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## RESEARCH NOTE

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# PREPARATION AND CHARACTERIZATION OF SiO<sub>2</sub>-CaCl<sub>2</sub> NANOCOMPOSITE BY THE SOL-GEL METHOD

S.H. Tohidi\*, F. Ziaie and A. Abdolmaleki

Material Research School, Nuclear Science and Technology Institute

P.O. Box 31485-498, Karaj, Iran

htohidi2003@yahoo.com, htouhidi@nrcam.org, a.abdolmalaki@gmail.com

\*Corresponding Author

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**Abstract** The SiO<sub>2</sub>-CaCl<sub>2</sub> hybrid porous materials were prepared by the sol-gel method. This process was conducted by the hydrolysis and condensation of Tetraethyl orthosilicate (TEOS) by replacement of ethanol from alcogel and drying at the ambient temperature to obtain xerogel structure. The alcogel samples were synthesized from TEOS, EtOH, H<sub>2</sub>O, HCl, NH<sub>4</sub>OH and CaCl<sub>2</sub>, while the total molar ratio of the compounds was 1: 9: 4: 8 x 10<sup>-4</sup>, 8 x 10<sup>-3</sup>, respectively. Xerogel containing 30 wt % of CaCl<sub>2</sub> (dry matter) was prepared and characterized by Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Fourier Transmittance Infra Red spectrum (FT-IR), Energy Dispersive X-ray (EDX) and Thermal Gravimetric Analysis (TGA) systems. The results obtained from SEM and EDX showed the micrograph of CaCl<sub>2</sub> on the silica and chemical elemental analysis, respectively. On the other hand, The TEM micrograph confirmed average particle size of SiO<sub>2</sub>-CaCl<sub>2</sub> about 50 nm and FT-IR spectrum described the functional groups of the nanocomposite. The thermal analysis of SiO<sub>2</sub>-CaCl<sub>2</sub> nanocomposite was performed using TGA system and the results showed that the suitable temperature for initial thermal treatment was about 200°C.

**Keywords** Synthesis and Characterization, Sol Gel Process, Nanocomposite

**چکیده** در این تحقیق ماده متخلخل ترکیبی شامل کلرید کلسیم روی بستر سیلیکا توسط روش سل-ژل تهیه شد. این فرآیند توسط آبکافت و تراکم تترااتیل اورتوسیلیکات با حذف اتانول از الکوژل توسط عملیات خشک کردن در شرایط محیطی حاصل شد تا نمونه ها به صورت زیروژل تهیه گردند. نمونه های الکوژل از ترکیب تترااتیل اورتوسیلیکات/اتانول/ آب/اسید کلریدریک/هیدروکسید آمونیوم و کلرید کلسیم آماده شدند که نسبت مولی کل ترکیبات به ترتیب ۱/۴/۹/۸ x ۱۰<sup>-۴</sup>/۸ x ۱۰<sup>-۳</sup> بود. زیروژل شامل ۳۰ درصد وزنی کلرید کلسیم بود که توسط میکروسکوپ الکترونی عبوری و روبشی، طیف سنجی مادون قرمز با انتقال فوری، آنالیز عنصری و آنالیز حرارتی خصلت یابی گردید. نتایج حاصل از آنالیز میکروسکوپ الکترونی و روبشی، میکروگراف های کلرید کلسیم روی بستر سیلیکا و آنالیز عنصری ترکیب درصد وزنی را نشان دادند. هم چنین میکروسکوپ الکترونی عبوری اندازه میانگین ذرات را ۵۰ نانومتر تایید کرد. طیف سنجی مادون قرمز با انتقال فوری گروه های عاملی روی نانو کامپوزیت را مشخص نمود. آنالیز حرارتی نمونه توسط سیستم آنالیز حرارتی گراویمتری انجام شده و نتایج دمای مناسب برای شروع عملیات حرارتی را در حدود ۲۰۰ درجه سانتی گراد تعیین نمود.

## 1. INTRODUCTION

The sol-gel technology is attended as a simple and high efficiency method for synthesis of materials at low temperatures [1, 2]. The sol-gel process is a wet chemical method that a precursor with M(OR)<sub>n</sub> 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 which contain metal oxide clusters of M—O—M [4]. The sol-gel materials exhibit a disordered structure and a continuous

distribution of pore sizes which gives rise to structural heterogeneity of the surface [5]. Amorphous silica is 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 (e.g.  $\text{CaCl}_2$ ) has been investigated most recently [7]. These materials have virtually two phase solids consisting of a porous host matrix (silica gel  $\approx 70$  wt %) and a hygroscopic substance (HS  $\approx 30$  wt %) introduced into the pore space by the conventional impregnation using 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 and a straightforward entrapment of the target compound within the sol-gel matrix, which hopefully should result in atomic dispersion across the sample [9]. In the present paper, preparation and characterization of  $\text{SiO}_2\text{-CaCl}_2$  nanocomposites by the sol-gel route was investigated and the structural properties of the obtained materials were studied.

## 2. EXPERIMENTAL DETAILS

In this investigation, the raw materials containing Tetraethyl orthosilicate (Fluka, 98%) (TEOS), Ethanol absolute (Merck) (EtOH), calcium chloride (Merck), HCl (Merck, 35%),  $\text{NH}_4\text{OH}$  (Merck) were used with mentioned specifications. At first, the samples were prepared by the sol-gel method as  $\text{SiO}_2\text{-CaCl}_2$  nanocomposite xerogel [3]. Two different samples of inorganic nanocomposite (IN) were prepared by the sol-gel route. The first sample was used as the blank sample and the second one, was formed to achieve a target  $\text{CaCl}_2$  content of 30 wt % (dry matter). The alcogel samples were synthesized from TEOS, EtOH,  $\text{H}_2\text{O}$ , HCl,  $\text{NH}_4\text{OH}$  and  $\text{CaCl}_2$  following the two-step preparation procedure [4]. The total molar ratio of

the compounds was 1: 9: 4:  $8 \times 10^{-4}$ ,  $8 \times 10^{-3}$ , respectively. In the first step, TEOS was hydrolyzed with  $\text{H}_2\text{O}$  by closed reflux for 2 hours at  $50^\circ\text{C}$ . Then, the solution was mixed with the remaining EtOH,  $\text{NH}_4\text{OH}$  and aqueous solution of  $\text{CaCl}_2$  35 wt % to obtain 20 ml samples which were kept at  $25^\circ\text{C}$ . The gelation took place within 1.5-2.5 hours and the 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  $200^\circ\text{C}$ . Figure 1 shows the schematic representation of the preparation procedures.

- The infrared spectrum was measured in a FT-IR spectrometer of Gensis system-model ATI, using 0.05 g of powder sample with 0.3 g of KBr.
- TEM micrograph was obtained from a TEM instrument of Phillips system- model Em 208S, operating at 100 KV power. The dry samples were ground and suspended in dry Cyclohexane, and sonicated for 1-2 min. Then the solution was allowed to settle and a droplet of the resulting supernatant was placed on a holey carbon film and dried.
- Scanning electron microscopy was performed by SEM XLC Philips instrument.
- The acidity of the solution (pH) was measured by Omega pH meter, model 744.

The condensation of the samples was done in an heat furnace (Oxaiton model) with high thermal capacity ( $1500^\circ\text{C}$ ).

## 3. RESULTS AND DISCUSSIONS

The bonding and molecular structure study of  $\text{SiO}_2\text{-CaCl}_2$  nanocomposite was done in bonding vibrational mode in the range of 500 to  $4000\text{ cm}^{-1}$  by FT-IR spectrum.

Figure 2 presents the FT-IR absorbance spectrum for  $\text{SiO}_2\text{-CaCl}_2$  in powdered sample. Three main regions from 500 to  $1500\text{ cm}^{-1}$  with the names of (R), (B) and (S) can be observed. Each of the three major features related to the transversal optical (TO) absorption bands is shown in Figure 2 which can be characterized in terms of a particular vibration

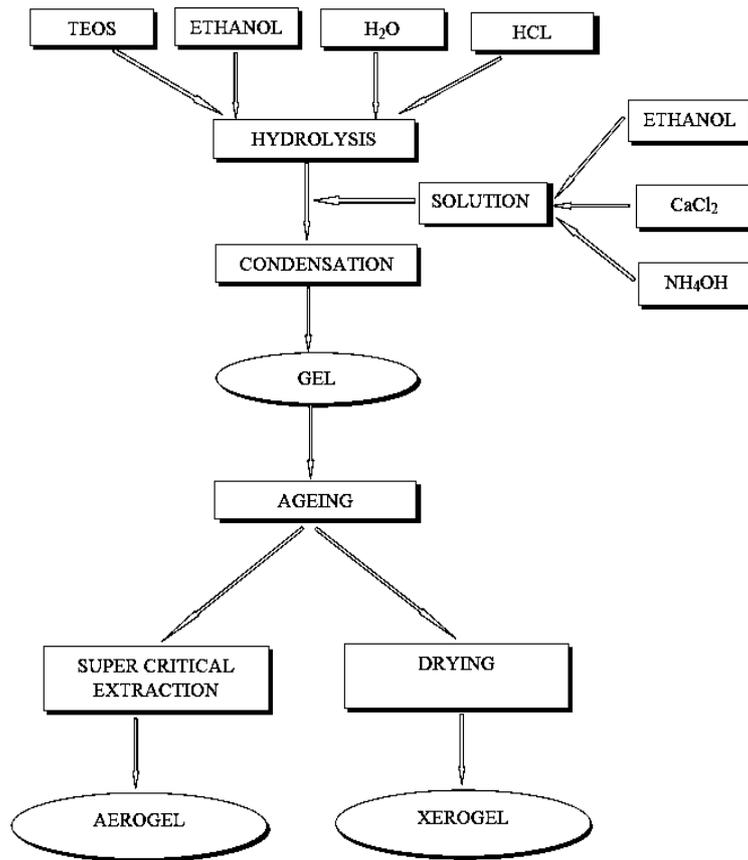


Figure 1. Schematic representation of the preparation procedure of  $\text{SiO}_2\text{-CaCl}_2$  nanocomposite.

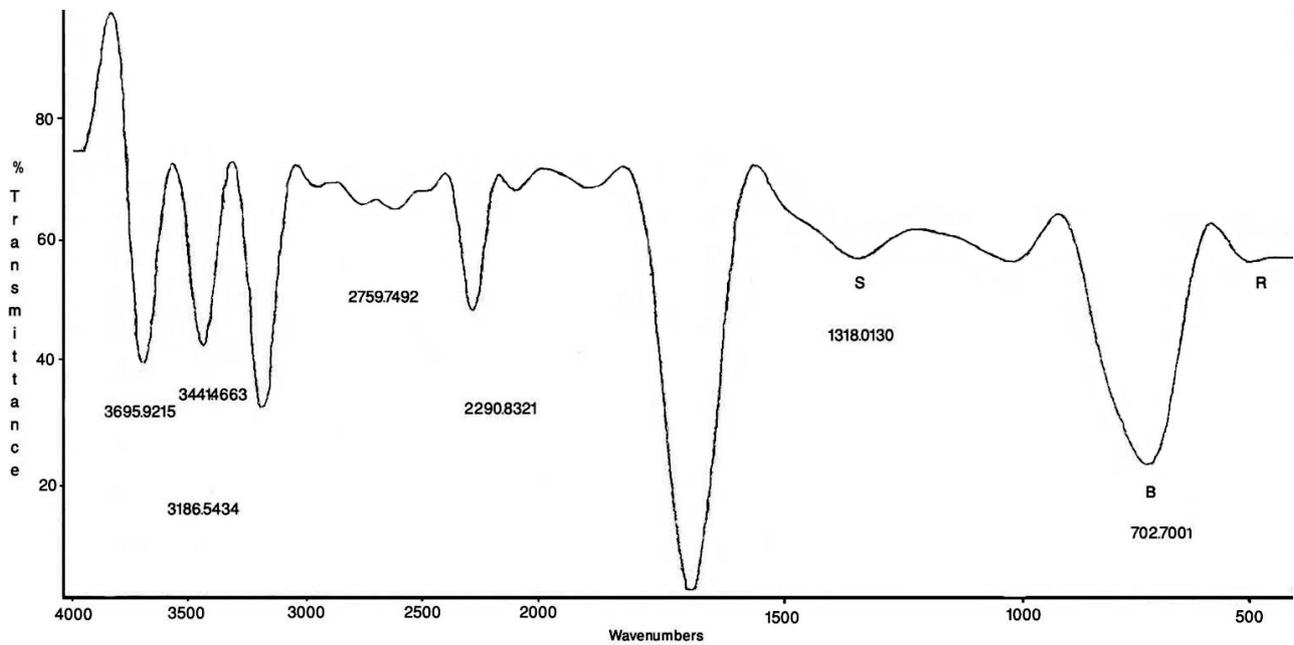


Figure 2. The FT-IR spectrum of  $\text{SiO}_2\text{-CaCl}_2$ .

mode of the Oxygen (O) atom with respect to the Silicon (Si) atom that can be bridged. Rocking (R) of the (O) atom about an axis through the two Si atoms characterize the vibration behavior of the lowest frequency to central bond at  $550\text{-}600\text{ cm}^{-1}$ . Bending (B) of the (O) atom along a line bisecting the axis was formed by the two Si atoms which characterize the vibrational mode of the middle TO band centered at  $700\text{-}850\text{ cm}^{-1}$  [9]. The remaining TO band and its high frequency shoulder are due to an asymmetrical stretch (S) mode at  $1200\text{-}1350\text{ cm}^{-1}$ . It has been reported about a FT-IR spectrum in which a shoulder, in the frequency range of  $1150\text{ to }1250\text{ cm}^{-1}$ , has an amplitude comparable or bigger than the main stretching band at  $1000\text{ cm}^{-1}$  [10]. This has been achieved in vitreous samples prepared by the sol-gel method using specific preparation conditions. The TEM micrograph of dried  $\text{SiO}_2\text{-CaCl}_2$  sample is shown in Figure 3. This figure confirms the formation of average particle size of about 50 nm. Also, a highly porous material with various pore sizes and an average pore size of 50 nm can be observed.

The guest substance such as calcium chloride disperses atomically within the host silica matrix and change or cure the properties of the silica. This action can enhance the water adsorption capacity of the silica surface. The nanocomposite can be applied in aquatic ambient as an adsorbent [9]. Figure 4 presents the data of EDX which includes the elemental weight percent and elemental atomic percent. Elemental analysis presents the weight percents of O, Si, Cl and Ca.

This data is shown in Figure 3 and confirms the ratio of  $\text{O/Cl (wt \%)} = 3.34$  and  $\text{Si/Ca (wt \%)} = 9.93$ . It also presents that the structure of the nanocomposite is a porous material that  $\text{CaCl}_2$  particles are doped into porous  $\text{SiO}_2$  matrix. The SEM micrograph is shown in Figure 5. The SEM micrographs are used for studying the morphology of samples. Initial electrons that return from the sample (BSE) and second electrons with low energy (SE) are collected and present a micrograph. These images present an inorganic polymerization that can form inorganic network containing  $\text{CaCl}_2$  particles. The particles of calcium chloride that were doped into silica support were studied by scanning electron microscopy. This result can be compared with results of LiBr nanocomposite structure on the silica matrix [10].

The exact composition of nanocomposite depends

on the annealing temperature. Particles of calcium chloride on the silica matrix can be produced by thermal treatment. These metallic nanocomposites have a structure with excellent stability and reproducibility [11]. The thermal analysis of  $\text{SiO}_2\text{-CaCl}_2$  nanocomposite was performed using TGA system and the results showed that the suitable temperature for initial thermal treatment was about  $200^\circ\text{C}$ . The thermal analysis presented weight loss of about 4 % at  $40\text{-}80^\circ\text{C}$  that was due to the remove of water and then the weight was slightly increased at  $100^\circ\text{C}$ . After this, a constant reduce in weight was observed between  $100\text{-}280^\circ\text{C}$  that was related to the remove of solvent. Also, the thermal analysis presented weight loss about 31.5 % at  $300\text{-}1000^\circ\text{C}$  which was due to the decomposition of the organic compounds [12].

As depicted in Figure 6, at  $20\text{-}100^\circ\text{C}$  heat flow increases because the materials need to be heated for breaking of their bonds, but at  $100\text{-}200^\circ\text{C}$ , the heat flow is constant. Also, the thermal analysis showed, as the heat flow increased to about 20 mW at  $200\text{-}300^\circ\text{C}$ , the material needed more heat to release the solvent.

At temperatures above  $300^\circ\text{C}$ , the curve showed a slight growth in heat flow at  $700^\circ\text{C}$  which was due to the decomposition of the organic elements and at  $700\text{-}1000^\circ\text{C}$ , the decomposition of the nanocomposite was completed.

#### 4. CONCLUSIONS

The straightforward entrapment of calcium chloride in silica matrixes was performed by the sol-gel method which resulted in hybrid materials. This process was conducted by the hydrolysis and condensation of Tetraethyl orthosilicate (TEOS) by replacement of ethanol from alcogel and drying at ambient temperature to obtain xerogel structure. FT-IR spectrum was used to describe (describes) the functional groups of the nanocomposite. Three main region from  $500\text{ to }1500\text{ cm}^{-1}$  with the names of (R), (B) and (S) can be observed. Each of the 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 with respect to the Silicon (Si) atom that can be bridged.

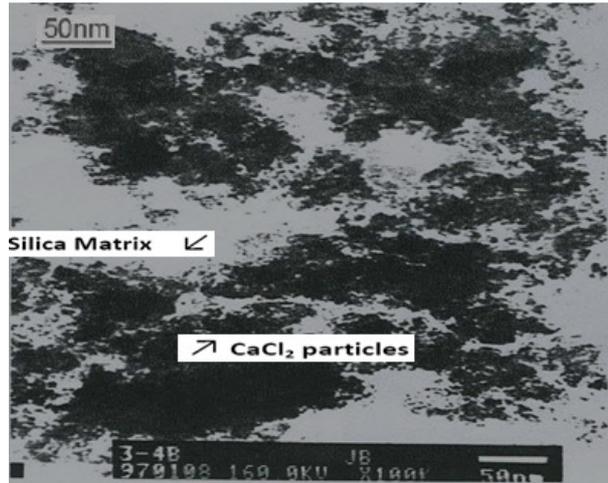


Figure 3. The TEM micrograph of SiO<sub>2</sub>-CaCl<sub>2</sub> nanocomposite.

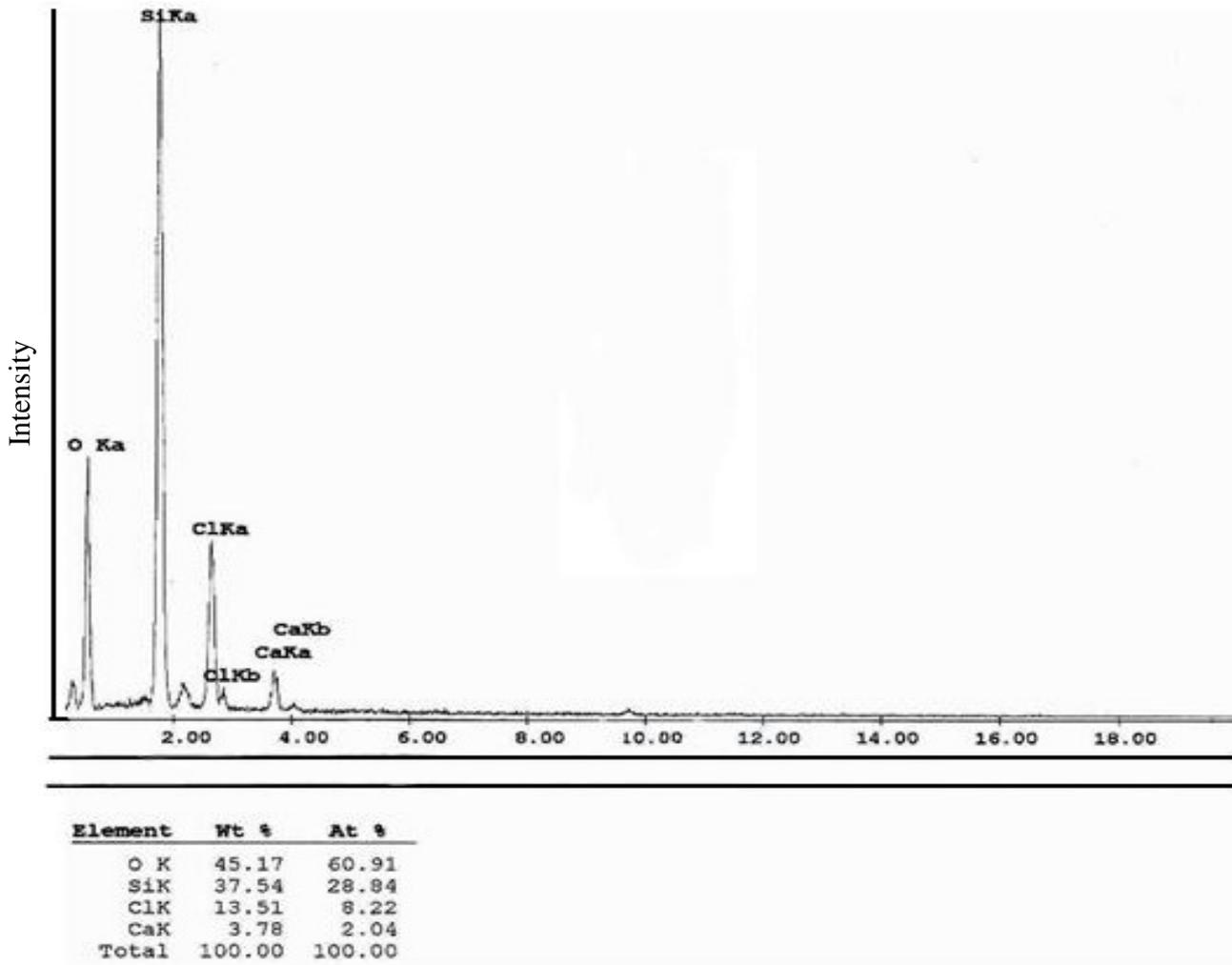


Figure 4. The EDX analysis of SiO<sub>2</sub>-CaCl<sub>2</sub>.

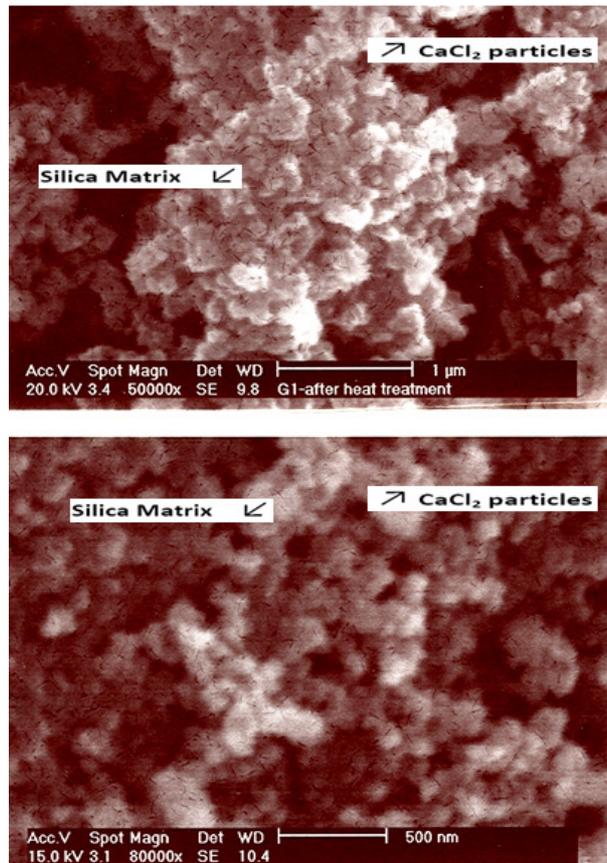


Figure 5. The SEM micrograph of SiO<sub>2</sub>-CaCl<sub>2</sub>.

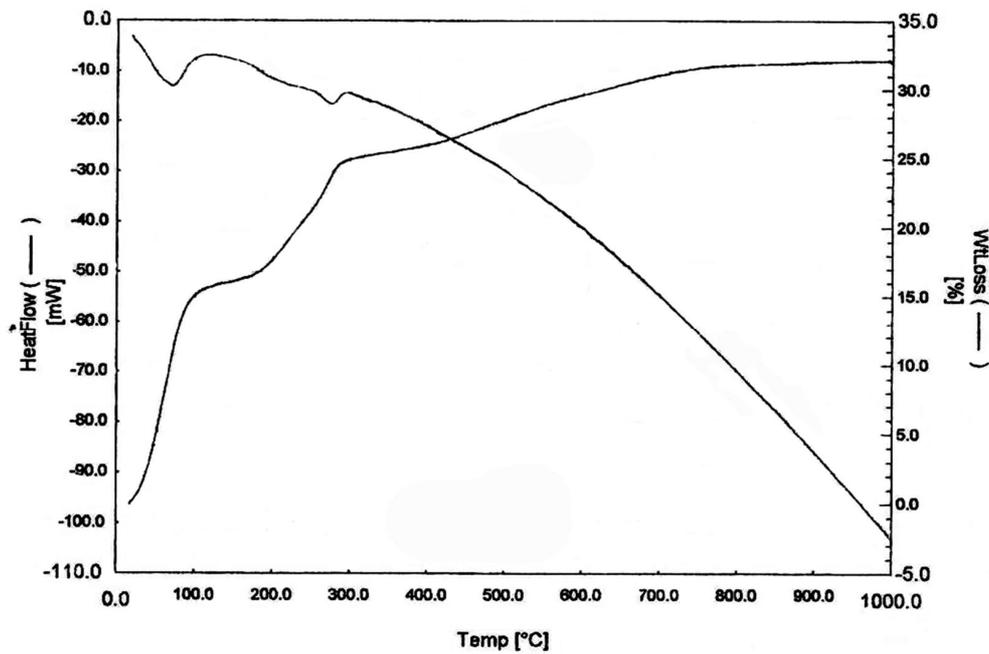


Figure 6. The thermal analysis (TGA) of SiO<sub>2</sub>-CaCl<sub>2</sub> nanocomposite.

The TEM micrograph of dried sample SiO<sub>2</sub>-CaCl<sub>2</sub> confirms the formation of average particle size of about 50 nm. Also, a highly porous material with various pore sizes and an average pore size of 50 nm can be observed.

Elemental analysis presents the weight percents of O, Si, Cl and Ca. It confirmed the ratio of O/Cl (wt %) = 3.34 and Si/Ca (wt %) = 9.93. Elemental analysis also presented that the structure of the nanocomposite was a porous material that CaCl<sub>2</sub> particles are doped into porous SiO<sub>2</sub> matrix. The SEM micrographs are used for studying the morphology of samples. These images present an inorganic polymerization that can form inorganic network containing CaCl<sub>2</sub> particles. The thermal analysis of SiO<sub>2</sub>-CaCl<sub>2</sub> nanocomposite was performed and the results showed that the suitable temperature for initial thermal treatment was about 200°C. This compound can be easily regenerated, dried at 200°C and reused. Finally, a highly porous material with doped CaCl<sub>2</sub> particles and various pore sizes was formed. The average particle size was estimated to be 50 nm.

## 5. REFERENCES

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