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Abnormal FT-IR and FTRaman spectra of ionic liquids confined in nano-porous silica gel

Feng Shi, Youquan Deng*

Centre for Green Chemistry and Catalysis, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou, 730000, China

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Abstract

A new concept of designing and synthesizing highly dispersed ionic liquids was developed through physical confinement or encapsulation of them into silica gel matrix with sol–gel process. A series of silica gel confined ionic liquids were synthesized through this process and characterized by diffuse-reflectance infrared Fourier transform spectroscopy (DRIFTS) and FTRaman analysis, and abnormal FT-IR and FTRaman spectra were observed. The silica gel matrixes confined ionic liquid BMImBF₄ were further characterized by BET analysis after the ionic liquid was almost completely washed out by acetone under refluxing conditions and meso-porous silica gel matrixes were obtained according to the N₂ adsorption measurements, which suggested that the particle-size of the dispersed ionic liquids was in nano-scale. In consideration of the results obtained together, it could be found that the abnormal FT-IR and FTRaman spectra were changed with the pore-size of the silica gel matrix. For example, obvious abnormal FT-IR and FTRaman spectra appeared when the particle-size of ionic liquid BMImBF₄ is smaller than 11 nm while they disappeared again if the corresponding particle-size >11 nm. These results indicated that nano-effect, or restriction effect, produced from the nano-pores of silica gel was the reason for the abnormal FT-IR and FTRaman spectra. © 2004 Elsevier B.V. All rights reserved.

Keywords: Ionic liquids; Silica gel; Abnormal spectra; Nano-material; Characterization

1. Introduction

As a bridge between single molecules and infinite bulk systems, the physicochemical properties, e.g. optical properties, of nano-materials, which usually closely connected with the particle size of the nano-materials, could significantly differ from those of the atomic-molecular and bulk materials and offers significant potentials in building new types of devices with atomic or molecular precision [1–3]. In previous studies, nano-materials concerned were basically solid and reports on nano-fluids or liquids confined in narrow space, which may also exhibit different or novel physicochemical properties in comparison with the bulk fluids or liquids, however, are still quite scarce [4–6] probably due to the difficulties in obtaining nano-liquid particles with enough stability and in characterizing experimentally.

Room temperature ionic liquids are becoming increasingly important and of particular interests due to their thermal stability, negligible vapor pressure, selective dissolvability, peculiar ion environment, diversity, and more and more applications in catalysis, organic synthesis, electrochemistry, sensing material, lubrication, life science and solar cell, etc. [7–10], have been explored. This un-traditional, stable liquid material also offered new opportunity for synthesis of stable nano-liquid and our efforts in this study is to design and synthesize a narrow space confined ionic liquid system. The key concept of designing and synthesizing such silica gel confined ionic liquid system involves the physical confinement or encapsulation of ionic liquid with a traditional sol-gel process based on the hydrolysis of silicate esters to produce a solid matrix with desired sizes of pores or cavity and channels, which should be big enough to contain ionic liquids (Fig. 1). Therefore, they are intrinsically different from those previously reported supported or immobilized ionic liquid catalysts [11], which were obtained by covalently bonding of

^{*} Corresponding author. Tel.: +86 931 4968116; fax: +86 931 4968116. *E-mail address:* ydeng@ns.lzb.ac.cn (Y. Deng).

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Fig. 1. Illustration for synthesis of silica gel confined ionic liquids.

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} X=BF_4: n=1 \ EMImBF_4; \ n=3 \ BMImBF_4 \\ n=9 \ DMImBF_4; \ n=15 \ CMImBF_4 \\ X=PF_6: n=3 \ BMImPF_6 \end{array} \\ \\ \begin{array}{c} BMImBF_4: 8\%BMImBF_4/silica \ gel, \ 17\%BMImBF_4/silica \ gel, \ 35\%BMImBF_4/silica \ gel, \ 53\%BMImBF_4/silica \ gel, \ EMImBF_4: \ 17\%EMImBF_4/silica \ gel \end{array} \end{array}$$

DMImBF₄: 17%DMImBF₄/silica gel CMImBF₄: 17%CMImBF₄/silica gel BMImPF₆: 17%BMImPF₆/silica gel

Fig. 2. Ionic liquids used and silica gel confined ionic liquids synthesized.

ionic liquid fragment such as dialkyl imidazolium cation to the surface of silicon dioxide or by dipping the porous silicon dioxide in the mixture of ionic liquid containing the catalysts.

Raman and infrared spectroscopy [12,13], they could provide information on molecular vibrations and now have



Fig. 3. DRIFTS spectra of ionic liquid $BMImBF_4$ before and after confinement.

been the most widely used techniques and methods for non-destructive determination of molecular structure, were used for characterizing the nano-liquid system because nanomaterial usually exhibited special optical properties. As expected, abnormal spectra were observed and it could be regulated by the particle-size of ionic liquid or the pore-size of the silica gel.

2. Experimental

A mixture of 10 ml of tetraethyl silicate (TESO) and 7 ml of EtOH was heated to 60 °C and then 0.2-4 g of ionic liquids were transferred into the TESO immediately. After the formation of a clean and homogeneous liquid mixture, 2 ml of concentrated hydrochloride acid (36–38%) diluted by 3.5 ml of distilled water was added and the mixture became coagulated gradually. After aged at 60 °C for 12 h, the resulted solid material was dried in vacuum at 150 °C for 3 h and about 4–7 g of catalyst was obtained. The samples for BET surface



Fig. 4. FTRaman spectra of ionic liquid BMImBF₄ before and after confinement.

analysis: the silica gel confined ionic liquids were washed under refluxing in acetone at $60 \,^{\circ}$ C for 3–8 h, the solids were filtrated and dried in air at $80 \,^{\circ}$ C for 24 h.

DRIFTS analysis was conducted with Nexus 870. FTRaman characterization was carried out over a Nicolet 950. N_2 adsorption measurements were obtained using a Micromeritics ASAP 2020 instrument.

Two kinds of ionic liquids were used here to synthesize the silica gel confined ionic liquid system and following samples were obtained (Fig. 2).

3. Results and discussion

A typical ionic liquid, BMImBF₄, was firstly confined into the nano-pores of silica gel and characterized by DRIFTS, Fig. 3. It can be seen that negative-going bands [14–17] at 1135 cm⁻¹, which was stretching vibration of B–F bonds

17%wtCMImBF4

CMImBF4

17%wtDMImBF4

DMImBF4

17%wtEMImBF4 /silica gel

EMImBF4

2500

3000

3500

/silica gel

/silica gel

Fig. 5. FTRaman spectra of different ionic liquids before and after confined in silica gel.

2000

Raman shift (cm⁻¹)

1500

1000

500

in BF₄⁻, 1182 cm⁻¹ (in-plane C-H deformation vibration of imidazolium ring), 1290 cm⁻¹ (symmetrical C-H vibration of imidazolium ring), 767 cm^{-1} (stretching vibration of BF₄⁻), 858 cm⁻¹ (C–H in-plane vibration of imidazolium ring), and a broad band attributable to the C-H bending vibrations of CH₃ at 1476 cm⁻¹, were almost disappeared when ionic liquid BMImBF4 was confined into the silica with a content of 8%. At the same time, the bands at 1576 cm^{-1} , which was the in-plane C-C and C-N stretching vibrations of the imidazolium ring, was still relatively strong after the ionic liquid was confined. If the contents of ionic liquids confined in silica gel were increased, it can be seen that the band at 1575 cm^{-1} became stronger and band at 767 cm^{-1} appeared again while other peaks still not appeared even the content of ionic liquid reached to 53%. Based on these results, it can be conjectured that the vibrations of the ionic liquid molecular confined were severely affected due to the narrow space of nano-pores in silica gel.

FTRaman analyses of a series of silica gel confined BMImBF₄ ionic liquid with different loadings (Fig. 4) also revealed that the Raman spectra of 8-37 wt.% BMImBF₄/silica were markedly different with pure bulk ionic liquids while almost same spectrum as bulk ionic liquid was obtained when the content of ionic liquid was 53%. In comparison with corresponding bulk ionic liquids, the bands [18-22] at 2971 cm⁻¹ (symmetrical stretching vibration of alkyl chain), 1569 cm⁻¹ (C-C and C-N stretching vibrations of the imidazolium ring), $1420 \,\mathrm{cm}^{-1}$ (symmetrical deformation vibrations of alkyl chain), 1024 cm⁻¹ (in-plane wagging vibrations of alkyl chain) and 768 cm^{-1} (out-plane C–H bending vibrations of imidazolium ring) are remarkably inhibited or even disappeared and then appeared again, while the bands at $2936 \,\mathrm{cm}^{-1}$ (combination band of 1457 and $1480 \,\mathrm{cm}^{-1}$), $1457 \,\mathrm{cm}^{-1}$ (out-plane vibration of imidazolium



Fig. 6. FTRaman spectra of 17 wt.% $MImBF_4/silica$ gel before and after washing under refluxing in acetone.



Fig. 7. BET pore-size distribution of silica gel confined ionic liquid BMImBF₄ after washing.

ring) and 878 cm^{-1} (not clear at this stage) for BMImBF₄ appeared or strengthened and then disappeared again, when the loadings of ionic liquids confined increased from 8, 17 wt.% and then to 35 and 53 wt.%. These results were similar as those obtained from the DRIFTS characterization. Ionic liquids EMImBF₄, DMImBF₄ and CMImBF₄, in which their side chains contained different carbon numbers, were also used to investigate the restrictive effect of narrow space and similar results as that using ionic liquid BMImBF₄ were achieved (Fig. 5). If the anion of the ionic liquid, BF_4^- , was substituted by PF₆⁻, the FTRaman spectra of the ionic liquid before and after confinement were quite different as that using ionic liquid BMImBF4 and the abnormal FTRaman spectra were still remained even when the content of $BMImPF_6$ in silica gel reached to 53%. All these results showed that the occurring of abnormal optical spectra of ionic liquids confined in narrow space of silica gel were universal.

In order to investigate the inner reason for the abnormal FT-IR and FTRaman spectra of the silica gel confined ionic liquids, BET surface analysis was further conducted after ionic liquid BMImBF₄ in silica gel was almost washed out (determined by FTRaman analysis, Fig. 6) by acetone under vigorous refluxing. The easy leaching of ionic liquid BMImBF₄ showed that there was no chemical bonding between silica gel and ionic liquid BMImBF₄, i.e. this ionic liquid was physically confined or encapsulated into the nano-



Fig. 8. FTRaman spectra of ionic liquid $BMImPF_6$, 17 wt.% $BMImPF_6$ /silica gel and 17 wt.% $BMImPF_6$ /silica gel after washing.



Fig. 9. Bet pore size distribution of pure silica gel and 17 wt.% BMImPF₆/silica gel after washing.

pores of silica gel, and the abnormal optical spectra were not caused by chemical reaction of ionic liquids with the silica gel. As the results shown, typical structures of meso-porous materials were formed [23,24] and the average pore sizes of silica gel ranged from 2.9 to 10.9 nm with the increasing of the amounts of ionic liquid contained (from 8 to 53 wt.%, Fig. 7). The pore size distributions were quite narrow and then became widen when the amounts of ionic liquids contained in silica gel excess 35 wt.% or near to 53 wt.%, respectively. This means that the particle sizes of ionic liquids confined in the silica gel matrix may range between about 2.9-10.9 nm and nano-effect may be the reason for abnormal FTRaman and FT-IR spectra. As to the BET characterization of 17 wt.% BMImPF₆/silica gel after removal of the ionic liquid by washing, meso-porous material was also obtained while the pore-size was lager in comparison with the silica gel that containing ionic liquid BMImBF₄ and its average pore-size reached to 34.3 nm (Figs. 8 and 9). The sample with higher BMImPF₆ contents (53 wt.%) was also investigated by BET analysis and the corresponding average pore-size decreased to 26.2 nm, it was why its abnormal FTRaman spectra maintained, while the reason for the decreasing of the average pore-size when further increasing the amounts of ionic liquid BMIMPF₆ was not clear at this stage. As to the BET characterization of DMImBF₄/silica gel and CMImBF₄/silica gel, the average pore size distributions and surface area could not be determined exactly because these ionic liquids could not be washed out completely (especially for silica gel confined CMImBF₄ ionic liquid, determined by FTRaman analysis) without destroying the structure of the silica gel matrix. These results suggested that the silica gel matrix was connected with inlet and outlet, which could be small enough to restrict ionic liquid DMImBF₄ and CMImBF₄ while big enough to let ionic liquid BMImBF₄ and BMImPF₆ to be transported out. The HRTEM characterization also showed that the silica gel confined ionic liquid BMImBF₄ was uniform and porous.

In consideration of all the results achieved above, it can be seen that the abnormal FTRaman and FT-IR spectra of nano-pores confined BMImBF₄ were completely disappeared when the diameter of the nano-pores reached to about 11 nm while the abnormal FTRaman spectra of nano-pores confined BMImPF₆ were still maintained even its diameter exceeded 30 nm, which indicated that different particle-sizes were needed for different ionic liquids to exhibit the abnormal FTRaman and FT-IR spectra.

4. Conclusions

In conclusion, abnormal FTRaman and FT-IR spectra of silica gel confined ionic liquids were found and their characteristic bands could be regulated by the particle-size of the ionic liquid (or the pore-size of the silica gel) and therefore, the nano-effect was the reason for the abnormal FT-IR and FTRaman spectra.

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