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Synthesis of Nano-fillers from Local Materials by Two Different Methods

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Abstract: *Two nano-fillers were synthesized using two different methods. In sol-gel method, times of milling and calcinations were studied. In sonochemical method, times of ultrasound, calcinations and temperature were studied. The bentonite and kaolinite samples were characterized by X-ray powder diffraction, Transmission electron microscopy (TEM) and the results recorded from the above mentioned methods were compared.*

Keywords: *Nano catalyst , Synthesis of Nano fillers.*

1. INTRODUCTION

The two main approaches for producing Nanomaterials are top-down and bottom-up [1]. Top-down approach is to start from the macro-size to the nano-size. Each method rely on the chemical, thermal and electrical processes and the targeted physical features [2]. The high-energy milling is the main process in the top-down approach, also it may include: ion implantation[3], lithography[4], laser ablation[5], sputtering, vapor condensation, etc[6]. In contrast, bottom-up approaches are synthesized from the atomic/molecular-size to the nano-size [7]. It requires an accurate multidisciplinary research of the molecules structure, assembly and dynamic behavior. Bottom-up approach contains sol-gel, precipitation [8], electrical deposition [9], cluster assembly/consolidation [10], self-assembly [11], self-alignment [12], chemical vapor deposition [13], atomic layer deposition [14], anodizing [15] and etc. Also, new hybrid techniques to fabricate nanomaterials merge between top-down and bottom-up approaches have been developed [16].

Different authors prepared nano-fillers with different methods. Nano-particles of bentonite have been prepared by solvothermal method in different conditions in order to regenerate waste engine oil [17-19]. The adsorbents porosity was developed using nitric and sulfuric acid acidification [20].

Shao et al. [21] used nano-bentonite to prepare clay composite with a high requirement of montmorillonite (MT). Bentonite slurry concentration of 7%, stirring and centrifugal time of 20 and 30 min, respectively, were applied, none dispersant agent was requested. The MT content in the composite reached as high as 98.7%. The structural characterization and morphology of composite were observed by means of X-ray diffraction (XRD), scanning electron microscopy (SEM). Higher MT content matrix was obtained using bentonite purification.

Bukit, et al. [22] prepared Nano-bentonite as filler and reinforcement of thermoplastic high density polyethylene (HDPE). The purification have been done using HCl solution, then calcination at 600 ^{o}C for 2 h and finally, milling for 10 h to get natural nano-bentonite with good mechanical and thermal properties to be used as a filler for HDPE in the automotive industry.

Clay-based nanostructures were prepared from kaolinites of varying structural order by different methods. The kaolinite-urea precursor obtained by dry grinding intercalated further with triethanolamine. The tetraalkylammonium salt was synthesized in the interlamellar space. Exfoliation was achieved by the use of sodium polyacrylate. In other method, the kaolinite-potassium acetate precursor, obtained via two different methods, first was intercalated further with ethylene glycol (EG) and then *n*-hexylamine (HA). Intercalation with EG was also achieved by heating either directly or with microwaves. The morphology depends on the degree of structural order of the original clay, the precursor and the heat treatment. Higher structural order facilitates the formation of a tubular morphology, while mechanical treatment and microwave agitation may result in broken tubes. Molecular mechanical calculations showed that organo-complexes may be exfoliated to a *d* value of 10 –11Å[23].

Nano-bentonite/polyester composite was prepared using different percentage of bentonite (5, 10, 15, and 20%). The indirect activation was repeated five times using HCl and $NaCo_3$ [24].

Nano-bentonite was also prepared by co-precipitation method. Bentonite was dried at 100 ^{o}C for a week, then, crushed and milled. The powder is activated chemically by dissolves 50 g of bentonite in 100 ml of HCl (10 M), at 300 rpm and 70 ^{o}C. The powder is calcined at 600 ^{o}C for 1 h with fix increment of 150 ^{o}C. Finally, the powder undergoes milling for 30 min[25].

In order to synthesize silica nanoparticles from bentonite, a series of thermal and acid treatment processes was performed to increase the silica and lower the alumina content. The obtained silica rich clay was treated in NaoH solution (10 & 40 wt%) to form sodium silicate solutions [26].

Nano-particles of bentonite have been prepared by nano-grinding. The bentonite particles had been ground to the size ranging from 4 to 9 nm [27].

Natural kaolinite was treated chemically with H_2O_2, followed by thermal treatment at 500 ºC and then mechano-chemically by ball milling with/without $CaSO_4$ in order to improve the catalytic activity of modified kaolinite as a solid acid catalyst[28].

Different types of nano-organo bentonite were prepared from the Egyptian bentonite; it was purified using a conventional method via the treatment with HCl and distilled water. The modification of the clay was carried out using different types of organo-modifiers [29].

However, the synthesis of nano-materials requires high energy, costly materials and difficult working conditions that could be hard to be available. Also, the trend of nano-clay applications in the modern industries, were motivated us to prepare local, cheap and available nano-clay using simple techniques. Nano fillers were prepared from local clays such as bentonite and kaolinites using two different techniques (sol gel and sonochemical).

Modification of sol-gel method [30], was investigated by purification of clay with HCl and stirring for 15 min, drying at 60 ^{o}C for 1 h, then calcination at different temperatures (250-600 ^{o}C) for 2 h, finally, milling in a ball mill for (2-10 h). In the sono-chemical method [31], the clays were prepared as suspension of clay and ethyl alcohol and sonicated by ultra sonic device for (0.5-4 h), then dried for alcohol removal for 30 min at 60 ^{o}C, after that calcined at different temperatures (250-800 ^{o}C) for (1-4 h), the resulted samples were characterized by XRD, Transmission electron microscopy (TEM). Analysis of the results has been done to get the optimum synthesis parameters.

2. EXPERIMENTAL PART

A. Materials:

Bentonite was obtained from Cairo with the following chemical composition:

Table (1): The chemical composition of raw bentonite

Chemical composition	SiO_2	Al_2O_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	TiO_2
Percentage (%)	54.91	17.01	9.31	0.99	2.47	1.03	2.75	0.48	1,53

Kaolinite was obtained from Asyut with the following chemical composition:

Table (2): The chemical composition of raw kaolinite

Chemical composition	SiO_2	Al_2O_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	Cr

Percentage (%)	41.05	34.84	2.40	1.29	0.72	0.05	0.04	0.76	0.054

B. Methods:

- Sol-gel method was modified in which a suspension of kaolinite, and suspension of bentonite in hydrochloric acid (commercial, 36% assay), were prepared and agitated with a magnetic stirrer for 15 min, dried for an 1h at 60 ^{o}C, calcinated at [150, 200, 250, 350, 400, 500 and 600 ^{0}C] for 2 h, then milled in a ball mill for [2, 4, 5, 6, 8 and 10 h].

In the second method (sonochemical) [31], A suspension of kaolinite, and suspension of bentonite in ethyl alcohol (ethanol 98% assay) were prepared, stirred with a magnetic stirrer for 15 min. The suspension was ultrasonically irradiated for [0.5, 1, 1.5, 2, 2.5, 3, 3.5 and 4 h] with a high-intensity ultrasonic probe immersed directly into the solution under various conditions, and then dried at 60 ^{o}C for 30 min for alcohol removal and finally calcined for [1, 1.5, 2, 2.5, 3, 3.5, and 4 h] at 800 ^{o}C.

A quantitative phase analysis was performed using XRD (X – Ray diffractometer, Pananlytical Embryean, Model No: 202964). The particle size was calculated using Scherer formula

$D= 0.891\lambda/\beta\cos\theta$,

Where: D is the average grain size, λ is the X-ray wavelength (0.15405 nm), and θ and β are the diffraction angle and full-width at half maximum of an observed peak, respectively [32-34].

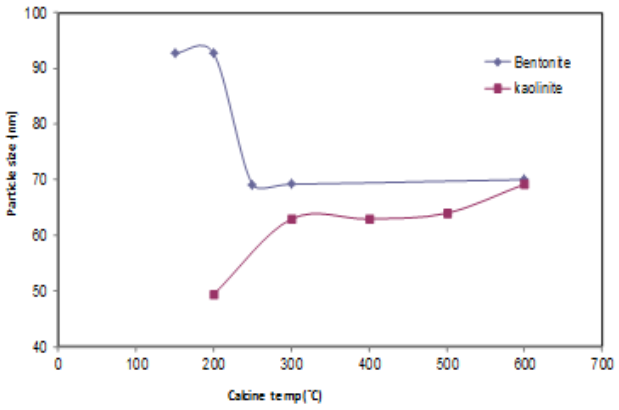
3. RESULTS AND DISCUSSION

The prepared clays samples at different working parameters were characterized. Also, the effect of these parameters on the properties of resulted samples was investigated.

A. The effect of calcination temperature:

Fig (1) shows the effect of different calcination temperature on the clays particle size. The effect differs from material to other as previous studies proved that thermal treatment affect the strength parameters of clays. It was found that kaolinite becomes non-plastic at 400°C and bentonite at 500°C [35]. Grain size growth with increasing thermal treatment plays indeed a major role. Thermal treatment of kaolinite and bentonite up to 400°C drastically reduces their swelling behavior. Strong correlations between the angle of shearing resistance and thermal treatment of both materials and correlation coefficients have been demonstrated. However, the kaolinite and bentonite can be used as good stabilization materials if they are thermal treated; kaolinite up to 400°C and bentonite up to 500°C[35].

As shown in Fig. (1), the temp was more effective on kaolinite than bentonite as kaolinite more sensitive for high temperature. In bentonite case, the particle size decrease with the increase of temp as particles divided to smaller size with increasing temperature. It was found that bentonite is more stable under high temp, in case of kaolinite reach near softening point so particles agglomerated making the size increase with temperature increase.



Fig(1): The effect of calcination temp on the particle size of clays using sol gel method.

B. The effect of milling time :

Fig (2) shows the effect of milling time on the clays. At early time, the particle size increase with increasing milling time as particles agglomerated at the beginning of milling, then it decrease with increasing milling time. In case of bentonite the particle size increased sharply then decreased with time contrast in case of kaolin it increased slightly then decreased which indicate that bentonite particles were more compacted than kaolinite particles referring to its properties. Finally, decreasing in particle size with increasing calcination temperature or milling time which may be attributed to the formation of new phase with new properties as its crystalline structure did not effected by temperature or milling sharply and formed material in nano-size conserved its crystalline structure.

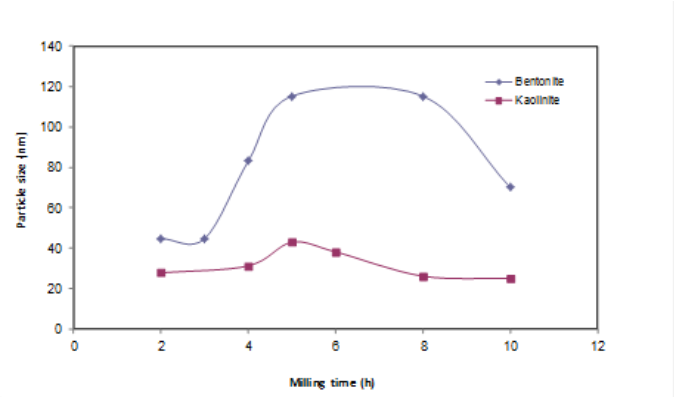


Fig (2): The effect of milling time on the clays particle size using sol gel method.

C. Effect of sonication time

The effect of sonication time on the particle size of the clays (Fig. 3) shows that bentonite to kaolinite have different attitudes, as in case of bentonite the curve show that particle size decrease with increasing sonication time (the time that the material exposed to ultrasonic waves) and nearly constant but in case of kaolinite the particle size firstly increased with increasing sonication time then nearly constant then decreased with increasing time of sonication.

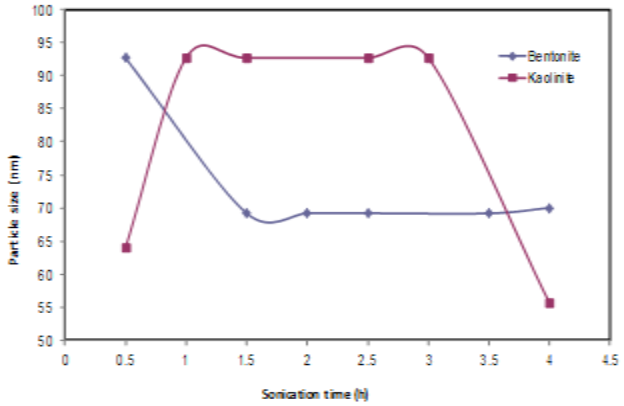


Fig (3): The effect of sonication time on the particle size of clays using ultrasonic method.

The results showed that the particles of kaolinite more adhesive than bentonite as it agglomerated firstly then dispersed finally with increasing time of sonication.

D. The effect of calcination time

As shown in Fig. (4), the calcination time affect the clay particle size and it's nearly the same effect for both materials, with only one hour shift. The particle size increased then decreased with increasing time as in the beginning of calcination the particles being agglomerated due to liquid content then it get red off liquids and particles become individual.

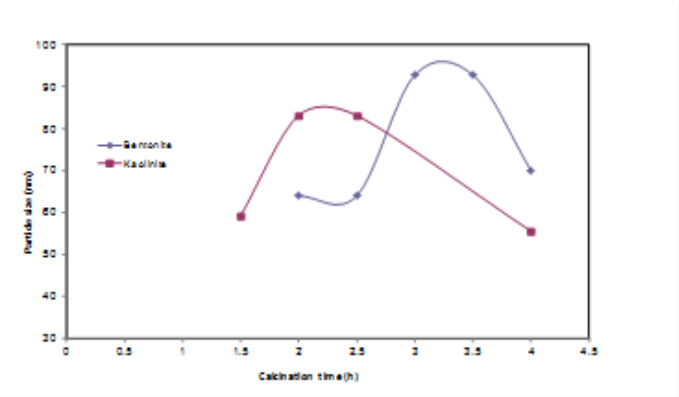


Fig (4): The effect of calcination time on the particle size of clays using ultrasonic method.

The XRD analyses of the produced samples at the optimum conditions are shown in Fig. (5-8), the materials in that size conserved its crystal structure as sharp beaks and it resemble to the peaks of the raw clay before treatment. Additionally, they didn't affected by applied working parameters like high temp, milling, or exposing to ultrasonic powers and it could be useful in many applications.

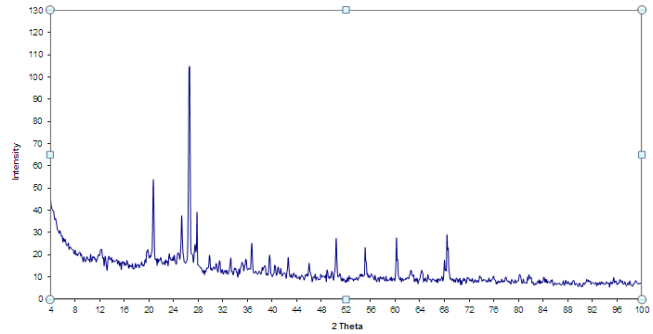


Fig (5): The XRD of bentonite optimum sample prepared by sol gel method.

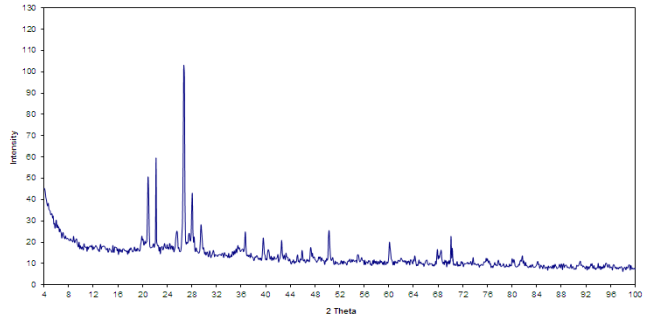


Fig (6): The XRD of bentonite optimum sample prepared by ultrasonic method.

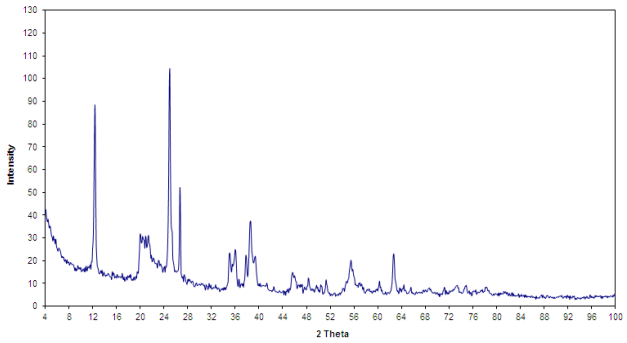


Fig (7): The XRD of kaolinite optimum sample prepared by sol gel method.

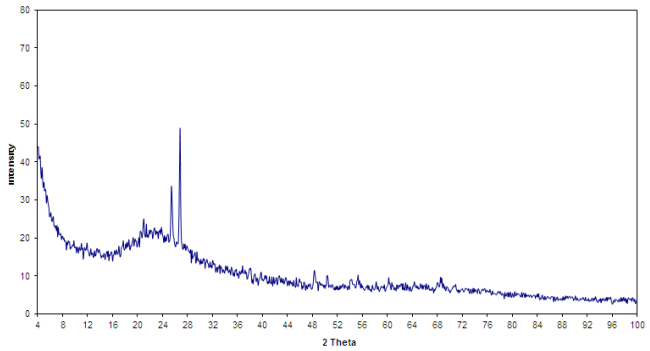


Fig (8): The XRD of kaolinite optimum sample prepared by ultrasonic method.

- Transmission electron microscopy (TEM) images:

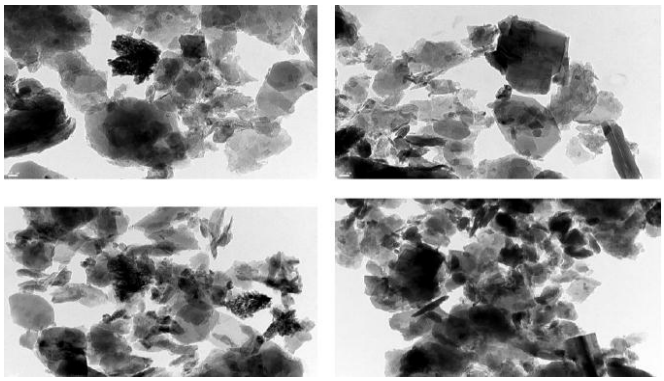


Fig (9): TEM for bentonite nano particles.

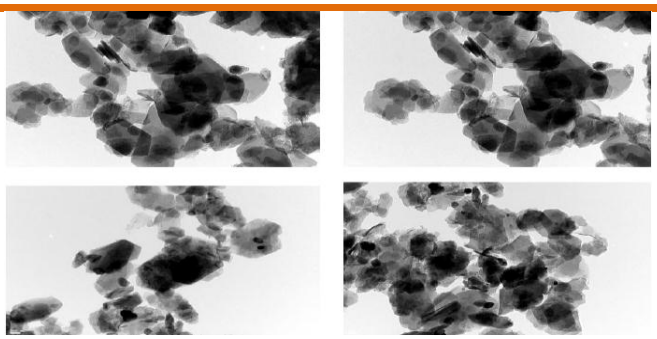


Fig (10): TEM for kaolinite nano particles.

Figures (9-10) shows: Transmission electron microscopy (TEM) images confirm X- ray diffraction results and provide a unique opportunity to directly visualize nano-particle morphology; these techniques can provide a representative perception of the morphology being analyzed, images show the particle shape of bentonites, kaolinite which enlarged a certain multiples, image is generated based on the interaction pattern of electrons that transmit through the specimen giving 3-D image construction possible and show particle size ranging from 50 to 100 nm and that confirms the results we got from X- ray diffraction patterns.

4. CONCLUSIONS

Nano-fillers from cheap and available precursors like bentonite and kaolinite were successfully synthesized by sonochemical and modified sol gel methods. The results were confirmed be XRD analyses and Transmission electron microscopy (TEM). The sonication of bulk bentonite and kaolinite would produce nanostructures. The morphology change upon sonication and chemical conditions of sol gel. The method can potentially be used in the industrial scale because it does not need special operating conditions, such as elevated temperature, special surfactants, long reaction time or temperature and pressure controlling.

The optimum conditions of bentonite production using sol gel method are (calcination at 300 ºC and milling for 2.5 h), and for ultrasonic method (sonication for 2 h and calcination up to 2.5 h). The optimum conditions of kaolinite production (calcination at 300 º C and milling for 4 h) for sol gel method, and (sonication for 4 h and calcination up to 4 h) using ultrasonic method.

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