SILICA AEROGELS SYNTHESIZED WITH BUTYL-4-METHYLPYRIDINIUM TETRAFLUOROBORATE

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ABSTRACT

The supercritical drying effects were investigated, on a series of samples synthesized with: tetramethoxysilane and methyltrimethoxysilane, used as precursors, and butyl-4-methylpyridinium tetrafluoroborate (BMPyBF4) ionic liquid (IL), as gelation catalyst. These results show that the IL addition has a significant impact on the structure of the aerogel as a function of used nIL/nSi molar ratio.

Keywords: aerogels, specific surface area, BET method, BJH method.

INTRODUCTION

Ionic liquids have been described as designer solvents [1], and this means that their properties can be adjusted to find the expectations of a certain process. The pyridinium ends of the cations behave as Brönsted acidic catalysts to accelerate the hydrolysis of silica precursors and BF4 anions behave as Lewis base catalysts and accelerate the condensation reactions of silica [2].The CO2 supercritical drying method to yield aerogels eliminates most of the liquid phase, including ILs from wet gel, without shrinking the sample, comparatively to drying by evaporation [3].

MATERIALS AND REAGENTS

A series of gels were prepared by mixing 0.13 moll tetramethoxysilane, TMOS, 1.15 moll distilled water, 0.4 moll acidic water (pH adjusted to 2.8 by addition of HCl) and 0.01615 mmoll trimethoxymethylsilane, MTMS. After mechanical stirring (at 20±1 ◦C, 800 rpm), in a round bottom flask, a homogenous sol was obtained (15 min of magnetic agitation). BMPy BF4 was added into the mixed solution to a various IL/Si molar ratio [4]. The obtained sols were left to gel, in covered vessels, at room temperature. In the case of xerogels samples (named, 1x, 2x and 3x, respectively), the wet gels were dried at 60°C, for 26 h.

Other already gelled samples (named, 1a, 2a and 3a, respectively) were washed with 20 mL methanol every day, during 10 days. This stage is essential in order to further exchange the methanol for liquid CO_2. After, the drying of gels under CO_2 supercritical conditions was realised.

Other series of samples (named, 1s, 2s and 3s, respectively) were synthesised (using the same recipe, were the BMPyBF4 was added into the mixed solution to a various IL/Si molar ratio) *under ultrasonic field action*, in the following sonication conditions: total transferred energy, 25 KJ; activation duration: 23 minutes and finally the obtained wet sonogels being dried at 60 degree Centigrade. For all synthesised samples, the hydrolysis ratio was ~30.

CO_2 supercritical drying. First of all, the remained solvent mixture within the obtained wet gels pores was replaced with methanol. The resulted wet gels containing methanol were placed in a Supercritical Point Dryer (SC Popsoft SRL) and liquid CO_2 was introduced to gradually replace the methanol. For this reason, the gels were left for 30 min in liquid CO_2. Maintaining CO_2 flux injection and the pressure at 55 bar, the methanol was replaced by CO_2. The latter step was repeated two times to fully exchange methanol for liquid CO_2. Afterwards, the temperature and pressure were raised in two steps, at 37 °C and 90 bar, respectively, and maintained in these conditions for 15 min. Finally, the supercritical CO_2 was purged as a gas by slowly decreasing the pressure; with 5 bar/ min (the pressure must be released slowly so as to maintain the temperature at 37 °C, that is higher than the critical point temperature of CO_2).

The ultrasonic activation The samples were sonicated using VCX – 750 type apparatus with titanium sonotrode, working at 20 kHz, and 750W, 25 % amplitude; pulse duration: on cycle - 15 sec, off cycle-5 sec.

The nitrogen adsorption/desorption isotherms were recorded with a Quantachrome Nova 1200 apparatus. The BET surface (S_{BET}), the total pore volume (V_p) and the pore diameter (D_p) were calculated using a NovaWin software.

RESULTS AND DISCUSSION

The gel texture was investigated by recording and analysing the nitrogen adsorption-desorption isotherms (see Tables I and II) and measuring: the surface area (SSA), by: Brunauer, Emmett and Teller (BET) and Barrett, Joyner and Halenda (BJH) methods. Porosity characteristics like the average pore diameter (nm) and the specific pore volume (cm^3/g), were determined by BJH method. From both adsorption and desorption branches was observed that for aerogels, at low concentrations, multibet SSA is increasing with concentration of IL, than, when the Il concentration reached at 0.018 mol ratio the SSA decrease. Comparatively, in the case of xerogel and sonogel samples it was observed similar behaviour, but it can clearly seen that SSA BJH in the case of aerogels increase is more drastically than in the case of xerogels and sonogels.

The average pore diameter (nm) was determined by BJH method, also from both adsorption and desorption branches of the isotherms. The aerogels pore diameter presents a maximum corresponding to 0,018 nIL/nSi molar ratio. For the xerogel and sonogel samples the pore diameter is increasing with IL concentration (see Figure 1). The specific pore volume (cm^3/g) was also determined by BJH method, from the adsorption and desorption branches of the isotherms. The aerogels pore volume has maxima at 0.0.018 molar ratio, as for the xerogel. The sonogels pore volume is increasing with IL concentration (see Figure 2).

Table I. Surface area (m^2g^{-1}) determided by multibet method

nIL/nS	xerogel	sonogel	aerogel
0,007	535.75	542.6	50.27
0,018	436.5	373.08	689.04
0,070	265.36	267.33	601.30

Table II. Surface area (m^2g^{-1}), average pore diameter (nm) and specific pore volume (cm^3/g) determined using **BJH** method, of xerogels, sonogels and aerogels samples synthesised with IL, as a function of the molar ratio of molls IL/molls Si, from the **adsorption (ADS)** and **desorption** (DES) branches of the isotherms.

		Surface area (m^2g^{-1}) BJH			**Average pore diameter (nm) BJH**			**Specific pore Volume (cm^3/g) BJH**		
	nIL/nSi	**xerogel**	**sonogel**	**aerogel**	**xerogel**	**sonogel**	**aerogel**	**xerogel**	**sonogel**	**aerogel**
ADS	**0,007**	200.72	316.18	98.91	3.62	3.39	3.23	0.21	0.36	0.13
	0,018	395.39	347.82	398.40	3.61	5.58	4.18	0.48	0.56	0.60
	0,070	270.89	314.83	217.65	4.62	9.47	3.62	0.36	0.7	0.25
DES	**0,007**	308.37	462.84	70.99	3.63	3.86	3.71	0.29	0.44	0.10
	0,018	540.27	488.77	599.30	3.67	4.34	3.86	0.54	0.63	0.68
	0,070	373.18	398.5	271.35	4.64	7.87	3.63	0.41	0.75	0.27

CONCLUSIONS

A series of aerogels, in a range of molar ratio of IL to Si atoms nIL/nSi = 0.007, 0.018 and 0.07, were synthesized. Gels synthesized with IL and dried under CO_2 supercritical conditions had a high surface area compared to xerogels and sonogels with the same used molar ratio. In our case it clearly appeared that the aerogels synthesized with a low BMPyBF4 content had a much higher specific pore volume and high average pore diameter than those made with a high BMPyBF4 content.

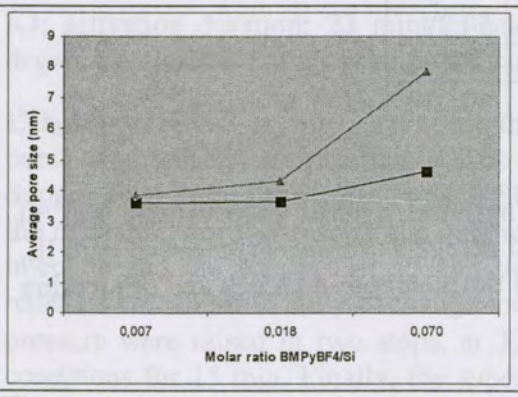

Figure 1. Average pore size (nm) determined from the **desorption** branch of the nitrogen absorption isotherms, as a function of the molar ratio nIL/nSi for sonogels (triangle), xerogels (squares) and aerogels (simple line) made with various IL/Si molar ratio.

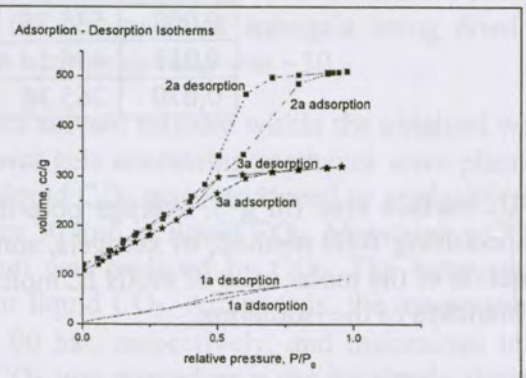

Figure 2. Results of the nitrogen adsorption and desorption isotherms of the aerogels

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