

Influence of supercritical CO₂ and the type of the imidazolium based ionic liquids on the gelation time and the properties of one - pot synthesized silica ionogels

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ABSTRACT

Silica ionogels were synthesized using the one step sol-gel route. Imidazolium based ionic liquids (ILs) containing different cations and anions were used in order to investigate their effect as co-solvent and co-catalyst on the gelation time and on the solid properties (pore size, surface area, pore volume, hydrophobicity) of the final material. The influence of the ionic liquid concentration on the gelation time was also determined. Experiments under high pressure in presence of supercritical carbon dioxide were additionally performed. The obtained ionogels were dried with supercritical CO₂ and analyzed by scanning electron microscopy (SEM) and nitrogen adsorption –desorption isotherms (BET).

INTRODUCTION

Organic – inorganic nano composites are a novel class of hybrid materials. Silica ionogels are porous materials with intrinsic hybrid character, in which the ionic liquids are confined in a solid – like matrix. Therefore the ionogel features derive from the combination of the properties of the ionic liquid and the component forming the solid network. These materials have found applications in areas of optical and electrochemical sensing, solid state electrolytes, etc. The most common method for the synthesis of silica ionogels is the sol-gel route. During this process two chemical reactions occur – hydrolysis and condensation. The gelation time of the ionogels depends on many factors like silica source, solvent, catalyst, temperature, nature of the ionic liquid etc. Also the properties of the final product are depending not only on the synthesis conditions but also on the aging time, drying procedure, etc. [1 - 5].

In the present work silica ionogels were prepared by the sol – gel process using imidazolium ionic liquids, containing different cations and anions. The influence of supercritical carbon dioxide on the gelation time and the properties of silica ionogels was investigated for first time in the present study.

MATERIALS AND METHODS

The ionogels were prepared by a one - step sol - gel method. Tetramethyl orthosilicate (TMOS) 98% (Merck Millipore, Germany), ethanol 99.8% (Sigma Aldrich), citric acid and deionized water were used as received. The ionic liquids 1 - butyl - 3 - methylimidazolium hexafluorophosphate [C₄mim][PF₆], 1 - butyl 3 - methylimidazolium bis(trifluoromethylsulphonyl)imide [C₄mim][Tf₂N], 1 - hexyl - 3 - methylimidazolium tetrafluoroborate [C₆mim][BF₄] were synthesized at the Chair of Inorganic Chemistry III of the Ruhr-University Bochum. The experiments with supercritical carbon dioxide (CO₂) (99.9%, Yara/Hydro) and also the supercritical drying were performed in a 300 ml high pressure view cell. The synthesis temperature at ambient pressure was 70°C. For the synthesis in presence of supercritical CO₂, the temperature was kept at 70°C and the pressure was 80 bar. The molar ratio between the compounds was the same for all of the experiments. Only the concentration of the ionic liquid was varied – 1 mol TMOS :x mol IL, where x = 0.01, 0.05, 0.1 and 0.2. For the both type of synthesis the silica precursor was mixed with water, ethanol, citric acid and the relevant amount of IL. The mixture was stirred at room temperature for 15 min. at 800 rpm. and after that transferred to an oven or in a high pressure view cell until the gelation occurs. The samples were covered with ethanol and left for aging for 3 days. After that the ethanol was extracted from the pores with supercritical CO₂ by 40°C and pressure of 90 bar. The obtained ionogels were characterized using a JSM-6510 scanning electron microscope (SEM), nitrogen adsorption –desorption isotherms (BET). The MAS-NMR spectra were recorded on a Bruker DSX 400MHz spectrometer, utilizing ZrO₂ rotors of 2.5 mm diameter at 293 K. During measurement the rotors were rotated at 25000 Hz. The NMR(MAS) spectra was measured applying pulse programs written by H.-J. Hauswald at the Department of Analytical Chemistry of the Ruhr-University Bochum.

RESULTS

The reference sample was prepared without ionic liquid. The TMOS, water, ethanol and the citric acid were mixed and stirred for 15 min. with a magnetic stir bar at 800 rpm. After that the sample was put in an oven at 70°C, in order to ensure faster gelation time, until the gelation occurs [6]. The gelation time for the reference sample was 240 min. The samples with IL were made with four different concentrations of the ionic liquid. The gelation times for the ionogels with [C₄mim][PF₆] at ambient pressure and in presence of CO₂ are given in Figure 1.

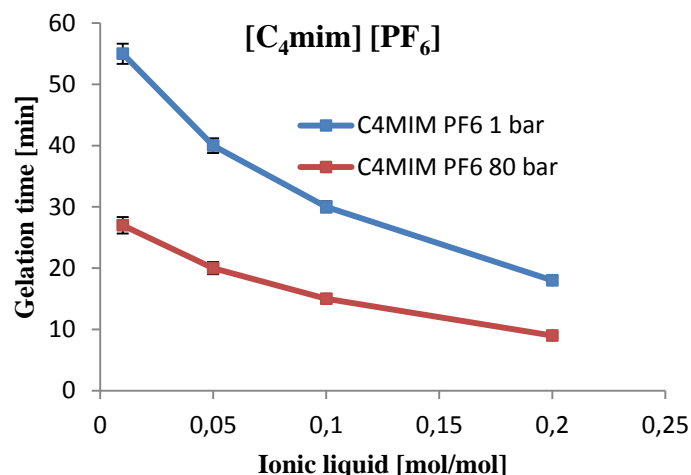


Figure 1 Gelation times of ionogels with 1 - butyl – 3 -methylimidazolium hexafluorophosphate

From those results it is obvious that a small amount of the ionic liquid leads to shorter gelation times, compared to the reference sample. Further increasing of the IL concentration provides faster gelation time. The anion of the ionic liquid contains F⁻ which, according to the literature, is able to increase the coordination of the Si and leads to faster hydrolytic and condensation reactions [7]. The synthesis in presence of supercritical carbon dioxide reduce further the gelation time, which is twice shorter compared to the gelation time at ambient pressure. From the obtained results it can be concluded that the supercritical CO₂ favors the reactions during the sol - gel process.

The results from the experiments with IL, containing the larger anion [Tf₂N] are shown in Figure 2:

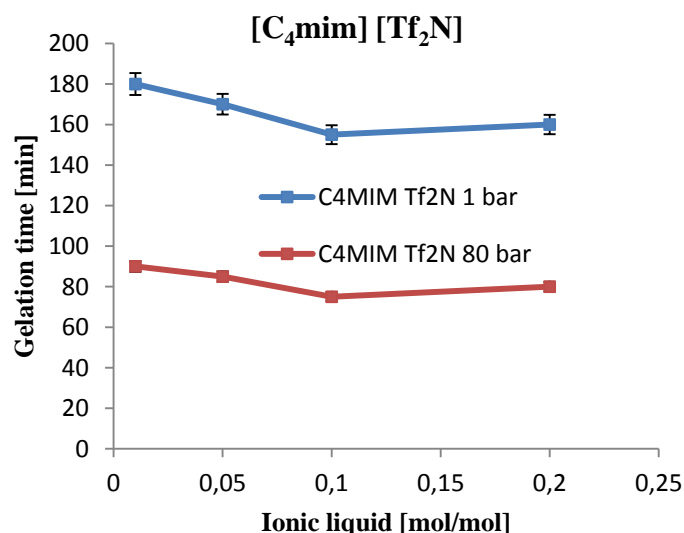


Figure 2 Gelation times of ionogels with 1- butyl -3-methylimidazolium bis(trifluoromethylsulphonyl)imide

By changing the hexafluorophosphate anion with the bigger hydrophobic bis(trifluoromethylsulphonyl)imide anion, leads to a much longer gelation time, but it remains shorter compared to the reference sample. One possible explanation of these results can be that the $[\text{Tf}_2\text{N}]$ anion provides weaker hydrogen bonds than $[\text{PF}_6]$, which can postpone the condensation reaction during the sol – gel process [8]. The optimum in the gelation time is reached by 0.1 IL concentration. After this point the gelation time increase again. A possible explanation therefore can be the reaching a saturation point of the IL concentration, after which the catalytic action of the IL is decreasing. The same trend was observed also by the experiments with CO_2 , where the gelation time is reduced to half for all IL concentrations.

In Figure 3 the gelation times with an ionic liquid, containing the longest alkyl chain, compared to the other two, and tetrafluoroborate as anion are shown

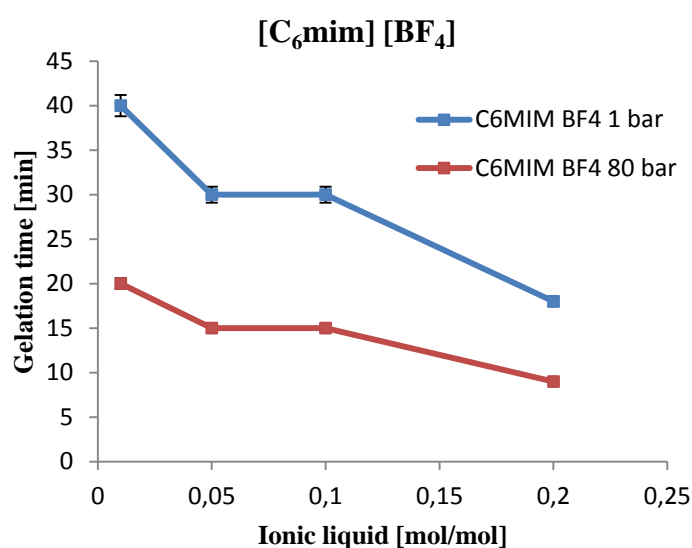


Figure 3 Gelation times of ionogels with 1 - hexyl – 3 -methylimidazolium tetrafluoroborate

At low IL concentrations the gelation time is about 40 min, which is decreasing to 20 min when the IL ratio is increased to 0.2. Gelation time remains the same by 0.05 and 0.1 IL concentration, which was not observed by the other two ionic liquids. The same constant gelation time between 0.05 and 0.1 is observed also by the synthesis under pressure. The presence of supercritical CO_2 has positive influence on the gelation time by all IL concentrations. The shortest obtained gelation time with 0.2 $[\text{C}_6\text{mim}][\text{BF}_4]$ in CO_2 is 10 min, which is 24 times less, compared to the reference sample.

From all of the experiments in presence of supercritical CO_2 at a pressure of 80 bar (Figure 1 – 3) can be concluded that the obtained gelation times for all samples were twice shorter than the gelation times without CO_2 . On one hand the CO_2 can act as a co – solvent and co – catalyst, which can lead to an acceleration of the hydrolytic and the condensation reactions during the sol – gel process. According to the literature, the CO_2 is also solvable in imidazolium based ionic liquids and probably can support their catalytic influence [9].

To analyze the pore characteristics of the synthesized ionogels N₂ adsorption / desorption measurements were carried out. These results are given in Table 1. All of the presented results are made with a molar ratio of 0.1.

Table 1: N₂ adsorption – desorption data of ionogels with different ILs with and without CO₂

Sample name	Surface area [m ² /g]	Pore volume [cm ³ /g]	Pore diameter [nm]
IGC ₄ MIMPF ₆	720,87	3,56	19,76
IGC ₄ MIMPF ₆ CO ₂	662,20	2,89	17,49
IGC ₄ MIMTF ₂ N	725,12	3,54	19,54
IGC ₄ MIMTF ₂ NCO ₂	561,61	3,20	22,80
IGC ₆ MIMBF ₄	545,35	3,96	29,10
IGC ₆ MIMBF ₄ CO ₂	541,23	4,12	30,52

The sample with [C₄mim][PF₆] in presence of CO₂ has a smaller pore diameter and lower surface area than the same sample prepared by the conventional method. The ionogel prepared with the biggest and the most hydrophobic anion - bis(trifluoromethylsulphonyl)imide shows a bigger surface area and a smaller pore diameter compared to the same in CO₂. For this ionogels prepared with [C₆mim][BF₄] the presence of CO₂ has a slight influence on the specific surface and the pore diameter.

The ionogel's microstructures were analyzed with SEM. The pictures of ionogels with [C₄mim][PF₆] without CO₂ (left) and [C₄mim][PF₆] with CO₂ (right) synthesized in CO₂ are shown in Figure 4. The obtained results show that the gels have a fine and homogenous structure, which is also in agreement with the BET results.

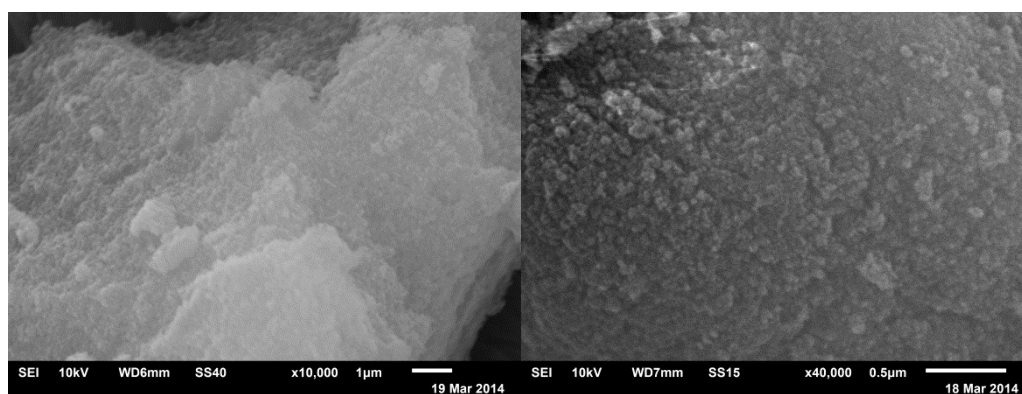


Figure 4 SEM pictures of silica ionogel samples synthesized with [C₄mim][PF₆] without and with CO₂

To prove that the ionic liquid is still confined in the gel, after the aging time and the supercritical extraction, NMR analysis were performed. The NMR spectrum is given in Figure 5

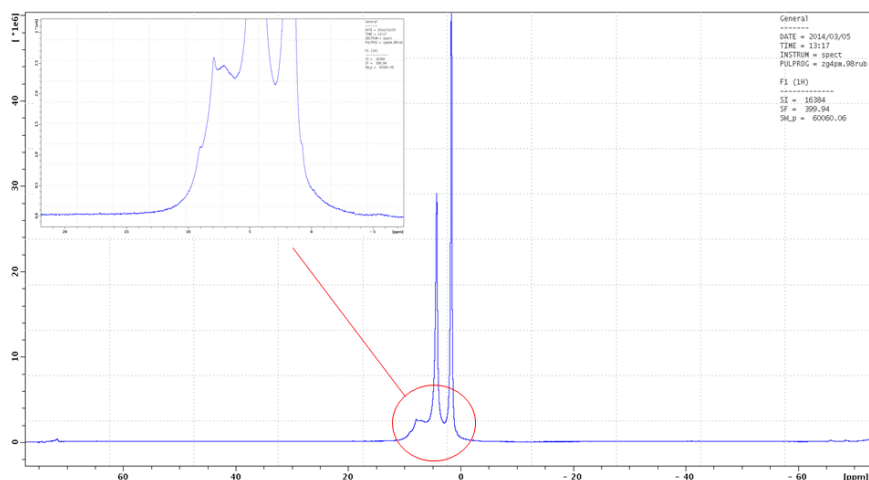


Figure 5 NMR spectra of the sample IGC₄MIMPF₆CO₂ after supercritical extraction

The peak at 8 - 9 ppm probably corresponds to the aromatic imidazolium ring, which is a prove, that the ionic liquid remains in the structure of the gel.

CONCLUSION

Imidazolium based ionic liquids [C₄mim][PF₆], [C₄mim][Tf₂N] and [C₆mim][BF₄] have been successfully applied as co – catalysts during the sol – gel process and can reduce the gelation time of one – pot synthesized silica ionogels. The presence of supercritical carbon dioxide decreases further the gelation time and has influence on the surface area of the obtained gels. The ionogels, containing the IL with the most hydrophobic anion have the longest gelation times and the samples synthesized with the smaller and less hydrophilic anion [PF₆] have shorter gelation time and the smallest pore diameter. The alkyl chain length of the IL has no significant influence on the gelation time, but the longer alkyl can provide ionogels with similar porous characteristics at ambient pressure and in presence of CO₂. The NMR measurements proved that the ionic liquids are confined in the ionogels structure after the drying process.

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