not seen). The latter process, labelled as B', would generate the solvated cation $[\text{TiCp}_2\text{Cl}(\text{THF})]^+$. Upon addition of 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1H-5imidazol-3-ium tetrafluoroborate as co-solvent the CV for titanocene dichloride complex was also recorded (Fig. S8). Firstly, and for comparison purposes, the electrochemical response of ILBF_4 was studied in a THF solution, obtaining a silent voltammogram in the range under study [35]. The CV reported in Fig. 10(B) shows at a scan speed of 100 mV/s the reduction peak A slightly shifted from -1.56 to -1.59 V. However, in contrast with that observed in the absence of ionic liquid, the reduction stage was irreversible in all ranges of scan speed measured. When the scan is reversed two anodic peaks A' and B' at $E_{\text{ox}}(\text{B}') = -0.96$ V can be predicted. As previously published, the addition of a co-solvent with coordinative properties shifts the equilibrium $[\text{TiCp}_2\text{Cl}_2] + e^- \rightleftharpoons [\text{TiCp}_2\text{Cl}_2]^-$ to the right due to its interaction with the titanium centre [36]. $[\text{TiCp}_2\text{Cl}_2]^-$ oxidation wave decreased at the expense of a new wave at a higher potential value (less negative) assigned to the new $[\text{TiCp}_2\text{Cl}(\text{L})]$ solvent coordinated species. Peak B' can be seen to be due to the reaction $[\text{TiCp}_2\text{Cl}(\text{L})] \rightleftharpoons [\text{TiCp}_2\text{Cl}(\text{L})]^+ + e^-$. The electron uptake is followed by the ligand exchange $-\text{Cl}^+/\text{L}$, where L is the solvent or the ILBF_4 (coordinated through the 4,5-dihydro imidazolium unit or through the interaction with BF_4^- anion) (see Insert Fig. 10(A)). The process is controlled by diffusion as is demonstrated in the linear plot of $I_{\text{red}}(\text{A})$ vs, square root of scan rate through the origin ($I = -3.65E^{-5} - 2.60E^{-4}v^{1/2}$, $R^2 = 0.9900$). The calculation of the diffusion coefficient showed that in the presence of ILBF_4 it decreases from $2.46E^{-7}$ to $1.17E^{-7}$ m^2/s which supports the existence of some kind of interaction between the metallic complex and the ionic liquid (Fig. S9) as previously observed by our group [37]. Recently, Masuda and coworkers [38] have measured the

CV of titanocene in 1-butyl-1-methylpyrrolidinium tris(pentafluoroethyl)-trifluorophosphate and 1-butyl-1-methylpyrrolidinium triflate. These authors propose the formation of $\text{TiCp}_2\text{Cl}(\text{OTf})$ in the presence of the ionic liquid with anion triflate which possesses coordinative properties. When the electrochemical experiment is conducted with a similar concentration of ILCl as co-solvent, the CV of titanocene remains unchanged, nor the E_{red} neither the peak intensity of reverse oxidation scan shows any variation (Fig. S10). These results demonstrate that the electronic properties on the titanium centre, practically, remain unchanged for both ionic liquids since the potential reduction value remains unaltered for ILCl, and just slightly modified for ILBF_4 . Thus, there is a stronger interaction between titanocene and ILBF_4 (possibly through the 4,5-dihydro-imidazolium ring and through the anion BF_4^-) than with titanocene and ILCl, as previously observed by NMR studies.



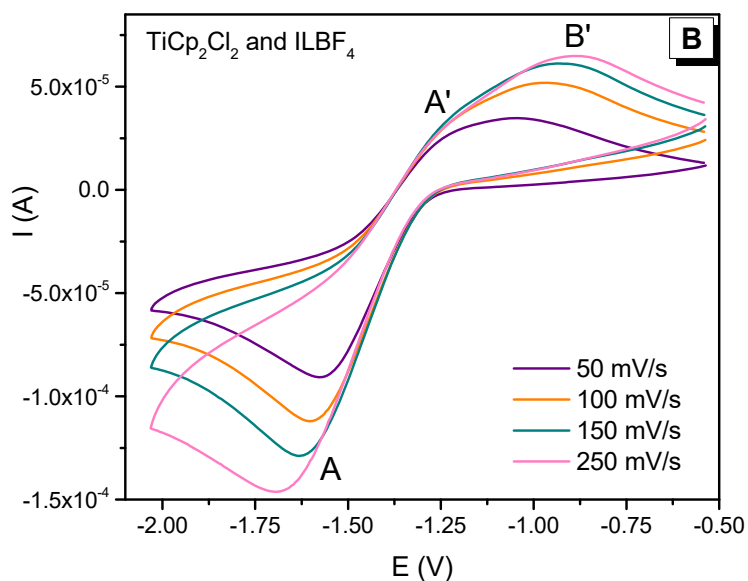


Fig. 10. (A) CV of pristine TiCp_2Cl_2 and upon addition of ILBF_4 scan rate 100 mV/s in THF as solvent and with Fc/Fc^+ as external standard. (B) CV of TiCp_2Cl_2 in THF as solvent with ILBF_4 as co solvent, scan rate from 50-250 mV/s. Bu_4NPF_6 as electrolyte (0.2 M), GC as working electrode, Pt as counter electrode.

Bearing in mind, the important differences that may exist between solid state and solution, where polar solvents have been used to carry out our preliminary and model studies, we performed a similar study to determine the existence of interactions between immobilized titanocene and ionic liquid. For that, a comparison of ^{13}C and ^{19}F -CP-NMR spectra and differential pulse voltammetry of $\text{TiCp}_2\text{-MSN}$ and $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$ have been accomplished. ^{13}C CP-NMR spectra of $\text{TiCp}_2\text{-MSN}$ (Fig. S11) and $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$ (Fig. 3) show, as expected, that there is no difference between the chemical shifts of cyclopentadienyl ligand bonded to titanium before and after immobilization of ILBF_4 . Fig. 11 shows ^{19}F CP-MAS NMR spectra of $\text{ILBF}_4\text{-MSN}$ and $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$. As can be seen, two peaks at -150 and -142.8 ppm are observed for $\text{ILBF}_4\text{-MSN}$. Unlike the ^{19}F -NMR spectra in CDCl_3 solution whereas one signal attributed to the tetrafluoroborate anion is observed, the spectra of the ionic liquid grafted to the silica surface suggest the existence of two different types of fluorine atoms in the anion BF_4^- . Previously, He et al. [39] proposed that ILBF_4 forms $\text{C-H}\cdots\text{F}$ hydrogen bonds between the 4,5-dihydro-imidazolium cation and BF_4^- anion. Furthermore, the presence of

mesoporous silica nanoparticles with free surface silanol groups still available for further reaction, additional hydrogen bonds can be established and the cation-anion interactions in the ionic liquid and silica-ionic liquid hydrogen bond may compete with each other. In ILBF₄-MSN, we propose that the anion BF₄⁻ near the silica surface interacts with the silanol groups via the formation of hydrogen-bonded fluorine atoms and gives rise to two different resonances in the ¹⁹F-CP-NMR spectrum. The hydrogen-bonded fluorine atoms in BF₄⁻ anions resonate at -150 ppm, while those which are not hydrogen bonded contribute to the peak at -142 ppm, as previously observed by Pruski and co-workers in the immobilization of [Pd(dppp)(S₂C-NEt₂)]BF₄ onto silica [40]. The ¹⁹F CP-MAS NMR spectrum recorded for ILBF₄-3%TiCp₂-MSN (Fig. 11) shows a similar pattern, but two new peaks are observed at -122 and -160 ppm which can be attributed to free F⁻ anion [41]. Although, the origin of F⁻ anions remains unclear, it could be formed by defluorination reaction of BF₄⁻ anion with Lewis acid titanium centre, located close in spatial proximity on the silica surface, or/and with water (BF₄⁻ + H₂O → BF₃(OH)⁻ + HF) or silanol groups since this signal at -122 ppm is also observed in the spectra of ILBF₄-MSN, although much less intense.

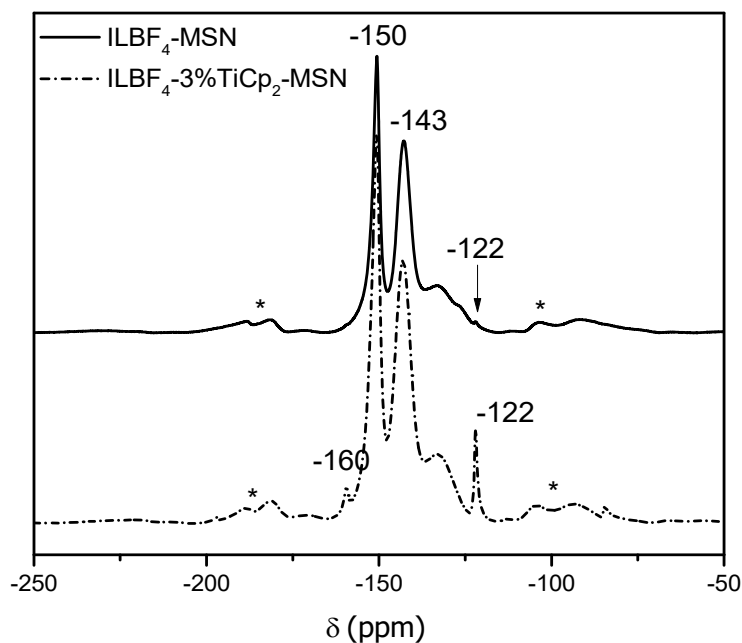


Fig. 11. ¹⁹F CP-MAS NMR spectra of TiCp₂-MSN and ILBF₄-3%TiCp₂-MSN materials (*side

bands).

Voltammetry techniques have been also used to characterize the heterogeneous catalysts prepared in this work by means of modified carbon paste electrodes (MCPE) with embedded titanium modified nanoparticles as working electrodes. These techniques are based on the theoretical model developed by Lovric and Scholtz [42,43] and Oldham [44] for the coupled transport of ions and electrons in redox conductive microcrystals transferred mechanically onto the surface of a graphite electrode. This model explained the electrochemical reduction of a solid compound immobilized on an electrode surface by mixed ionic/electronic conductivity and the uptake or expulsion of electrons and electrolyte cations at the three-phase junction; where electrode, solid and electrolyte solution meet. The experiments were carried out at room temperature, using a three-electrode-single compartment electrochemical cell. A modified carbon paste electrode (MCPE), an Ag/AgCl/KCl (3 M) as reference electrode and a platinum rod as counter electrode and a buffer phosphate solution (pH 7.4) as electrolyte, the slightly basic pH avoids the formation of non-soluble titanium oxides species and additional adsorption phenomenon onto the electrode surface.

The measurements were recorded immediately after immersion of the fresh electrode surface into the electrolyte aqueous solution. As can be seen in Fig. 12, differential pulse voltammogram of TiCp₂-MSN material shows a reduction peak at -0.94 V attributed to the redox system Ti(IV)/Ti(III) present in pseudotetrahedral "[TiCp₂(OSi)₂"]". This value is similar to that obtained for TiCp₂-SBA-15 in previous studies and suggest that there is no influence of the mesoporous silica material in the potential reduction value obtained and hence in the electronic properties of the immobilized titanocene [37]. Under identical experimental conditions, no peaks were observed with an ILBF₄-MSN modified carbon paste electrode. Therefore, the peaks observed in ILBF₄-x%TiCp₂-MSN have been assigned to the redox system Ti (IV)/Ti (III) demonstrating that titanium is readily accessible to electron transfer reactions in aqueous medium. The materials containing the ionic liquid grafted onto silica surface and different titanium loading, ILBF₄-3%TiCp₂-MSN and ILBF₄-0.6%TiCp₂-MSN, show one peak associated to the reduction of grafted titanium (IV) complexes, but in this case unexpectedly, there is a clear shift of the peak to more positive potential values, -0.84 V, which indicates lower

electron density at the titanium atom. Our group has performed previous electrochemical studies of immobilized titanium isopropoxide and titanocene dichloride on to mesoporous silica materials in the presence of grafted 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride [26,37] These studies have demonstrated the capability of this ligand as electron donor ligand, since it shifts to more negative values the reduction potential of grafted titanium complexes. In this study, for the materials functionalized simultaneously with titanocene and the bulky ionic liquid, 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate, the results suggest the weak coordination of the 4,5-dihydro-imidazolium cation. In addition, the results obtained in solution are corroborated, where the influence of ILBF₄ on the cathodic potential change of the half reduction wave for titanocene is very small. As previously discussed, there is no difference between differential pulse voltammograms recorded for ILBF₄-3%TiCp₂-MSN and ILBF₄-0.6%TiCp₂-MSN which supports that the titanium loading does not render different structural forms on the silica surface.

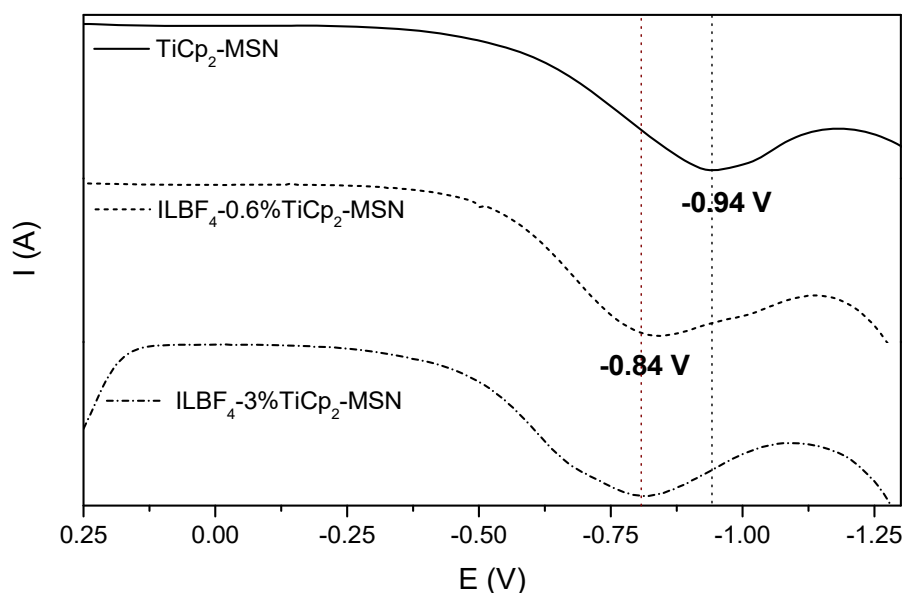


Fig. 12. Differential pulse voltammograms (75 mV modulation amplitude) of immobilized titanium silica materials $\text{TiCp}_2\text{-MSN}$, $\text{ILBF}_4\text{-3\%TiCp}_2\text{-MSN}$ and $\text{ILBF}_4\text{-0.6\%TiCp}_2\text{-MSN}$

immediately after immersion in aqueous phosphate buffer pH 7.4 as electrolyte vs Ag/AgCl/KCl (3M) as reference electrode.

To gain insight into the nature of the catalytic active titanium species under experimental conditions chosen in the catalytic assays, DP voltammograms were recorded for ILBF₄-3%TiCp₂-MSN as a function of time in aqueous media. The profile obtained for ILBF₄-3%TiCp₂-MSN showed a decrease of the peak current observed at -0.84 V as a function of time. As can be seen in Fig. 13, the decrease took place at very short time, after immersion, and in water. This suggests a fast hydrolysis of the major species "[TiCp₂(OSi)₂]", formation of [Ti(OH)₂(OSi)₂] and also a rapid transformation of these monomeric species, probably, to originate dimeric or polymeric μ-hydroxo and μ-oxo species of the type [Ti(OH)(OSi)]₂(μ-O)₂ (similarly to the behaviour of TiCp₂Cl₂ in solution [45,46,47]). Since the peak observed for TiCp₂-MSN appears at -0.94 V, the only observable peak in ILBF₄-3%TiCp₂-MSN (-0.84 V) does not exhibit any shift with time, and taking into account that ILBF₄ does not modify the reduction potential value of titanocene in solution. We assume that this peak at -0.84 V is due to monomeric [TiCp(OH)(OSi)₂] or [Ti(OH)₂(OSi)₂] more than due to "[TiCp₂(OSi)₂]" species. This grafted titanium complex bearing cyclopentadienyl ligands seems to be elusive in this material in water since it evolves very fast towards [Ti(OH)₂(OSi)₂]. This last dihydroxo titanium grafted complex further evolves to give μ-hydroxo and μ-oxo dimeric or polymeric species as [Ti(OH)(OSi)]₂(μ-O)₂. In fact, the DP voltammogram measured immediately after immersion shows an additional small peak at -0.70 V which can be attributed to these newly formed species. Previous work reported by our group [37], when a similar stability study in water was performed for TiCp₂-MSN, in the presence of donor ligand 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride, showed that the signal attributed to [Ti(OH)₂(OSi)₂] was visible a few minutes after immersion, but this signal (slightly shifted from -0.94 to -1.01V) remained as the only observable peak after two hours. These results suggest higher stability of pseudotetrahedral [Ti(OH)₂(OSi)₂] species against further reaction when 1-methyl-3-[(triethoxysilyl)propyl]imidazolium chloride is simultaneously tethered to the silica surface, probably due to the donor properties of the imidazolium unit. Here, 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate used to prepare the catalyst ILBF₄-3%TiCp₂-MSN does not

increase the electronic density of grafted titanium species, quite the opposite, it seems to favour the hydrolysis processes, to give rise to new active species on the silica surface.

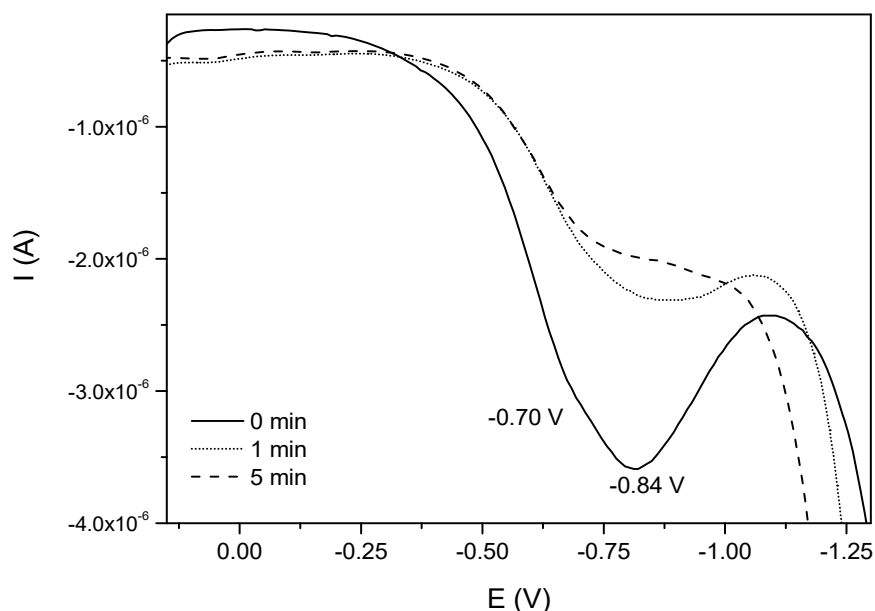


Fig. 13. Differential pulse voltammograms (75 mV modulation amplitude) of immobilized titanium silica materials ILBF₄-3%TiCp₂-MSN as a function of time after immersion in aqueous phosphate buffer pH 7.4 as electrolyte vs Ag/AgCl/KCl (3M) as reference electrode.

Finally, we have recorded the ^{47/49}Ti NMR spectra of the materials TiCp₂-MSN and ILBF₄-3%TiCp₂-MSN synthesized to complete the titanium environment characterization. In Fig. 15, the ^{47/49}Ti MAS NMR spectra show poorly resolved and broadened signals with overlapping resonances for both titanium isotopes: ⁴⁷Ti and ⁴⁹Ti [48]. Considering this, the use of ^{47/49}Ti NMR has been limited to examining compounds of high symmetry and low molecular complexity in solution and in solid state [48,49] the broadening of the lines is associated with the distortion of the local titanium environment. The poor resolved resonances and the high line width values $\Delta\nu_{1/2}$ measured for these materials indicate asymmetrical electron distribution at the titanium centre in these materials. In both cases, the shape of resonances ^{47/49}Ti NMR measured was dominated by quadrupolar effects, which made it difficult to study by this technique. The structure of the molecular species anchored on the mesoporous silica

nanoparticles and draw clear conclusions about the effect of the incorporation of the ionic liquid on the chemical and electronic environment of the titanium centre.

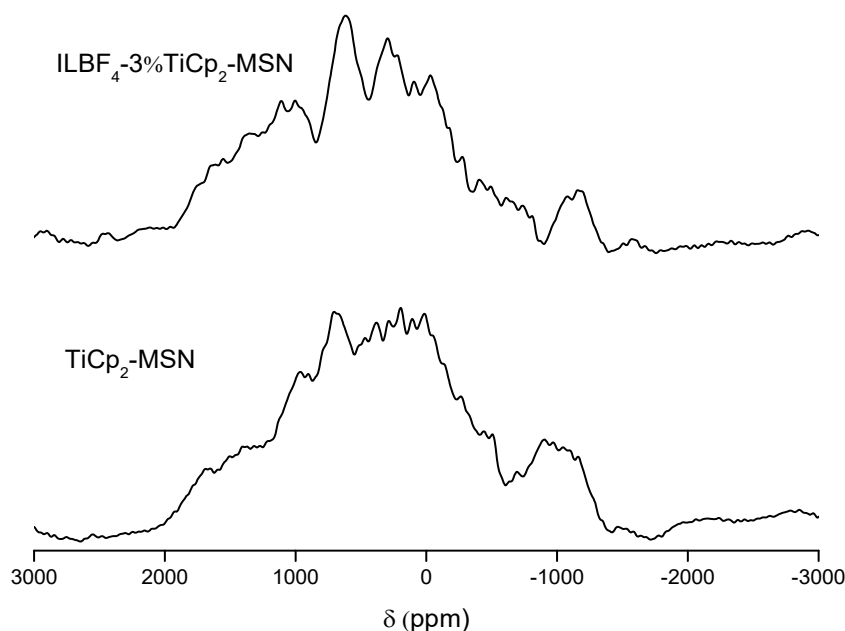


Fig. 15. $^{49/47}\text{Ti}$ MAS NMR spectra of titanium supported MSN catalysts.

As mentioned in the introduction section, in an attempt to improve the catalytic oxidation of sulfur compounds, highly inert due to its aromaticity, a dual activation has been the choice of some authors [50,51]. Reaching the conclusion that metal catalyst and ionic liquid, both cation and anion [52], play an important role in the process since they may activate synergistically sulfur derivatives and promote the ODS. Based on the results and the studies performed in this work, a dual activation mechanism is proposed due to the properties of immobilized titanium as Lewis acid centre and the versatile properties of immobilized 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate which is capable of activating the DBT molecule by partially destroying its aromaticity, through DBT-cation and DBT-anion interactions. In addition, the ionic liquid is capable of interacting with the titanium centre (possible through the tetrafluoroborate anion) and also acts as amphiphilic molecule improving the diffusion processes towards the silica surface (see Fig. 17).

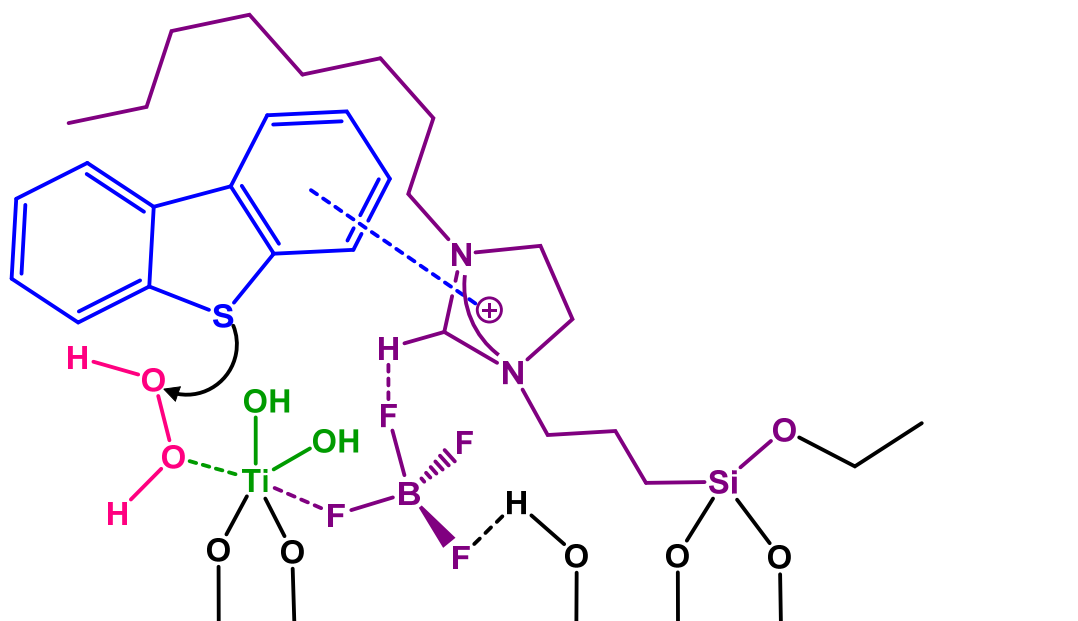


Fig. 17. Proposed activation mechanism for ODS of DBT with ILBF₄-TiCp₂-MSN and H₂O₂ as oxidant (without co-solvent).

4. Conclusions

Lewis acid titanium and 4,5-dihydro-imidazolium tetrafluoroborate ionic liquid functionalized mesoporous silica materials have been prepared and fully characterized. The interactions between DBT and immobilized titanium and ionic liquid have been studied by means of DRUV-vis, ¹³C and ¹⁹F-CP-MAS-NMR and solid state voltammetry techniques. For comparative purposes, a three compound model system in solution, formed by titanocene dichloride, DBT and ionic liquid, has also been studied by NMR and cyclic voltammetry techniques. The ODS of DBT using H₂O₂ and ILBF₄-3%TiCp₂-MSN as catalyst in L-S phase shows nearly quantitative conversion to sulfone using H₂O₂ as oxidant. The catalyst is recovered and reused with a slight loss of activity after three consecutive runs. A dual activation mechanism is proposed due to the properties of immobilized titanium as Lewis acid centre and the versatile properties of immobilized, 1-octyl-3-(3-(triethoxysilyl)propyl)-4,5-dihydro-1*H*-imidazol-3-ium tetrafluoroborate capable of activating the DBT molecule and the metallic promoter and also capable of acting as an amphiphilic molecule improving the diffusion processes.

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