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Catalytic Decomposition of H_2O_2 on $MnFe_2O_4$ Nanocomposites Synthesized by Various Methods in the Presence of Silicate and Zeolite Supports

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ABSTRACT

In this research iron manganese oxide nanocomposites were prepared by co-precipitation, sol-gel and mechanochemical methods by using iron (III) nitrate, iron (II) sulfate and manganese (II) nitrate as starting materials. These nanocomposites were prepared in the presence of various catalyst beds. The polyvinyl pyrrolidon (PVP) was used as a capping agent to control the agglomeration of the nanoparticles. Nanocatalysts were identified by FT-IR, XRD,SEM and TEM. The sizes of nanoparticles were determined by XRD data and Scherer equation. The prepared nanocatalysts were tested for decomposition of hydrogen peroxide. The hydrogen peroxide decomposition activity of samples was determined by evolved oxygen volumetry technique. Also based on surface area analysis and BET data, using of sodium metasilicate bed led to the high surface area and catalytic activity. Therefore Coprecipitation method in the presence of sodium metasilicate introduce as preferred method. To optimize the catalytic activities of nanoparticles factors such as concentration, cations ratio, pH and calcination temperature were investigated.

Keyword: Hydrogen peroxide; Decomposition Nanocatalysts; Co-precipitation method; Iron manganese oxide; Catalyst Supports; Surface area analysis (BET).

1. INTRODUCTION

Decomposition of hydrogen peroxide to supply oxygen for the atmosphere is more suitable method than superoxide or cholorate piles. For the decomposition of hydrogen peroxide the active inorganic metal oxides of manganese, iron, cobalt and lead are used. If these metal oxides are prepared at nanoscales their performance will be strengthened and can accelerate the catalytic decomposition of hydrogen peroxide [1]. Catalytic Substrates or beds such as zeolites also increase the surface area of the nanoparticles and their uniform size distribution that improves the catalytic activity

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in the decomposition of hydrogen peroxide.

Ahmed et al [2] synthesized iron-manganese oxides by combustion and sol-gel methods. In combustion method, stoicheiometric amounts of manganese acetate $Mn(CH_3CO_2)_2{\cdot}4H_2O$, ferric nitrate $Fe(NO_3)_3{\cdot}9H_2O$ and urea were mixed in an agate mortar for few minutes. Urea was added to the mixture (as fuel) and mixed again thoroughly then transferred to a quartz crucible and synthesized at 500°C for 1/2 h. At this temperature, the mixture was reacted leading to the combustion and the reaction was complete in 3-5 min. A foamy and highly porous precursor mass was obtained. The ferrite powder was calcined at 900°C. In sol-gel method the raw materials, $Mn(CH_3CO_2)_2{\cdot}4H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$, were first dissolved in ethylene glycol and de-ionized water under stirring until a homogeneous mixture was observed, heated to 70°C for 12 h and dried at 80°C for 24 h. The resulting gel was calcined at 600°C. The smallest nanosize was obtained in combustion method (41 nm).

Shin-Liang Kuo et al [3] synthesized $MnFe_2O_4$-carbon black (CB) composite powders by a co-precipitation method in alkaline aqueous solutions. $MnSO_4$ was dissolved along with $FeCl_3$ with a stoicheiometric ratio of 2:1 in 1M HCl aqueous solution with bubbling N_2. The solution was then added into another solution that contained 1.5 M NaOH and suspended CB powder under vigorous stirring. Black precipitate was formed immediately upon mixing. The powder was prepared by drying at 50°C. A subsequent calcination process was carried out at different temperatures for 2 h in N_2 atmosphere.

The decomposition of hydrogen peroxide by manganese oxide at pH= 7 is represented by a pseudo first order model [4]. The maximum value of the observed first order rates constants (k_{obs}) was 0.741 min^{-1} at 11.8 of $[H_2O_2]/[MnO_2]$ when $[H_2O_2]/[MnO_2]$ were ranged from 58.8 to 3.92. The direct relation of both the concentration of the initial hydrogen peroxide and manganese oxide on the decomposition rates allows the first order kinetics to be modified:

$$-\frac{d[H_2O_2]}{dt} = k_{MnO_2}[\equiv MnO_2]\cdot[H_2O_2]$$

$$k_{obs} = k_{MnO_2}[\equiv MnO_2] \qquad (1)$$

Pretty lahirri et al [5] synthesized a set of ferrites of different composition by coprecipitation method. Ferrites have wide applications in transformer and communication field. Nanoparticles of spinel. Manganese ferrite ($MnFe_2O_4$) is a common spinel ferrite material and has been widely used in microwave, magnetic recording and catalyst applications.They found that some ferrous spinels act as catalysts for the decomposition of H_2O_2 and their effectiveness is dependent on the composition of the catalyst. The catalytic activity of the ferrous spinels for hydrogen peroxide decomposition was evaluated by rate of evolution of oxygen from the liquid phase. The rate of evolution of gaseous O_2 was monitored with a gasometric assembly.

Nasr-Allah M. Deraz [6, 7] studied the hydrogen peroxide decomposition activity by oxygen gasometry of the reaction kinetics at 20-40°C on the pure and ZnO-doped cobaltic oxide catalysts. The results revealed that the treatment of Co_3O_4 with ZnO at 40-700°C brought about a significant increase in the specific surface area of cobaltic oxide.

In the present work, iron manganese oxide nanocomposites synthesized using different preparation methods to achieve the high surface area and catalytic activity in decomposition of hydrogen peroxide. For this purpose different synthesis methods, catalytic supports and parameters such as concentration, cations ratio, pH and calcination temperatures were investigated to optimize the catalytic activity for increasing the rate of hydrogen peroxide decomposition.

2. EXPERIMENTAL PROCEDURES

2.1. Reagents and instruments

$Mn(NO_3).4H_2O$, $Fe(NO_3)_3.4H_2O$ and polyvinyl pyrolidone (PVP) as a capping agent were purchased from Merck company. Ethylene glycol, sodium metasilicate and Zeolite 13X prepared from Fluka company. The IR and UV spectrums were recorded by IR-Perkin Elmer and UV-Shimadzu respectively. The nanocomposites were characterized by XRD and scanning electron microscopy (SEM) analysis.

2.2. Preparation of $MnFe_2O_4$ nanocomposites

2.2.1. Coprecipitation method

An appropriate amount of $Mn(NO_3).4H_2O$ and $Fe(NO_3)_3.4H_2O$ were dissolved in water and heated to 40°C. While the solution was being stirred rapidly, 20 mL of NaOH 0.1 M was added to the solution. After 30 minutes the reaction was halted; filtering and washing steps at pH= 7 were carried out. As a result the precursors of $MnFe_2O_4$ i.e. $Mn(OH)_2$ and $Fe(OH)_3$ were produced which were left for 24 h at 60°C±10°C to be dried. The dried precursors were calcinated and annealed at 300°C for 2 h a heating and cooling rate of 10°C/min to obtain $MnFe_2O_4$.

The ionic equation of the reaction is as followed:

$$Mn^{2+} + 2Fe^{3+} + 8OH^- \rightarrow Mn(OH)_2\downarrow + 2Fe(OH)_3\downarrow \rightarrow MnFe_2O_4 + 4H_2O \tag{2}$$

2.2.2. Sol-gel method

$Mn(NO_3).4H_2O$ and $Fe(NO_3)_3.4H_2O$ were dissolved in ethylene glycol as a gelling agent. While stirring deionized water was added until a homogeneous mixture was observed this was heated at 70°C for 12 h and dried at 80°C for 24 h. The resulting gel was ground and reheated at 100°C for 24 h and slowly cooled. Final calcination was carried out at 500°C for 2 h at a heating rate of 10°C/min which was followed by cooling step to room temperature at the same rate.

2.2.3. Mechanochemical method

$Mn(NO_3).4H_2O$ and $Fe(NO_3)_3.4H_2O$ were mixed and ground to have an uniform powder. Addition of some distilled water converted the powder to gel form which was dried at 50°C for 4h that was calcinated at 300°C for 2 h to obtain $MnFe_2O_4$.

To increase the nanoparticles active surfaces in above method an optimized amount of sodium metasilicate, foam form of sodium metasilicate gel and zeolite as catalytic beds were added to metal salts. To have a gel form of the mixture some deionized water was added to the mixture. The obtained mixture was dried at 50°C and calcinated at 300°C for 2 h to build the desired phase.

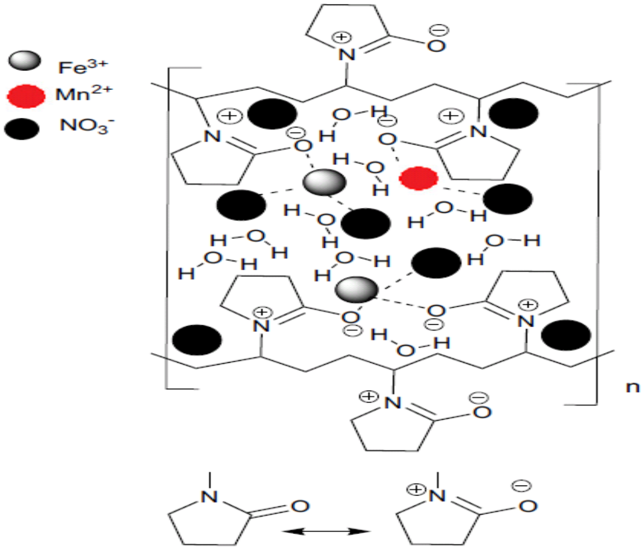


Figure 1: *Proposed mechanism of PVP intractions with metal ions [8].*

2.2.4. Coprecipitation method in the presence of PVP

The procedure of this method is similar to the Coprecipitation method. The difference is the acting of PVP as a capping agent that controls the size of nanoparticles and prevents from agglomeration. The interactions between PVP and metal ions are represented schematically in Figure 1, which shows that the manganese (II) and iron (III) ions are bound by strong ionic bonds between the metallic ions and the amide group in a polymeric chain or between the polymeric chains. This uniform immobilization of metallic ions in the cavities of the polymer chains favors the formation of a uniformly-distributed, solid solution of the metallic oxides in the calcination process.

2.3. Measurment of catalytic activity of the nanocatalysts on decomposition of hydrogen peroxide

The catalytic activity of the nanoparticles on hydrogen peroxide decomposition was evaluated by rate of evaluation of oxygen from the liquid phase. A measured amount of catalyst (0.1 g) was injected into a thermostated reaction vessel containing 10 mL of 5% H_2O_2 (pH= 6.64) for each specimen. H_2O_2 was standardized immediately prior to use by standard $KMnO_4$ solution. The peroxide decomposition is represented by:

$$H_2O\ (aq) \rightarrow H_2O\ (l) + 1/2\ O_2\ (g) \tag{3}$$

H_2O_2 undergoes an exothermic reaction to form O_2 and H_2O. The rate of evolution of gaseous O_2 was monitored with a gasometric assembly. The time dependent volume, V_t of the evolved oxygen was monitored at 0.5 min intervals in all cases.
The catalytic activity was calculated by Eq. 4:

$$a = k/(t.m) \tag{4}$$

where a is the activity, k is a constant, t is a reaction time and m is mass of catalyst (In this experiment it is 0.1 g).

3. RESULT AND DISCUSSION

3.1. IR investigation

The IR transmission spectra were measured for sample calcined at 300°C. Two bands with wave numbers 470 cm^{-1} and 562 cm^{-1} are attributed to Fe-O and Mn-O on octahedral and tetrahedral sites with spinel structure ($MnFe_2O_4$) respectively (Figure 2).

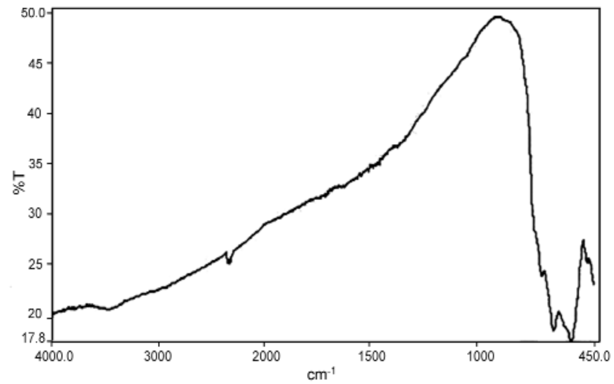


Figure 2: *IR spectrum of $MnFe_2O_4$*

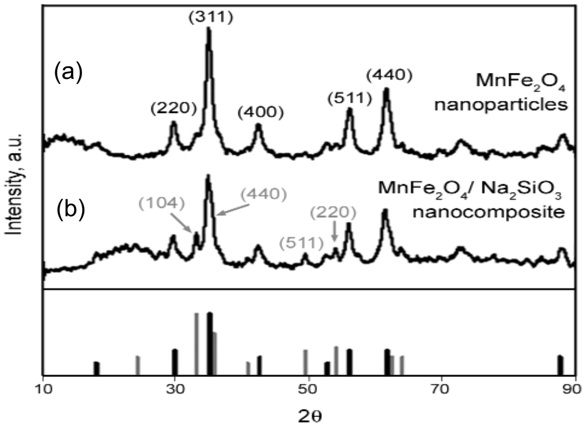


Figure 3: *XRD of $MnFe_2O_4$ (a: pure b: in the presence of sodium metasilicate).*

3.2. XRD investigation

The peaks that are present and are labeled by codes 220, 311, 400, 511, 440 belong to $MnFe_2O_4$ with spinel structure (Figure 3). Basedon data obtained from JCPDS-JCDD (joint committee for powder diffraction international center for diffraction data) our sample exhibits a cubic structure (space group:

Fd3m, JCPDS: 10-319) and no extra high exists along the peak that implies the sample doesn't contain any impurity. Using Scherer equation the average size of nanoparticles was determined to be 45 nm. The XRD of the sample that was prepared by coprecipitation method and PVP capping agent demonstrates a decrease of 15 nm in particle size that may be related to capping agent.

3.3. Investigating the UV spectrum

Considering the low solubility of transitional elements in organic solvents and water, for analyzing the UV spectrum the sample should be left in suspended and disperse situation in ultrasonic bath. Also, surface active and surfactant agents like PVP can be used for this purpose. In electromagnetic region of the spectrum, the molecules experience the electronic transition. Charge transition band in maximum wavelength absorb (347 nm) and observation of broad peaks before and after the incident indicates the formation of ferrite compound [9] (Figure 4).

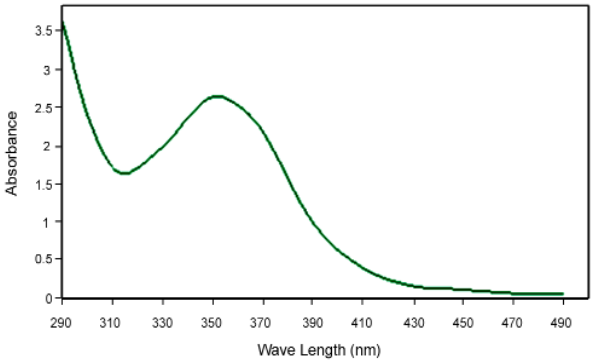


Figure 4: *UV spectrum for $MnFe_2O_4$*

3.4. SEM analysis

Analyzing the morphology aspect of the nanoparticles by studying the SEM (micrographs) indicates that the synthesized nanoparticles are quasi-spherical and the size is less than 100 nm. That means the synthesized catalysts have nano dimension. The information obtained from XRD also confirms the above findings. The results obtained from the calculation of average size of nanoparticles by the aid of SEM images and analytical Clemex image software is as followed: The size of samples prepared by coprecipitation method and synthesized in presence of a capping agent are 50 nm and 40 nm respectively (Figures 5 and 6).

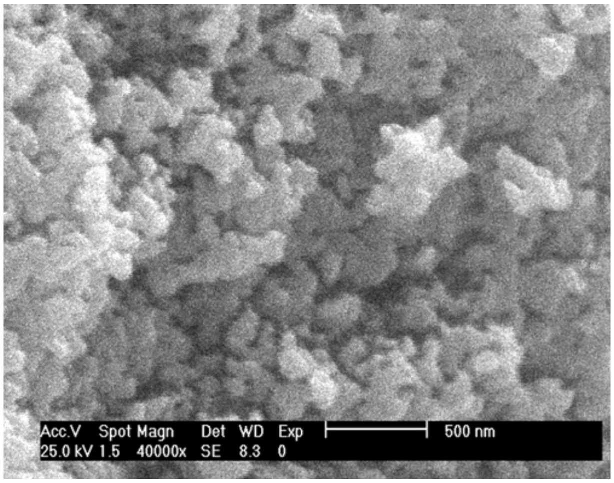


Figure 5: *SEM of $MnFe_2O_4$ (coprecipitation method).*

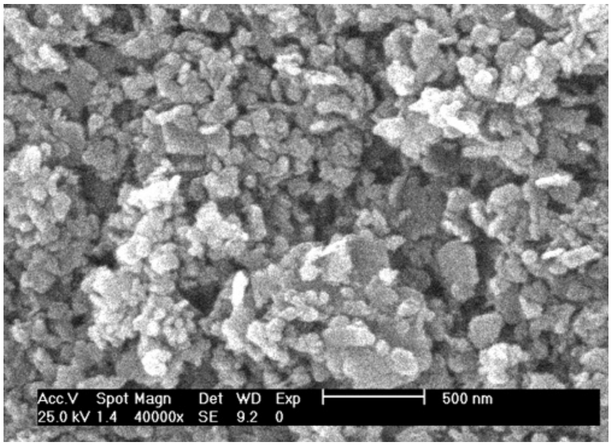


Figure 6: *SEM of $MnFe_2O_4$ in the presence of PVP.*

It should be mentioned that the deter mination of nanoparticles size by aid of SEM is related to morphology of the particles that means the reported size of the nanoparticles verified by XRD and SEM techniques are related to uniform distribution of particle size. At this section of the article SEM images of nanoparticles that are formed in the presence of catalytic beds are investigated. SEM images demonstrated the fact that the morphology of majority of nanoparticle beds is quasi-spherical. Another determination by SEM images is related to the size particles i.e. the formed particles exhibit nano dimension and to be exact the size is under 100 nm. The size of particles formed on silica and porous beds are smaller than those formed on zeolite bed (Figures 7, 8 and 9).

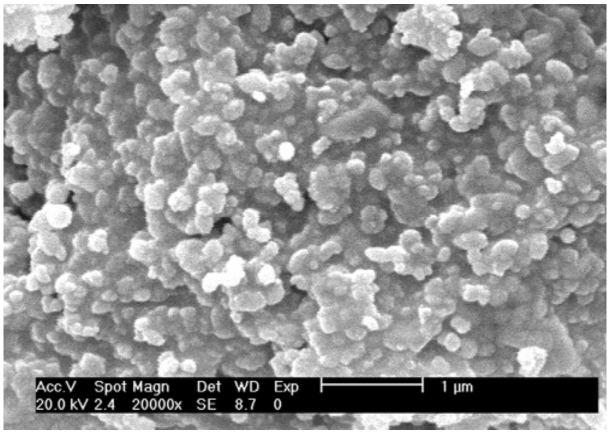


Figure 7: *SEM of nanocomposite with sodium metasilicate support.*

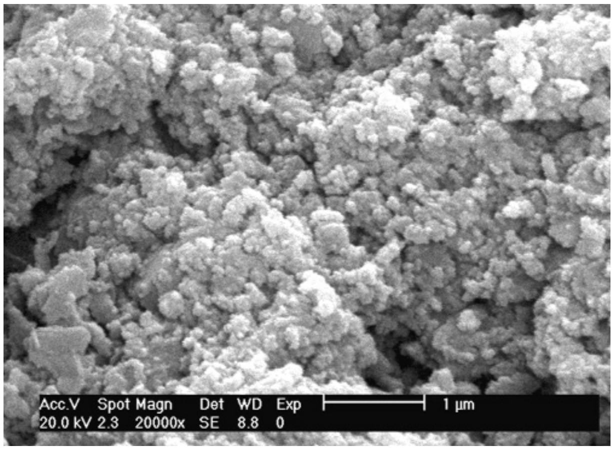


Figure 8: *SEM of nanocomposite with porous beds.*

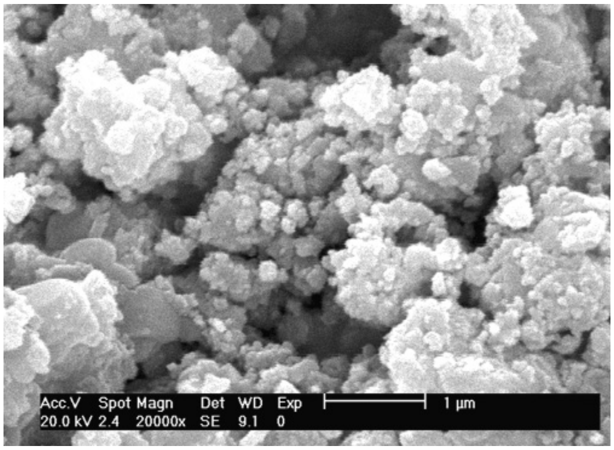


Figure 9: *SEM of nanocomposite with zeolite support.*

Also, dispersion and distribution of nanoparticles size in silica and porous beds are more than the other beds. Hence it can be concluded that the above reasoning are effective in incrementation of catalytic activities of silica and porous beds. In order to have a sharper remark the analysis of samples surface area should be considered.

3.5. The role of catalyst support on surface area and particle size

Presence of catalytic support of sodium metasilicate illustrates various advantages associated with nanoparticles such as simple work up procedure, short reaction times, reduced particle size, high total surface area (m^2), high specific surface area (m^2/g), high product yield and easy recovery and reusability of the catalyst. The use of sodium meta silicate reduces the size of nanoparticles from 43 nm to 12 nm; increases the catalytic activity;

Table 1: *surface area analysis (BET)-iron manganese oxide nanocaomposites in the presence of sodium meta silicate catalyst support.*

Sample	Weight (gram)	Adsorb gas	Relative (p/p_0) Pressure	Total Surface area (m^2)	Specific surface area (m^2/g)
in the absence of support	0.107	Nitrogen	0.15	0.5407	5.0531
in the presence of support	0.105	Nitrogen	0.5	11.2864	107.4899

increases the distribution of nanoparticles on the support (the morphology of system improves).The data that confirm the above claims are listed in Table 1 and shown in Figures 10 and 11. Furthermore presence of catalytic support increments the amount of evolved oxygen (Figure 12).

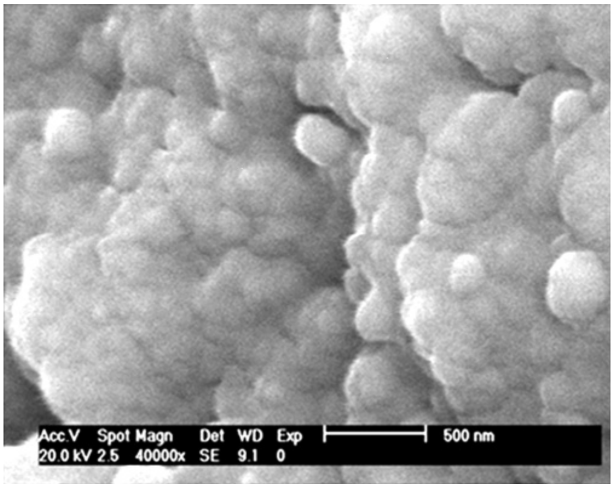


Figure 10: *SEM of iron-manganese oxide nanocomposites in the absence of sodium meta silicate catalyst support.*

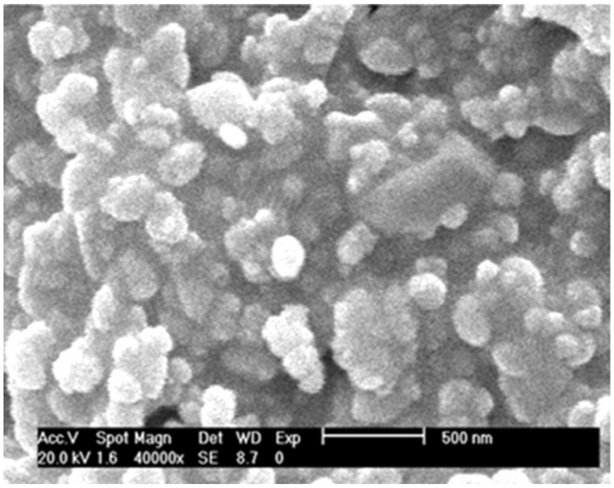


Figure 11: *SEM of iron-manganese oxide nanocomposites in the presence of sodium meta silicate catalyst support.*

It should be mentioned that three other catalyst beds i.e. meso porous, molecular sieves and zeolit 13X were also investigated, but none of them had the effectiveness of sodium metasilicate on decomposition of H_2O_2 and as a result the amount of evolved oxygen was in excess. Among the catalyst beds the zeolit 13X bed had the less effect (Figure 12).

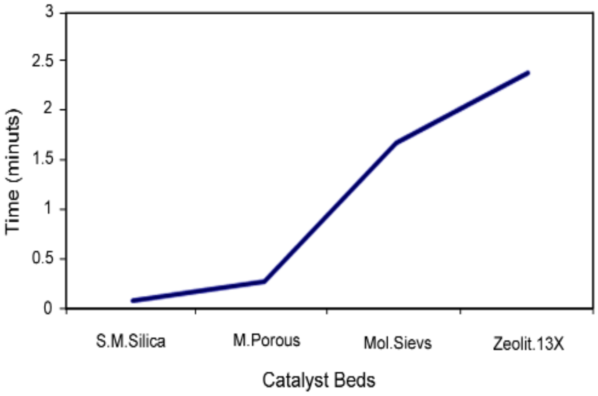


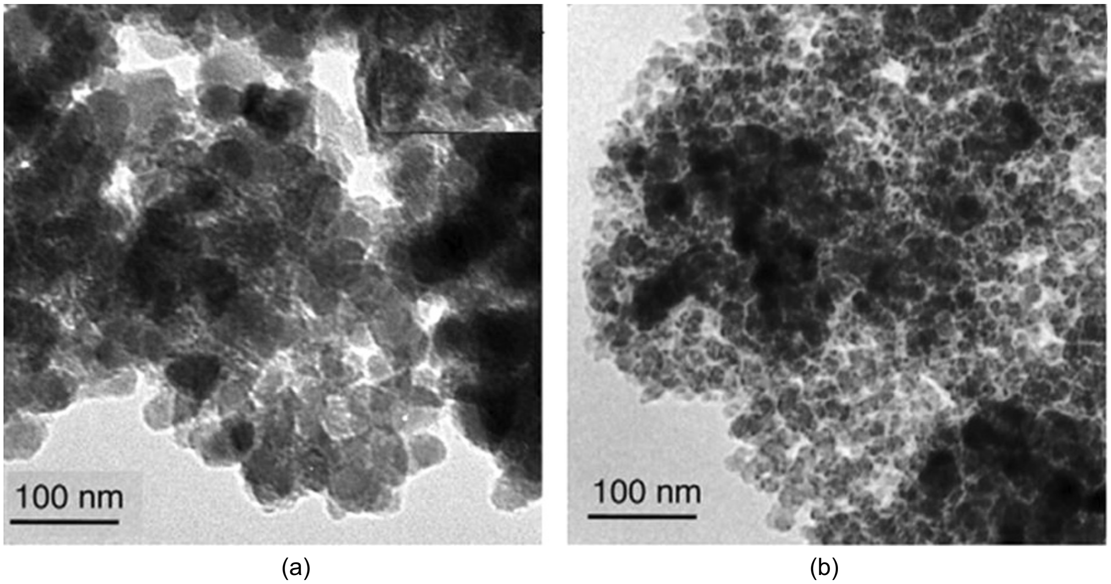
Figure 12: *Catalytic activity of iron-manganese oxide nanocomposites in the presence of catalyst beds on hydrogen peroxide decomposition.*

TEM images obtained for the ferrite nanoparticles and sodium metasilicate ferrite nanocomposites are shown in Figure 13a and b respectively. The $MnFe_2O_4$ sample consists of nanoparticles of approximately 40 nm which aggregate to form large clusters. The size of these nanoparticles as deduced by TEM inspection is in agreement with that calculated by XRD analysis. The TEM image obtained for the $MnFe_2O_4$/sodium metasilicate composite (Figure 13b) shows that the $MnFe_2O_4$ are dispersed along the silicat, which exhibits a large porosity.

3.6. Investigating the different variables providing optimized conditions to accelerate H_2O_2 decomposition

3.6.1. Effect of calcination temperature

In order to determine the optimized calcinations temperature, different calcinations temperatures were implemented on hydroxide precipitation produced via co-precipitation method. Catalytic activities was at maximum when the temperature of calcination reached 300°C. At this temperature decomposition of hydrogen peroxide occurred at lower temperature which evolves more oxygen. In higher calcination temperature the nanoparticles stick together, so their sizes increments and the



(a) (b)

Figure 13: *TEM image of the iron-manganese oxide nanoparticles (a: pure b: in the presence of sodium metasilicate).*

surface area for catalytic activities are reduced. At lower calcination temperature oxidize phases is not formed (Figure 14).

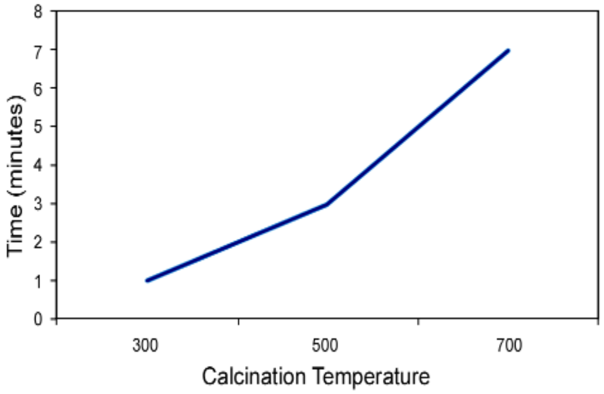


Figure 14: *Effect of calcination temperature on catalytic activity of hydrogen peroxide decomposition (samples obtained from co-precipitation method).*

3.6.2. Optimization of pH in co-precipitation method

Decomposition of hydrogen peroxide is a variable of pH. It was mentioned that the optimized pH for the most catalytic activity of the samples is on the basic region of 9-10 the samples in acidic region (low pH) has the least catalytic activity.

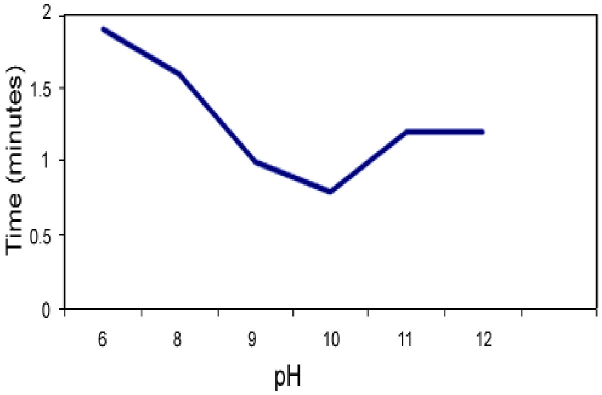


Figure 15: *Effect of pH on catalytic activity of hydrogen peroxide decomposition (samples obtained from co-precipitation method).*

3.6.3. Effects of catalyst bed amounts and different types of starting materials for supporting process

It was observed that for having the maximum catalytic activity the amount of metal salts should be four times of catalytic bed (Figure 16). In fact the amount of catalytic bed should be exact because if it is more the catalyst active sites are covered and surface and catalytic activities are reduced; Furthermore if it is less than the optimized amount the surface activity is not altered by it. It was

Table 2: *Feasibility of reusing nanocatalysts.*

Sample	Initial weight	Reaction Time	Secondary weight	Reaction Time
Coprecipitation method	0.1(g)	30(s)	0.098(g)	33(s)
Sol-Gel	0.1(g)	150(s)	0.099(g)	155(s)
Silica Support (preferred method)	0.1(g)	12(s)	0.091(g)	13(s)
Zeolit 13X	0.1(g)	120(s)	0.088(g)	123(s)

observed that if $FeSO_4$ is used as a reactant instead of $Fe(NO_3)_3$ the surface activity is reduced dramatically; the reason could be related to the poisoning nature of sulfate. In co-precipitation method, catalytic activities are not poisoned because of the washing and filtering processes. It was confirmed that suitable starting material is utilization of metal salts instead of metal hydroxides and metal oxides, the reason that in metal nitrates the ions are more freer to move about, therefore the ion-exchange was carried-out better (Figure 17).

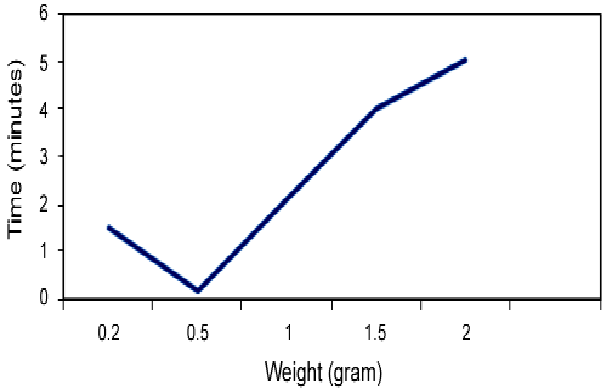


Figure 16: *Optimization of support weight in 2g catalyst.*

3.7. Feasibility of reusing nanocatalysts

In order to examine the reusability of nanocatalysts in decomposition of hydrogen peroxide, a few of synthesized samples were chosen coincidentally, and catalytic decomposition reaction was carried out on them. At the end of reaction the samples was collected, dried and weighted, then they were reused for the decomposition of hydrogen peroxide, as the last step of the experiment the difference between the catalytic activity and the weight of nanocatalysts were considered. The slight difference in initial and final weights of nanocatalysts indicates that both the primary nanocatalysts and synthesized samples have the catalytic activity in hydrogen peroxide decomposition. The results are summarized in Table 2.

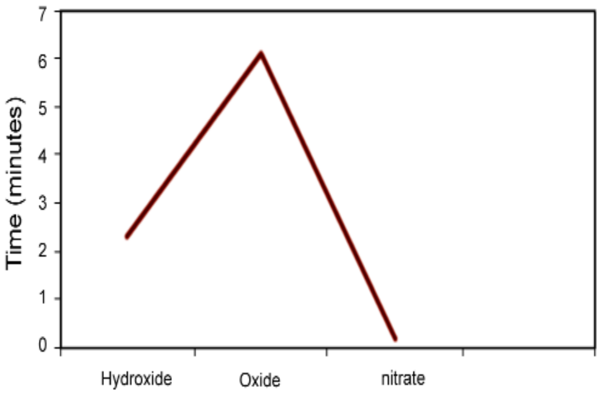


Figure 17: *Form of starting materials for supporting process.*

4. CONCLUSIONS

For carrying out the hydrogen peroxide decomposition reaction in short time (rapid reaction), $MnFe_2O_4$ nanocomposites were used. In order to reach the maximum speed in hydrogen peroxide decomposition reaction, and as a result collecting the maximum possible amount of oxygen in short time, nanocatalysts with the highest catalytic activity should have been used. Hence, major variables that were so effective in catalyst synthesis should be considered, and optimized. Conditions of each variable that had a major effect in incrementation of catalytic activity were investigated that caused the augementation of nanoparticles active surface area and their uniform distribution on catalytic supports that are followed:

1. The best method for synthesis of nanocatalysts was Coprecipitation method in the presence of silicate that provided the maximum catalytic activity for decomposition of H_2O_2. The suitable pH for nanoparticles precipitation was around 9. The optimized calcinations temperature was about 300°C. In lower temperature suitable oxidized phase was not formed and in higher temperature the nanoparticles were sticked together and as a result the size of nanoparticles was incremented.
2. For controlling the nanoparticle size PVP capping agent was applied by using co-precipitation method. PVP agent also caused a 15 nanometer reduction in nanoparticles size.
3. To accelerate hydrogen peroxide decomposition sodium metasilicate was used as a catalytic support. In presence of sodium metasilicate shorter time needed to decompose a certain amount of H_2O_2. Decomposition of H_2O_2 was implemented at the least time when the amount of catalyst was four times of the support because large amount of support cover the active sites of catalysts.
4. Investigating the reusability of nanocatalysts indicated that second use of them was accompanied by a slight poisonous that was negligible; therefor the nanocatalysts could be used for a few times. It was also observed that the difference in weight of consumed nanocatalysts is so small that demonstrated the nanocatalysts participated in the reactions as catalysts and not reactants.

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