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phosphonate (DMMP) as an organo-phosphorous pollutant (OPP) on the

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surface of nano-structured Co₃O₄ and MnCo₂O₄ catalysts

and neutralization

Abstract

In this work, the practicality of catalytic surfaces of nano-structured Co_3O_4 and $MnCo_2O_4$ for the adsorption and neutralization reactions of dimethyl methyl phosphonate (DMMP) as a toxic agricultural organo-phosphorous pesticide has been investigated. The Co_3O_4 and $MnCo_2O_4$ NPs have been successfully prepared by precipitation method using cobalt nitrate and manganese nitrate as the precursors and then characterized by SEM-EDX and XRD. The application of the synthesized nanoparticles as solid catalysts for the adsorption and neutralization of dimethyl methyl phosphonate (DMMP) was assayed in different solvents and monitored by ³¹PNMR and IR analyses. The experimental results have shown that 39%, 47% and 62% of DMMP have been adsorbed on the surface of Co₃O₄ nanoparticles in isopropanol, chloroform and decane solvents after 5 h, respectively. While, higher amounts (80%, 92% and 100%) were removed in the same solvents respectively, MnCo₂O₄ nanoparticles were chosen as the catalytic surface. This demonstrates that the choice of nanoparticle and solvent (MnCo₂O₄ nanoparticles and decane) have a great impact on the neutralization of DMMP.

Keywords: Co₃O₄; MnCo₂O₄; nanoparticles; precipitation; dimethyl methyl phosphonate (DMMP); adsorption; neutralization.

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Adsorption

Payame Noor University

Introduction

Any one of numerous pesticides are organic derivatives of the acids phosphorus. Organophosphorus pesticides are used to chemical warfare nerve agent simulants, combat crop pests, plant diseases. ectoparasites of domestic animals (body parasites), weeds, and synanthropic insects, mites, and ticks. They are also utilized as bactericides and plant growth regulators. Organophosphorus pesticides have low stability in the environment, which prevents their accumulation in amounts dangerous for living organisms. Most of them decompose after application, with the formation of nontoxic products such as phosphoric acid, Their carbon dioxide. and water. disadvantages include the relatively high toxicity of many such pesticides for humans and animals necessitate the observation of safety precautions during application[1]. The dimethyl methyl phosphonate (DMMP) as an agricultural organo-phosphorous pesticide considered as a toxic pollutant that reveals hazardous effects on the environment and biological media. DMMP molecule has the bind to acetylcholinesterase ability to (AChE) enzyme that leads to the disruption in nervous impulses and inhibition of the normal function of nerve cells [2]. In Figure

1, the molecular structure of DMMP is shown.



Figure 1. The molecular structure of DMMP

Various methodologies have been designed for the decomposition of DMMP in the recent years [3-5]. Liquid detoxification has been long used as major route for this purpose through utilizing a series of chemicals such as bleach. DS2 and hypochlorite. However, certain disadvantageous like chemical contamination arising from these materials, reveal the necessity of researching for new substitutions for liquid detoxification. An alternative approach is the use of solid inorganics for the adsorption and degradation of organophosphorous pesticides and clean-up of hazardous waste pollutants [6]. Accessible surface and sufficient reactivity toward pollutant detoxification are kev two properties of the sorbent materials for such

applications. Strong absorbance removes the pollutant agent rapidly from the affected surface and creates immediate relief. Once trapped within the porous solid, the adsorbate undergoes chemical reactions could render it harmless [6]. Literally, various experiments have shown that powders of metal oxides such as MgO [7], CaO[8], Al₂O₃ [9] and TiO₂ [10] when penetrated by pesticides initiate reactions found in liquid detoxification schemes in addition to binding pollutants to their surfaces. Moreover the catalysis process will be suspected by means of sustaining some reactions [8].

It is expected that powders of nanocrystalline inorganics would be more effective than powders of conventional micro-crystals owing to lager surface area and massive quantities of available reactive sites due to surface, corner and edge defects in the lattice [8, 11]. A key reason for the change in the chemical and physical properties of small particles as their size decreases - is the increased fraction of the surface atoms, which occur under conditions (coordination number, symmetry of the local environment, etc.) differing from those of the bulk atoms [9, 10]. The surface atoms are unsaturated and exhibit high chemical activity and adsorption capacity and are thus subject to combination with other substances

by static electricity [11]. Recent investigations have explored the promising decomposition applications of the nano-sized metal oxides such as AP-MgO, AP-CuO, AP-Fe₂O₃ and AP-Al₂O₃ [12-17].

In recent years, cobalt oxide (Co_3O_4) and manganese-cobalt oxide (MnCo₂O₄) spinel nanoparticles [3-14] have been extensively studied owing to their potential uses in many fields including solar energy cells as photoelectric energy conversion materials [7, 8]. A variety of methods have been reported for the preparation of Co₃O₄ and MnCo₂O₄ nanoparticles including chemical spray pyrolysis [15], chemical vapor deposition (CVD) [16], micro-emulsion synthesis [17], solvo-thermal synthesis [18], hydrothermal method [19], mechano-chemical method [20] and chemical combustion synthesis [21]. Nevertheless, nearly all of these methods need specific instrumentation and harsh conditions. Martin-de-Vidales et al. [14] prepared Co₃O₄ and MnCo₂O₄ nanoparticles by sol-gel method. They reported that using this route, size, morphology and crystal structure of the products could be easily controlled.

In the present study, the characterization of the synthesized Co_3O_4 nanoparticles and $MnCo_2O_4$ nanoparticles by the precipitation method at 400 °C is investigated. Co_3O_4 and $MnCo_2O_4$ nanoparticles were then evaluated as solid catalysts for the adsorption and neutralization of DMMP at room temperature (RT) in different solvents including isopropanol, chloroform and decane.

Experimental

Materials and Reagents

 $Co(NO_3)_2.6H_2O$, $Mn(NO_3)_2.4H_2O$, NaOH, KOH, isopropanol, chloroform, decane. CDCl₃, phosphoric acid and dichloro methane were purchased from Merck (Merck, Darmstadt, Germany). Dimethyl methyl phosphonate (DMMP) was obtained commercially from Sigma-Aldrich Co. (USA). All the chemicals and reagents were of chemical grade and were used as received.

Instrumentation

Different characterization techniques were used to elucidate the physicochemical properties of the produced catalysts. The morphology and size of the prepared catalysts were studied via SEM images using a scanning electron microscope coupled with energy dispersive X-ray spectrometer (SEM-EDX, HITACHI S-300N). The powder X-ray diffraction pattern (XRD, Philips PW 1800) study was carried out on an X-ray diffractometer using CuK radiation (30 mA and 20 kV and =1.54056 Å). The analyses were conducted at 2° min⁻¹ in the range of $2 = 10-80^{\circ}$. In order to investigate the reaction of the organo-phosphorous pesticide with the catalysts, phosphorous-31 nuclear magnetic resonance spectroscopy (³¹PNMR, Bruker 250 MHz) and centrifuge (Universal, CAT. NO. 1004) instrument was used. The IR spectra were scanned on a PerkinElmer model 2000 FT-IR spectrometer (USA) in the wavelength range of 450 to 4000 cm⁻¹ using KBr pellets.

Preparation of Co₃O₄ and MnCo₂O₄ nanoparticles

Prior to the adsorption and neutralization reactions, Co₃O₄ nanoparticles and MnCo₂O₄ nanoparticles have been synthesized by the precipitation method as previously reported [14]. In a typical synthesis procedure, first, 2 g of $Co(NO_3)_2.6H_2O$ as the source of Co^{2+} ions was dissolved in 100 mL of deionized water. In the next step, 100 mL of 3.2 M KOH aqueous solution was then added dropwise to the precursor solution. Pink precipitate appeared immediately which was oxidized Co(OH)₃ easily by air and low heat or by weak oxidizing agents. As a result, a dark brown precipitate which was produced was separated and washed with deionized water, then dried in an oven at 60°C for 30 min. For the formation of $Co(OH)_3$ from $Co(NO_3)_2.6H_2O$, the following reaction mechanisms be formulated can as represented in (1-3):

Co(NO₃)₂.6H₂O+KOH Co(OH)NO₃+KNO₃ (1) Co(OH)NO₃ + KOH Co(OH)₂ + KNO₃

(2)

 $4Co(OH)_2 O_2 + H_2O 4Co(OH)_3$ (3)

On the one hand, in order to prepare the cobaltic-cobaltous oxide (Co_3O_4) , the dark brown cobaltic hydroxide was calcined at 400 °C for 5 h.

On the other, to synthesis the $MnCo_2O_4$ nanoparticles, 1g of $Mn(NO_3)_2.4H_2O$ and 2 g of $Co(NO_3)_2.6H_2O$ were dissolved in 100 mL of deionized water. Under stirring vigorously, NaOH was added until a homogenous mixture was observed then it was dried at 60 °C for 30 min. Finally, the calcination of this powder was also carried out at 400 °C for 5 h.

Preparation of DMMP/catalyst sample (reaction procedure)

Sample preparation meets four steps: (1) 0.03 M phosphoric acid (H₃PO₄) as the blank solution was prepared through dilution of 0.05 mL of H₃PO₄ with 25 mL of deionized water. The blank solution was injected to a capillary column whose tips were closed by heat (S1). (2) DMMP solutions were prepared *via* addition of 30 μ L of DMMP to

10 mL of different solvents including isopropanol, chloroform and decane (S2). (3) S2 solutions were mixed with 0.35 g of Co_3O_4 nanoparticles and MnCo₂O₄ nanoparticles in a 50 mL Erlenmeyer flask and stirred rapidly at room temperature for 5 h (S3). (4) 1 mL of S3 mixture was placed in a centrifuge tube and centrifuged at 600 rpm for 4 min. after that, 0.3 mL of the above sample and 0.1 mL CDCl₃ were added to a NMR tube along with the capillary column (S1 solution) as the blank solution. Finally, the presence of DMMP molecule in the samples was revealed by ³¹PNMR instrument [10].

Results and discussion

SEM Analysis

In Figure 2, in order to investigate the morphology and structure at 400 °C the SEM images of synthesized nanoparticles are given with different resolution. Analyzing the morphology aspect of the synthesized Co_3O_4 nanoparticles (Figure 2a, 2b and 2c) and $MnCo_2O_4$ nanoparticles (Figure 2d, 2e and 2f) indicates that the sample were quasispherical in shape. The results have also emphasized that both two catalysts have nano-sized particles.



Figure 2. SEM images of: (a), (b) and (c) Co_3O_4 nanoparticles, and (d), (e) and (f) $MnCo_2O_4$ nanoparticles with different resolution

EDX analysis

The energy energy dispersive X-ray (EDX) microanalysis was performed to confirm the presence of cobalt, manganese and oxygen elements in the synthesized samples. As

illustrated in Figure 3, there was no unidentified peak observed in the EDX spectra (only C element has been revealed which was corresponded to adsorbed atmospheric CO_2). This fact clearly confirms the prepared purity and composition of Co_3O_4 and $MnCo_2O_4$ nanoparticles. EDX

analysis data for the Co_3O_4 and $MnCo_2O_4$ nanoparticles are shown in Table 1.



Figure 3. EDX analysis of: (a) Co₃O₄ nanoparticles and (b) MnCo₂O₄ nanoparticles

Samples/Elements (wt%)	Cobalt (Co)	Manganese (Mn)	Oxygen (O)	Carbon (C)
Co ₃ O ₄	71.53	-	27.24	1.23
MnCo ₂ O ₄	43.12	22.49	32.50	1.89

X-ray diffraction (XRD) patterns

The structures of the nano-structured catalysts have been assayed *via* X-ray

diffraction patterns of each sample at 400 °C as shown in Figure 4. The crystalline size was determined from full width at half

maximum (FWHM) parameter with the most intense peak obtained in XRD patterns. The average particle size of Co_3O_4 nanoparticles and $MnCo_2O_4$ nanoparticles was calculated from line broadening of the peak at 2 =10-80° using Debye-Scherrer formula (4) [22]:

$$\boldsymbol{d} = \frac{0.94\lambda}{\beta \cos\theta} \tag{4}$$

Where d is the crystalline size, is the wavelength of X-ray Cu K source (= 1.54056 Å), is the full width at half maximum (FWHM) of the most predominant peak at 100% intensity and is Bragg diffraction diffraction angle at which the peak is recorded. There was no characteristic peaks corresponded to of impurity were found, confirming that high-purity products be obtained. In two of the XRD patterns, seven peaks were revealed at approximately $2 = 23.11^{\circ}, 28.45^{\circ}, 37.36^{\circ}, 45.55^{\circ}, 55.52^{\circ},$ 58.68° , and 63.74° , which correspond to the Bragg's reflection plane (111), (220), (311), (400), (422), (511) and (440) for cobalt oxide

and four peaks at $2 = 16.36^{\circ}, 33.38^{\circ}, 43.19^{\circ}$ and 76.73° are ascribed to the Bragg's reflection plane (110), (310), (300) and (421) for the manganese oxide (MnO) nanoparticles, respectively. Using this formula, the smaller average particle sizes were estimated to be 27.29 nm and 22.19 nm for Co_3O_4 nanoparticles and $MnCo_2O_4$ nanoparticles, which coincide well with the standards data (JCPDS no.74-2120) and (JCPDS no.23-1237), respectively. The of the XRD peaks may also contain contributions from lattice microstrain. The average microstrain () of the Co_3O_4 and MnCo₂O₄ nanoparticles were calculated using the Stocks-Wlison equation(5) [23]:

$$= /4 \tan (5)$$

Using this equation, the average microstrain was calculated about 0.25 and 0.31, respectively. The size obtained from XRD measurement in good agreement with the results from the SEM study.



Figure 4. XRD patterns of: (a) Co₃O₄ nanoparticles and (b) MnCo₂O₄ nanoparticles

³¹PNMR and IR studies

³¹P nuclear magnetic resonance (³¹PNMR) was utilized as a rapid and suitable analytical technique to explore the adsorption and neutralization chemistry of the DMMP as an agricultural organo-phosphorous pesticide (OPP) on the surface of Co_3O_4 nanoparticles and $MnCo_2O_4$ nanoparticles in isopropanol, chloroform and decane solvents at room temperature (RT, (25±1 °C)). To investigate the amount percent of the neutralized organophosphorous pesticide, the under peak integral two sample of DMMP and H_3PO_4 were given. ³¹PNMR spectra demonstrate the chemical shifts for DMMP and phosphoric acid (H_3PO_4) which were =33 ppm and =0 ppm, respectively [24]. The quantitative works of ³¹PNMR spectroscopy were performed in the presence of H_3PO_4 as a suitable inorganic internal standard for the determination of reaction efficiency. After the reaction, increasing the contact time leads to decrease the intensity of the area under curve (AUC) integral of DMMP as compared to the area under curve (AUC) integral of H₃PO₄ as the blank solution. Moreover, the concentration of DMMP also decreased after the reaction. The spectra and AUC data are shown in Figures 5-10 and Tables 2 and 3, respectively. These results emphasize that 39%, 47% and 62% of DMMP have been removed on the surface of $C_{0_3}O_4$ nanoparticles in isopropanol, chloroform and decane solvents, respectively. However, results for the removed DMMP on the surface of MnCo₂O₄ nanoparticles in the same solvents are higher, 80%, 92% and 100%, respectively. This provides more surface and adsorptive sites and possesses a higher catalytic ability to adsorb and remove DMMP. Polarity of the media is another issue extracted from these results. Although the transition state of the polar reaction is involved, the polar solvent hinders the reaction. These data illustrate that polar solvents can compete with reactive sites on the surface of the catalysts including Bronsted and Lewis acid sites. In particular, blocking of Lewis acid sites would hinder the

coordination of DMMP. Since isopropanol is such a strong hindrance to the reaction, this tends to lend further support to the idea that isopropanol simply blocks access to the surface of the catalyst. At the end of, the adsorption of DMMP on the catalyst surface was studied by IR spectrum. In Figure 12, the IR spectra of Co₃O₄ nanoparticles before and after the adsorption of DMMP were shown. As depicted in (Figures 12 a and 12 b), two strong absorbed peaks at 571 and 663 cm⁻¹ clearly indicates of an interfacial chemical bond between cobalt and oxygen (Co-O) modes $(Co^{2+} and Co^{3+} ions)$, respectively. Also, the absorption peak displayed at 3449 cm⁻¹ is assigned to hydroxyl (O-H) stretching vibration on the surface of metallic particles should be assigned to absorbed H₂O by the sample or KBr pellet. The new peaks in 3537, 1262 cm⁻¹ and 1178 cm⁻¹ are seen (Figure 12 b). The observed IR data lead to an understanding of the adsorption and of DMMP reaction on the Co_3O_4 nanoparticles surface. Hence, the structure of catalyst almost remains intact after the reaction with DMMP.

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Figure 5. ³¹PNMR spectra for the adsorption of DMMP on the Co₃O₄ nanoparticles in isopropanol solvent: a) 0 h and b) 5h



Figure 6. ³¹PNMR spectra for the adsorption of DMMP on the Co_3O_4 nanoparticles in chloroform solvent: a) 0 h and b) 5h

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Figure 7. ³¹PNMR spectra for the adsorption of DMMP on the Co_3O_4 nanoparticles in decane solvent : a) 0 h and b) 5h



Figure 8. ³¹PNMR spectra for the adsorption of DMMP on the MnCo₂O₄ nanoparticles in isopropanol solvent: a) 0 h and b) 5h



Figure 9. ³¹PNMR spectra for the adsorption of DMMP on the MnCo₂O₄ nanoparticles in chloroform solvent: a) 0 h and b) 5h



Figure 10. ³¹PNMR spectra for the adsorption of DMMP on the MnCo₂O₄ nanoparticles in decane solvent: a) 0 h and b) 5h

50

40

.0000

0

-20

-40

Integral

ppm

80

60

Table 2. ³¹ PNMR spectra results for	: DMMP/Co ₃ O ₄ nan	oparticles sample in	different solvents after 5 h
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Decane solvent				chloroform solvent		isopropanol solvent			
remained DMMP %	DMMP Concentrat ion% (M)	MMPOM AUC Intg/phos phoric acid blank AUC Intg	remained DMMP %	DMMP Concentration % (M)	MMPOM AUC Intg/phosphor ic acid blank AUC Intg	remained DMMP %	DMMP Concentration % (M)	MMPOM AUC Intg/phosphor ic acid blank AUC Intg	Sample
100.00	0.0300	2.8232	100.00	0.0300	3.2242	100.00	0.0300	2.7775	a
39.22	0.0117	1.1074	52.52	0.0157	1.6963	61.32	0.0173	1.7034	b

Table 3. ³¹PNMR spectra results for DMMP/MnCo₂O₄ nanoparticles sample in different solvents after 5 h

Decane solvent			chloroform solvent		isopropanol solvent				
remained DMMP %	DMMP Concentratio n% (M)	MMPOM AUC Intg/phos phoric acid blank AUC Intg	remained DMMP %	DMMP Concentration % (M)	MMPOM AUC Intg/phosphor ic acid blank AUC Intg	remained DMMP %	DMMP Concentration % (M)	MMPOM AUC Intg/phosphor ic acid blank AUC Intg	Sample
100.00	0.0300	2.9288	100.00	0.0300	2.8538	100.00	0.0300	2.8171	а
00.00	00.00	0.0000	08.31	0.0024	0.2372	19.43	0.0058	0.5475	b



Figure 11. The curve of neutralized DMMP% versus solvent type for Co_3O_4 and $MnCo_2O_4$ nanoparticles after 5 h



Figure 12. IR spectra of Co₃O₄ nanoparticles: (a) before and (b) after the adsorption of DMMP

Mechanism of the adsorption and neutralization procedure

According to this observation, there are two proposed mechanisms and structures for adsorption and neutralization chemistry of DMMP on the surface of Co_3O_4 nanoparticles and $MnCo_2O_4$ nanoparticles, as illustrated in Scheme 1. In route A, bonding between the oxygen atom of the phosphoryl group in DMMP and hydroxyl group (MnOH or/and Co-OH) of the catalyst surface (Bronsted acid sites) causes a rearrangement in DMMP molecule which is followed by the loss of CH₃OH group and the dehydration reaction. This will make DMMP molecule to bridge an O—P—O group on the surface of the catalyst which leads to the formation of the degradation product. In route B, the oxygen atom of the phosphoryl group in DMMP binds to manganese and cobalt (Mn^{2+} or/and Co^{3+}) atoms of the nanoparticles (Lewis acid sites) which involves the loss of methoxy group from the adsorbed DMMP

molecule and its adsorption as a methoxy species on the surface of the catalyst. It is obvious that only the M-O-P-O-M bridging species are observed on the surface. Thus the hydrolysis of the adsorbed DMMP molecule affects only the free methoxy groups on the surface and not the phosphorous-bound methoxy groups (Me-P)[25]. This compound is not seen in the analysis, because that is directly connected on the catalysts surface and not be removed easily from the surface even if it be washed dichloro methane solvent with [10].



Scheme 1. Proposed mechanisms and structures for the adsorption and neutralization of DMMP on the catalysts surface (M=Mn or/and Co)

Conclusion

In summary, Co_3O_4 and $MnCo_2O_4$ nanoparticles were synthesized by the precipitation method calcinations at temperature of 400°C and characterized by SEM-EDX and XRD techniques. The synthesized nanoparticles were then employed as the catalysts for the adsorption and neutralization of DMMP as an organophosphorous pesticide (OPP) in different solvents. The results obtained by ³¹PNMR and IR analyses denote that MnCo₂O₄ nanoparticles have a higher catalytic potential for the adsorption of DMMP molecules compare to Co₃O₄ nanoparticles. Also it is realized from experiments that polar solvents hinder the access to the active sites on the surfaces of nanoparticles, hence, decane was chosen as the proper solvent.

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References

C. Fest, K. J. Schmidt, *The Chemistry of Organophosphorus Pesticides*. Berlin, **1973**.
 F. Ahmed, P. K. Gutch, K. Ganesan, R. Vijayaraghavan, *J. Therm. Anal. Calorim.*, **2012**, *107*, 141–147.

[3] G. Wulfsberg, *Inorganic Chemistry*, *University Science Books*, 691(**2000**). [4] C.N.R. Rao, J. New Directions in Solid State Chemistry, Cambridge University Press, **1997**, 296-301.

[5] C. Liu, J. Am. Chem. Soc., 2000, 122,6263-6267.

[6] Y.C. Yang, J.A. Baker, J.R. Ward, *Chem. Rev.*, **1992**, *92*, 1729-1743.

[7] G.W. Wagner, P.W. Bartam, O. Koper,K.J. Klabunde, *J. Phys. Chem.*, **1999**, *103*,3225-3228.

[8] G.W. Wagner, O.B. Koper, E. Lucas, S. Decker, K.J. Kabunde, *J. Phys. Chem.*, 2000, 104, 5118-5123.

[9] G.W. Wagner, L.R. Procell, R.J.
OÕConnor, S. Munavalli, C.L. Carnes, P.N.
Kapoor, K.J. Klabunde, *J. Am. Chem. Soc.*, **2001**, *123*, 1636-1644.

[10] M. Sadeghi, M. Hosseini, H. Tafi, *Int. J. Bio-Inorg. Hybd. Nanomat.*, **2013**, *2*, 281-293.

[11] K.J. Klabunde, J. Stark, O. Koper, C.
Mohs, D.G.Park, S. Decker, Y. Jiang, I.
Lagadic, D. Zhang, *J. Phys. Chem.*, **1996**, 100, 12142-12153.

[12] A. Mirzaei, M. Feyzi, F. Shayegh, H. R.Bozorgzadeh, A. Bigbabaei, *American Scientific Publishers.*, 2004, 10, 767–780.

[13] I. Luisetto, F. Pepe, E. Bemporad, *J Nanopart Res.*, **2008**, *10*, 59–67. Adsorption and neutralization chemistry of dimethyl methyl phosphonate (DMMP) as an ...

[14] E. Rios, P. Lara, D. Serafini, A. Restovic, J. Gaytier, *J. Chil. Chem. Soc.*, **2010**, *2*, 55-67.

[15] V.R. Shinde, S.B.Mahadik, T.P.Gujar,C.D. Lokhande, *Applied Surface Science.*, 2006, 252, 7487-7492.

[16] J. Ahmed, T. Ahmed , K.V. Ramanujachary, S.E. Lofland, A.K. Ganguli, *Journal of Colloid and Interface Science.*, **2008**, *321*, 434-441.

[17] L. Sun, H.Li, L.Ren, C.Hu, *Solid state Science.*, **2009**, *11*, 108-112.

[18] A. Rumplecker, F.Kleitz, E.L. Salabas,

F. Schuth, Chem. Mater., 2007, 19, 485-496.

[19] H. Yang, Y.Hu, X. Zhang and G. Qui, *Mate. Lett.*, **2004**, *58*, 387-389.

[20] T.Li, S.Yang, L.Huang, B.Gu ,Y.Du ,*Chinese Phys. Lett.*, **2004**, *21*, 966-969.

[21] N. Camelia, T. Rusu, Jr. Yates, J. Phys. Chem. B., 2000, 104, 12292-12298.

[22] N.R.E.Radwan,M.S.El-

Shall,H.M.A.Hassan, *Applied Catalysis* A:General., **2007**, *331*, 8-18.

[23] H.R. Shakur, *Physica E.*, **2011**, *44*, 641–646.

[24] M. Sadeghi, M. Hosseini, *J. Nano. Struc.*, **2013**, *2*, 439-453.

[25] M. Sadeghi, S. Yekta, N. Shahabfar, M.

Hosseini, H. Adeli, M. J. Taghizadeh, Int. J.

Bio-Inorg. Hybd. Nanomat., **2014**, *3*, 117-123.