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Synthesis and Characterization of 1-Methyl-3-Methoxysilyl Propyl Imidazolium Chloride – Mesoporous Silica Composite as Adsorbent for Dehydration in Industrial Processes

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Ionic liquid – mesoporous silica composite was synthesized as a new adsorbent for dehydration in industrial processes. An ionic liquid (IL) with proved dehydration properties has been covalently anchored to mesoporous silica. The parameters of the synthesis were studied to produce a solid and stable composite. The material was then characterized by SEM, BET, FTIR, NMR, Raman, XRD, XRF, MALDI and LDI confirming the presence of a covalent bond between the ionic liquid and the solid matrix. Evaluations have shown that the material kept the IL dehydration property.

Keywords: *Ionic liquid, composite, Immobilized, Porous silica*

Introduction

Silica is an inorganic material broadly used as catalytic support or material for chromatographic columns. Its preparation involves polycondensation of sylanol groups (-Si-OH) from orthosilicic acid ($Si(OH)_4$). Through the synthesis, the silicon precursor can interact with porogenic agents or surfactants when added to the reaction media. This sort of substances form micelles, which keep trapped in the growing structure of siloxanes. As a result, a hybrid material is obtained, its organic component can be extracted with solvents otherwise can be calcined to give rise to a solid structure based on an irregular arrangement or irregular channels with silica walls. [1,2]

Ionic liquids (IL) are a synthetic group of chemicals with a growing interest due to their unique properties including melting points below 100°C, negligible vapor pressures, high thermal stabilities, high viscosities, and the great number of anions and cations available [3] that allow tailoring the ionic liquids based on the applications. Due to all these properties, there is a broad field of potential applications; our interest is as an extracting media. [4] The ionic liquid chloride 1-methyl-3-methyl imidazolium has been reported as a material with dehydrating properties [5, 6]

Industrial applications of ionic liquids offer environmental advantages but still have room for improvement, mainly due to their high costs and high viscosity that make applications expensive energetically and economically. In an effort to solve these issues, preparation of immobilized functional ionic liquids (IFILs) has emerged as a better option.[7, 8] These kind of solid composites can be easier handled, separated, regenerated and re-used, the anchoring processes have been used in catalytic processes including esterification, nitration, enzymatic reactions among others [9-11]. The grafting method or valent anchoring method avoid IL leaching and involves an anchor group covalently attached to the surface that is used as the cation in the formation of the ionic group, in this way a thin fil of IL is formed on the surface of the support. Here we report the synthesis and characterization of a solid composite based on a mesoporous silica material, covalently bonded to the ionic liquid chloride 1- methyl-3-methoxysilyl propyl imidazolium with application in dehydration processes of industrial interest including natural gas or bioethanol among others.

1. Experimental

1.1 Synthesis of chloride 1-methyl-3-methoxysilyl propyl imidazolium

Stoichiometric amounts of (3-chloropropyl) trimethoxy sylane (Merck S.A) and 1-methyl imidazolium (Merck, S.A.) were mixed and heated at 78°C under inert atmosphere and reflux. The produced chloride 1-methyl-3-methoxysilyl propyl imidazolium was rotoevaporated, washed and dried under vacuum. A yellow viscous material was obtained with 78% yield. [12,13]

1.2 Synthesis of mesoporous silica

For this synthesis, according to the nature of the surfactant and pH of the synthesis media, three main types of interactions are involved. In alkaline media, where the siliceous species bear negative charges (I^-), the interactions with cationic surfactant (S^+) are electrostatic (S^+I^-); [14] non-ionic surfactants (S^0) used in neutral media, allow hydrogen bonds and Van der Waals interactions (S^0I^0). [15] In acidic media, the interaction between the silica and the surfactant is mediated by X^- anions as described by $S^+X^-I^+$ [11]; in this case glycerol was used as porogenic agent (a renewable, non-toxic, highly available and cheap material) [16] and TEOS (tetraethoxysilane) (Merck S.A) as siliceous source. In the first step, hybrid

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micelles were formed by interaction between the glycerol and TEOS under controlled pH. In the second step, the condensation reaction occurred by addition of NaF, which is both the starter of the poly-condensation reaction and the precursor of the material with meso- structural properties.

After evaluation of different reaction parameters it was determined that using CH_3COOH at pH 2 as a reaction media, molar ratios TEOS: Glycerol and NaF:TEOS of 1:6 y 1:10, respectively and dried at 90°C for 12 hours, allows to synthesize SiO_2 with 85% yield.

2.3 Synthesis of 1-methyl-3-methoxysilyl propyl imidazolium chloride – mesoporous silica composite

A mix of Ionic liquid/silica with a molar ratio of 0,2 was heated at 90°C for 24 hours, the produced composite was filtered and then washed with methanol.

2.4 Characterization

FTIR and Raman spectra were recorded on a Tensor 27 Bruker with an ATR cell and a Raman confocal microscope LabRam High Resolution (HR) from Horiba, respectively. X-ray diffraction (XRD) patterns were recorded on a BRUKER model D8 ADVANCE equipped with a graphite monochromator powder diffraction system using Cu Kα1 radiation of 0.15406 nm wavelength operated at 40 kV y 30 mA. The BET (Brunauer–Emmett–Teller) specific surface areas were calculated using adsorption data in a relative pressure range of P/P0 = 0.05–0.25. Pore size distribution curve was calculated from the adsorption branch using the BJH (Barrett–Joyner–Halenda) method. The total pore volumes were estimated from the amounts adsorbed at a relative pressure (P/P0) of 0.99. Quantitative analysis was performed by XRF on a dispersive wavelength instrument 4KW BRUKER model S8 TIGER. Scanning electron microscopy (SEM) was performed using a FE-SEM QUANTA FEG 650 (FEI) system with a LFD detector, at 7 kV equipped with EDX. NMR spectra were recorded on a Bruker Advance III 400 MHz Ultrashield. Mass spectra were recorded using LDI (Laser Desorption Ionization) and MALDI with CHCA as matrix using a Bruker Ultraflextreme MALDI TOF-TOF (Bruker Daltonics, Billerica, MA).

2. Results and discussion

The ionic liquid was synthesized as explained before; the characterization included FTIR spectrum, the assignment of the spectrum bands corresponds with functional groups presents in its structure. KBr liquids cell: 3363 (OH), 3140 (C=C), 2947 (CH_2), 2841 (CH_3), 1568 (C=C) 1460 (CH_3), 1182 (Si-O-CH_3), 1070 (Si-O-CH_3), 810(Si-C). These observations indicate that the organic silica structure keeps unchanged during the anchoring process. NMR spectrum allowed correlation of every type of signal to the corresponding protons in the molecular structure as shown in Figure 1.

^{1}H NMR (400 MHz, D_20): δ (8.67, 2H) δ (7.56-7.29, 2H) δ (4.13, 4H) δ (3.82, 6H) δ (3.54-3.36, 2H) δ (3.25, 9H) δ (1.87, 4H) δ (0.73-0.46, 4H). Signals integration showed duplicity for the corresponding signals of propyl imidazolium, which is explained by considering the presence of a cluster. Analysis by MALDI using CHCA as matrix was performed to confirm the cluster formation; the approach shown between 300 and 400 m/z in Figure 2 presents the m/z 369 corresponding to the cluster mass: the proposed structure for it is shown in Figure 3.

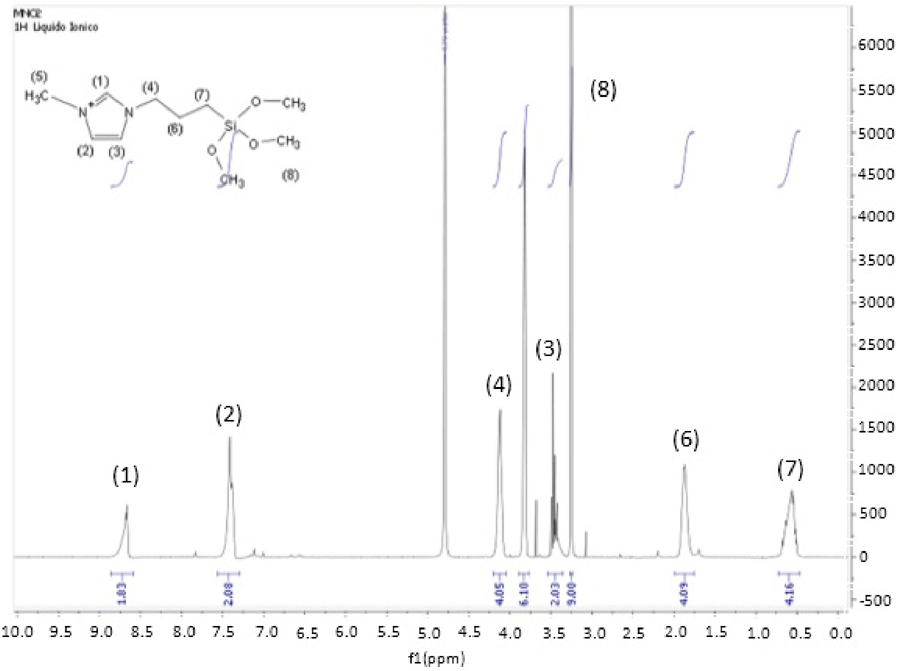

Figure 1. Spectrum NMR of 1-ethyl-3-methoxysilyl propyl imidazolium

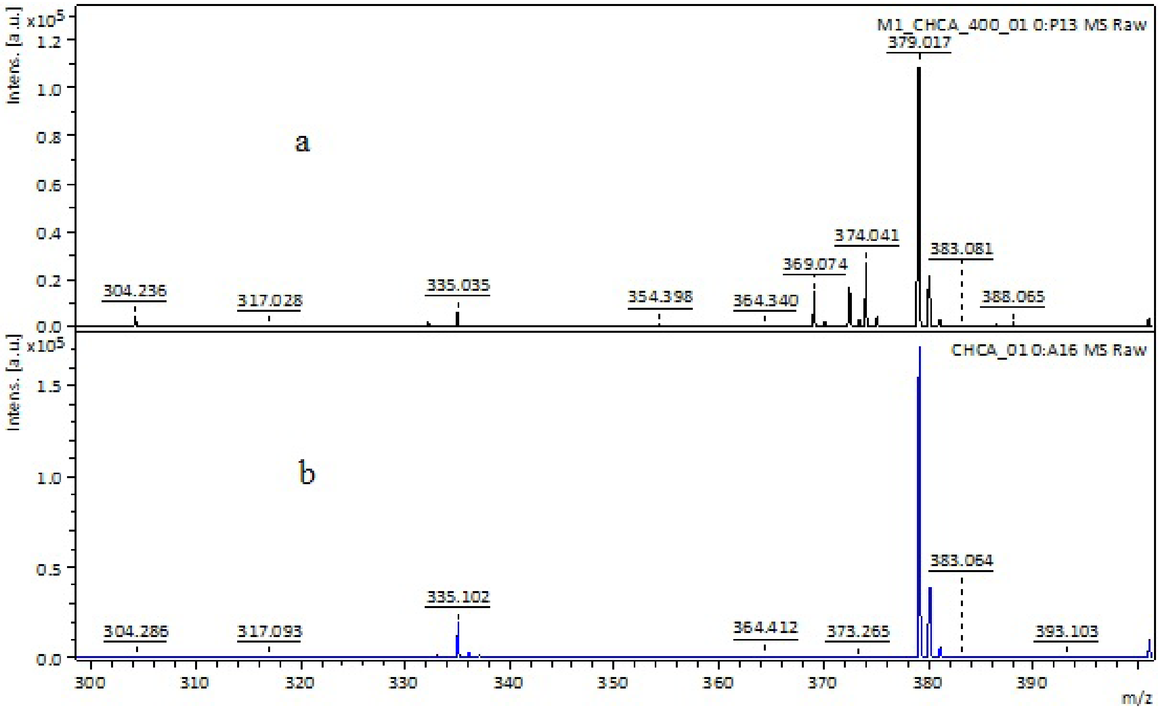

Figure 2. MALDI spectra: a. Spectrum of 1-methyl-3-methoxysilyl propyl imidazolium with the matrix CHCA b. Spectrum MALDI of the matrix CHCA. Approach between 300-400 m/z.

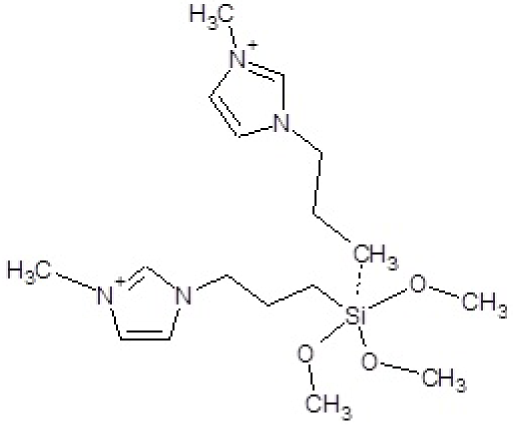

Figure 3. Proposed structure for the ionic liquid cluster

Additional characterization of the ionic liquid included analysis by laser desorption ionization (matrix free used for small molecules). The molecular mass of the ionic liquid is 280 Da, however the molecular ion is neutralized by the chloride counter ion, in consequence, the expected molecular ion must be 245 m /z as observed in the corresponding spectra shown in Figure 4.

SEM as shown in Figure 5 allowed observation of the synthesized silica morphology; amorphous particles are observed most of them with micrometric size as shown at different optical magnifications, the average sized is between 90-120 µm, aggregates are not observed meaning a proper dried process of the gel. BET analysis determined an average surface area of 104.02 m^2/g and an average pore size of 28 nm. Quantitative analysis by FRX showed a Si content of 44, 7% a 4,3% of error when compared with the theoretical value.

Qualitative analysis by XRD showed a profile characterized by a broad band typical of an amorphous material. Comparison with profiles reported at the PDF-2 del International Center for Diffraction Data (ICDD) database determined the presence of quartz SiO_2 in addition to a second phase of Malladrite (Na_2SiF_6), as a result of the reaction of SiO_2 with the catalyst NaF. See Figure 6.

Once the ionic liquid and the solid matrix were synthesized, the immobilization was realized through a process named *grafting*. In this process a covalent bond is created and the ionic liquid in confined in the matrix material [17]. The idea was to prepare a heterogeneous material supporting the ionic liquid on a high surface area and good mechanical stability material. Through the process, the active sites are increased in this case for dehydration purposes using the ionic liquid more efficiently with less quantity.

SEM images in Figure 7 let see the morphology and surface patterns of ionic liquid on SiO_2, in addition, it is clear from the image that the SiO_2 structure did not suffer any kind of modification after the immobilization process as reported before for other type of matrices. [18] Images in Figure 9 showed non-homogeneous aggregates of micrometric size uniformly distributed on a particle of SiO_2. BET analysis determined a surface area of 71.23 m^2/g and a pore size of 8.74 nm.

The covalent linkage of the ionic liquid moieties to the silica framework and the ionic liquid moieties content in the composite were assessed by [19] Si NMR technology as shown in Figure 8. The spectrum displayed five distinct resonances centred at -111, -102, -93, -67 and -57 ppm that can be

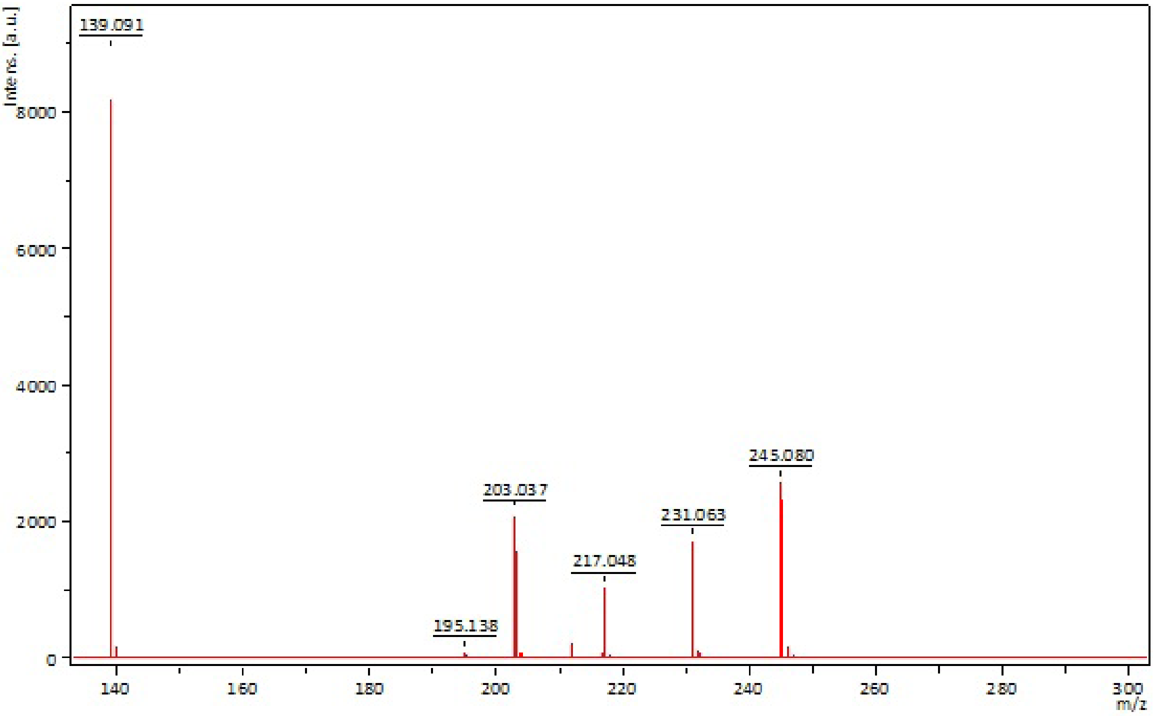

Figure 4. LDI spectrum of 1-methyl-3-methoxysilyl propyl imidazolium

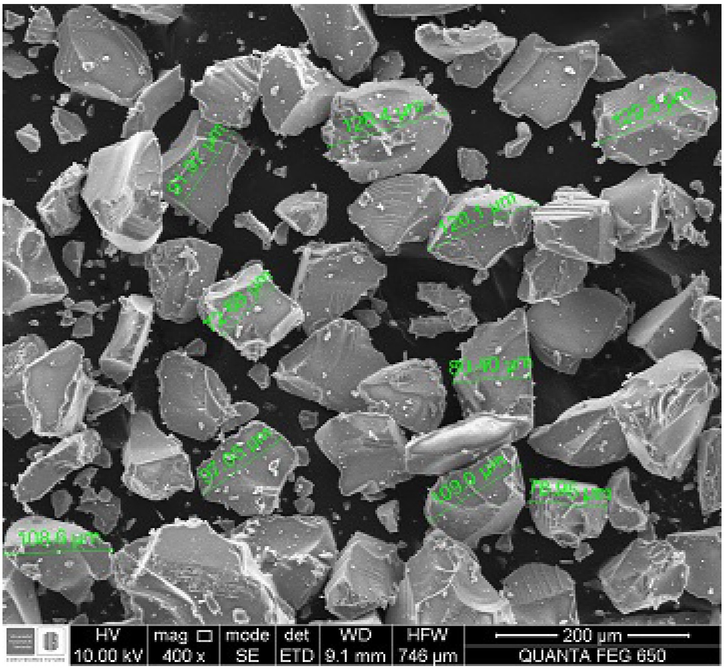

Figure 5. SEM Image of synthesized SiO_2 particles at 200 µm

assigned, respectively to, $Si(OSi)_4$ [Q^4], $(HO)Si(OSi)_3$ [Q^3], $(HO)_2Si(OSi)_2$ [Q^2], $RSi(OSi)_3$ [T^3] and $RSi(OSi)_2(OH)$ [T^2] environments about silicon. The appearance of T^m signals ($RSi(OSi)m(OH)_3$-m being R the structure of the IL and taking m values of 3 and 2 to form the structures) evidences the existence of Si-C in the framework and thus the effective incorporation of the ionic liquid moieties. The relative integrated intensities of organosiloxane (T^m) and siloxane (Q^n) signals calculated in the form of $T^m/(T^m+Q^n)$ allowed the quantitative assessment of the incorporation degree of the ionic liquid moieties. The measured ionic liquid moieties content was 0.21 mmol/mol of SiO_2, which is close to that expected on the basis of the initial mixture (0.80 mol/mol of SiO_2). [19-21]

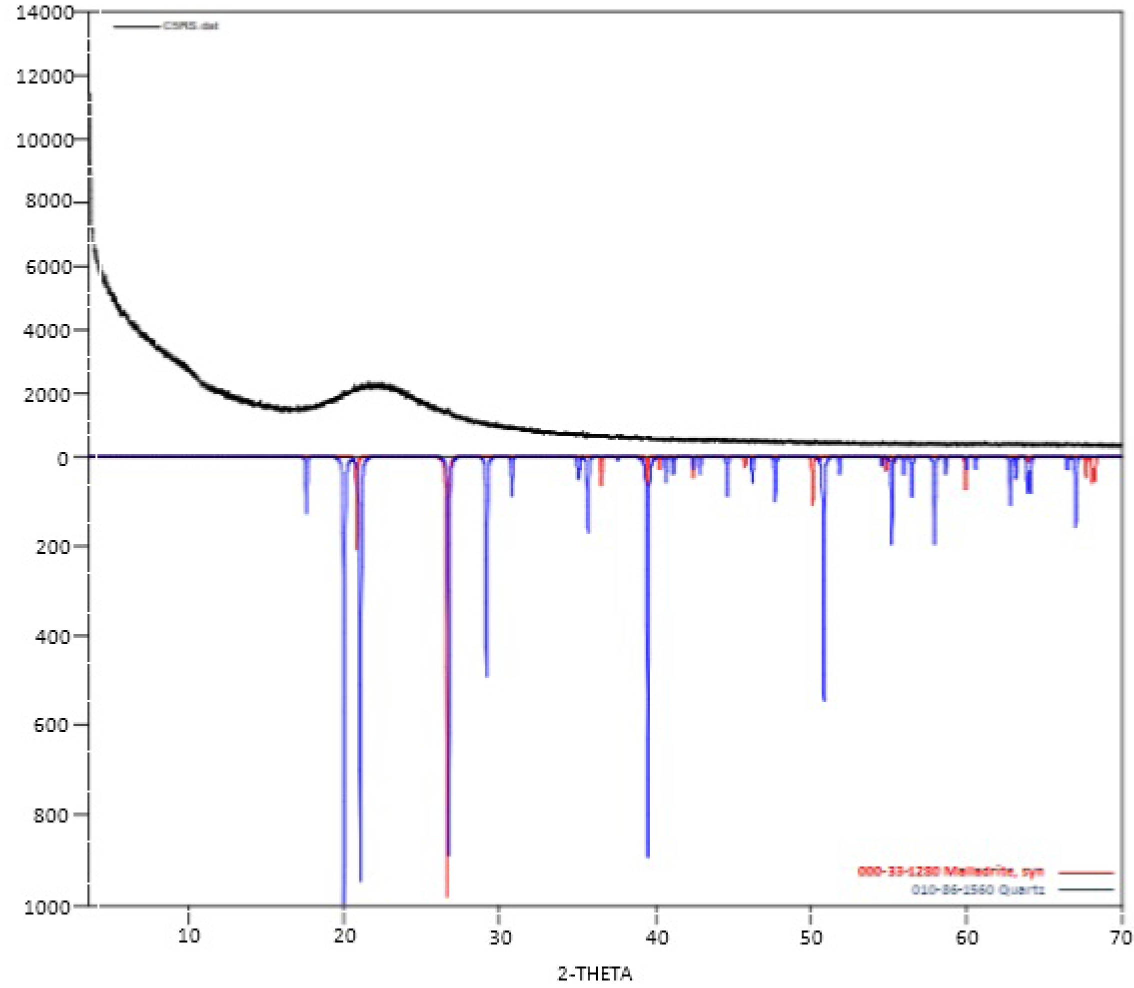

Figure 6. Diffraction profile of synthesized SiO_2.

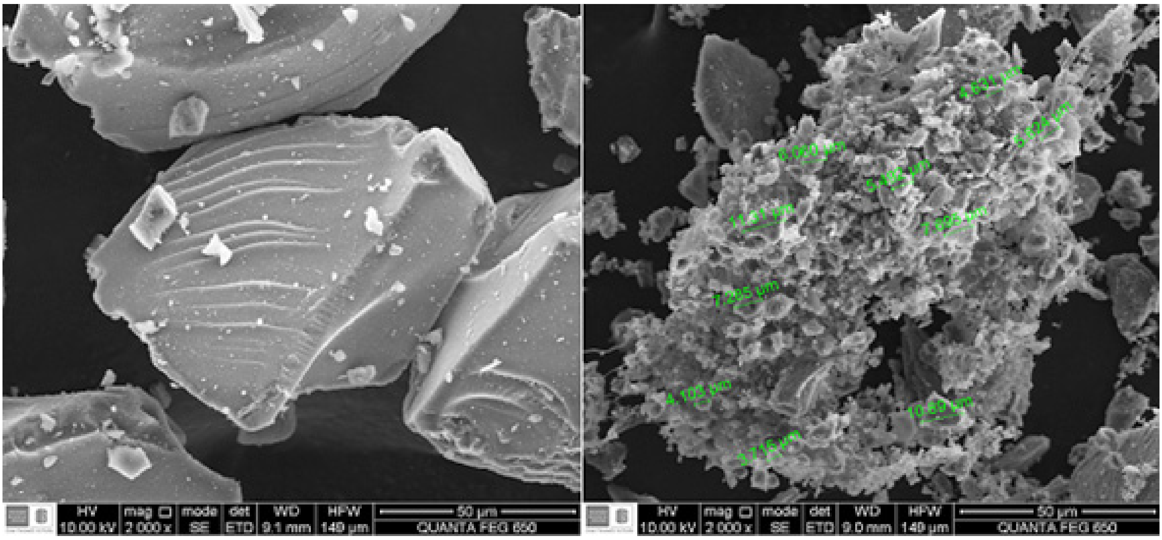

Figure 7. SEM images: on the left pure SiO_2, on the right the composite (immobilized IL)

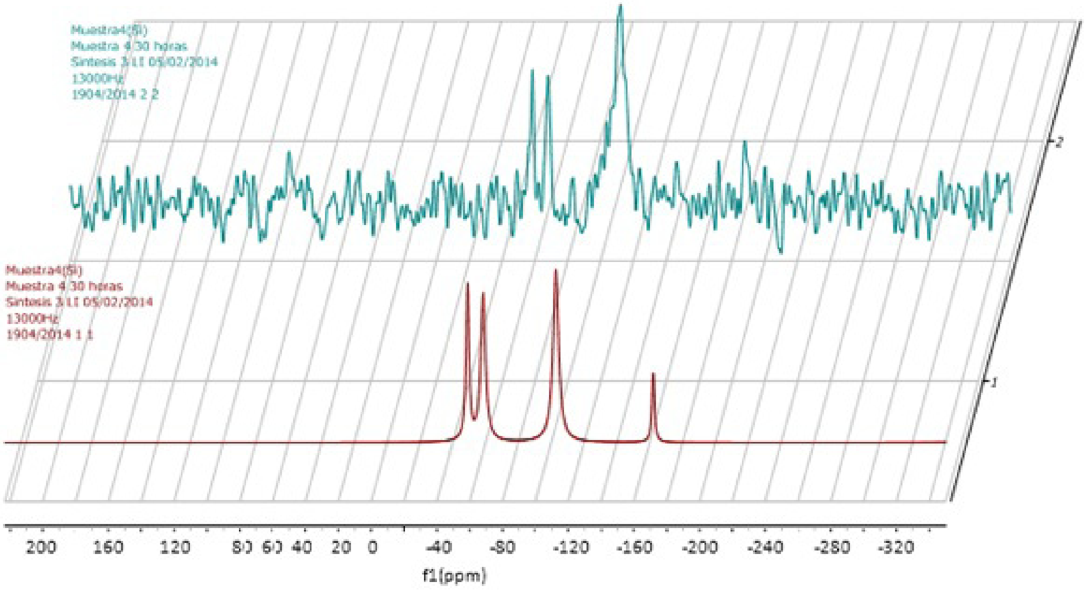

Figure 8. RMN- 29Si spectrum IL immobilized on SiO_2 surface

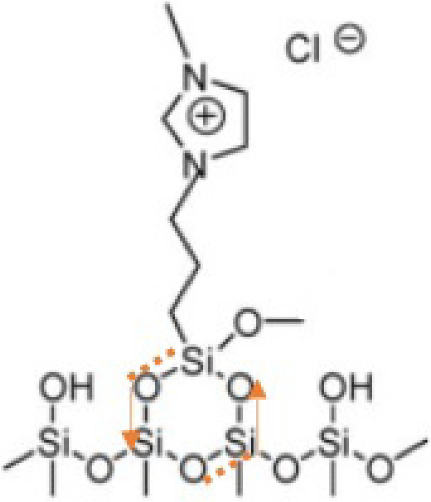

Figure 9. Proposed structure of the ionic liquid immobilized on SiO_2

Raman characterization of the composite before and after the immobilization process was performed; spectra are shown in Figure 10. In addition to proper SiO_2 signals appear two bands at 597 and 623 cm^{-1} from quadrant in-plane bend vibrations in imidazolium ring. The spectra is typically dominated, by a very strong band in the 1050 and 980 cm^{-1} region that involves the 2,4,6 carbon radial stretch from the imidazolium ring, in addition to the weak Si-O signals at 790 and 880 cm^{-1} [22], these observations allowed to confirm the presence of the ionic liquid on SiO_2 surface.

Evaluation of the composite has been performed by determining the dehydration percentage of bioethanol 93.45%. 0,15 g of the composite was set in a quartz reactor with an internal diameter of 4 mm. The reactor temperatures evaluated were 60, 70 y 80°C, with feed flows of bioetanol of 0.1, 0.2, 0.3 y 0.4 mL/min and –N_2- as carrier gas at 130, 100 y 80 mL/min. The experimental design showed that nitrogen flow at 80 ml/min, the reactor at 80°C and bioethanol flow at 0.1 mL/min that amount of composite is capable of removing above 61% of the water as shown in Figure 11.

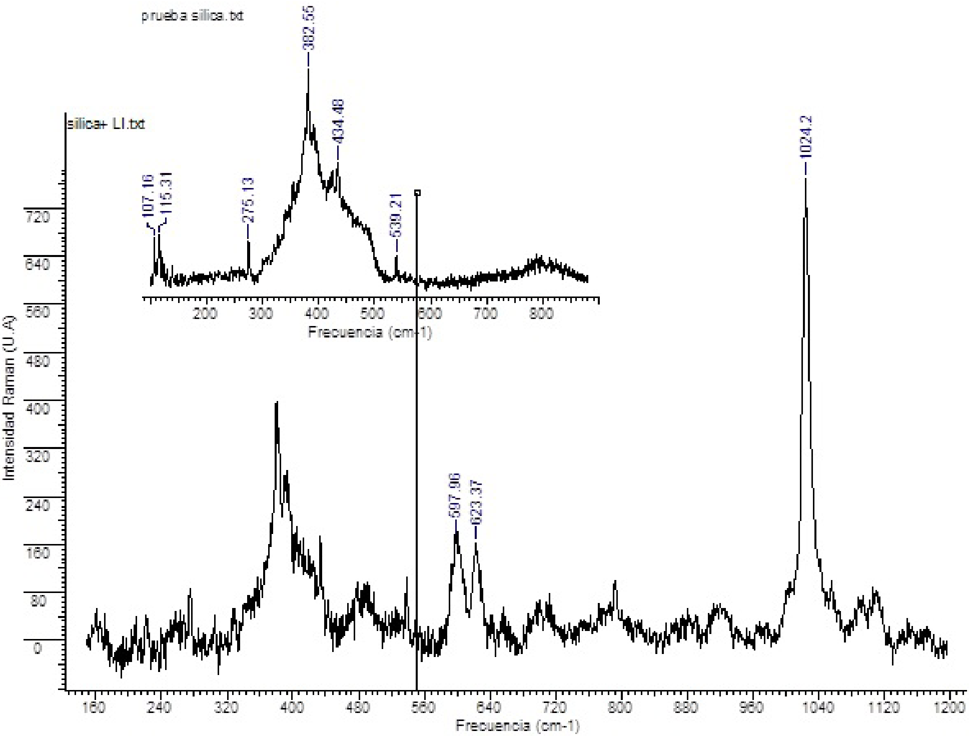

Figure 10. Raman spectra of SiO_2 and ionic liquid immobilized on SiO_2

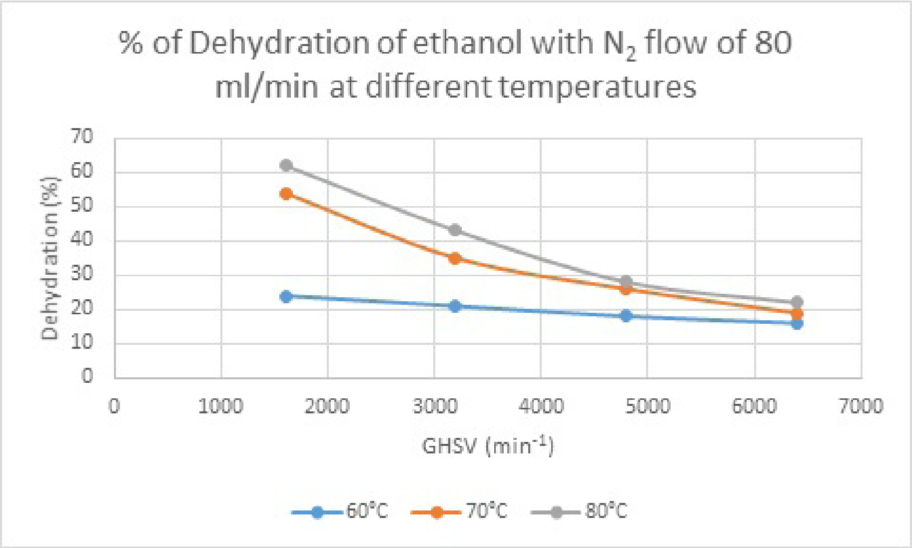

Figure 11. Dehydration of ethanol (93.45%) using the composite on a fix bed reactor with a nitrogen flow of 80 ml/min at different temperatures.

Conclusion

A composite was prepared by bonding the 1-methyl-3-methoxysilyl propyl imidazolium to the mesoporous matrix of silica. A covalent bond between the methoxisylil and the hydroxy groups on the silica has been created by the grafting method. The composite material led to a more heterogeneous environment for the dehydration been with the mass ratio used ($IL/SiO_2 = 0.2$) a solid material, of easy preparation and handling and with application in a fix bed reactor.

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