RESEARCH NOTE

EFFECT OF INORGANIC HYBRID LiBr ON THE SILICA MATRIX XEROGELS

S. H. Tohidi*, A. J. Novinrooz and A. Nabipour

Material Research School, Nuclear Science and Technology Institute, P. O. Box: 31485- 498, Karaj, Iran
htouhidi@mail.nrcam.org, anovinrooz@nrcam.org, a_nabipour@yahoo.com

*Corresponding Author

(Received: July 02, 2009 – Accepted in Revised Form: December 15, 2011)

doi: *10.5829/idosi.ije.2012.25.01b.06*

Abstract The SiO_2-LiBr hybrid porous materials were prepared by the sol-gel method. This process was obtained by the hydrolysis and condensation tetraethyl orthosilicate (TEOS) with replacement of ethanol from alcogel by drying at ambient temperature to obtain xerogel structure. The alcogel samples were synthesized from TEOS, EtOH, H_2O, HCl, NH_4OH and LiBr. The total molar ratio of the compounds was 1: 9: 4: 8×10^{-4}, 8×10^{-3}. Xerogel contain 30 % wt of LiBr (dry matter) was prepared and characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Furier Transmittance Infra Red (FTIR), Energy Dispersive X-ray (EDX) and Thermal Gravimetry Analysis (TGA) systems . The results obtained from SEM were shown the micrograph of LiBr on the silica matrix. Chemical elemental analysis data was resulted by EDX. On the other hand, the TEM have confirmed average particle size of SiO_2-LiBr about 50 nm and FTIR spectrum describes functional groups of nanocomposite. The thermal analysis of SiO_2-LiBr nanocomposite was performed using TGA system. The results show that the suitable temperature for initial thermal treatment is about 200 °C.

Keywords Inorganic hybrid, Lithium bromide, Silica, Xerogel

چکیده در این تحقیق مواد متخلخل ترکیبی شامل برمید لیتیوم روی بستر سیلیکا توسط روش سل- ژل تهیه شد. این فرآیند توسط آبکافت و تراکم تتراتیل اورتوسیلیکات با حذف اتانول از آلکوژل توسط عملیات خشک کردن در شرایط محیطی حاصل شد تا نمونه ها به صورت زیروژل تهیه گردد. نمونه های آلکوژل از ترکیب تتراتیل اورتوسیلیکات/اتانول/ آب/اسید کلریدریک/هیدروکسید آمونیوم و برمید لیتیوم آماده شدند که نسبت مولی کل ترکیبات به ترتیب ۱/۹/٤/ $\times ۱۰^{-٤}$/۸ $\times ۱۰^{-۳}$/۸ می باشد. زیروژل شامل ۳۰ درصد وزنی برمید لیتیوم است که توسط میکروسکوپ الکترونی عبوری و روبشی و طیف سنجی مادون قرمز با انتقال فوریه و آنالیز عنصری و آنالیز حرارتی خصلت یابی می شود. نتایج حاصل از آنالیز میکروسکوپ الکترونی روبشی میکروگراف های برمید لیتیوم روی بستر سیلیکا و آنالیز عنصری ترکیب درصد وزنی را نشان می دهد. هم چنین میکروسکوپ الکترونی عبوری اندازه میانگین ذرات را ۵۰ نانومتر تایید می کند. طیف سنجی مادون قرمز با انتقال فوریه گروه های عاملی روی نانو کامپوزیت را مشخص می نماید. آنالیز حرارتی نمونه توسط سیستم آنالیز ترمال گراویمتری انجام شده و نتایج دمای مناسب برای شروع عملیات حرارتی را در حدود ۲۰۰ درجه سانتی گراد پیشنهاد می نماید.

1. INTRODUCTION

The Sol gel technology is attended as a simple and high efficiency method for synthesis of materials in low temperatures [1, 2]. The Sol gel process is a wet chemical method that a precrousor with M(OR)n structure lead to inorganic network including metal oxide [3]. These materials are converted to gel network by alkoxide reaction in presence of water molecules and, finally, can be inverted to solid state. There is an inorganic polymerization that can form oxide network contain metal oxide clusters M—O—M [4]. The sol-gel materials exhibit a disordered structure and a continuous distribution of pore sizes which give rise to structural heterogeneity of the surface [5]. Amorphous silica has been well known for displaying a heterogeneous surface at the atomic

level with silanols being the main centers for water physisorption [5]. This chemical inhomogeneity of the surface is likely to be even stronger in the more complex, hybrid materials, owing to the presence of calcium chloride, or any other guest substance dispersed atomically within the host silica matrix [6]. Upgrading of silica gels by incorporating inorganic hygroscopic compounds (eg., LiBr) have been investigated most recently [7]. These materials have virtually two phase solids consisting of a porous host matrix (silicagel ˜ 70 wt %) and a hygroscopic substance (HS, 30 wt %) introduced into the pore space by the conventional impregnation with aqueous solution [8]. Apparently, such an approach is convenient but too simple to ensure the desired end content of the HS and its uniform distribution within the sample. Sol-gel science offers an alternative equally simple and more effective approach, a straightforward entrapment of the target compound within the sol-gel matrix, which hopefully should be resulted in its atomic dispersion across the sample [9]. In the present paper, we have reported on the preparation and characterization of SiO_2-LiBr nanocomposites by the sol-gel route. The obtained structural properties of the materials were also studied.

2. EXPERIMENTAL DETAILS

In this investigation, the raw materials contain tetraethyl orthosilicate (Fluka, 98 %) (TEOS), ethanol absolute (Merck) (EtOH), lithium bromide (Merck), HCl (Merck, 35 %), NH_4OH were used with mentioned specification. At first, the samples have been prepared by the sol-gel method as SiO_2-LiBr nanocomposite xerogel [3]. Two different samples of inorganic nanocomposite (IN) were prepared by the sol-gel route. The first sample is due to blank sample and the second, was formed to achieve a target LiBr content 30 wt % (dry matter). The alcogel Samples were synthesized from TEOS, EtOH, H_2O, HCl, NH_4OH and LiBr following the two-step preparation procedure [4]. The total molar ratio of the compounds was 1: 9: 4: 8 x 10^{-4}: 8 x 10^{-3}. In the first step, TEOS was hydrolyzed with H_2O by reflux for 2 hours at 50 °C. Then the solution was mixed with the remaining EtOH, NH_4OH and aqueous solution of LiBr 30 wt % to obtain 20 ml samples which were kept at 25 °C. The gelation took place within 1.5-2.5 hours. Alcogel sample was aged for 6 days at ambient condition and finally, they were dried at room temperature for 35 days. To remove residual water and ethanol, the sample was dried for 2 hours at 200 °C. Figure 1 shows schematic representation of the preparation procedures.

-The infrared spectrum was measured in a FTIR spectrometer of Gensis system- model ATI, using 0.05 gr. of powder sample with 0.3 gr. of KBr.

-TEM micrograph was obtained on a TEM instrument of Phillips system- model Em208S operating at 100 Kv power. The dry samples were ground suspended in dry cyclohexane, and sonicated for 1-2 minute. Then, the solution was allowed to settle and a droplet of the resulting supernatant was placed on a holey carbon film and dried.

- Scanning electronic microscope (SEM) is performed by SEM XLC Philips instrument.

- The acidity of solution (PH) was measured by Omega PH meter-model 744.

-The condensation of samples was done in a Oxaiton heat furnace with high thermal capacity (1500 °C).

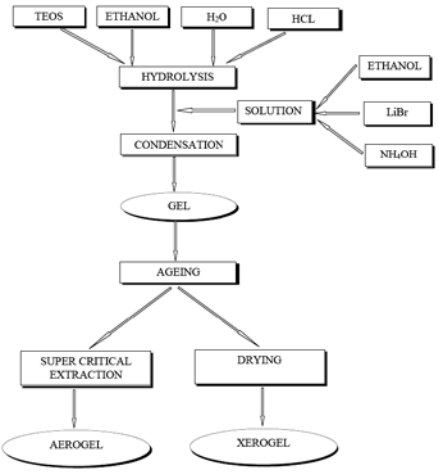

Figure 1. Schematic representation of the preparation LiBr on the silica matrix xerogel

3. DISCUSSION AND RESULTS

The molecular structure study of SiO_2-LiBr nanocomposite was done in bonding vibrational mode in the range of 500 to 4000 cm^{-1} by FTIR spectrum.

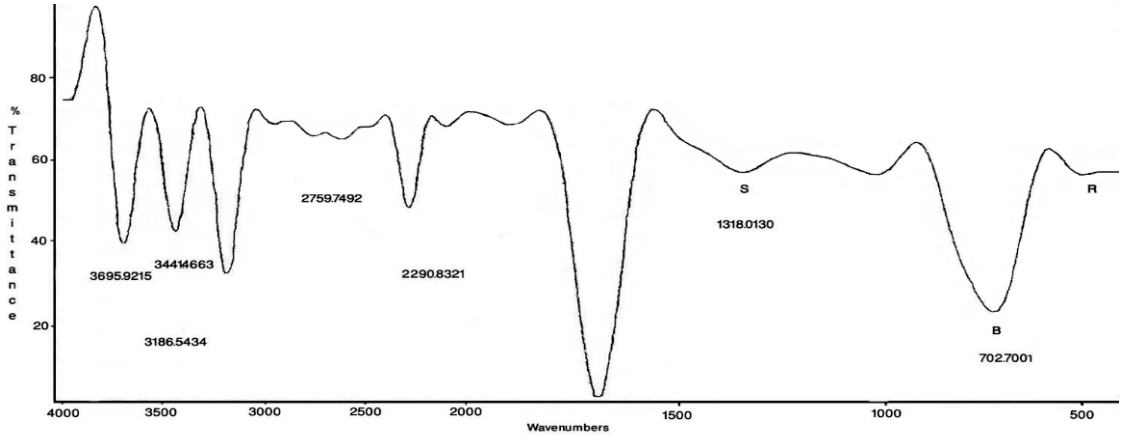

Figure 2. The FT. IR spectrum of SiO_2-LiBr

Figure 2 presents the FT.IR absorbance spectrum for SiO_2-LiBr in powdered sample form. We can see three main regions from 500 to 1500 cm^{-1} to name (R), (B) and (S) respectively. Each of three major features related to transversal optical (TO) absorption bands was shown in the Figure 2 which can be characterized in terms of a particular vibration mode of the Oxygen (O) atom respect to the Silicon (Si) atom that they can be bridge. The rocking (R) of the (O) atom about an axis through the two Si atoms characterize the vibration behavior of the lowest frequency to bond central at 550-600 cm^{-1}. The bending (B) of the (O) atom along a line bisecting the axis was formed by the two Si atoms characterizes the vibration mode of the middle (TO) band centered at 700-850 cm^{-1} [9]. The remaining TO band and his high frequency shoulder are due to an asymmetrical stretching (S) mode at 1200-1350 cm^{-1}. It has been reported the FTIR spectrum in which a shoulder, in the frequency range of 1150 to 1250 cm^{-1}, has an amplitude comparable or bigger than the main stretching band at 1000 cm^{-1} [10]. This has been achieved in vitreous SiO_2 samples prepared by the sol gel method using specific preparation conditions. The TEM micrograph of dried sample SiO_2-LiBr was shown in Figure 3. This figure confirms the formation of average size about 50 nm. Also, we can see a porous material with high porosity which porous size is very different and the average porous size is about 50 nm.

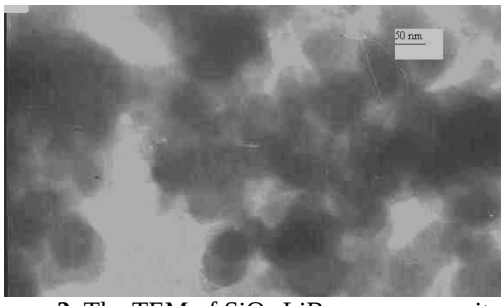

Figure 3. The TEM of SiO_2-LiBr nanocomposite

The guest substance such as Lithium bromide (LiBr) dispersed atomically within the host silica matrix which change or cure the properties. This action can be caused the curing of water adsorption of silica surface and we can apply this nanocomposite in aquatic ambient as adsorbent [9]. The SEM (Scanning Electron Microscope) micrograph has been shown in Figure 5. The scanning electron microscope (SEM) pictures were used for study of sample morphology which initial electrons (BSE) and second electrons with low energy (SE) were collected and present a micrograph. These images were presented an inorganic polymerization which can form inorganic network contain LiBr particles. We have studied the particles of lithium bromide which are doped to silica support by scanning electron microscope. Also, these results have been compared with results of LiBr nanocomposite

structure on the silica matrix [10]. The exact composition of nanocomposite depends on the annealing temperature. We have produced the particles of lithium bromide on the silica matrix by thermal treatment. These hybrid nanocomposite have a structural stability and reproducibility [11]. The thermal analysis of SiO_2-LiBr nanocomposite was performed using TGA system and the results shown that the suitable temperature for initial thermal treatment is about 200 °C.

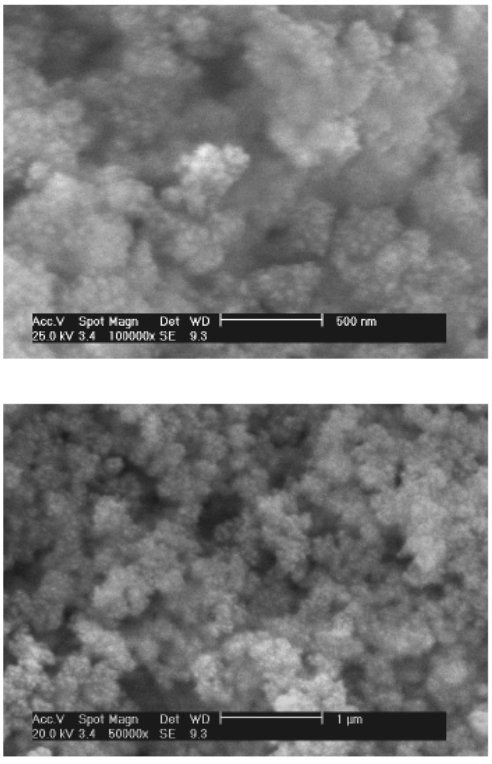

Figure 4. The SEM micrograph of SiO_2-LiBr

Figure 5 presents data of EDX contain elemental weight percent and elemental atomic percent. Elemental analysis presents weight percent of O, Si and Br. This data was shown in Figure 3 and confirms the ratio of O/Br (wt %)= 4.5, Si/Br (wt %)= 4.5 and O/Br (At %)= 22.5, Si/Br (At %)= 12.8. These data show atomic percent Si/O= 1/2 and also, presents that the structure of nanocomposite is a porous material SiO_2 which LiBr particles were doped into porous SiO_2 matrix. Moreover, lithium is very light element, that can't be detected by EDX and there is not any pick due to lithium.

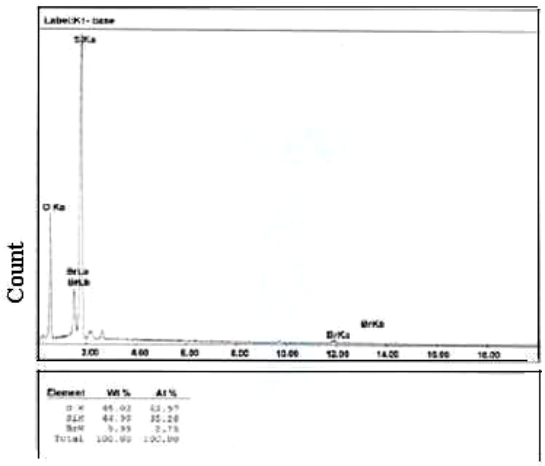

Figure 5. The EDX of SiO_2-LiBr nanocomposite

The thermal analysis presents weight loss about 4 % at 40-80 °C which is due to water removing. An increase slightly was also at 100 °C. After this, a constant reduce was observed between 100-280 °C which related to solvent removal. Also, the thermal analysis presents weight loss about 31.5 % at 300-1000 °C which due to decompose of organic compounds [12]. As we see in Figure 6, at 20- 100 °C, heat flow increase because the materials need to heat for breaking of bonds. However, at 100-200 °C, the heat flow is constant. The thermal analysis presents an increase in heat flow about 20 mW at 200-300 °C and the material need to more heat for release the solvent. After 300 °C, the curve shows a slight growing at heat flow at 700°C which due to decompose of organic elements. Finally, at 700-1000 °C, the decomposition of nanocomposite has been completed.

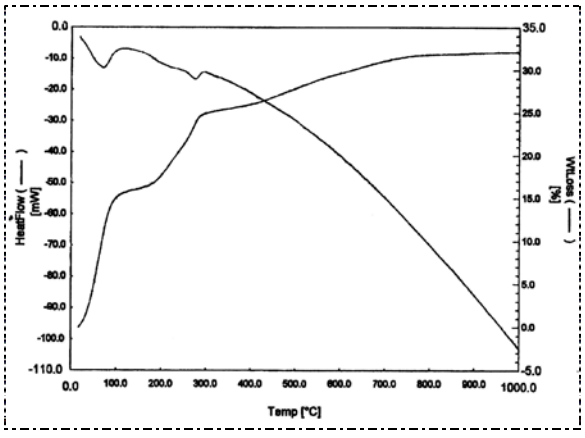

Figure 6. The thermal analysis (TGA) of SiO_2-LiBr nanocomposite

4. CONCLUSIONS

The straightforward entrapment of lithium bromide in silica matrixes was performed by the sol-gel method results in hybrid materials. This process was obtained by the hydrolysis and condensation tetraethyl orthosilicate (TEOS) with replacement of ethanol from alcogel by drying at ambient temperature to obtain xerogel structure. FTIR spectrum describes functional groups of nanocomposite, and three main regions were observed from 500 to 1500 cm^{-1} to name (R), (B) and (S) respectively. Each of three major features related to transversal optical (TO) absorption bands which can be characterized in terms of a particular vibration mode of the Oxygen (O) atom respect to the silicon (Si) atom that they can be bridge. The TEM micrograph of dried sample SiO_2-LiBr confirms the formation of average size about 50 nm. We can see a porous material with high porosity and various porous sizes. The average particle size is about 50 nm. Elemental analysis presents atomic and weight percent of O, Si and Br. This obtained data confirms the ratio of O/Br (wt %)=4.5. EDX can not present a profile of lithium element, because carbon and lighter elements energies are lower than EDX systematic energy. The structure of nanocomposite is a porous material which LiBr particles were doped into porous SiO_2 matrix. The scanning electron microscope (SEM) pictures were used for study of sample morphology. These images present an inorganic polymerization which can form inorganic network contain LiBr particles. The thermal analysis of SiO_2-LiBr nanocomposite was performed. The results show that the suitable temperature for initial thermal treatment is about 200 °C. This compound can be easily regenerated, dried at 200 °C and reused. Finally, we have a porous material with high porosity which LiBr particles doped in it. The porous size is different with average particles size of 50 nm.

5. REFERENCES

1. Brinker, C. J. and Scherer, G., "The physics & chemistry of sol gel processing", Sol Gel Science, Academic Press, San-Diago, (1990).
2. Zelinski, B. J. J.andUlhmann, D. R., "Gel technology in ceramics", ***Journal of Physics and Chemistry Solids***, Vol. 45, (1984), 1069-1090.
3. Schmidt, H., "Inorganic- Organic composites by sol gel technology", ***Materials Research Society. Symposium Proceedings,*** Vol. 3, (1990), 171-175.
4. Tohidi, S. H., Novinrooz, A. J. and Derhambakhsh, M., "Preparation steps and study of molecular structure of metal ions doped in a matrix", ***International Journal Engineering, Transaction B***, Vol. 19, (2006), 53-60.
5. Jarzebski, A. B., Lorenc, J., "Surface fractal characteristics of silica aerogels***", Langmuir***, Vol. 13, (1997), 1280-1285.
6. Sanchez, C., Babonneau, F., Banes, F., Doeff-Barboux, S. and Ribot, F., "Chemistry of hybrid organic-inorganic materials synthesized via sol- gel", ***Materials Science Forum***, Vol. 313, (1994), 153-162.
7. Mrowiec-Bialon, J., Jarzebski, A. B., Pajak, L., "Water vapor adsorption on the composites", ***Langmuir***, Vol. 15, (1999), 6505-6509.
8. Martinez, J. R., Ruiz, F., Vorobiev, Y. V. and Gonzalez-Hernandez, J., "Infrared spectroscopy analysis of the local atomic structure in silica prepared by sol- gel", ***Journal of Chemical Physics***, Vol. 109, (1998), 7511-7514.
9. Martinez, J. R, Ruiz, F., Gonzalez-Chavez, M. M. and Valle-Aguilera, A., "Mapeo structural de silica xerogelutilizandoespectroscopia", ***Revista Mexicana de Fisica,*** Vol. 44, (1998), 575-581.
10. Mrowiec-Bialon, J., Lachowski, A. I., Jarzebski, A. B., Aristov, Y. I., "Preparation and properties sol-gel adsorbents of water vapor", ***Journal of Colloid and Interface Science***, Vol. 218, (1999), 500-503.
11. Serna, C., Fornes, V. and Fernandez-Navarro, J. M., "Sol gel transition in simple Silisate", ***Journal of Non-Crystalline Solids***, Vol. 63, (1984), 4559.
12. Dudley, H. W., Fleming, I., "Spectroscopic methods in organic chemistry", 4th Edition, McGraw-Hill, New York, (1987).