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Immobilization of a titanium complex on the surface of nan magnetite and characterization of the resulted material

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ABSTRACT

Nan magnetite is a class of nanoparticles which has interesting behavior using magnetic fields. In such a way, each nanoparticle becomes a single magnetic domain and show superpara magnetic behavior, so it can be attracted to external magnetic field and will be easily redispersed after the removal of this field. Magnetitenanoparticles were prepared by co precipitation of Fe^{2+} and Fe^{3+} with NH_4OH and then, Silica was coated on to the surface of the magnetite Nan particles by Tetraethylorthosilicate. Then superpara magnetic magnetite Nan particles were functionalized with 3-aminopropyltrimethoxysilane so that, at the next step, acetyl ferrocene can attach to magnetite nanoparticles with forming bound. The resulted nonmaterial was characterized with different physicochemical techniques such as FT-IR and atomic absorption spectroscopies, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), vibrating sample magnetometry (VSM) and thrmogravimetric analyses (TGA and DTA). VSM analysis showed super paramagnetic properties of the materials and TEM and SEM analyses indicated the relatively uniform spherical nanoparticles with 15 nm average size.

Keywords: Nano Magnatisi, Silica, Super Para Magnatisi, Titanil Asetil Asetonat.

INTRODUCTION

Nano technology is a new technology which has spread all over the world and in a more precise interpretation, it is not a part of future, it's the future [1]. Nano has been derived from Greek work "Nanos" which means "dwarf". This paper describes the synthesis of titanium supported catalyst onto MCM-41 via chemical bonding. This has been done by first modifying the support in one step with a mixture of silanes—the synthesized triazine propyl triethoxysilane as a functional linker and methyltrimethoxysilane or hexamethyldisilazane as a capped agent to increase the hydrophobicity of the support and to mask the remaining silanol groups. Finally, titanium tetraisopropoxide has been immobilized by the reaction with the modified MCM-41. The materials without functional linker have also been prepared by reaction in one step of the capped agent and the titanium alkoxide precursor with the mesoporous silica. All the materials have been characterized by elemental analysis, X-ray diffraction, nitrogen adsorption techniques, FT-IR, ICP-MS, DRUV-Vis, ^{29}Si and ^{13}C MAS NMR, and TGA. The materials have been tested as cyclohexene epoxidation catalyst using tertbutylhydroperoxide as oxidant [2, 3, 4 and 5]. Titanium-containing mesoporous molecular sieves are of great significance in selective catalytic oxidation processes with bulky molecules. Recent researches and developments on the designing and synthesis of Ti-containing mesoporous materials have been reviewed. Various strategies for the preparation of Ti-containing mesoporous materials, such as direct synthesis and post-synthesis, are described. Modifications of Ti-containing mesoporous materials by surface-grafting and atom-planting are also discussed. All approaches aimed mainly at the

improving of the stability, the hydrophobicity, and mostly the Catalytic activity. Structural and mechanistic features of various synthetic systems are discussed. Ticontainingmesoporous materials in liquid phase catalytic oxidation of organic compounds with H₂O₂ as an oxidant is briefly summarized, showing their broad utilities for green synthesis of fine chemicals by catalytic oxidative reactions [6, 7, 8 and 9].

MATERIALS AND METHODS

Magnetite Nan particles preparation

First 420 ml distilled water which had been distilled twice was poured into a flask with two opening mouth which had 1000 ml capacity. From one opening mouth nitrogen was entered into the flask and was refrigerated in the other opening mouth. It must be noticed that the upper part of refrigerated mouth must be nearly closed in order to keep nitrogen gas. It must be done carefully. Then the flask was put in a water bath with 85°C. Then nitrogen was injected directly onto 85°C stirring water for 45 minutes by a mixer. After 15 minutes nitrogen injection was done through the mouth of the flask and by means of a balloon. Then 15.5 gr FeSO₄ and 21.7 gr FeCl₃ was added to the mentioned flask. 60 minutes opportunity was given to the salts to be solved completely. After 60 minutes the solution changed into brown which shows complete solution of iron salts II and III. In this stage ammoniac 25% merck was added into the flask drop by drop and completely black sediment appeared. This black sediment was transferred into the flask and a strong magnet was put under the flask in order to magnetize the obtained ferrous to the magnet. (Quick sedimentation indicates that the sediment has magnetic feature. The solution on the sediment was evacuated and the sediment was washed twice with distilled water that has been distilled twice and it was washed once with NaCl 2% in order to exit NH₃ completely from that space. At the end some sediment was taken to be the range after being dried.

Covered with silica magnetite nanoparticles preparation SCMNP.

The prepared magnetite nanoparticles were poured into the flask and then 16 ml TEOS 20% and the 200 ml glycerin was added and PH of the above mentioned solution was regulated in 4.5 PH by acetic acid glacial. At this time nitrogen was injected into the solution for 15 minutes and after 15 minutes. Nitrogen injection into the solution was done by a balloon. The temperature of the solution was regulated on 90°C. The solution was reflected for 2 hours. After 2 hours, the sediment was settled by a magnet and the solution on the sediment overflowed and the sediment was washed with distilled water that had been distilled twice and then it was washed with ethanol or methyl alcohol. This was repeated three times. It is washed with Ethanol or methyl alcohol, because in this case the sediment is dried better and sooner.

The synthesis of Nan magnetite particles covered with silica and the significant factors with amino propyl tri methoxysilane.

Nan magnetite particles covered with silica were poured into 150 ml solution of amino propyl tri methoxysilane in Ethanol to prepare 2% solution, 300 ml Ethanol and 12 ml amino propyl tri methoxysilane (ATPS) were synthesized. Then PH was regulated on 4.5 that it was done by acetic acid glacial. Reaction temperature will be 60°C and the time of reflexion will be 23 hours. The reaction was done under nitrogen gas (using a balloon). After 2 hours reflexion above the sediment overflowed. The sediment was washed twice with water which had been distilled twice and it was done twice with methyl alcohol. Then the sediment was dried and prepared for the next stage.

The synthesis of magnetite nanoparticles reformed with amino propyl tri methoxysilane which contain tytanil acetyl acetone.

In the final stage, One gram of amines having magnetite nanoparticles which had been dried and was in the form of powder was poured into the 100 ml flask which contained 30 ml methyl alcohol. The contents of the flask were stirred for half an hour by a mixer. In this stage, 0.524 grs tytanil acetyl acetone was added into the solution in the flask and reflexion was done for 24 hours in 100°C. After reflexion, the sediment was washed with methyl alcohol and after being dried. VSM, FT-IT-SEM, TEM, XRD analysis were done on it.

The study of synthesized combinations formation mechanism and identifying them.

The synthesis of reformed magnetite particles done by fixing tytanil acetyl acetone complex on magnetite nanoparticles. The scheme of fixing tytanil acetyl acetone complex on magnetite nanoparticle level has been shown in Figure 1. Proving expected products formation was done by different techniques.

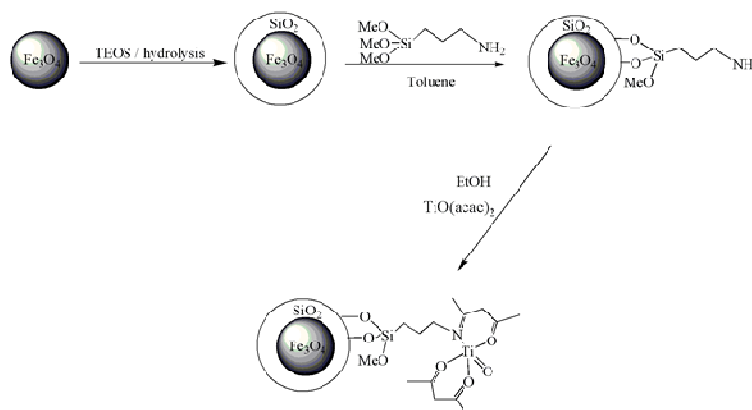


Figure 1. General design of stabilizing stonacetyl titanic on magnetic nano particle surface

Magnetite Nan particles synthesis (MNPs)

The total reaction of magnetite nanoparticles is done by the sedimentary method. Iron salts (II) and (III) have been used in this reaction with 1 to 2 stoichiometrically ratio $\text{Fe}^{2+} + 2\text{Fe}^{3+} + 8\text{OH}^- \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2\text{O}$.

Magnetite magnetic nanoparticles are sensitive to oxygen and some of them may oxidize to $\text{Fe}(\text{OH})_3$ when exposed to air. In order to prevent oxidation of these nanoparticles, deoxygenating from water is done in the first stage of the reaction by direct nitrogen injection into the water. Also as the reaction goes on, nitrogen injection is done indirectly by putting a balloon above the fridge that contains nitrogen gas. Base atmosphere this reaction has been prepared by ammoniac which is formed by adding it to the reaction solution which contains nanomagnetite Fe^{3+} and Fe^{2+} . The final solution of this reaction is nanomagnetite that is black sediment and it has magnetite feature. The scheme of the reaction in the first stage has been showed in Figure 2.

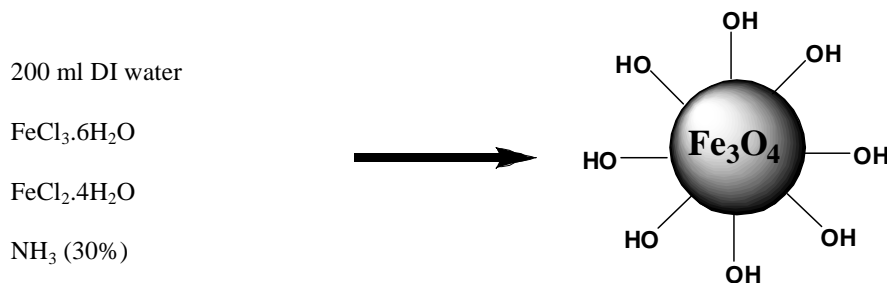


Figure 2. General design of nonomagnetitsynthese

RESULTS AND DISCUSSION

The study of FT-IR spectrum of magnetite nanoparticles.

The absorption bands related to Fe-O link is observed in magnetite particles in 570 cm^{-1} and 375 cm^{-1} . In nanomagnetite FT-IR spectrum, these absorption peaks are moved to higher wave numbers. As it is observed in this spectrum, these absorption peaks have been appeared in 422 cm^{-1} and 587 cm^{-1} . The most important effect the break of many links between surface atoms which result in chrymstqr electrons new arrangement on nanoparticles surface. When magnetite particles size decreased into nano dimensions, absorption bands in FT-IR spectrum change into higher wave Figures. So a water movement in absorption bands related to Fe-o links is seen in magnetite magnetic nanoparticles. The peaks related to iron oxide vibrations depend on the kind of oxide and also bar of central metal which is appeared in 422 cm^{-1} areas for Fe^{2+} . It is seen as a single peak and it is seen in a more frequency for Fe^{3+} compared to Fe^{2+} and it appears in 587 cm^{-1} . Also absorption bands near 1624 cm^{-1} are related to the flexural vibrations (H-O-H) of water molecule coordinated to ferrous metal which has been joined by means of hydrogen

link and absorption bands of 3396 cm^{-1} related to tensile vibrations (O-H) of water molecule coordinated to ferrous. It has been gotten from water remaining which has been come to existence in the sample Figure 3.

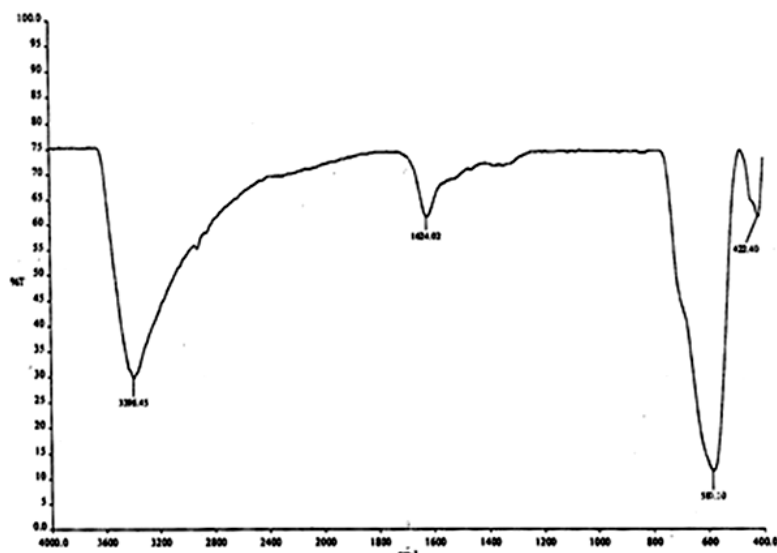


Figure 3. FT-IR spectrum of nonmagnetic

Magnetite nanoparticles covered with silica (SCMNPs)

Formation mechanism

The magnetite nanoparticles obtained in the first stage, are covered with a layer of silica by means of tetraethylortho silicate (TEOS) combination. Covering these nanoparticles with silica is done to prepare a neutral layer between reaction solution and metal oxide core. Also, this silica cover on nano magnetite surface brings an ideal atmosphere to existence for reforming the surface and it also fixes the heat of magnetite particles. Silica cover also prevents formed peroxide breakdown on the surface. One of the most important effects of covering magnetite nanoparticles with silica is the ease of managing separation surface. The outer surface of these nanoparticles has less hydroxyl groups. The number of these hydroxyl groups on silica surface is more compared to magnetite nanoparticles. Also covering the nanoparticles with silica, improves the capability of these particles distribution in water solution. In this condition, first TEOS molecules are hydrolysis of according to the following reaction.

Also, adding glycerin makes it possible for the magnetite nanoparticles to break well and the silica covers their outer surfaces effectively. Adding acid regulates PH in the solution for hydrolyzing the hydrides on the surface of magnetite nanoparticles and TEOS molecules and it joins these molecules effectively to each other Figure 4.

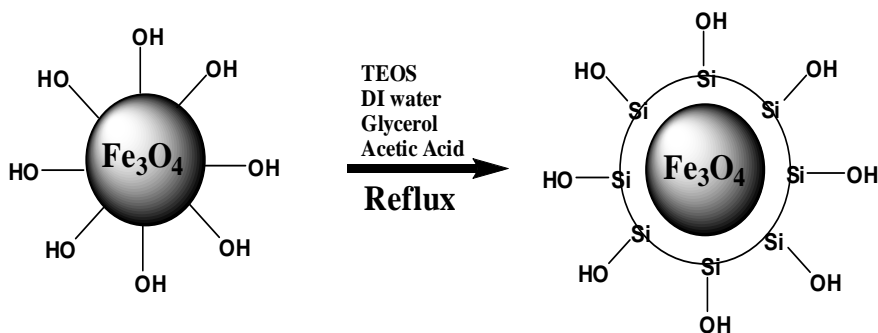


Figure 4. A pattern of a process for solication of magnetic nano particle.

Survey FT-IR spectrum related to magnetite nanoparticles covered with silica has been shown in 5 Figure. Some peaks are created. The wide peak seen in 3391 cm^{-1} relates to (O-H) tensile vibrations of water molecule coordinated to ferrous. The observed peak in 1627 cm^{-1} relates to (H-O-H) flexural vibrations of water molecule

coordinated to ferrous metal which has been joined through hydrogen link. The wide peak seen in 1049 cm⁻¹ relates to (Si-O-Si) tensile vibrations on iron oxide surface. The observed peak in 587 cm⁻¹ relates to (Fe⁺³-O) vibration and the peak seen in the areas near 449 cm⁻¹ relates to (Fe⁺²-O) tensile vibration.

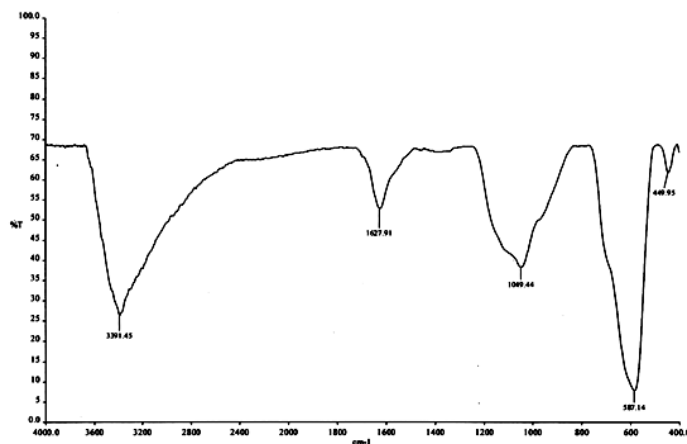
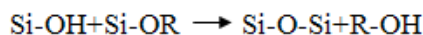


Figure 5. FT – IR spectrum of magnetite nanoparticle covered by silica.

Magnetite nanoparticles covered with silica and having an agent with amino propyl triethoxysilane (APTS-SCMNPs).

Formation mechanism

Managing separation these magnetite nanoparticles which is somehow reforming the outer surface of these nanoparticles makes it possible to join different molecules to them. What is considered more here, is making it possible to join these molecules to inorganic ligands to prepare fixed heterogeneous catalysts on nanomagnetite. One of these combinations which reforms effective surface and has been used a lot is amino propyl tri methoxysilane (APTS). Reforming nanomagnetites surface by APTS is a very complex process. Empirical factors such as temperature. Reaction duration. APTS molecules density and the nature of agent groups are effective on silanemolecules reactivity on inorganic surfaces. The reaction between alkoxysilane and a solid material does not obey just a special mechanism and many intermediate are formed in this reaction. In this study silane tab method by means of acidic water solution has been applied to fix. APTS molecules on magnetite nanoparticles covered with silica. This reaction has been shown in a scheme in Figure 4. The reaction between APTS molecules and nanomagnetite is done in two stages. First avrgarnvsilaneis hydrolysis of in a aqueous solution of an acid. The acid used here plays the role of a catalyst for hydrolyzing process. As a result of hydrolysis of kind's density, silanepolymers are formed. In hydrolysis reaction, alkvkxy groups have been substituted by hydroxide groups to formsylanvlactive groups. These groups react with each other and form Si-O-Sisylvksanlinks. Alcohol and water are produced as lateral products in this reaction.



In the second stage, the product of APTS molecules hydrolysis reaction stands on the surface of magnetite nanoparticles which are covered with silica, and a covalent bond happens between OH groups on the surface of magnetite nanoparticles which contain silica and OH groups in APTS structure. This covalent link is done following dehydrogenation reaction on nanomagnetites surface. The final product of the mentioned reactions is black sediment, dense and it has a high magnetite power when an outer magnetic field is present.

The study of FT-IR spectrum of magnetite nanoparticles covered with silica and the significant with amino propyl tri ethoxysilane (APTS-SCMNPs) combination.

The FT-IR spectrum related to magnetite nanoparticles reformed with APTS molecules has been shown in Figure 7. The peak related to N-H tensile vibration appears in 3390 cm⁻¹ area. The other peak relates to C-H tensile vibrations of propyl branches on the surface which appears in 2933 cm⁻¹ area. The other one relates to C-H a flexural vibration that is observed in 1465 cm⁻¹ area. The peak related to Si-CH₂ tensile vibration appears in 1410 cm⁻¹ area. Tensile vibration to C-C links has appeared in 1335 cm⁻¹ area. Tensile vibration related to Si-O has appeared in 1059.17 cm⁻¹ area. Tensile vibration related to Fe-O has appeared in 585 cm⁻¹ areas. The seen peak in 1627 cm⁻¹ relates to H-O-H flexural vibration of water molecule coordinated to ferrous which has joined through hydrogen links.

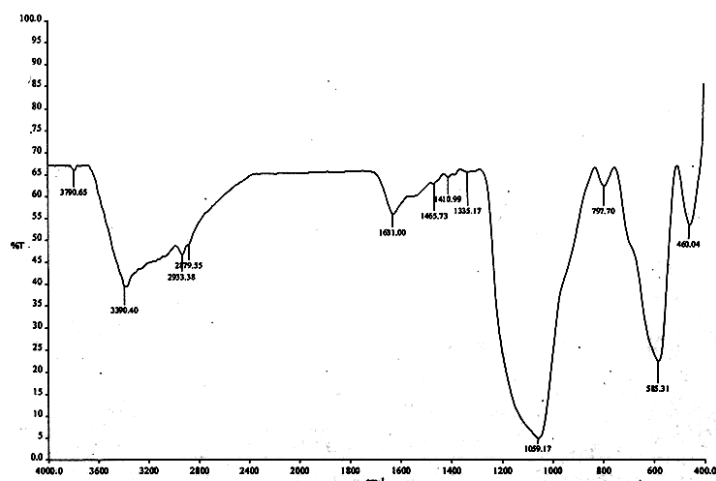


Figure 7. FT-IR spectrum related to nano magnetite modified by APTS molecules.

The study of FT-IR spectrum related to nanomagnetite covered with silica and having an agent with amino propyl which contains tytanil acetyl acetone

When magnetite nanoparticles which contain silica were having an agent with amino propyl tri methoxysilane, these nanoparticles had reaction with acetyl acetone. The reaction between amine group of having an agent magnetite nanoparticles and carbonyl group of tytanil acetyl acetone formed C=N link and an organic – inorganic hybrid. The resulted FT-IR spectrum has been shown in Figure 8. The peak created in 3381 cm⁻¹ is related to (O-H) tensile vibrations. The tensile vibration related to (C-H) has appeared in 2920 cm⁻¹ area. The peak related to C=N link's tensile vibration has appeared in 1302 cm⁻¹ area. The tensile vibration related to Si-O has appeared in 1049 cm⁻¹ area. The peaks related to Fe-O tensile vibrations have appeared in 569 cm⁻¹ and 476 cm⁻¹ areas.

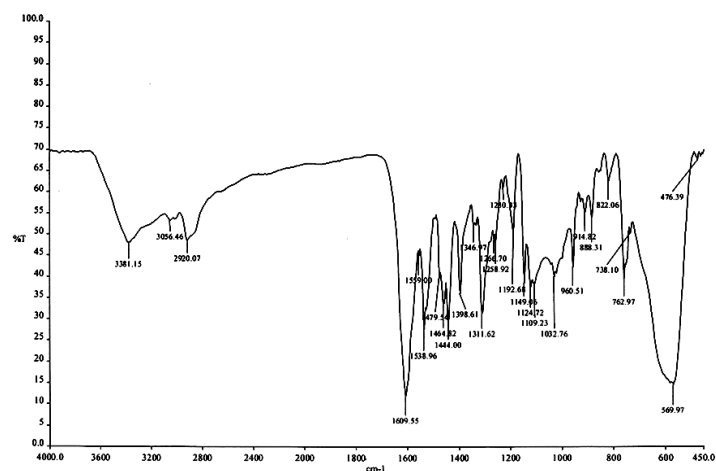


Figure 8. FT-IR spectrum of magnetite nano particle functionalized with amino propyl-3-methoxysilane containing stonctactylitanil.

The study of XRD pattern of reformed nanomagnetite with amino propyl silane which contains tytanil acetyl acetone.

Diffraction of X-ray (XRD) in the prepared sample has been shown in the diagram. The peaks created show crystal structure of magnetite particles. The resulted Figures out of X-ray diffraction pattern conform to the Figures presented for magnetite nanoparticles in the articles, and it indicates that the magnetite reformed with tytanil acetyl acetone groups has kept its upside down spinel structure Figure 9.

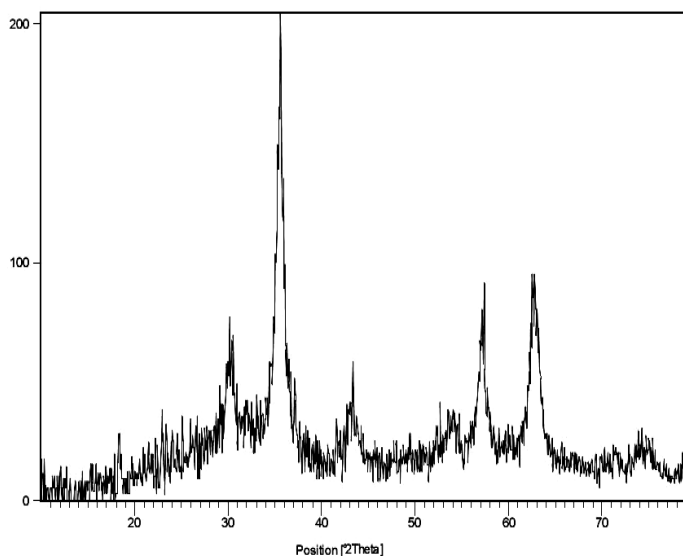


Figure 9. XRD pattern of magnetite nanoparticle modified with amino propyl silane containing stannic acetyl titanil.

The study of TEM image of magnetite nanoparticles reformed with amino propyl silane which contains tytanil acetyl acetone.

To study the size of nanoparticles precisely, the microscopic image of passing electron (TEM) of the resulted combination has been studied which is shown in Figure 10. TEM image of prepared nanoparticles shows that the shape of the particles are nearly spherical and their size is estimated nearly 10-15 nanometers.

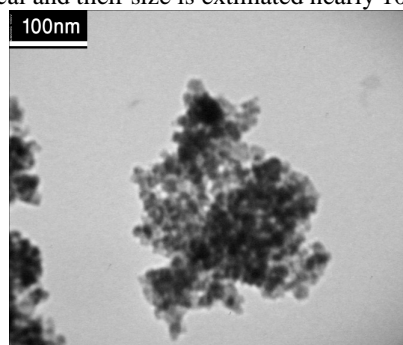


Figure 10. TEM picture of magnetite nanoparticle modified with amino propyl silane containing stannic acetyl titanil.

The study of SEM image of the magnetite nanoparticles reformed with amino propyl silane which contains tytanil acetyl acetone.

To study morphology of the surface and structural study of the magnetite nanoparticles, SEM means electron microscopic image was also studied. The SEM image of the nanoparticles has been shown in Figure 11 and it shows that the particles are spherical and conform to the microscopic image of passing electron.

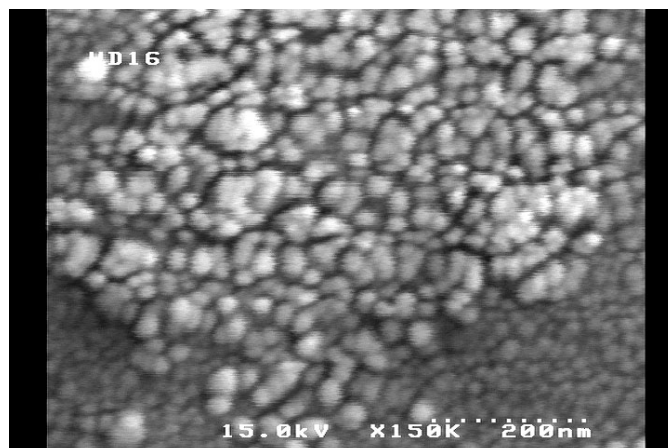


Figure 11. SEM picture of magnetitono particle modified with amino propyl silan containing stonacetyl titanil.

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