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Preparation nanostructured materials By sol–gel crosslinking process inpresent N,N-dimethyl amino pyridiniumionic liquid as a catalysis

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Abstract

Silica porous materials with use of the some of ionic liquids (ILs) based N, N-dimethyl aminopyridinium cation (DMAP) with high thermal stability was prepared.

First according to a proper sol-gel method, various RTILs with anions such as= Br, BF_4 as a new kind of recyclable templates in present of trimethoxysilane (TMOS) as the sol-gel precursor and deionized water were employed. Then ILs was removed from the silica matrix by calcination method.

The resulting gels were characterized by using thermogravimetric analysis, infrared spectroscopy. The calcined gels were analyzed using scanning electronmicroscopy and X-ray diffraction. In the continuous, reaction was fallowed under acidic conditions at temperature above the melting point of the functional IL such as; 2–ethoxyethyl-4-(N, N-dimethyl amino) pyridinumtetrafluoroborate with larger hydrophilic polar region in a so-called nanocasting sol-gel technique, that silica Nanostructured materials with highly ordered monolithic was obtained.

Keywords: Sol-Gel process; N, N-dimethyl amino pyridinium ionic liquid; Nanostructured material; Silica; Ionogel

Introduction

Silica based sol–gel technique has attracted a considerable interest because it has proven to be a convenient route for the preparation of hybrid compounds which combine characteristics of organic and inorganic components and applied widely in many fields, such as optical devices, sensor sciences and catalysis [1–3]. Sol–gel process is mild, which proceeds by hydrolysis of an alkoxide precursor and followed by polycondensation of the hydroxylated monomers to form a porous gel. Under this mild polymerization process, sol–gel hybrids could be easily produced by impregnates of organic reagents or copolymerization with the high reactivity of silanol by covalent bonding. The studies suggested that the properties of the sol–gel hybrids could be tuned by designing the sol–gel matrix with suitable materials.

Ionic liquids (ILs) are composed entirely of ions, which exist in liquid state at temperatures around 298 K and below. As a potentially environmentally benign reaction media, ILs have attracted more considerable attention for their unique chemical and physical properties, such as high thermal stability, high ionic conductivity, negligible vapor pressure and adjustability of characteristics via choice of the anion and cation combination etc [4-5].

Recently, ILs have been used in the preparation of sol–gel materials [6–13]. In sol–gel applications, ILs have served as solvents [6, 8, 12], pore templates [7, 9], drying control chemical additives [10], and possibly as a catalyst [12]. In several cases, ILs had significant effects on the porous structure of sol–gel materials [7,10,12], reduction in cracking and shrinking [10,11,14] during solvent evaporation from the sol–gel pores, and sol–gel reactionkinetics [10,12,15,16].

Based on unique properties of ionic liquid and advantages of sol–gel technique, new kind of hybrid materials that combine ILs with sol–gel appeared and had promising applications in preparation of nano-materials, catalysis and biosensor [17–22], Shi et al. also synthesized [RDMAP][X] based sol–gel hybrids material and characterized the resulting matrix representingcrack-free morphology because the viscous IL prevented the cracking of the sol–gel derived glasses [19-21].

In this work, according to a proper sol-gel method, various RTILs with various cations and anions as templates were used. (Scheme 1). And effect of the cations and anions in ILs on morphology and structure of the calcined silica Nanostructured materials investigated. We showed that these compounds not only for solvent, but also act as catalysis in sol-gel processes.

Experimental

Materials and reagents

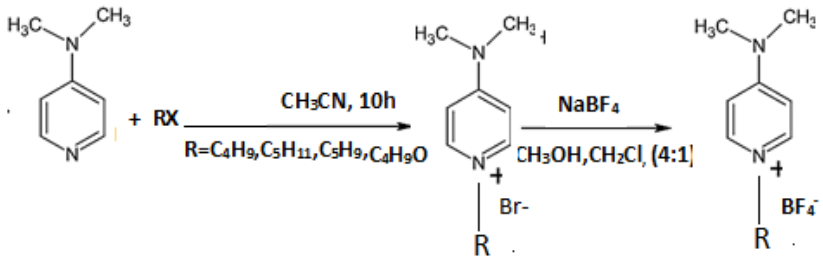
All the chemicals used in the present work were purchased from Merck and used as received.

Measurements

Thermogravimetric analyses (TGA) of the air-dried gels were performed on a TGA/SDTABSI thermogravimetricAnalyzer (METTLER TOLEDO). Samples were heated under an argon atmosphere on room temperature to 650 ℃ at 10 ℃ min^{-1}. X-ray diffraction

(XRD) patterns were performed on a D_8ADVANCE (BRUKER axs) powder X-ray diffractometer. Diffraction patterns were recorded with Cu Ka radiation (40 mA, 40 kV) over a 2θ range of 1.2 ^{0} -15^0 at a scan rate of 2℃/min.

The calcined gels were characterized using scanning electron microscopy (SEM) (Philips XL30 S-2500), infrared spectroscopy (BRUKER PS15), infrared spectroscopy (IR) (BRUKER PS15) with a Perkin-Elmer. DSC differential scanning calorimeter at a heating rate of 10˚C/min in air.



Scheme (1).Reactions processes for Ionic liquids Synthesis

Synthesis of ionic liquid compounds:

The synthetic procedure of ILsfollowed a reported route[23]. 1.22g, (10 mmol) DMAP(dimethyl amino pyridine)was added to a 50 ml three- necked round-bottom flask containing (10mmol) of anyone of compounds; 1-Bromobutane, 1-Bromopentane, 1-Bromo ethoxyethane, 1-Bromopentyne, respectively in acetonithrile and 1-Bromododecane,in dichloromethane as solvent of reaction. The mixture was heated to reflux with constant stirring for 10 h, and then cooled to room temperature. The volatile component was removed under reduced pressure to give the crude product. This compound was dispersed into ethyl acetate- isopropanol with ratio of (1:1) from which IL_nrecrystallized.

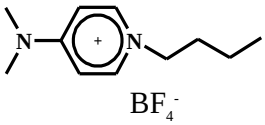
Then (10 mmol) of ILs in 10 ml dry CH_2Cl_2 was added to a solution of $NaBF_4$ (1.09g, 10mmol) dissolved in 40 ml of dry methanol. The mixture was stirred at room temperature for 20 h and then all solvents were removed. The resulting residue was dissolved in CH_2Cl_2 and it was filtered to remove NaBr, and ionc liquids of $[C_2C_3DMAP][BF_4]$,$[C_2OC_2DMAP][BF_4]$ was resulted, but $[C_4DMAP][BF_4]$, $[C_5DMA][BF_4]$was purified by column chromatography (Al_2O_3), with acetonithrile as the movable phase.

Preparation of silica Nanostructured materials with ILs ([RDMAP][X]) as the catalysis

In a typical synthesis with IL_1 as catalysis, tetramethylorthosilicate (TMOS) was used as the sol-gel precursor. Compound IL_1 (0.2 g, 1.69 mmol) was dissolved in 0.3 ml deionized water and a few minutes was heated until 60 ℃. This was allowed to cool to room temperature, then (0.625 ml) TMOS monomer was added and the mixture vortexed until a monophasic solution was obtained. Gels were stored in covered vials with punched pin-holes

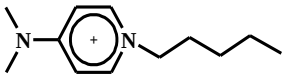
for a one week period to allow slow evaporation of the volatile components.

IL_1 was removed from the silica by calcinations of the sample at 550°C with a temperature ramp of 5 °C/min, and then was allowed to cool to roomtemperature with a temperature ramp of 20 °C/min. The final product was ground into a powder for further characterization. The other Nanostructured materials were prepared by repeating above procedure with the corresponding IL_s as catalysis.



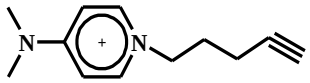
BF_4^-

$C_4DMAPBF_4$; IL_1



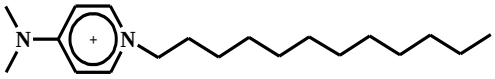
Br^-,BF_4^-

$C_5DMAPBr$, BF4 ; IL_2,IL_3



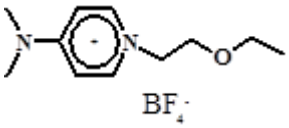
BF_4^-

$C_2C_3DMAPBF_4$; IL_4



Br^-

$C_{12}DMAPBr$; IL_5



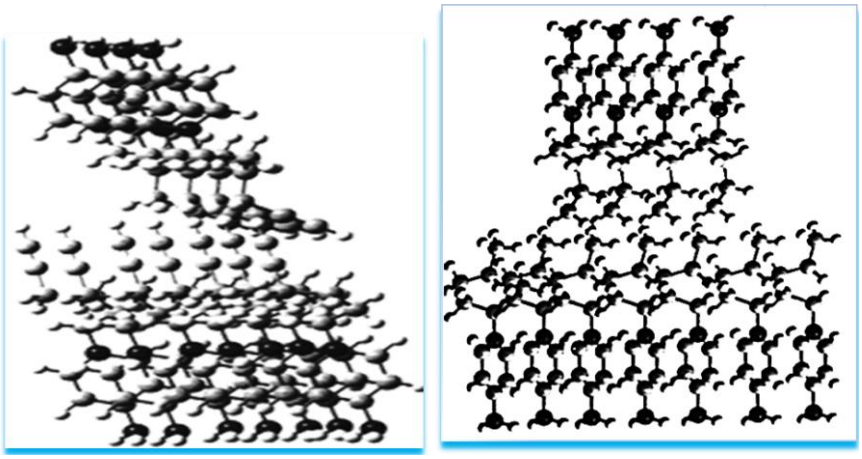
BF_4^-

$C_2OC_2DMAPBF_4$; IL_6

Scheme .2. Chemical structures of a) IL_1: 1-butyl -4-(N,N-dimethylamino) pyridiniumtetrafluoroborate($C_4DMAPBF_4$), b) IL_2: 1-pantyl -4-(N,N-dimethylamin) pyridiniumbromid and c) IL_3: 1-panty-4 -(N,N-dimethylamino) pyridiniumtetrafluoroborate ($C_5DMAPBr,BF_4$), d) IL_4 :1- pantinyl -4-(N,N- dimethylamino) pyridiniumtetafluoroborate ($C_2C_3DMAPBF_4$), e) IL_5:1-dodecyl -4-(N,N-dimehylamino) pyridiniumbromide($C_{12}DMAPBr$), f) IL_6: 2–Ethoxyethyl-4-(N,N-dimethylamino) pyridiniumtetrafluoroborate ($C_2OC_2DMAPBF_4$).

Preparation (Sg - C_2OC_2DMAP) nanocomposite under acidic condition

In this procedure 0.2g $C_2OC_2DMAPBF_4$ was mixed with 10ml of tetraethyl-orthosilicate (TEOS) and 7ml ethanol under mild magnetic stirring. After homogenization,2 ml of concentrated hydrochloride acid (36–38%) diluted by 3.5ml of distilled water was added and the mixture became coagulated gradually.After aged at 60 ℃ for 12 h, the resulted solid material was dried in vacuum at 120℃ for 4 h. Then $C_2OC_2DMAPBF_4$ were extracted from silicamatrix by refluxing the synthesized Sg-C_2OC_2DMAP BF_4 (0.5g) in 200 mL of methanolic solution of HCl (0.5M) for 48 h.



Scheme.3.tridimensional schemes of theπ -πstacking of the N, N-dimethylaminopyridinium rings and alkyl chains in pentyl and compare it with b) pentyn. (blanlk bulb is nitrogen atoms).

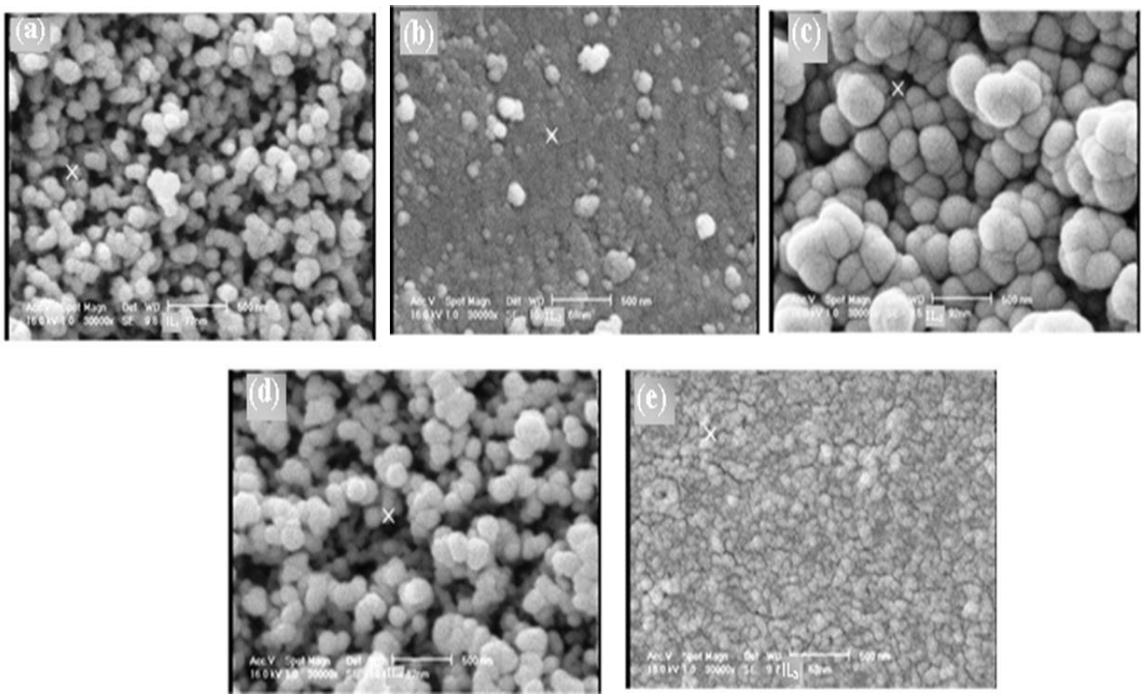


Figure (1). SEM images of the resulting morphology of the synthesized calcined silica Nanostructured materials in a molar ratio described of silicon precursor tetramethylorthosilicate to water and IL_n (n =1,2,3,4,5); scale bars: 500 nm.

Results and discussion

Some ionic liquids: ([R DMAP][X]) in which R = Bu,pentyl,), pentynyl, 2–ethoxyethyl, and dodecyl were synthesized. DMAP was reacted with alkyl bromides in which R=Bu, pentyl, pentylyl, ethoxyethyl, and dodecyl to produce some novel ionic liquids with bromide as an anion. Then anion exchange reaction was done with some anions such as $NaBF_4$ (Scheme1). These compounds were characterized by ^{1}H, ^{19}F NMR and IR

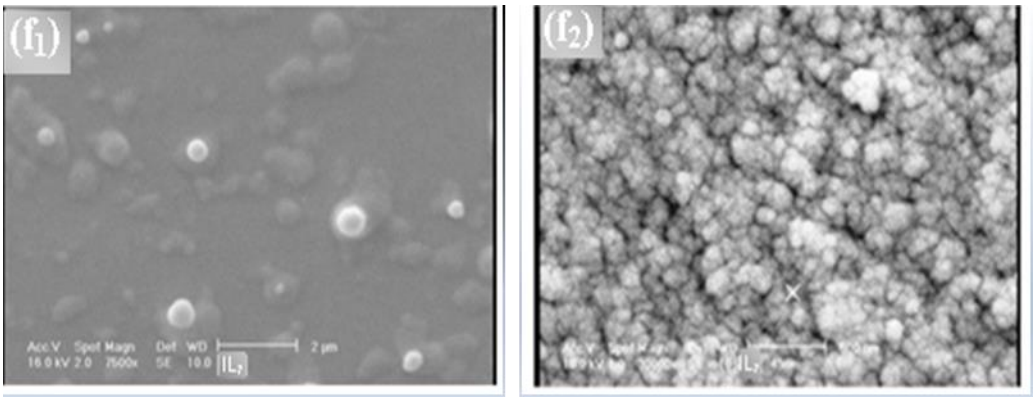
spectroscopic methods. The results are given below (Scheme1):

C_4DMAPBF_4 (n=1)

IR (KBr) cm^{-1} = 3030 (Ar C-H); 2932 (aliphatic C–H); 1651, 1571(Ar C=C); 726 (B-F).

^{1}HNMR (400 MHz, $CDCl_3$); δ (ppm): 0.70 (t, 3H, CH3-CH_2-); 1.09 -1.18 (m, 2H, -CH_2-CH_3); 1.59 -1.67 (m, 2H, -CH_2-CH_2-CH_3); 3.05 (s, 2×3H, CH_3-N); 4.02 (t,2H –CH_2-N); 6.7(d, 2H,
C-H Ar); 8.12 (d, 2H, C-H Ar).

^{19}FNMR (400 MHz, $CDCl_3$); δ = -152.55 ppm.



Figure(2). SEM images of the resulting morphology of the synthesized calcined silica Nanostructured materialsin a molar ratio described of silicon precursor tetramethylorthosilicate to water and IL_6(f_1) and also in present molar ratio described of silicon precursor tetraethyl silicate to EtoH/ HCL/H_2O and IL_6 (f_2); scale bars: 500 nm.

C_5DMAPBF_4 (n=2)

IR (KBr) cm^{-1} =3015 (Ar C-H); 2932 (aliphatic C–H); 1653, 1571 (Ar C=C); 729 (B-F).

^{1}HNMR (400 MHz, $CDCl_3$); δ (ppm): 0.660 (t, 3H, CH3-CH_2-); 1.080-1.15 (m, 2×2H, - $(CH_2)_2$-CH_3); 1.64 -1.67 (m, 2H, -CH_2-CH_2-N); 3.1 (s, 2×3H, CH_3-N); 3.9(t, 2H, -CH_2-N); 6.7 (d, 2H, C-H Ar); 7.8 (d, 2H, C-H Ar).

^{19}FNMR (400 MHz, $CDCl_3$): δ = -152.91 ppm.

C_2C_3DMAP BF_4(n=3)IR (KBr) cm^{-1} = 3019 (Ar C-H); 3157 (H-C≡C); 2929 (aliphatic C–H); 1977(C≡C), 1654, 1549(Ar C=C); 770(B-F).

^{1}HNMR (400 MHz, $CDCl_3$); δ (ppm): 1.9(t, 2H, -CH_2-CH_2-N); 3.1 (s, 2×3H, CH_3-N); 4.2-4.3(t, 2H, -CH_2-N); 4.9(t, 2H, -CH_2-C≡C); 5.6-5.7 (m, 1H, H-C≡C); 6.9(d, 2H, C-H Ar); 8.4 (d, 2H, C-H Ar).

^{19}FNMR (400 MHz, $CDCl_3$); δ = -152.57 ppm.

C_2OC_2DMAP BF_4 (n=4)

IR (KBr) cm^{-1} = 3085(Ar C-H); 2932 (aliphatic C–H); 1649, 1571 (Ar C=C); 1118 (C-O); 567(B-F).

^{1}HNMR(400 MHz, $CDCl_3$); δ (ppm): 0.9(t,3H,CH_3-CH_2-); 3.3(s, 2×3H, CH_3-N); 3.33-3.38(q, 2H -O-CH_2-CH_3); 3.7(t, 2H,-CH_2-N); 4.4(t, 2H, -O-$\underline{CH_2}$-CH_2-N); 6.8(d, 2H, C-H Ar); 8.4 (d, 2H, C-H Ar).
^{19}FNMR (400 MHz, $CDCl_3$); δ = -152.46 ppm.

C_{12}DMAPBr (n=5)
IR (KBr) cm^{-1} =3011 (ArC-H); 2916, 2849(aliphatic C-H); 1653,1570 (ArC=C).

^{1}HNMR (500 MHZ, $CDCl_3$); δ(ppm): 0.92(t, 3H, CH_3-CH_2-); 1.2-1.3(m, 16H, -CH_2-CH_2-);
1.8-1.9(m, 4H, -$\underline{CH_2}$-$\underline{CH_2}$-CH_2-N); 3.2 (s, 3×2H, CH_3-N); 4.3(t, 2H, CH_2-N); 7(d, 2H, C-H Ar); 8.4(d, 2H, C-H Ar).
In the next step by using these novel ILs sol-gel process were done (Scheme4). This process was started with TMSO, H_2O, and ILs.

Table.1.Characterization of thermal stability silica Nanostructured materials; $T_{g\ is}$ temperature decomposition of the ILs. Sg: Sol-gel;[RDMAP]: R=$C_{4,\ C5,\ C12}$,C_2C_3, C_2OC_2; [X]= Br, BF_4

Sg –[RDMAP][X]	**Tg (°C)**
Sg - C_5DMAP Br	358
Sg - C_4DMAP BF_4	420
Sg - C_5DMAP BF_4	438
Sg - C_2C_3DMAP BF_4	412
Sg - C_2OC_2DMAP BF_4	368
Sg - C_{12}DMAP Br	460

Characterization of gels
SEM characterization of calcined silica Nanostructured materials
Figure (1) shows the the SEM images of the resulting calcined silica Nanostructured materials froma molar ratio described of silicon precursor tetramethylorthosilicate, water, and ionic liquid based N,N-dimethylaminopyridinium cation for (a) IL_1, (b) IL_2, (c) IL_3, (d) IL_4, (e) IL_5, (f) IL_6. The ILs was used as a template in a traditional manner. SEMs of the gels revealed a mareked effect as the structure of IL was changed. Also these images show that the average particle size is below 100 nm.
Naught observation of particle in image of (f_1) relatead to hydrophilic polar region of IL_5 ; C_2OC_2DMAPBF_4, with the ether moiety close to the N,N- dimethyl aminopyridiniumgroup, is significantly larger of others. And as a result, increase the polar region of ionic liquid increase percent hydrogen bonding of pyridinum ring with Si-OH groups. That was prevented the formation of Si-O-Si bonds from condensation polymerization pathway. Also such hydrogen bonding would help disrupt any ring stacking compared to other ILs.Zhou et al [24] suggested a worm-hole effect (ordered periodicity) and the formation of long channels (image of a, c, d).
On the other hand performance of reaction under acidic condition, in the presence of organic solvent of ethanol and IL_6 as a catalysis and also stabilization the reaction temperature in 60$^{\circ C}$ for 12 h during the aging process, hydrolysis process accelerate, and the

aging gelation was accomplished. During this period IL is molten and acts as an active supermolecule catalysis. In addition IL has a longer time for orientation porous silica framework. And as a result, silica framework was obtained with more ordered, highly porous, more uniform surface (image of f_2).

According to image of (e) in present IL_5 with long molecular chain as template; the macroporosity decreased, and a more uniform topography was observed [25]. This problem related to an increased thermal stability of IL with long molecular chain linked to N, N-dimethyl aminopyridinium cation to allow the condensation, and densification process are done in longer time in high temperatures.

In the C_2C_3DMAP BF_4 (IL4) duo to formation $\pi-\pi$ stacking pyridinium rings with pentyne alkyl chain according to Scheme (2), a ununiform morphology, size and shape was obtained(image of d).

X-ray diffraction data of calcined silica Nanostructured materials

XRD spectrum in (Fig.3) do not show any clue for the formation of crystallized silica, indicating that the silica gel materials obtained in the presemce of IL_n based N,N- dimethyl aminopyridinium cation as template are amorphous, and even after being calcined at 550°C do not observe any peak [26]. But silica porous material that synthesized in the presence of C_{12}DMAPBr template exhibits a distinct diffraction peak at $2\theta = 2.409^0$ with the corresponding d spacing about 17.5 nm, which in good agreement with the SEM observation.

Thermogravimetric analysis of the gels

The results of thermogravimetric analyses (TGA) traces of the air-dried gels are shown in table- (1). $T_{g\ is}$ decomposition temperature of the IL as the matrix of sol gel. As a result the thermal stability ILs based N, N- dimethyl aminopyridinium cation is higher than ILs based imidazolium cation. Also the large polar region in C_2OC_2DMAP based IL, due to more hydrogen bonding with matrix silica cause higher thermal stability in silica network.

On the other hand ionic liquids of long molecular chain as template was obtained micellar and packing structures from silica sol gel materials and remove this ILs was achived in higher temperatures according with result of table(1). Also exchanging anion from Br to BF_4 was increased thermal stability, that attributed to the $\pi-\pi$ stacking of the pyridinium rings and formation of hydrogen bonding between the tetrafluoroborate anion and the hydroxyl groups of the silica. The schematic illustration of the mechanism is presented in the Scheme (2), that indicates $\pi-\pi$ stacking of the pyridinium rings is more efficient than stacking of the imidazoliumrings.

Invistigation of Infrared spectroscopic characterization

Infrared spectroscopy of the non-calcined gels (Fig. 4-a) showed small peaks at areas 2900 and 2800 cm^{-1}, corresponding to the N,N-dimethylaminopyridinium cation alkyl groups and any residual methoxy groups of the silica monomer. This show that in non-calcined gel, IL is in matrix. IL is blocking the complete reaction of the monomer. These peaks are presented in all non-calcined gels.But the optimum hydrolysis conditions corresponding in the acidic environment, tesespeakes are invisible (Fig. 4-c). Also, the two characteristic bands of the N,N-dimethylaminopyridinium ring around 1600-1570 cm^{-1} could not be observed in the spectra of calcined gels(Fig. 4-b).Ofcourse this bonds adsorption in hybrid C_2OC_2DMAP- Sg under acidic condition are as one broadband, indicating that a strong interaction between the pyridinium group and the silica matrix (Figure. 4-c).

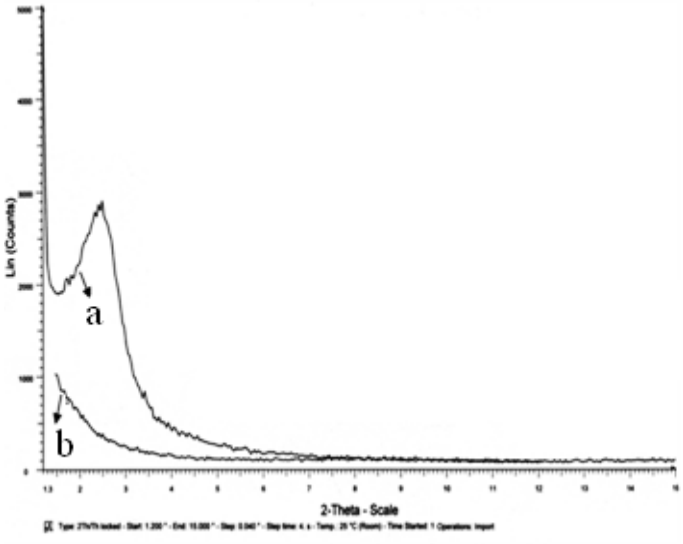


Figure (3). XRD patterns of calcined silica sol–gel materials of the(a) Sg-C_{12}DMAPBr, (b) Sg-[RDMAP][X]. [RDMAP]; R=$C_{4,\ C5,}$ C_2C_3, C_2OC_2 [X]= Br, BF_4

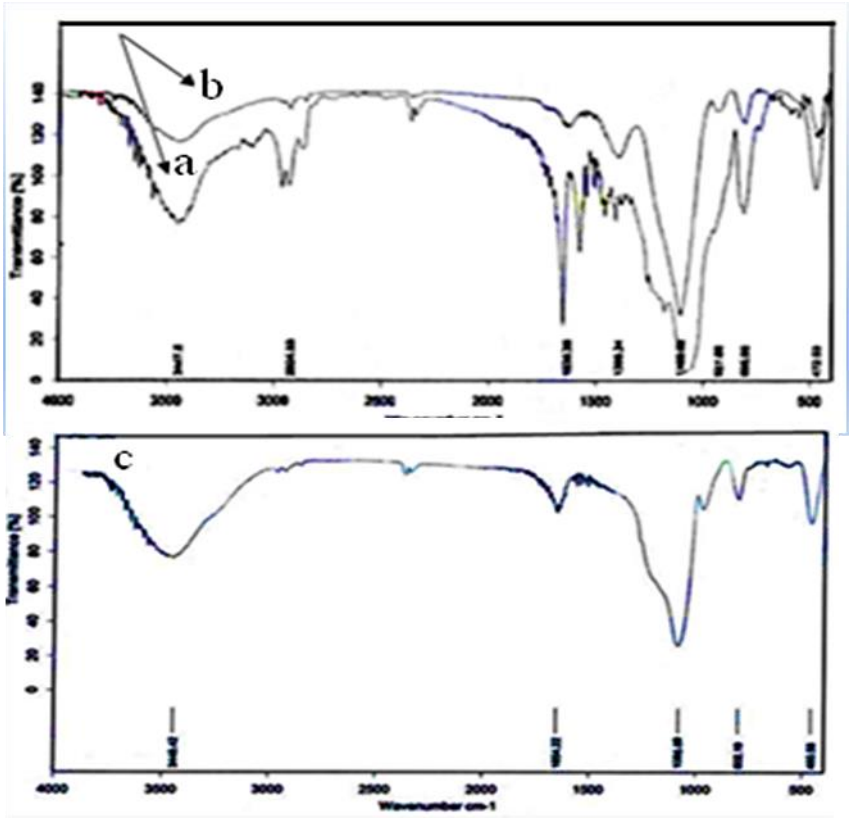
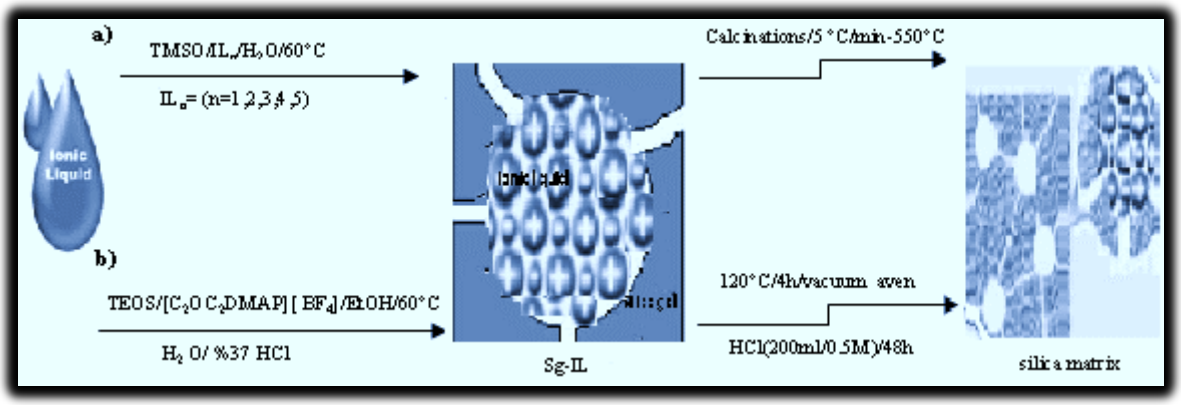


Figure (4). IR spectra of silica sol–gels: (a) non-calcined silica sol–gel; (b) calcined sol–gel synthesized with IL; (c)Sg-C_2OC_2DMAP nanocomposite under acidic condition.



Scheme. 4-a, b.Illustration of the synthesis of silica-gel-confined ionic liquids.as catalysis: Sg:Sol-gel; IL:[RDMAP][X]:R=C_4,C_5, C_{12},C_2C_3, C_2OC_2; [X]= Br, BF_4

Conclusion

Silica Nanostructured materials with various RTILs based N, N-dimethyl amino pyridinium cation with high thermal stability as templates were synthesized according to a proper sol–gel method.

The results show that, with using various kind of ILs, various morphology, particle size, and shape was obtained. The best result was obtained in which functional ILs was used. In this case a uniform morphology, size, and shape were produced. This is especially interesting case in selective drugs loading, drugs delivery systems, and selective analytical application. In comparison hydrophilic polar region and hydrophobic region of ionic liquids C_2OC_2DMAP, C_{12}DMAPBr, as surfactant in synthesis of silica Nanostructured materials,

it was observed that with increasing hydrophobic region of IL silica frameworks with miceller and highly ordered structures was obtained. On the other hand, variety of procedure is important in synthesis, and topography of Nanostructured silica materials. In this procedure the structure of ILs important factor. And as a result of the controlled periodic porosity silica materials was obtained by using of [C_{12}DMAP][Br] as template whit long alkyl chain and also highly ordered monolithic silica Nanostructures were prepared under acidic conditions at temperatures above the melting points of the IL ([C_2OC_2DMAP][BF_4]) in a so-called nanocasting sol-gel technique.

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