Synthesis of Nanosilica by Condensation Method For Crude Oil Adsorption

Nguyen Khanh Dieu Hong[*], Hoang Thi Phuong and Dinh Thi Ngo

*Hanoi University of Science and Technology, Hanoi, **VIETNAM***

Email: dieuhongprof@gmail.com

ABSTRACT

A novel condensation method using surface active agent CTAB for synthesizing nanosilica was reported. Effects of CTAB concentration in ethanol and TEOS/NH$_3$ molar ratio were investigated for improving the nanosilica structure. Results showed that the nanosilica could be well-structural controlled at the CTAB concentration in ethanol of 4% and TEOS/NH$_3$ molar ratio of 1.5/1 under pH = 9.5. Another new point of this report was to also investigate crude oil adsorption using the as-synthesized nanosilica. The adsorption was simulated as an oil spill contamination, so the nanosilica could be effectively used in case of the oil spill if the adsorption capacity was high enough. The adsorption pointed out a potential capacity of 9.32 for the nanosilica. Many techniques were used for characterizations of the materials including XRD, SEM, TEM, EDX, FT-IR and other standard ASTM methods.

Keywords: Nanosilica, TEOS, adsorption, oil spill, condensation.

INTRODUCTION

Recently, nanosilica based materials have attracted widely research interest because of many advanced properties such as high adsorption capacity, good surface area and low density [1-7]. Many efforts were established for improving characteristics and structure of this material including morphology, particle size and synthesis method. Actually, nanosilica materials could be produced by several routes including wet chemical procedure, sol–gel method, etc. [5-7]. Among them, the most common way was sol–gel polymerization of silicon alkoxides, especially tetraethyl orthosilicate (TEOS) because of its potential for strengthening the gel in sol-gel method against crack formation. The sol-gel method was preferred in comparison with original wet chemical one because of its good performance and fine morphology of the particles [5-7]. However, these methods were also all complicated, high cost considerably restricting their usage in large scale productions [3]. New procedures therefore should be developed based on some better solutions for simplicity, economy and high yield of nanoparticles.

In our present work, a novel but simple method was applied for preparing nanosilica – condensation using surface active agent CTAB. In fact, CTAB was commonly used for mesoporous silica synthesis because of its ability for forming large micelles at critical micelle concentration (CMC). Our modification was to control the concentration of CTAB being out of the range of the CMC. Therefore, the micelles could not

be produced but solution with low surface tension improving hydrolysis of precursors and condensation of immediate clusters.

A novel application of nanosilica was to apply in oil adsorption process simulated according to adsorption of oil spill over surface water. The investigation showed that nanosilica could play crucial role in this sector.

MATERIALS AND METHODS

Chemicals: Tetraethyl ortho-silicate (TEOS), ethanol, cetyl trimethylammonium bromide (CTAB) and NH_4OH solution 25% were all purchased from Merck and used without any further purification. Distilled water was produced in the laboratory.

Preparation of nanosilica: The nanosilica was prepared through condensation process at ambient temperature and pressure with these following steps:

Mixing a precise amount of distilled water and ethanol in an stirring supported beaker followed by stirring it vigorously at 400 rpm; this homogeneous mixture was gradually dropped with 5.6 ml TEOS and an exact amount of NH_3 25% solution; after 10 min of stirring, the pH value this mixture was controlled by the NH_3 solution until it ranged from 9.5 to 10.5.

Adding a series of CTAB solution in absolute ethanol with each of 2 mL containing 0%, 8% and 10% of CTAB by mass into the above mixture while keeping the stirring for 1 h next; then the whole mixture was quietly stored and closed up overnight; after this settling procedure, there was a layer of precipitate in the bottom of the beaker which was washed and filtered by absolute ethanol through a vacuum funnel until the pH of waste water was neutral.

Drying the precipitate after filtering at 100^oC for 10 h for evaporating surface water; then this white powder was calcined at 600^oC for 3 h in oven getting final product; there were many samples could be prepared depending on the varying of two important parameter consisting of CTAB concentration in ethanol in mother solution and molar ratio of $TEOS/NH_3$; for easily handling, these samples were assigned as SN-CTAB0, SN-CTAB4, SN-CTAB8, SN-CTAB10, SN-0.5/1, SN-1/1, SN-1.5/1 and SN-2/1 for nanosilica prepared with ethanol solution containing 0% - 10% CTAB and $TEOS/NH_3$ molar ratios of 0.5/1 – 2/1, respectively.

Application of nanosilica in oil adsorption process: The Vietnamese crude from Cuu Long basin was used as precursor for the adsorption. A simulation of oil spilling on surface water was established in a glass tank with diameters of 20cm×50cm×10cm for the real water level. The total surface area reached 1000 cm^2, and the water in the tank could be intently heated by an immersion heater for investigating effect of temperature on the adsorption.

A common adsorption process was described as followed: a precise and fixed amount of the crude oil was used for each experiment, and the oil was distributed over the water surface; then, an amount of 0.1 g of nanosilica was well distributed on the contaminated water surface. Because of low density and hydrophilicity, the nanosilica floated on the surface during the adsorption leading to gradually adsorbing the oil. The adsorption was also investigated through different parameters such as time, temperature and amount of the adsorbent (nanosilica); after each adsorption process, a filtering procedure was applied for separating the oil containing nanosilica from the water followed by drying at 100^oC for completely evaporating the rest water in the filter paper. A measuring procedures were established for the filter paper weight before (m1) and after (m2) filtering and drying.

323

Another procedure for determining the evaporated oil at 100°C was implemented using the beginning crude oil; the result exhibited a percentage of this part of the crude oil called as a%; then the total amount of the adsorbed oil could be calculated by this following equation: $m = [(m_2 – m_1) \times 100]/(100-a)$; the oil adsorption capacity therefore could be calculated as $r = m/0.1$ (0.1 grams were the weight of the nanosilica introduced to the adsorption);

The parameters of the adsorption process were investigated including temperature (from 25°C to 70°C), time (from 3 minutes to 2 hours) and mass ratio of the crude oil/nanosilica (from 3/1 to 15/1).

Characterization of materials: TEM images were captured using Field Emission JEOL 1100; XRD patterns were recorded using D8 Advance – Bruker; FT-IR spectra were measured in Nicolet 6700 FT-IR Spectrometer; EDX was recorded on Field Emission Scaning Electron Microscope S – 4800. Other ASTM methods were mentioned in the discussion.

RESULTS AND DISCUSSION

Effect of CTAB concentration in ethanol on nanosilica structure: Surface-active agent played a very important role in formation of nanosilica particles in condensation method because it could provide a micelle environment, especially with some unusual properties at critical micelle concentration. The surface-active agent helped condensed nanosilica well located on micelle clusters avoiding coagulation in the solution [8-10] therefore the nanosilica particles could be generated with small and uniform sizes. This study applied a common surface-active agent (CTAB) frequently used in nanoscale mesoporous materials such as MCM-41, SBA-15… to demonstrate how the nanosilica particles could be produced by using normal chemicals. Some XRD patterns of the four examples SN-CTAB0, SN-CTAB4, SN-CTAB8 and SN-CTAB10 were plotted in figure 1.
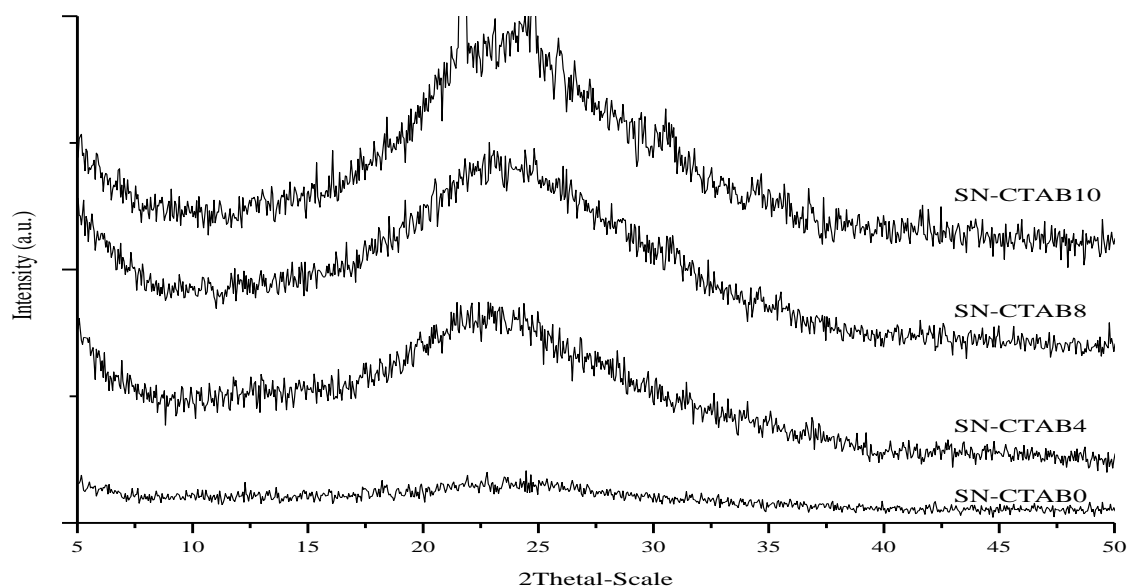

Figure 1. XRD patterns of nanosilica prepared at different CTAB concentration in ethanol

The XRD patterns clearly exhibited that the nanosilica samples existed in amorphous phase with an only wide band located at $2\Theta{\sim}25^{o}$ reliably attributed to amorphous silica [8, 11, 12]. That was to say that the particle size of the nanosilica was small. These observations were well adaptable with the results obtained from XRD patterns of other studies [13-16].

324

The pattern intensities of the nanosilica considerably changed when raising CTAB concentration from 0% to 4%. However, the amorphous background did not change clearly when raising the concentration from 4% to 10 %. That was to say that the amorphous structure could be stabilized under certain amount of this surface-active agent.

Morphology of the nanosilica samples were also observed through SEM and TEM images. Figures 2 and 4 described the SEM and TEM images of the four samples with different concentration of CTAB in absolute ethanol.
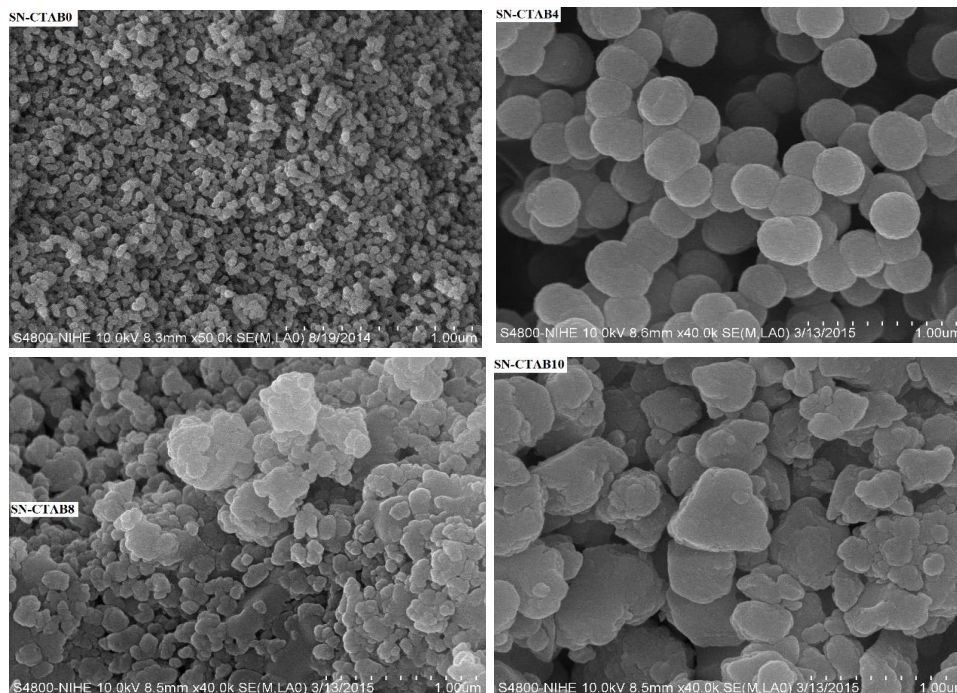

Figure 2. SEM images of nanosilica prepared at different CTAB concentration in ethanol

Observations from the SEM images indicated that with no CTAB usage in sample SN-CTAB0, particles tended to attach together becoming many large clusters. Therefore, there was difficult to determine size distribution of the nanosilica. Figure 3 could be used as another case for characterize the coagulation of the particles in the samples SN-CTAB0.
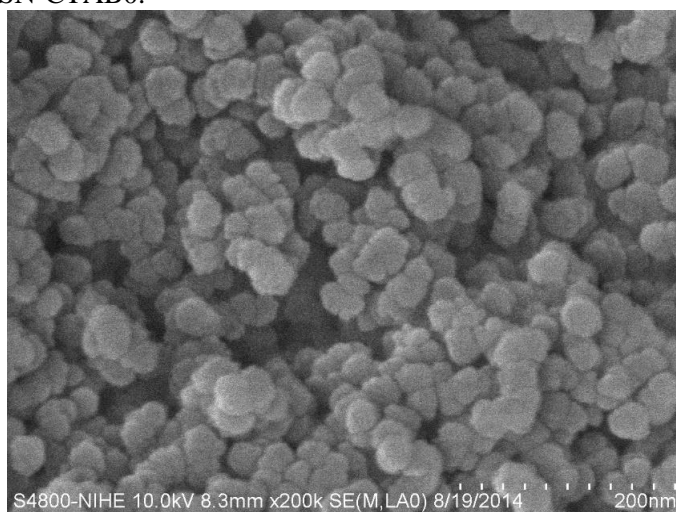

Figure 3. SEM image of sample SN-CTAB0

325

The SEM image of the sample SN-CTAB0 clearly exhibited that the material particles were constructed by many tiny parts coagulating together. This was a common phenomenon when preparing amorphous materials by condensation method without using any surface-active agent [8].

At higher concentration of CTAB in ethanol, for example 4% (sample SN-CTAB4), the nanosilica particles uniformly and separately distributed in a range of ~200-300 nm providing its porous structure. Raising CTAB concentration up to 8% in ethanol could induce decreasing in particle size, but size distribution of the particles was also ununiform and even partial coagulation. The case was much more worst in the sample SN-CTAB10 (10% CTAB in ethanol) because there was very difficult to distinguish the particles.

The phenomena could be explained as followed: in the first sample without using CTAB, the surface tension of the solution mixture was large enough to restrict diffusion of $Si(OH)_4$ fragments (generated from hydrolysis of TEOS in alkaline media) around the mixture resulting in coagulation tendency of the formulated particles; in the other samples introduced with CTAB at different concentration, the solution surface tension was lowered, so the diffusion of $Si(OH)_4$ into tiny clusters could be better; however, when the CTAB concentration was too high (exceeding the micelle critical point), the surface tension of the mixture sharply decreased tending to coagulate the small clusters again producing ununiform and large particle size of the as-synthesized nanosilica. Sample SN-CTAB4 contained many spherical and small particles therefore were the best candidate for the purpose of this material.
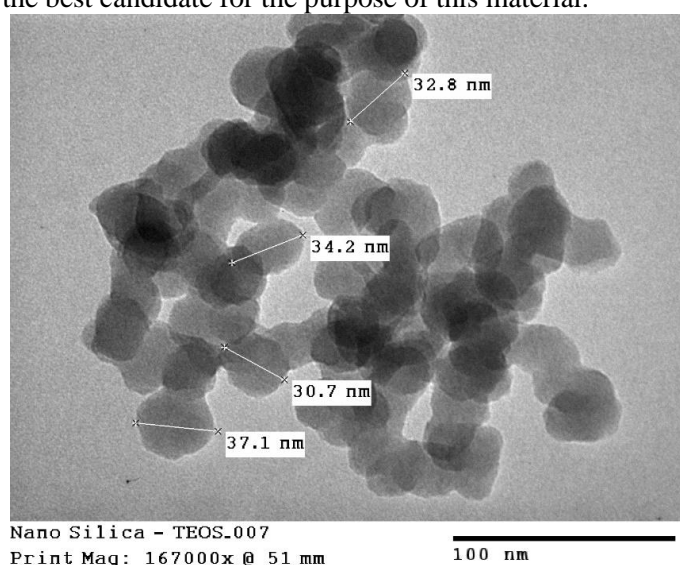

Figure 4. TEM image of sample SN-CTAB4

TEM image of this sample was exhibited in figure 4. The result showed that there were still many tiny particles being inside one large particle of the nanosilica material. That was to say that the synthesis process could be further improved to reduce the size of these particles.

Effect of TEOS/NH$_3$ molar ratio on nanosilica structure: By the method being familiar as applied when investigating the effect of CTAB concentration, the effect of TEOS/NH$_3$ molar ratio on the nanosilica structure was exhibited. By the condensation process, almost nanosilica materials existed in amorphous phase demonstrated by XRD patterns in the previous part and confirmed by many other studies [8, 11, 12]. Figure 5 also plotted many XRD patterns of different sample of nanosilica prepared at different TEOS/NH$_3$ molar ratios.

SEM images of the four samples were all exhibited in figure 6. The results showed the very same morphologies in comparison to those of the previous part; in which the nanosilica prepared at TEOS/NH$_3$ molar ratio of 1.5/1 reached the best uniform and well-distributed spherical particles. Therefore, the sample SN-1.5/1 was chosen for TEM image characterization.
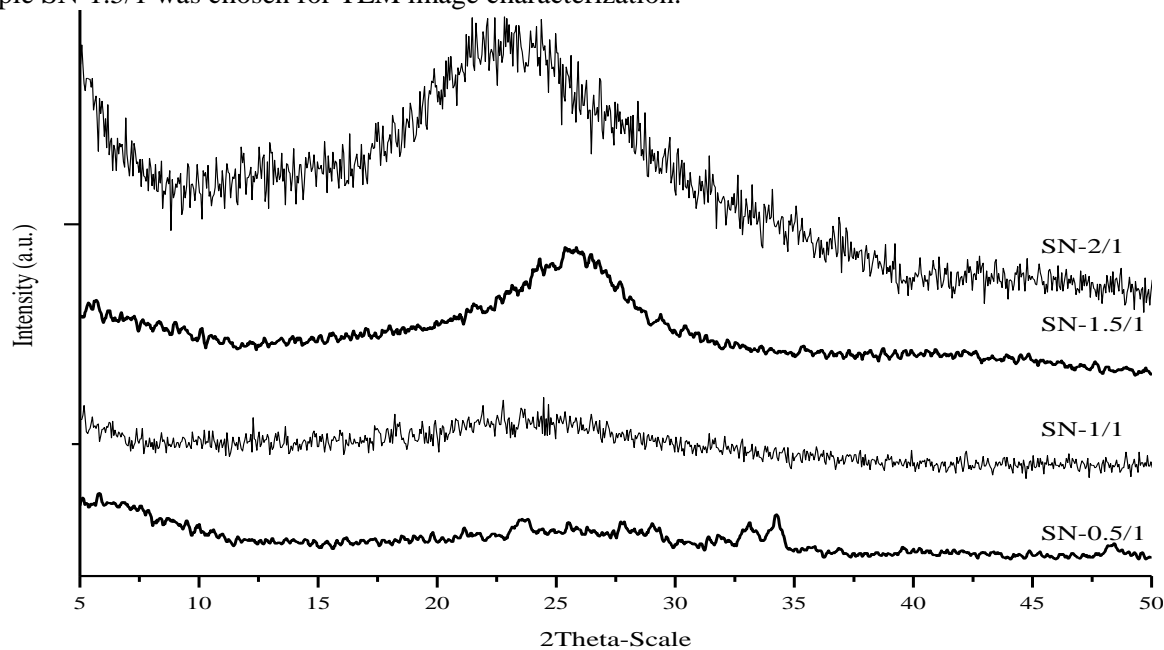

Figure5. XRD patterns of nanosilica prepared at different TEOS/NH$_3$ molar ratios
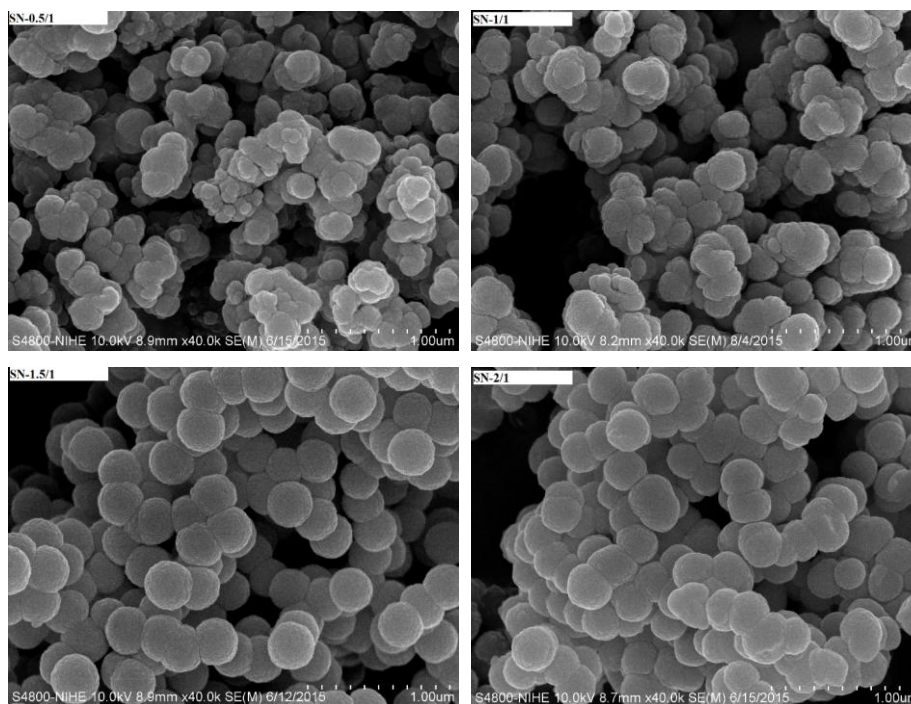

Figure 6. SEM images of nanosilica prepared at different TEOS/NH$_3$ molar ratios

TEM image of the sample SN-1.5/1 was revealed in figure 7. By observations, it could conclude that the nanosilica particles contained much more tiny particles in each cluster.
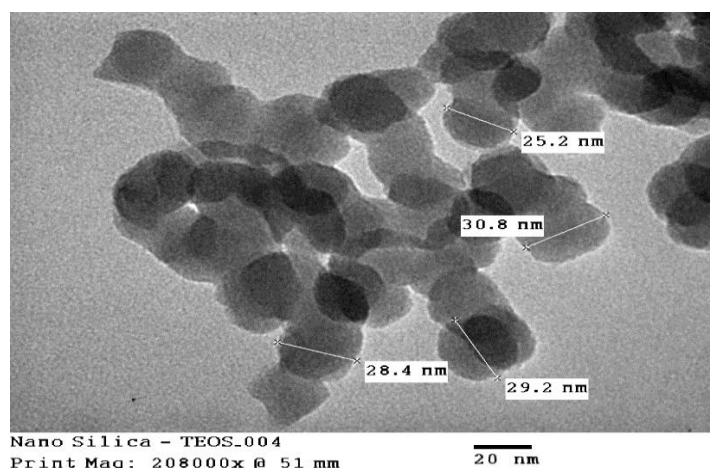
327

Figure 7. TEM image of sample SN-1.5/1

Explanations for these results could be withdrawn from the procedures happened during the condensation process. In the first step of the condensation, there was hydrolysis of TEOS followed by condensation of the $Si(OH)_4$ fragments forming the nanosilica frameworks under alkaline media. The hydrolysis took place at very low speed in comparison to that of the condensation process [8]. The two processes could be accelerated by using NH_3 as an effective catalyst, and the solution NH_3 therefore considerably played an important role on the whole reactions depending on its content in the solution.

Firstly, when NH_3 content was high with molar ratio of TEOS/NH_3 of 0.5/1, the velocity of both reactions such as hydrolysis and condensation was too high tending to partially coagulate the formed nanosilica clusters.

Secondly, when raising NH_3 content, both hydrolysis and condensation were taken place slowly, especially the hydrolysis. The consequence was that the condensation could be established quietly and smoothly, avoiding many side effect as coagulation.

Finally, when NH_3 content was too low, the reactions were on extremely low progress; many fragments formed but not being condensed together; then they could be coagulated again generating morphologies as in SEM image of sample SN-2/1. On the whole, the sample SN-1.5/1 could be considered as the best choice for the nanosilica synthesis process.

Other characterizations of nanosilica: As being investigated, the nanosilica sample prepared at chosen mentioned parameters in the previous part was used for further characterizations. EDX analysis of the material was done and revealed in figure 8.
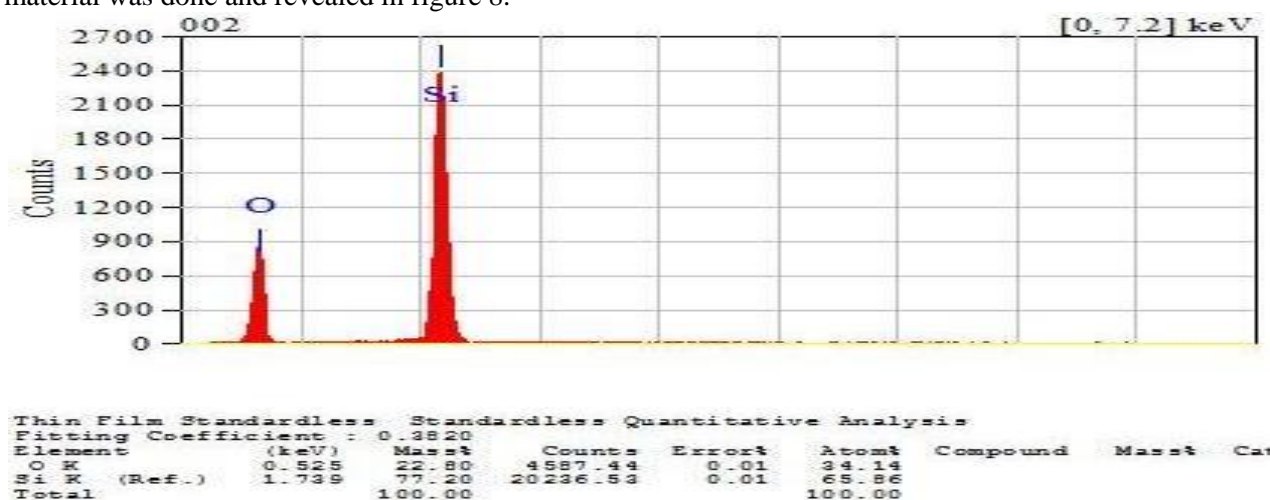

Figure 8. EDX analysis of the nanosilica

The analysis showed a high purity synthesized nanosilica. There were only two elements existed in the sample including O and Si with their weight content of 22.8% and 77.2% respectively. The molar ratio of Si/O was also considered as 65.86/34.14 = 1.93; this value was far different from the stoichiometry of Si/O in SiO_2. This unusual stoichiometry was discussed by using FT-IR method plotted in Figure 9.
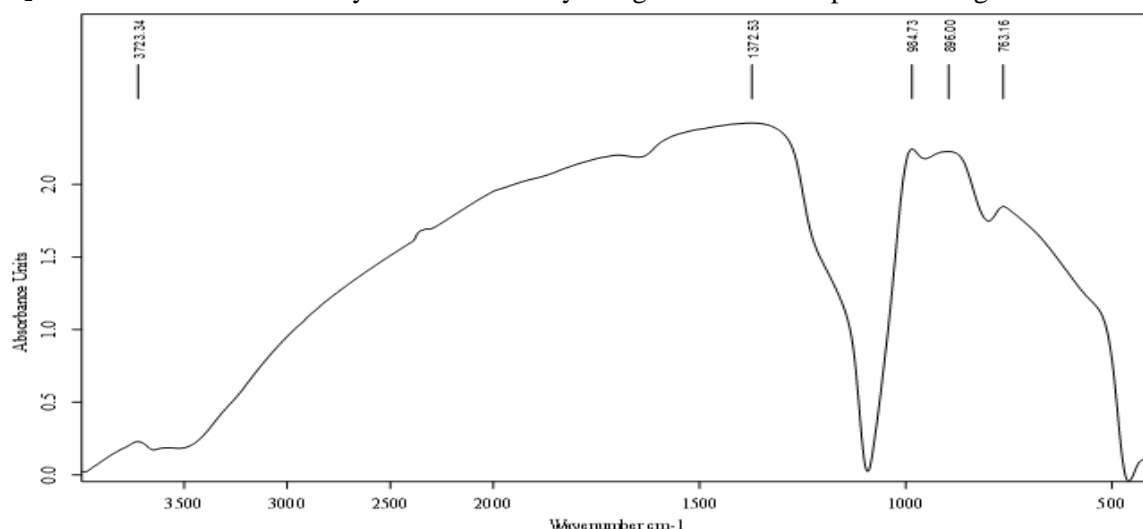

Figure 9. FT-IR analysis of the nanosilica

The FT-IR spectroscopy of the nanosilica revealed common bands of a typical silica such as bands at 1600 cm^{-1}, 896 cm^{-1} corresponding to vibrations of -OH and Si-OH groups; other bands were detected at 2250 cm^{-1}, 984 cm^{-1} and 480 cm^{-1} assigning to surface oxidation of the nanosilica with functions of Si-H when Si moiety was connected to surface Si through O bridges (H-Si-O-$Si_{surface}$).

The wavenumbers of the nanosilica at bands 984 cm^{-1} and 896 cm^{-1} were redshift in comparison to those of amorphous SiO_2. This could be explained by "confinement effect" – an effect happened when particle size was much smaller than the incident light source) [8, 11], or this could come from an unusual stoichiometry of SiO_x. The demonstration through EDX method confirmed the latter [8]. The connected hydrogen located on the nanosilica surface also considerably improved the surface-active property of the material. Some other specifications of the nanosilica before were also collected in table 1.

Table 1. Specifications of the nanosilica

No.	Properties	Methods	Nanosilica
1	Apparent density	D 1895	0.0826
2	Tensile Strength, kPa	D 638	22.3
3	Water solubility, %	D 5907	1.36
4	Index of Refraction	D 542	1.01
5	Linear thermal expansion	E 831	3.8×10^{-6}
6	Surface area, m^2/g	BET	197.4

The specification showed that the nanosilica was low solubility in water being well for the adsorption of oil on the surface water. The surface area of the nanosilica was also high in comparison to many amorphous silica materials [8], and it also provided great ability in the adsorption process.

Investigation of oil adsorption over nanosilica: The testing for oil adsorption of the nanosilica was established using sweet Vietnamese crude obtained from an oil field in Cuu Long basin with some properties measured in table 2.

329

Table 2. Specifications of Cuu Long basin crude oil

No.	Properties	Units	Methods	Values
1	Density, 20°C	-	D 3505	0.8386
2	Melting point	°C	D 87	24.8
3	Average molecule mass	g/mol	D 6579	250.9
4	Kinematic viscosity, 50°C	cSt	D 445	12.02
5	Sulfur content	%	D 4294	0.0403
6	Paraffinic content	%	D 5443	22.6
7	Asphalten content	%	D 6560	4.27

The adsorption investigation with the crude using the nanosilica was exhibited in table 3, figures 10 and 11.

Table 3. Investigation of oil adsorption using nanosilica

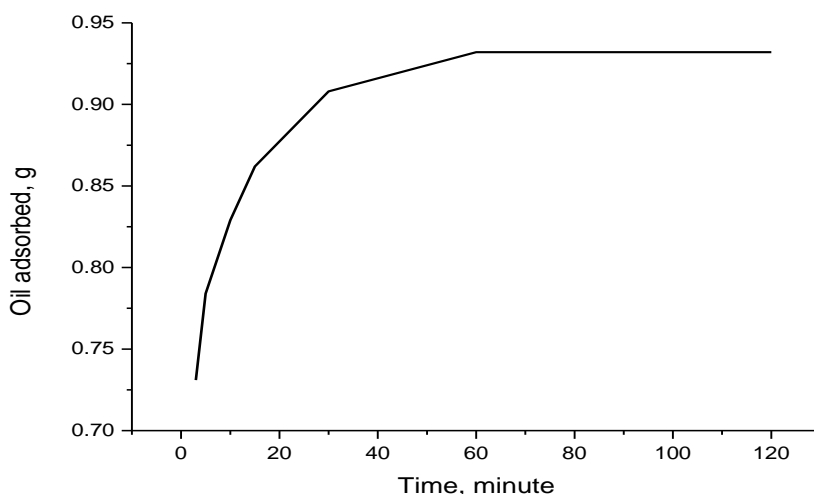| Time, min.	3	5	10	15	30	60	120
Oil adsorbed, g	0.731	0.784	0.829	0.862	0.908	0.932	0.932
Temperature, °C	25	30	40	50	60	70	-
Oil adsorbed, g	0.829	0.927	0.932	0.889	0.821	0.735	-

Figure 10. Oil adsorption at different times using nanosilica

The results obtained from figure 10 showed that the maximum adsorption capacity of the nanosilica was 9.32 after 40 min. The oil adsorbed amount increased by time because of extent contacting between oil and the nanosilica. However, the contact could only raise the adsorption capacity to a limit; then the adsorption has got balance.
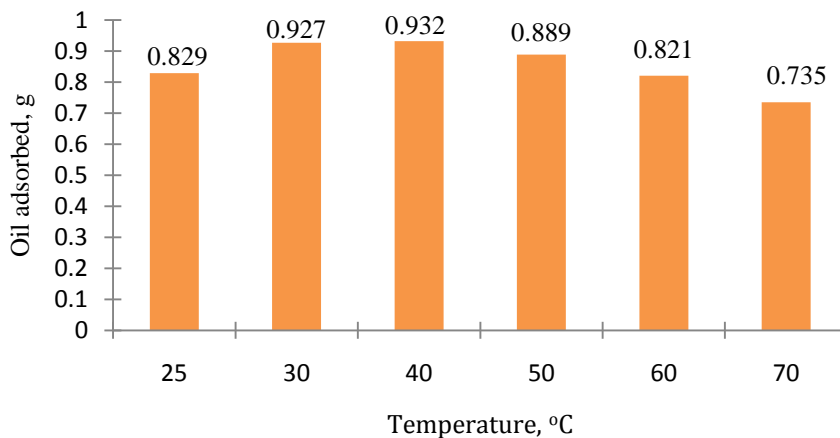

Figure 11. Oil adsorption at different temperatures using nanosilica

330

The adsorption process after being investigated with temperature also confirmed the 9.32 value was the highest capacity which the nanosilica could get. The suitable temperature was 40°C. If the temperature was higher, the adsorption was kinetically restricted, and at lower temperature, the oil tended to semi-solid avoiding the adsorption.

APPLICATIONS

The nanosilica material could be applied in many sectors including adsorption, oil spill remediation, and support for catalysts.

CONCLUSIONS

1. Successfully preparing nanosilica by condensation method using CTAB as surface active agent. Investigations resulted suitable CTAB concentration in ethanol and TEOS/NH$_3$ molar ratio of 4% and 1.5/1, respectively. Nanosilica possessed high surface area, hydrophobicity and low density which was useful for oil adsorption over surface water;

2. Investigating oil adsorption capacity of nanosilica pointed out that temperature and time being suitable of this process were 40°C and 40 minutes, respectively. The adsorption capacity of nanosilica reached 9.32 revealing its high potential in the oil spill treatment.

REFERENCES

[1]   M. A. Dabbaghian, A. A. Babalou, P. Hadi, E. Jannatdoust, A Parametric Study of the Synthesis of Silica Nanoparticles via Sol-Gel Precipitation Method, *Int. J. Nanosci. Nanotechnol.*, **2010,** 6(2), 104-113.

[2]   R. Stanley, A. Samson Nesaraj, Effect of Surfactants on the Wet Chemical Synthesis of Silica Nanoparticles, *International Journal of Applied Science and Engineering*, **2014,** 1, 9-21.

[3]   A.G. Dyachenko, M.V. Borysenko, S.V. Pakhovchyshyn, Hydrophilic/Hydrophobic Properties of Silica Surfaces Modified with Metal Oxides and Polydimethylsiloxane, *Adsorption Science & Technology*, **2004,** 22(6), 511-516 . DOI: 10.1260/0263617042879546.

[4]   L. P. Singh, S. K. Agarwal, S. K. Bhattacharyya, U. Sharma, S. Ahalawat, Preparation of Silica Nanoparticles and Its Beneficial Role in Cementitious Materials, Nanomater. *Nanotechnol.*, **2011,** 44-51. DOI: 10.5772/50950.

[5]   Ismail A.M. Ibrahim, A.A.F. Zikry, Mohamed A. Sharaf, Preparation of spherical silica nanoparticles: Stober silica, Journal of American Science, **2010,** 6(11), 985-989. ISSN: 1545-1003, 2375-7264.

[6]   E. A. Odo, D. T. Britton, G. G. Gonfa, M. Harting, Structure and Characterization of Silicon Nanoparticles Produced Using a Vibratory Disc Mill, *The African Review of Physics*, **2012,** 7, 45-56. ISSN 2223-6589.

[7]   C. Boissiere, M. Kummel, M. Persin, A. Larbot, E. Prouzet, Spherical MSU-1 Mesoporous Silica Particles Tuned for HPLC, *Adv. Funct. Mater.*, **2001,** 11(2), 129-135. DOI: 10.1002/1616-3028(200104)11:23.3.CO; 2-N.

[8]   B. Gorji, M.R. Allahgholi Ghasri, R. Fazaeli, N. Niksirat, Synthesis and Characterizations of Silica Nanoparticles by a New Sol-Gel Method, *Journal of Applied Chemical Research,* **2012,** 6(3), 22-26. P-ISSN: 2008-3815.

[9]   Jörg Knipping, Hartmut Wiggers, Bernd Rellinghaus, Paul Roth, Denan Konjhodzic, Cedrik Meier, Synthesis of High Purity Silicon Nanoparticles in a Low-Pressure Microwave Reactor, *Journal of Nanoscience and Nanotechnology*, **2004,** 4(8), 1039-1044 . DOI:10.1166/jnn.2004.149.

[10]   W. Stober, A. Fink, E. Bohn, Controlled growth of monodisperse silica spheres in the micron size range, *Journal of Colloid and Interface Science*, **1968,** 26, 62-69. DOI: 10.1016/0021-9797 (68) 90272-5.

[11]   J. Chrusciel, L. Slusarski, Synthesis of nanosilica by the sol-gel method and its activity toward polymers, *Materials Science*, **2003,** 21(4), 461-469.

[12]   N. Venkatathri, Synthesis of silica nanosphere from homogeneous and heterogeneous systems, *Bulletin of Materials Science*, **2007,** 30(6), 615-617. DOI: 10.1007/s12034-007-0097-3.

[13]   L. T. Zhang, W. F. Xie, Y. D. Wu, H. Xing, L A. W., W. Zheng, Y. S. Zheng, Thermal annealing of SiO_2 fabricated by flam hydrolysis deposition, *Chinese Physics Letters*, **2003,** 20(8), 1366-1368. DOI: 10.1088/0256-307X/20/8/354.

[14]   X. Shen, Y. Zhai, Y. Sun, H. Gu, Preparation of monodisperse spherical SiO_2 by microwave hydrothermal method and kinetics of dehydrated hydroxyl, *Journal of Materials Science & Technology,* **2010,** 26(8), 711-714. DOI: 10.1016/S1005-0302(10)60111-9.

[15]   H. Khorsan, N. Kiayee, A. H. Masoomparast, Optimization of amorphous silica nanoparticles synthesis from rice straw ash using design of experiments technique, *Particulate Science and Technology: An International Journal,* **2013,** 31, 366-371 . DOI: 10.1080/02726351.2012.755587.

[16]   S. Giri, Synthesis and Characterization of Zirconia Coated Silica Nanoparticles for Catalytic Reactions, M.Sc. Chemistry thesis, National Institute of Technology, Rourkela, India, **2008**.

AUTHOR ADDRESS

1.   **Nguyen Khanh Dieu Hong**
         Hanoi University of Science and Technology,
         Hanoi, Vietnam
         Email: dieuhongprof@gmail.com