SYNTHESIS AND CHARACTERIZATION OF ADSORBENTS BASED ON IONIC LIQUIDS ANCHORED ON MCM-41 FOR USE IN CO_2 CAPTURE

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ABSTRACT: CO_2 capture is one of the options for reducing emissions that contribute to global warming. Ionic liquids (ILs) are potential solvents for CO_2 absorption and, in order to benefit separation processes, the immobilization on solid adsorbents is proposed. The goal of this work is to synthesize and characterize ionic liquids anchored in mesoporous MCM-41 type material and evaluate the CO_2 adsorption by gravimetric method in a magnetic suspension balance. The characterization techniques performed by IR, NMR, TGA, N_2 adsorption and SEM shows that the ILs are covalently linked to the immobilized support, the support was changed the morphology and surface area and pore volume decreased by incorporating ionic liquids. The results of the CO_2 adsorption at low pressures were lower for supported ionic liquids, and with the increasing of pressure, pure MCM-41 material exhibited better adsorption capacity.

KEYWORDS: Ionic Liquids; MCM-41; Adsorption; Carbon Dioxide.

1. INTRODUCTION

The current mitigation scenario of the CO_2 emissions is based on the most efficient energy use, the substitution of fossil fuels by renewable sources, and also the exploration of technologies for carbon separation and storage. This includes carbon capture through ionic liquids in industrial processes of CO_2 separation from gas flows (Karadas, Atilhan e Aparício, 2010).

The study so far, to find new materials for CO_2 capture indicates as an option, the use of ionic liquids as solvents for absorption, CO_2 has a preferential solubility in these compounds. Thus, retains advantages of ILs, as green solvent due to the low vapor pressure and high thermal stability. ILs could be enhanced and modified by both their cationic and anionic moieties, they serve a broad range of applications, including uses in solid state (Karadas, Atilhan e Aparício, 2010).

The ionic liquids (ILs) are a class of materials with excellent perspective for carbon dioxide capture application, and an alternative to mitigate the increasing concentration of CO_2 in the atmosphere. Integrating ionic liquids in solid matrices appears as a new and challenging field, allowing the use of ionic liquids in heterogeneous systems for CO_2 capture.

There are several techniques to support IL, which sets the background of all applications, for example, supported ionic liquid phase, catalysts, membranes and many others (Mehnert, 2005). However, the process of immobilization normally is carried out by way of cationic or anionic incorporation, the IL is synthesized and then fixed
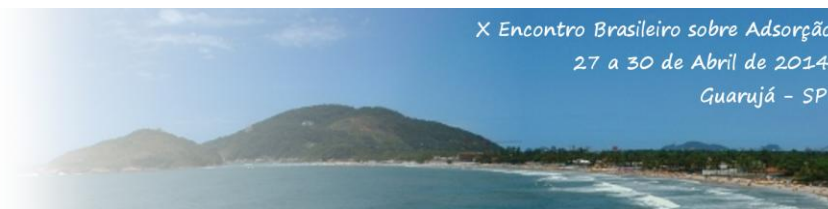
into the inorganic material, or by the cationic anchorage, or even the IL is used directly in situ polymerization in sol-gel process being this the support (Chiaro, 2011). On e Figure 1 are exposed some examples of supports and applications for each process.
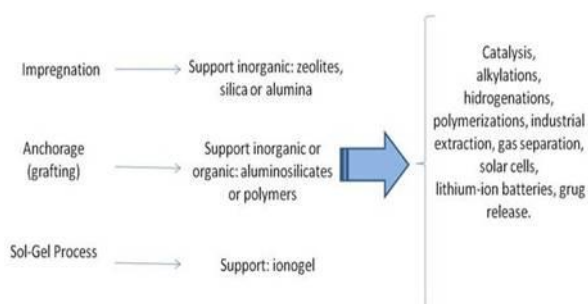

Figure 1. Types of immobilization, supports and applications (Chiaro, 2011).

The different immobilized ionic liquids can be classified by their interaction with the support material; the ILs can be bound to a surface either by covalent bonds between silanol groups and the anion or the cation of the liquid, or without covalent bonds in the form of supported liquid phases (Valkenberg, Castro and Hölderich, 2002).

It is worth stressing that silica was chosen due to their simple control of the synthesis parameters, moreover silica is easily modified by functionalized trialkoxysilanes (Litschauer and Neouze, 2008). The applications of supported ionic liquids on silica ranging from heterogeneous catalysts for various hydrogenation, hydroformylation and alkylation reactions, because they facilitate recovery of the catalyst and can be used in gas phase reactions. Furthermore, ILs are commonly known to guarantee the possibility of cation-anion numerous combinations, among them, change the size of the alkyl chain of cation and properties such as hydrophobicity and hydrophilicity on the surface can be enhanced (Valkenberg, Castro and Hölderich, 2002).

The ionic liquid should be synthesized with appropriate structure for immobilization, thus carries three steps: first the IL is silanized, second incorporation is made in the silica matrix, and, finally, exchange of the anion. The synthesis of supported ionic liquids occurs by ionic liquid immobilized via the cation through covalent bonds between the cation of IL and silanol group (Si-OH) on the surface of mesoporous material (Rodríguez-Perez et al. 2010).

Thus, the aim of this work is to synthesize and characterize structures of ionic liquids supported on mesoporous materials, checking the capacity of CO_2 adsorption on these materials.

2. EXPERIMENTAL SECTION

2.1. Chemicals

1-methylimidazole (Aldrich, 99%), 3-chloropropyltrimethoxysilane (Aldrich, 97%), LiNTf$_2$ (Aldrich, 99%), toluene (Merck, 99,9%), acetone (Vetec, 99,5%), dichlorometane (Vetec, 99,5%), diethyl ether (AGA, 95%), $MgSO_4$ (Acros Organics, 97%). The support MCM-41, aluminosilicate mesoporous was purchased from Sigma Aldrich. The solvents were dried before the synthesis.
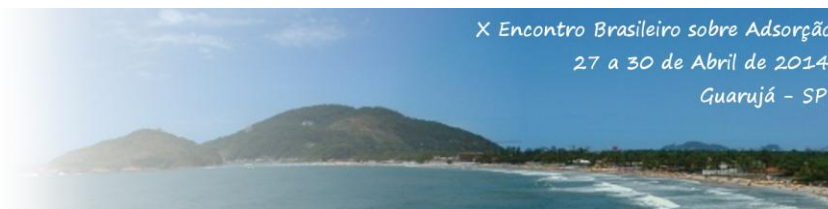
2.2 Ionic Liquid Synthesis

The IL (MeO)$_3$SipmimCl, 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride, was synthetized by the reaction of 0.87 g (0.0107 mol) 1-methylimidazole with 3.18 g (0.0160 mol) of (3-chloropropyl) trimethoxysilane with total reflux in toluene under nitrogen atmosphere for 48 h, following literature (Valkenberg, Castro and Holderich, 2002; Karimi and Enders, 2006; Lesniewski et al., 2007; Aimini et al., 2011). The reaction mixture was cooled down to room temperature and the organic upper phase was separated, leaving behind a yellow viscous ionic liquid phase. The ionic liquid phase was then washed with diethyl ether. Finally, the obtained product was dried at 50 °C for 8 h. The structure was confirmed by ^{1}H-NMR and FTIR.

^{1}H-NMR (400 MHz, DMSOd$_6$, 25 °C) δ (ppm): 0.58 (m, CH$_2$Si), 1.91 (m, CH$_2$CH$_2$N), 3.49 (s, SiOCH$_3$), 3.63 (s, CH$_3$N), 4.06 (t, CH$_2$N), 4.27 (t, CH$_2$), 7.39 (s, H5), 7.61 (s, H4), 10.39 (s, H2).

FTIR ν (cm^{-1}): 3031, Si-O; 2944-2839 for aliphatic C-H stretching (methyl and methylene groups); 1570-1457 C=C stretching and C-N of the imidazolium ring; 1175-1071 Si-OCH$_3$; 805 from chloride anion.

To a solution of 2.42 g (0.0086 mol) of the synthesized chloride salt dissolved in 50 mL acetone, 2.47 g (0.0086 mol) of LiNTf$_2$ was added and the mixture was left under stirring for five days at room temperature under nitrogen atmosphere.

After concentrating under vacuum the solid was solubilized in 50 mL of CH_2Cl_2 and washed with water until $AgNO_3$ test was negative. The organic phase was then dried over anhydrous $MgSO_4$, filtrated and its solvent was evaporated. The obtained product was dried under vacuum for 3 h at 40 ∘C. The ^{1}H-NMR data were as follows:

^{1}H-NMR (400 MHz, $CDCl_3$, 25 °C) δ (ppm): 0.52 (m, CH_2Si), 1.81 (m, CH_2CH_2N), 2.49 (s, $SiOCH_3$), 3.43 (s, CH_3N), 3.76 (t, CH_2N), 4.17 (t, CH_2), 7.52 (s, H5), 7.61 (s, H4), 8.39 (s, H2).

2.3 Ionic Liquids Immobilization on MCM-41

In a distillation apparatus, 2 g of commercial MCM-41 were dispersed in dried toluene. After the addition of 1 g $(MeO)_3SipmimNTf_2$ (50 %) and 0.4 g (20 %), the mixture was stirred at 90 °C for 16 h. In the following step, the solvent and the methanol created in the grafting step were distilled off, the remaining solid dried under high vacuum and the excess of IL removed by 8 h extraction with boiling dichloromethane and the material was dried under vacuum (Valkenberg, Castro and Hölderich, 2002), as show in Figure 2.

The structure of the mesoporous material MCM-41 before ionic liquid immobilization and the Supported Ionic Liquids (SILs) was confirmed by FTIR.
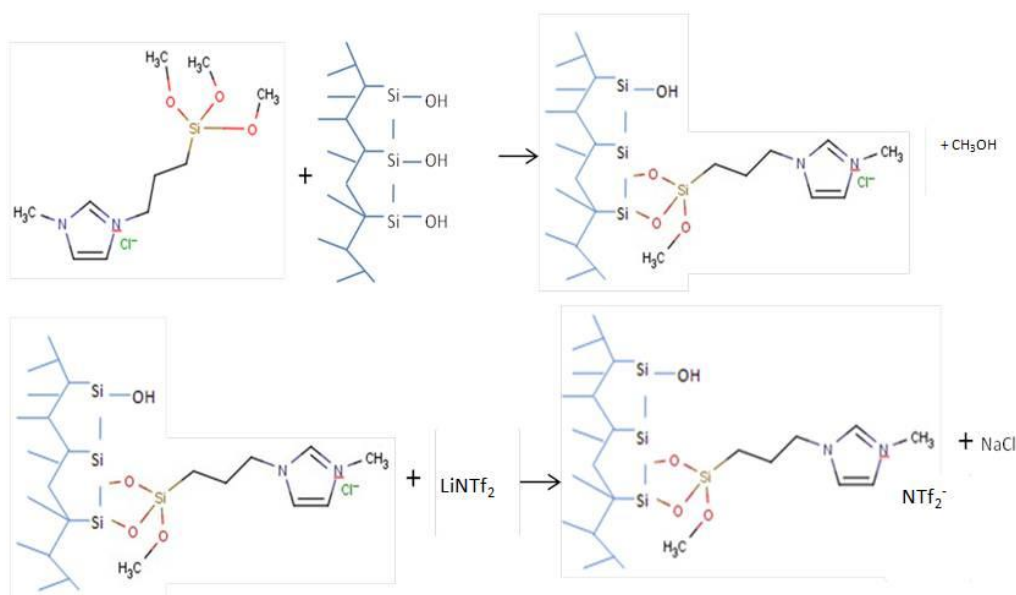

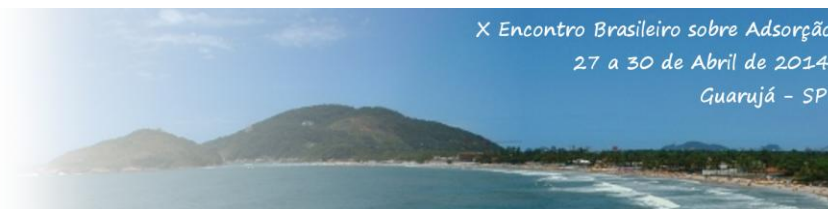**Figure 2.** Chemical equations that represent the immobilization of IL in commercial MCM-41.

2.4 Characterization

The FTIR spectra were performed on a Perkin-Elmer Spectrum 100 spectrometer in KBr pellet form. Thermal analysis, TGA were performed on TA Instrument, model Q600 SDT. The TGA ranging from room temperature to 1000 °C for 5 min with a heating rate of 10 °C.min^{-1} in a nitrogen atmosphere. NMR measurements were performed at room temperature on a Bruker Avance III 400 MHz spectrometer, with probe broadband (BBO 400 S1 BBF-HD-05 Z PLUS) and solid-state NMR for the observation of [29]Si resonances; cross-polarization magic angle spinning (CP-MAS) at 5 kHz was selected to record silicon spectra. SEM examination was carried out on a scanning electron microscope (Philips XL30) operated at 20 kV. The surface area and pore size were calculated from N_2 adsorption data at -196 °C (Micromeritics Instrument Corporation, TriStar II 3020). The density was determined on a Ultrapycnometer 1000–Quantachrome Corporation, volume cell of 20,5 cm^3 and pressure of 21,0 psi (1,45 bar).

2.5 CO_2 Adsorption

The sorption of CO_2 in the supported ionic liquids (SILs) were gravimetrically assessed in a

Magnetic Suspension Balance, (Rubotherm Präzisionsmeβtechnik GmbH, 35 MPa and 673 K) equipped with a single sinker device for adsorbate density determination and thermostatized with an oil bath (Julabo F25/± 0,01 °C). The apparatus of the PTGA (Pressure and Temperature Gravimetric Analysis) is show in Figure 3.
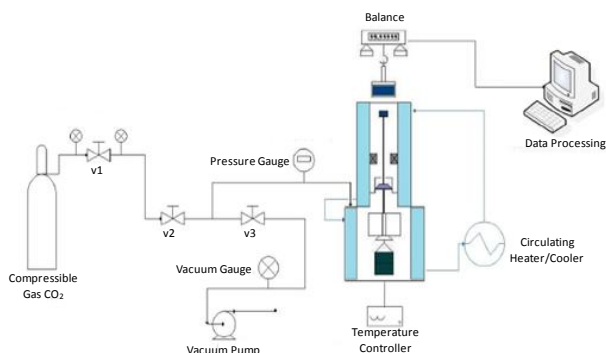

Figure 3. Experimental system for adsorption measurements in the PTGA.

When compared to other gravimetrical sorption methods, the MSB device has the advantage of allowing high pressure sorption measurements since the sample can be potted into a closed chamber coupled to an external precise balance (accuracy of ±10 μg). The SILs samples (0.06 to 0.09 g) were weighted and transferred to the MSB sample container and the system was subjected to a 10^{-7} MPa vacuum at the temperature of the sorption measurement, 298 K, for 24 hours. For all tests constant weight was achieved in this time. The CO_2 (Air liquids/99,998 %) was admitted into the MSB pressure chamber till the desired pressure, 0.1-2.0 MPa in this study, pressure gauges with an accuracy of 10^{-3} MPa.

The adsorption of CO_2 in the SILs for each isotherm and pressure considered was measured for 3 h after no more weight increasing for CO_2 sorption was observed. The mass and volume of the sample container, m_{sc} and V_{sc}, respectively, are fixed and known values for each temperature, determined from a test with empty system, without CO_2, the mass excess CO_2, $mCO_{2exc(P,T)}$ as described at equation (1).

$$mCO_{2exc(P,T)} = \{(m_{read} - m_{sc(P,T)}) + [\rho_{g(P,T)} \cdot (V_{sc(T)} + V_{s(P,T)})]\} - \{m_{s(vac,T)}\} \quad (1)$$

After each sorption test, CO_2 desorption was performed and for all the tests all the SILs returned to its original weight in the sample basket. The mass of CO_2 absolute in the SILs, ($mCO_{2\ abs}$), was calculated using the equation (2).

$$mCO_{2abs(P,T)} = mCO_{2exc(P,T)} + \rho_{g(P,T)} \cdot V_{ads(P,T)} \quad (2)$$

$$V_{ads\ (P,T)} = mCO_{2\ exc\ (P,T)} / \rho_L \quad (3)$$

Where the term m_{read} refers to the mass read on the balance, m_s is the mass of the solid in vacuum, ρ_g stands for CO_2 density, directly measured with the MSB coupled single-sinker device, ρ_L is the density of the adsorbed phase ($\rho_{ads} = \rho_L$), V_s is the adsorvent volume of solid sample of SIL, V_{ads} is the adsorbate volume. The term « ρg .V », for the equations 1 and 2 represents the buoyancy correction as described by Dreisbach and Lösch (2002).

It is interesting to note, that the volume of the adsorbed phase (V_{ads}) cannot be measured experimentally, therefore were sought theoretical models, mostly and in accordance with working pressures up to 6 MPa, they regard the density of the adsorbed phase constant and equal to the density of CO_2 in the boiling point at 1 atm, call density liquid CO_2 ($\rho_L = 1.227$ g/cm^3); the equation 3 refers to V_{ads} calculation applied in the equation 2 (Dreisbach and Lösch 2002).

3. RESULTS AND DISCUSSIONS

The results for the FTIR spectra for the SILs are showed at Table 1.

Table 1: Assignments of FTIR spectra for MCM-41 and SIL.

Assignments ν (cm^{-1})	MCM-41	LINTF2M50
n Si-OH silanol	3322	3553
n C-H		2934
		2853
n Si-O	1637	1631
n C-C e C-N		1572
imidazolium		1460
n Si-O-Si siloxano	1163	1182
n R$_3$Si-O-SiR$_3$ disiloxano		1047
n N-S		837
n C-S		791
n C-F		742

The assignments regarding at ILs, mainly the imidazolium ring bands around of 1572 and

1460 cm^{-1} and the alkyl chain about 2934 and 2853 cm^{-1} demonstrate that IL is present into MCM-41 support. The corresponding bands to anions also are well defined in the region between 837 and 742 cm^{-1}, thus indicates that ILs is immobilized.

In order to verify the efficiency of the immobilization process, comparing data obtained by the TGA for the samples with different concentrations of ILs , see Figure 4.
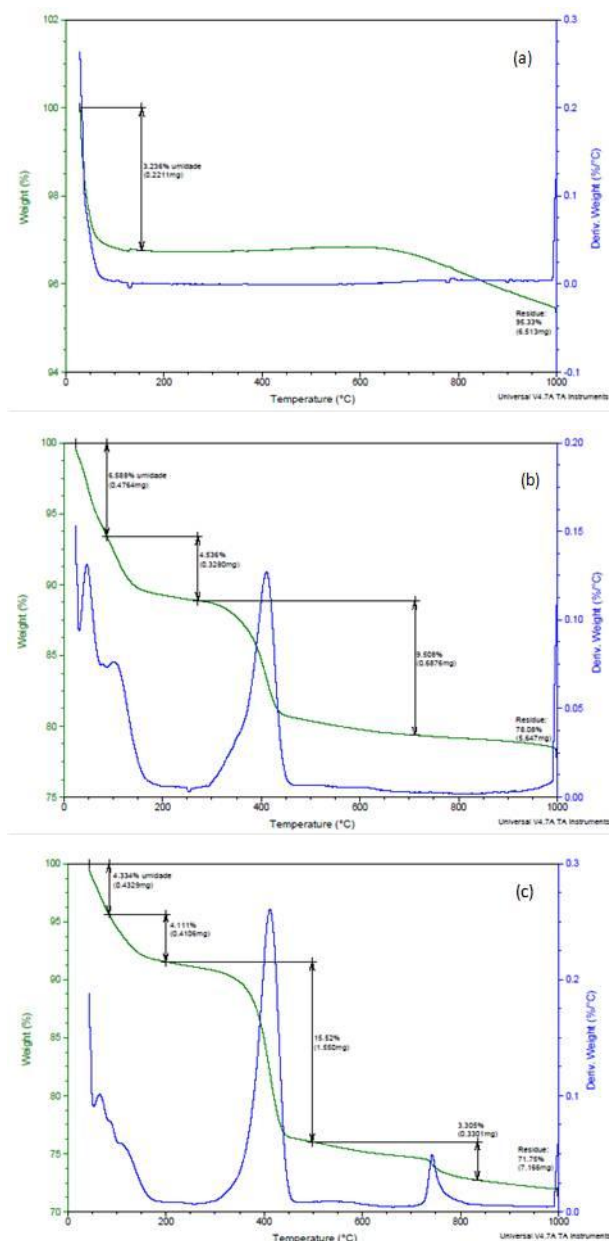

Figure 4. TGA for (a) MCM-41 neat; (b) LINTF2M20; (c) LINTF2M50.

The Figure 4 presents thermograms for samples of MCM-41 neat and with supported IL (20 and 50 %). We note that mesoporous material MCM-41 is more thermally stable, because it do not presents mass loss up to 1000 °C, whereas for the supported ILs both show a mass loss in degradation temperature of IL, 500 °C, however the mass loss for LINTF2M20 was much lower, consequently has less IL immobilized.

The NMR experiments in solid-state [29]Si CP-MAS enable to characterize the bonds of silicon atoms in the samples of ionic liquids incorporated into these support in order to prove to prove that the ILs were immobilized in these matrices.

In the Figura 5 the NMR spectra of mesoporous material MCM-41 neat (a) presents chemical shift at -92.07, -100.89 and -109.87 ppm for Q^2, Q^3 e Q^4, respectively, confirmed with literature data.
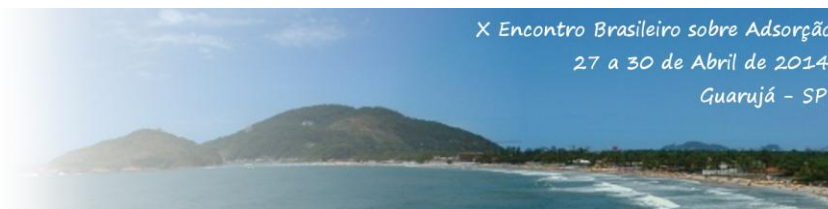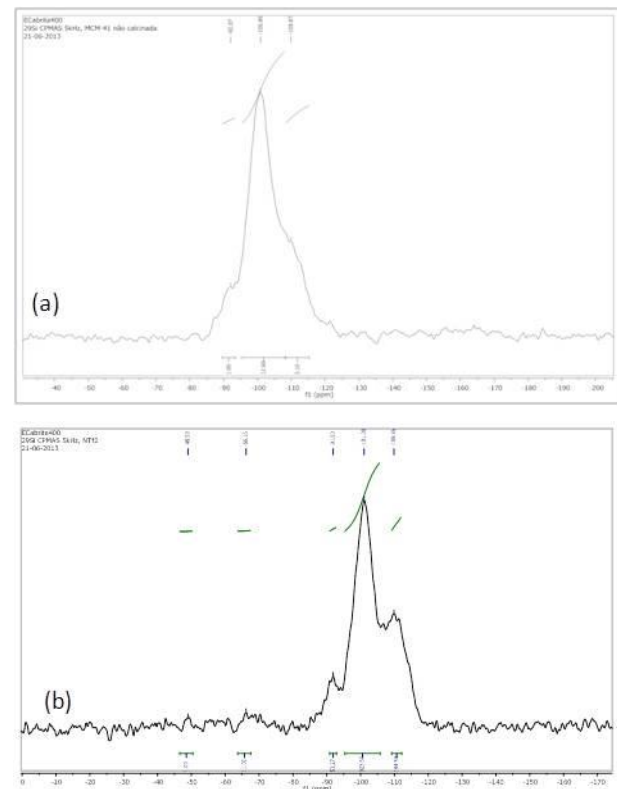

Figure 5. [29]Si-CPMAS spectra: MCM-41 (a) e LINTF2M50 (b).

In mesoporous material MCM-41 neat had the highest percentage of Q^3 (75 %), referring to silicon atom with only silanol group (Si-OH) to replacement. In the presence of 50 % of supported

IL some changes were observed in the compositions Q^n e T^n.

An example of NMR spectrum for supported IL, LINTF2M50 is showed in Figure 5 (b), in which we note that Q^2 and Q^4 decreases and, occurs an increase at Q^3 quantity, beyond the formation of the silicon chemical shift T^2 e T^3, in the region at -66.16 and -48.99 ppm, respectively, demonstrating that IL has affinity with the support, here illustrated by NMR technique, as will be shown below.

In order to investigate the morphology of the support and the covering by the ILs, the Figure 6 shows the images from Scanning Electron Microscopy (SEM).
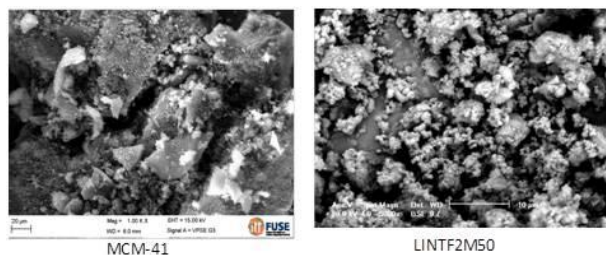

Figure 6. SEM for MCM-41 and LINTF2M50.

We can observe in this micrograph that LINTF2M50 shows a powder consisting of smaller agglomerated particles. There is no way to determine the presence of the IL in these images, however it can be concluded that the mesoporous material had its morphology altered by the presence of the IL compared with the image of pure MCM-41.

The physical characterization of the adsorbents was performed by analysis of N_2 adsorption for determination of the surface area and pore volume and, the density determined by Helium Picnometer. From the experimental data, summarized in Table 2, it can be observed that the values of BET surface area and pore volume of MCM-41 decrease with the incorporation of ionic liquids.

Table 2: Structural properties for supported ILs.

Materials	S_{BET} (m^2/g)	V_p (cm^3/g)	Poro size - BET (Å)	ρ_s (g/cm^3)*
MCM-41	841,76	0,952	45,24	0,340
LINTF2M50	233,75	0,249	42,62	1,493
* Determined by Helium Picnometer.				

The results represented in terms of absolute adsorption can be viewed in the graph illustrated in the Figure 7.
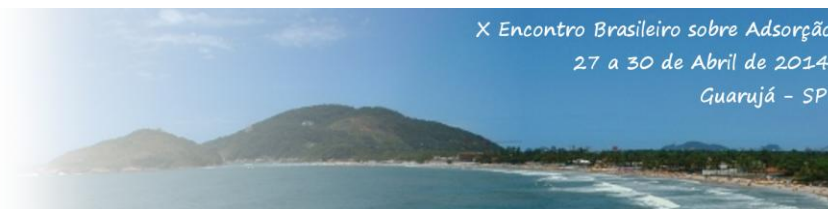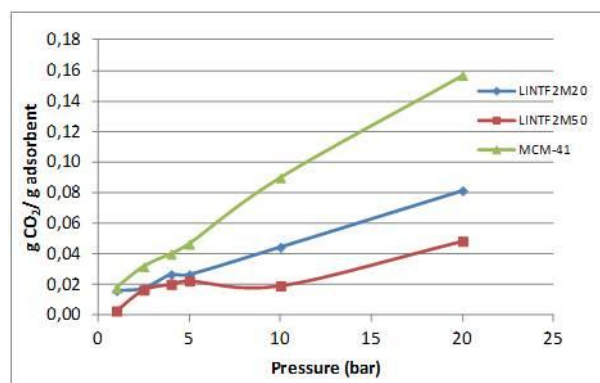

Figure 7. CO_2 adsorption in the PTGA at 25 °C.

From the curves of Figure 7 it can be seen that the capacity to adsorb CO_2 to supported IL is smaller than pure MCM-41, and with the pressure increases, the MCM-41 reaches higher values of CO_2 adsorbed which is a material already used as adsorbent for CO_2 capture processes (Xu et al., 2003; Yue et al., 2008; Wang et al., 2011; Shell et al., 2012). The lower values for LINTF2M50 are explained by the decreasing of surface area which caused a decrease in the pore volume of the MCM-41 material by IL compromising its adsorbent function.

For the same reason explained in the graphic above that the highest concentration of IL support in the amount of adsorbed CO_2 was smaller difference that stands out with increasing pressure. An example, at 5 bar LINTF2M20 presents value of 0,026 and LINTF2M50 0,022 g CO_2/g adsorbent, while at 10 bar the values are 0,044 and 0,019, respectively.

5. CONCLUSIONS

The characterization techniques performed by IR, NMR, TGA, N_2 adsorption and SEM shows that the ILs are covalently linked to the immobilized support, the support was changed the morphology and surface area and pore volume decreased by incorporating ionic liquids. The results of the CO_2 adsorption at low pressures were lower for supported ionic liquids, and with the increasing of pressure, pure MCM-41 material exhibited better adsorption capacity.

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