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The Synthesis of Mesoporous Sio2/Tio2 Composite Particles by Sol-Gel Method and Effect of Hexane on its Structural Properties

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Abstract

Due to their unique properties such as high surface area, uniform and adjustable pore structure, and permeability of various molecules within and on their surface, mesoporous materials have become of interest in various fields including electronics, separation, catalysis, medical applications such as implant coatings and drug delivery. Mesoporous SiO_2/TiO_2 particles were synthesized by sol-gel method using various amounts of surfactant cetyl tri methyl ammonium bromide (CTAB) as structure directing agent under acidic condition; moreover, hexane was applied as a swelling agent. The samples were investigated using XRD, SEM, FTIR, SEM and N_2 adsorption-desorption analyses, in addition, the incremental effect of surfactant and hexane were examined. The results obtained from the analysis clarified that an increase in amount of surfactant will lead to an increase in surface area, pore size and pore volume. Additionally, with adding hexane to the constant amount of surfactant; the results showed an increase in surface area, pore size and pore volume while order of the structure was maintained.

Keywords: Mesoporous; Surfactant; Swelling agent; N_2 adsorption-desorption

Introduction

Mesoporous materials were presented first with successful synthesis of mesoporous silica by Mobile Company in 1992. The synthesis is mainly based on self-ordering method and by organic surfactant was performed ordering of inorganic sections [1,2]. Following that extensive efforts have been done in producing mesoporous materials from transition metal oxide due to their unique properties. Silicon oxide and titanium oxide are the main mesoporous oxides particularly applied in extensive areas such as catalysis, sensors, solar cells and medical applications including biosensors, drug delivery and implant coatings [3-6]. High surface area, ordered pores, high volume of pores hence high absorption capacity, narrow pore size distribution, non-toxicity, and also high biocompatibility are considered some important features of these materials [7]. Among mesoporous materials, silicon oxide due to the possibility of achieving an ordered mesoporous structure and foam-like strong walls has been of special interest for researchers and craftsmen. Furthermore, titanium oxide is one of the most recognized industrial photocatalysts and extensive effort to increase this property. Recently, due to manufacturing problems of mesoporous titania and also regarding non-reinforced walls of these structures particularly in temperatures above 500 and non-stability anatase phase above this temperature, silicon mesoporous structure has been highly regarded as a strong and stable skeleton to put titania particles on its surface. The method prevents the growth of titania particles during calcination, therefore, anatase phase remains stable up to high calcination temperature [8,9]. One problem of mesoporous SiO_2/TiO_2 composite is that titania particles integrate into mesopore silica hence closing the pores which is aggregated due to the fact that the pores are small. Therefore, enlarging the pores to reduce the possibility of the pores being closed is considered one suitable solution to this problem. To do this, swelling agents such as alkanes are applied; however, not many researches have been done in this regard [10-13]. In the current research, first the composite was synthesized by various amounts of CTAB surfactant and hexane. Then, their structure and morphology were investigated using XRD analysis, infrared spectrograph using Fourier transform (FTIR), Scanning Electron Microscopy (SEM) and EDS. The surface area, pores size, and pores volume in samples were measured using N_2 adsorption-desorption analysis and the results obtained were investigated.

Experimental

Materials

Tetraethylorthosilicate (TEOS) and titanium tetraisopropoxide (TTIP) as silica and titania precursors were purchased from Merck Company. Also CTAB as structure directing agent, nitric acid (65%) as catalyst and hexane (99%) as swelling agent and absolute alcohol as solvent were purchased from Merck Company. 2-times distilled deionized water was also used as a solvent.

Sol- gel synthesis and formation

First, 48.5 ml deionized water and 7.2 ml alcohol were mixed together using stirrer and then the amounts of CTAB were added to it and they were slowly stirred to obtain a fully clear solution. Then, nitric acid was added drop wise and its pH was adjusted to 1 using a pH meter. In the next stage, TEOS was slowly added to the prepared solution and stirred in 500rpm for 1 hour to prepare silica sol. Molar ratio of the materials used (TEOS: CTAB: H_2O:EtOH:HNO_3) was 1: x: 120: 4: 0/75 respectively. Amounts of x were considered to be 0/25, 0/35, 0/45 in order to investigate the effect of the amount of CTAB and to reach to an optimal state. In order to prepare titania sol, the ethanol mixed with acid and then TTIP precursor was added drop wise to the solution and was severely stirred for 5 minutes. The prepared titania sol was added drop wise to silica sol and severely stirred for 2 hours. The molar ratio (Ti/Si) was 0/1. The prepared sol took under the process of aging for one week to become gel-like. The obtained gel was

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washed with deionized water and alcohol for 3 times and then filtered and the obtained powder was dried at 100 for 24 hours. Afterwards, it was calcined in the electrical furnace at 600 for 5 hours with a heating rate of 1 K/min. The synthesized powders were called ST0/25, ST0/35, ST0/45 the initials of which stand for silica, titania, respectively and the number shows the amount of CTAB. To investigate the effect of hexane on structural properties of the above composite in constant amount of CTAB, the different molar ratio hexane/CTAB of 5, 10 and 15 were prepared. The above solution mixed with TEOS and TTIP as explained before. The temperature of the solution remained constant at 15 using an ice/water bath. Other stages were performed like the previous samples. The powders prepared with hexane were named STH5, STH10, and STH15 in which H uses for hexane and the number following them shows molar ratio of the hexane used.

Samples analysis

To determine the phases and crystallite size of the samples, the ST0/45 and STH15 calcined at 600℃ and one other sample calcined at 700 , the XRD analysis (PW1800, Philips diffractometer Cu K∝), was used. Low-angle X-ray diffraction (X-Pert Pro MPD) was utilized in order to determine the order of the structure and lack of hexane's effect on pores orders. SEM, EDS (TESCAN VEGA/XMU) and FTIR analyses (SHIMADZU8400S) were applied in order to examine the morphology and to have a quantitative analysis of elements and the groups on the surface. The structure of the mesoporous samples was investigated using N_2 adsorption-desorption isotherms (Be1Japan) at 77K and also using Belsorp mini II.

Results and Discussion

Figure 1 illustrates XRD spectra for two ST0.45 and STH15 samples calcined at 600℃ and 700℃. Curves of the two samples A and B are amorphous not showing anatse crystal phase which is basically due to low calcination temperature, low amount of titania precursor and presence of large amounts of amorphous silica phase and the formation of Si-O-Ti bond.

Anatase-to-rutile phase transition occurs at about 500 while transition temperature increases in presence of silica due to formation of Si-O-Ti bond. In the sample calcined at 700 the peak of anatase phase is fully clear and its crystal size calculated by Scherrer formula was found to be 16nm. For two samples calcined at 600, solid-phase dispersion of titania on the surface of silica particles and inside the pores has been notified [14,15].

Low angle X-ray diffraction in order to investigate the effect and lack of hexane in meso-structure formed on the ordered of the structure which is illustrated in Figure 2 for ST0.45 and STH15 samples. As can be seen, there is an obvious peak at an angle of about 1 which is related to plane (100), in addition, both samples showed a broad peak at 2θ 2/5 which includes two broad peak planes of (110) and (200), moreover, these two planes have probably converted into a broad peak due to the presence of titania phase. The results obtained from the analysis suggest that the presence of hexane does not influence ordering of the structure and our mesoporous structure has maintained its order to a high degree. Particle morphology of ST0.45 and STH15 was analyzed using SEM which is illustrated in Figures 3 and 4. Surface morphology is worm-like which is the same for both samples and according to the studies performed this is attributed to molar ratio Ti/Si used [16]. EDS analysis was used in order to evaluate the elements in synthesized powders and the only observed elements in the synthetic powders include silicon, titanium and oxygen.

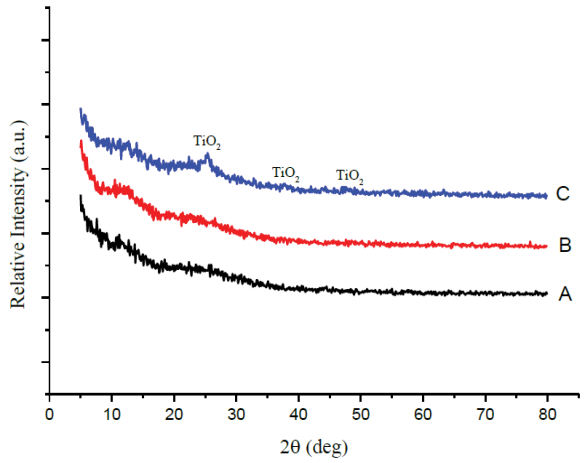

Figure 1: X-ray diffraction patterns: A) ST0/45 calcined sample at 600°C B) STH15 calcined sample at 600°C) Sample without hexane calcined at 700°C.

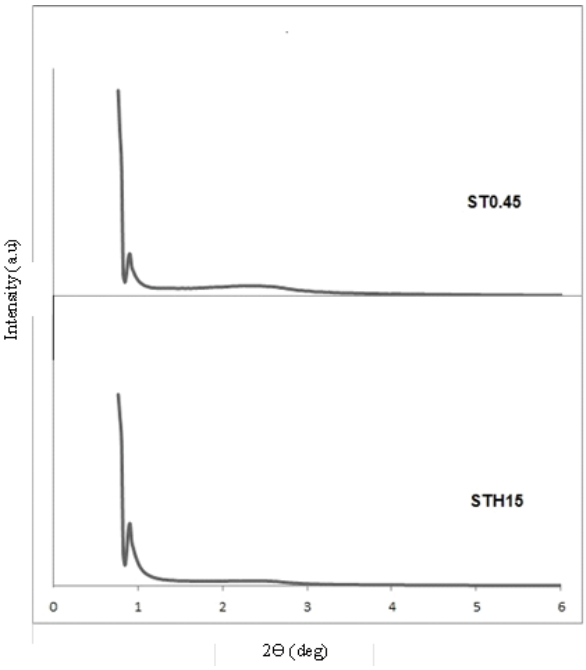

Figure 2: Low-angle X-ray diffraction for ST0.45 and STH15.

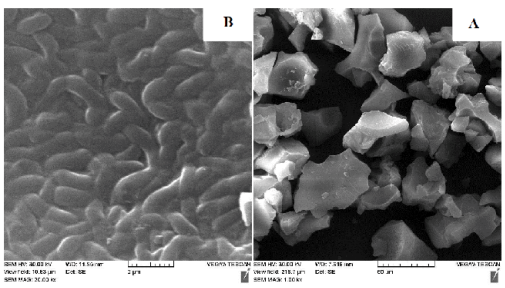

Figure 3: SEM images of ST0.45 at different magnification.

As can be seen in FTIR spectra of ST0.45 and STH15 samples illustrated in Figure 5, the spectra of both samples are the same. The peaks in 1080, 800 and 455 cm-1 were attributed to Si-O-Si stretching vibrations, in addition, the peaks related to 3430 and 1641cm-1 show the bonds attributed to hydroxyl and water. The sightly peak, i.e. peak 950cm-1 is also attributed to Ti-O-Si stretching vibration.

Figures 6 and 7 show N_2 adsorption-desorption curves of mesoporous silica-titania ST0.45 and STH15 samples. The curve of absorbance data shows that an increase in relative pressure will lead to a gradual increase in the amount of gas absorbed implying absorption through formation of several layers. A sudden increase of absorption occurs in ST0.45 and STH15 in a relative pressure of 0/3 - 0/4 which is due to capillary condensation of nitrogen in the pores and their curve is of IV type.

The desorption data graph locates on the absorbance data graph implying a uniform porous structure. As can be seen, an increase in the amount of surfactant will lead to a significant increase in the surface area (1179m^2/gr.), in addition, there has been an increase in size of pores and volume of pores. Pore size of ST0.45 sample is in the mesoporous area that having maximum surface area and pore volume. The critical micelle concentration (CMC) of CTAB surfactant is 0/03wt% and in a concentration above this level micelle is spontaneously formed and becomes spherical-shaped and upon further increase the spherical micelles become rod-like and their size will increase along with an increase in surfactant leading to an increase in pore size and surface area, moreover, an increase in surfactant leads to flocculation and larger size of the particles [17]. As we know, titania closes the pores and leads to even smaller pores, therefore, we applied different amounts of hexane in CTAB constant amount of surfactant with a molar ratio of

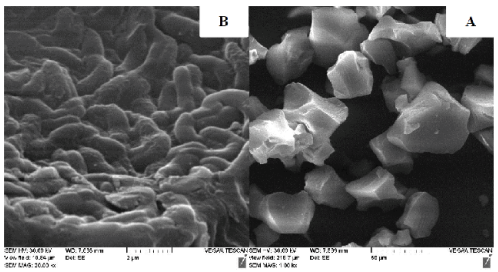

Figure 4: SEM images of STH15 at different magnification.

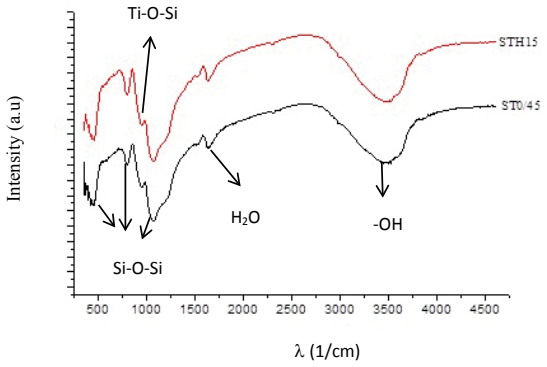

Figure 5: FTIR spectrum for mesoporous silica-titania composite in ST0.45 and STH15.

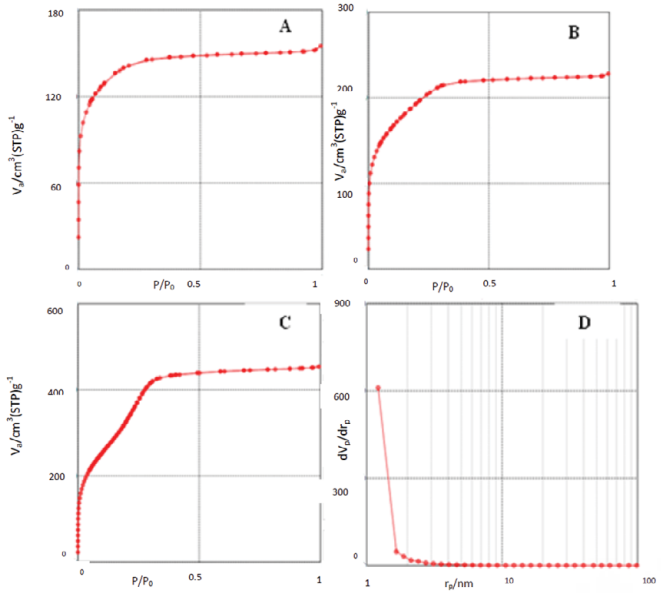

Figure 6: N2 adsorption-desorption isotherm of silica-titania samples A) ST0/25 B) ST0/35 C)ST0/45 D) Pore distribution curve.

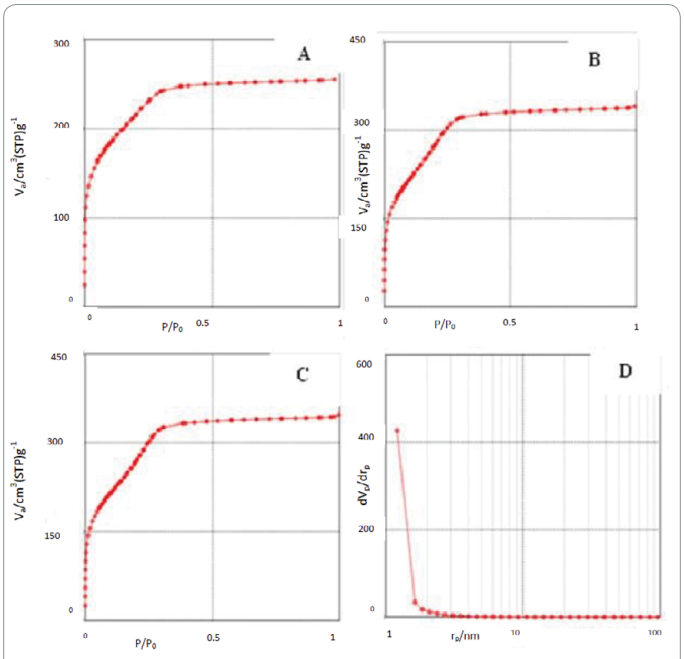

Figure 7: N2 adsorption-desorption isotherm curves of mesoporous silica-titania composites for samples A) STH5 B) STH10 C) STH15 D)Pore size distribution.

Type of Material	Surface Area (a_s BET) (m^2/gr)	Average Pore size (nm)	Total Pore Volume (cm^3/gr)
ST0/25	521	1.88	0.239
ST0/35	702	2	0.351
ST0/45	1179	2.376	0.7
STH5	775	2.03	0.39
STH10	982	2.13	0.52
STH15	988	2.16	0.533

Table 1: Features of silica-titania composite particles according to N2 adsorption-desorption data

CTAB/Si to investigate its effect on the surface area and pore size of the samples. As can be seen in Figure 7 and Table 1, the curve exits from microporous mode and leads to mesoporous mode. In mode A, there has been a little increase in absorption amount compared to ST0/25 and with adding hexane the amount of absorption in relative pressure of 0/3-0/4 has significantly increased. These isotherms like longmuir isotherms are of IV type showing mesoporous materials and like the previous samples, adsorption-desorption isotherms locate on each other implying uniform pores.

Conclusion

Mesoporous SiO_2/TiO_2 composite particles were synthesized using sol-gel method and in this context, an increase in the amount of surfactant led to an increase in surface area, pores size and pores volume. Furthermore, without affecting the order of the structure, hexane in CTAB constant amount led to an increase in the surface area, pores size and pores volume. In addition, formation of Si-O-Ti bonds increased thermal stability of anatase phase and these particles were uniformly distributed on the surface area and inside silica pores.

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