Microporous and Mesoporous Materials 195 (2014) 143–153

Contents lists available at ScienceDirect

Microporous and Mesoporous Materials

journal homepage: www.elsevier.com/locate/micromeso

Preparation and characterisation of ionic liquid confined hybrid porous silica derived from ultrasonic assisted non-hydrolytic sol–gel process

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ARTICLE INFO

Article history:
Received 3 August 2013
Received in revised form 4 April 2014
Accepted 15 April 2014
Available online 21 April 2014

Keywords:
Ionic liquid
Porous materials
Confinement
Ultrasound
Thermal analysis

ABSTRACT

A series of porous silica matrices have been synthesized using ionic liquid (IL) 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN]) by nonhydrolytic sol–gel method with and without ultrasonic irradiation during gelation. The properties of IL confined silica gel matrices so prepared have been studied using N_2-sorption measurement (BET characterisation for determining pore parameters), pulse echo technique (for sound velocity and hence elastic modulus determination), DSC, TGA, FTIR, TEM, SEM and fluorescence techniques. From the N_2-sorption measurement, it has been found that BET surface area increased (due to creation of pits on the surface caused by ultrasonic irradiation) while pore volume, average pore size and porosity for ultrasonicated samples decreased. Elastic modulus of the samples containing IL in silica matrices have been found to change with IL content. Glass transition temperature and thermal stability of the IL have been found to increase upon confinement in silica gel matrices. FTIR spectra (experimental as well as computed) show changes in vibrational bands of IL on confinement in pores of silica matrices. Particularly, for ultrasonic assisted samples, the bands related to the imidazolium ring, aliphatic chain and anion SCN of the IL are found to shift upon confinement. Optimised geometry of the IL in porous matrix shows interaction of these groups with the oxygen present on silica pore wall. Fluorescence spectra of samples containing IL shows a shift compared to the bulk IL.

1. Introduction

Ionic liquids (ILs) are salts that are liquid below 100 °C and are composed of organic cations & inorganic/organic anions [1–3]. ILs are highly attractive and versatile materials due to their exotic properties such as high chemical and thermal stability, high ionic conductivity, low vapour pressure, large electrochemical window, wide liquidus range, good capability of dissolving various organic/inorganic materials, etc. [1–4]. These are commonly used as green solvent because of ability to be recovered and recycled [5]. ILs have attracted much attention due to their tunable properties by choosing the specific combinations of cations and anions [4]. ILs are being used in many applications like catalysis, separations [4], sonochemistry [6] and as electrolytes in electrochemical devices such as batteries, fuel cells, super capacitors, dye sensitised solar cells [7–11], etc. However, liquidus nature of ILs results difficulty in many applications therefore, immobilisation of ionic liquids is necessary by some solid substrate. Subsequently, IL entrapped solid substrates termed as "Ionogels", are being extensively investigated [12,13]. The properties of ILs viz. phase transition temperature, thermal stability, optical properties, etc. have been found to change upon confinement [14–18]. In addition to above mentioned applications, ILs are also being used for the synthesis of nano porous materials having novel textural and structural characteristics [19].

Porous materials have attracted much attention of chemists and material scientists due to their interest in commercial applications in heterogeneous catalysis, chemical separations, nanoelectronics, chemical sensing, biomolecular immobilisation and as spatial host materials for substances or reactions [20]. Porous matrices can be classified into three categories based on their pore diameter (d): microporous, $d < 2$ nm; mesoporous, $2 < d < 50$ nm and macroporous, $d > 50$ nm [21]. Out of these, mesoporous materials have attracted much attention because of tailored pore structure and composition over a wide range of applications [20]. Dai et al. [22] for the first time synthesized porous silica gel using ionic liquid. Moreover, highly ordered monolithic super-micro-porous lamellar silica and monolithic mesoporous silica with wormlike porous structure were prepared by a nanocasting technique by Antonietti's group [23–25]. Many other studies have also been reported on the synthesis of porous materials using ionic liquids as a template [26–28].

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http://dx.doi.org/10.1016/j.micromeso.2014.04.026
1387-1811/

Since, rates of the chemical reactions such as hydrolysis and condensation in the sol–gel process are very important to synthesize different microstructures of gels; various methods have been used to control the sol–gel process. Ultrasonic irradiation is one of the useful method. Ultrasonic irradiation causes various chemical reactions under extreme conditions and has received increasing interest. For instance, many reactions can be completed under ambient conditions using ultrasonic irradiation. When ultrasonic irradiation of suitable intensity is applied during sol–gel reaction, sonogels (gels resulting due to ultrasonic irradiation) with unique properties such as porous property and density are obtained. Ultrasound irradiation results shorter gelation time in the preparation of sonogels [29]. In silica sonogel, finer sphere-shaped pore was obtained compared to the silica aerogels [30]. Ultrasound waves have proven to be very useful in the synthesis of organic/inorganic nanomaterials and in increasing reaction rates and yields of products thus decreasing the reaction time and introducing milder reaction condition [31]. Three stages of nucleation, growth and implosive collapse of cavitating bubbles are involved in acoustic cavitation. When ultrasonic waves are irradiated in driving chemical reactions, cavitation takes place due to collapse of vapour bubbles producing extreme pressure and hot spot which is accompanied by rapid heating and cooling created by cavitation bubble collapse [29].

In this paper, we report the synthesis of ultrasonicated (with low and high output power) and non-ultarsonicated IL (1-ethyl-3-methylimidazolium thiocynate; [EMIM][SCN]) confined silica gel matrices. Non-hydrolytic sol–gel process has been used for synthesis of ionogels due to its advantages over the conventional sol–gel process e.g. absence of water in initial reactant, fast gelation and simple route [32]. The ionic liquid ([EMIM][SCN]) was chosen in the present study due to its high ionic conductivity and low viscosity [33], which are very important factors for use in electrochemical devices, especially in rechargeable batteries and also to see the effect of IL on pore parameters of silica matrix. The effect of ultrasound irradiation on changes in the gelation time, pore parameters (viz. porosity, pore size distribution, N_2-sorption characteristics, surface area and pore volume) and morphological structure for different loadings of IL in silica gel matrices are also studied. In addition to the change in the characteristics of silica gel matrices, we have also observed changes in some physical properties viz. glass transition temperature, thermal stability, elastic modulus, cation ring and aliphatic chain related C–H vibrations and anion related vibrations of IL.

2. Experimental section

2.1. Chemicals

Chemicals used in the synthesis of ionogels were tetramethyl orthosilicate (TMOS; 98%) and formic acid (GR Grade) purchased from Merck Germany. Ionic liquid 1-ethyl-3-methylimidazolium thiocyanate ([EMIM][SCN] > 95%) was purchased from Sigma Aldrich. Before use, the IL was heated at a temperature of 100 °C for 12 h and vacuum dried at a pressure of 10^{-3} torr for 12 h to remove traces of water.

2.2. Synthesis

Ionic liquid confined porous silica gel matrices have been synthesized with (low and high power) and without ultrasonic irradiation using non-hydrolytic sol–gel process (ultrasonic irradiation was given during gelation process). Mixture of IL and formic acid was added to TMOS at a TMOS/HCOOH/IL molar ratio of 1:8:x (x = 0.5, 0.6, and 0.7 mol) in a reaction vessel at ambient temperature (25 °C). Further, resulting mixture was stirred for a short time and then left for gelation (in case of non-ultrasonicated sample), while for the ultrasonicated samples detailed procedure is discussed in the Supplementary Information. Nomenclatures of the synthesized samples have been given in Table 1. Photographs of the sample ingots (#SW2 and #SW3) obtained without ultrasonic irradiation are shown in Fig. 1. It can be seen from Fig. 1(a) and (b) that coloured (due to IL colour) stable monoliths are obtained. It has been observed that the gelation time for high power ultrasonicated samples gets reduced in comparison to the samples synthesized without ultrasonic irradiation. Gelation occurred in ~23 min for samples not exposed to ultrasonic irradiation whereas for low and high power ultrasonicated samples, gelation occurred respectively in ~20 min and ~15 min.

2.3. Characterisation

The BET surface area, pore volume and average pore size were measured on a Gemini VII 2390t, Micromeritics Instrument Corporation at 77 K. Before the pore parameter analysis, ionic liquid was extracted from IL confined samples by washing the samples in deionised water for several times and followed by ultrasonication in water for 30 min to ensure the complete removal of IL. Further, samples were subjected to vacuum drying at 100 °C for 24 h. After that, the samples were degassed under flow of dry N_2 for 24 h at 60 °C prior to N_2-physisorption study.

Bulk longitudinal elastic modulus of the samples is given by the relation $B = v^2 d$, where 'd' is the density of ionogel and v is the velocity of longitudinal ultrasonic waves through the samples. Density of the samples was determined by dividing mass of dried disc shaped ionogel ingots with its corresponding volume. The velocity of ultrasonic waves was measured with a standard pulse echo technique. JSR-Ultrasonics DPR 300 Pulser/Receiver along with 500 MHz Agilent digital storage oscilloscope (with a time resolution of 2 ns) was used for the ultrasonic velocity measurement. The accuracy of the ultrasonic velocity measurement was better than 0.5%. Piezoelectric ceramic transducer SH-6 (Valpe Fisher) operating at ~6 MHz (fundamental mode frequency) was used for producing longitudinal ultrasonic waves. Ultrasonic waves propagated in the disc shaped monolith ingot. After knowing the pulse transit time in echo mode; velocity (v) of ultrasonic waves was determined using the relation $v = 2x/t$, where x is the thickness of the disc shaped ionogels and t is the transit time.

DSC measurement of the samples was carried out on a Mettler Toledo DSC-1(with temperature measurement accuracy ±0.02 K). The samples were placed in 40 μL hermetically sealed aluminium pan with pinhole at the top of the pan. The samples inside the DSC-furnace were exposed under continuous flow of N_2 atmosphere. Before running the test, each sample was vacuum dried at 80 °C for 5 h. The measurements were carried out by first heating the samples at 100 °C for 15 min to remove the absorbed water

Table 1
Abbreviation used for various prepared samples.

Physical conditions	Sample abbreviation	Mole ratio TMOS/HCOOH/IL (1:8:x), x=
Without ultrasonicated	#SW1	0.5
	#SW2	0.6
	#SW3	0.7
Low power ultrasonicated	#SL1	0.5
	#SL2	0.6
	#SL3	0.7
High power ultrasonicated	#SH1	0.5
	#SH2	0.6
	#SH3	0.7