

Effect of Preparation Method on the Physicochemical and Catalytic Properties of Nanosized $\text{Fe}_2\text{O}_3/\text{MgO}$

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Abstract: $\text{Fe}_2\text{O}_3/\text{MgO}$ system was prepared by incipient impregnation, coprecipitation and hydrothermal techniques. The solids obtained were calcined at 500-900°C. The prepared catalysts were characterized using XRD, EDX, S_{BET} techniques and catalysis of H_2O_2 decomposition. The investigated catalysts contained nanosized MgO phase apart from the MgFe_2O_4 phase. The solids prepared by coprecipitation method were devoted with the highest concentration of surface iron-species and measured the highest specific surface areas. The lattice constant of MgO lattice in $\text{Fe}_2\text{O}_3/\text{MgO}$ system was dependent on both of preparation method and calcination temperature. The solids prepared by hydrothermal measured the highest catalytic activity towards H_2O_2 decomposition of. The apparent activation energy and the mechanism of the investigated catalyzed reaction didn't altered by variation of the preparation method.

Key words: Nano-catalysts • Hydrothermal • Coprecipitation • Impregnation • $\text{Fe}_2\text{O}_3/\text{MgO}$

INTRODUCTION

Several parameters such as [1] preparation conditions [2], thermal treatment [3], choice of the support material [4] and doping with certain foreign oxides [5] may affect the physicochemical, surface and catalytic properties of various catalytic systems towards certain catalytic reactions. From the interested catalysts supported transition metals oxides are well-known. These catalysts have both of surface acid-base [6] and oxidation-reduction properties [7]. Iron oxides-containing catalysts are used in oxidation processes [8, 9] and in microwave devices [10], CO gas sensors and pollution control devices [11]. Ferrites are known as products of interaction between divalent metal oxides and Fe_2O_3 . Prehistory of the parent oxides, their amounts and foreign oxides doping are parameters affect on ferrite formation [12, 13]. Ferrites are known as catalysts and also as permanent magnets used in computer [14]. Magnesia is used as a support and as a catalyst in many reactions such as dry reforming [15] and oxidative dehydrogenation of butane [16]. The nano-particles oxides activity is caused not only by high surface area but also by the high concentration of low coordinated sites and structural defects on their surfaces [17]. Nanomaterials exhibit novel electronic, optical,

magnetic and chemical properties [18] Nanocrystals of MgO are very strong adsorbents for SO_2 , chlorocarbons and polar organic compounds [19]. This interested property is due to high surface areas and enhanced surface reactivities toward incoming adsorbates [20]. Nanocrystalline magnesia adsorbed different organic compounds stronger and in much larger amounts than those of activated carbon samples [21], the large surface area gives a chance for the interfacial interactions [22]. Various methods have been used for preparation nanocrystalline magnesia such as impregnation [23], coprecipitation [24], hydrothermal [25], laser vaporization [26], sol-gel [27]. Hydrothermal route has been proposed for the preparation many catalysts [28]. The coprecipitation method gives a fine particle size of powders in nano-scale [29, 30]. Hydrothermal route is a technique used in synthesis of metal oxides having nanostructures; these metal oxides are used for many technological processes [31]. Hydrothermal technique gives highly homogeneous crystalline material at low reaction temperature; this material has narrow particles size distribution, uniform composition, high purity and controlled particle morphology. The hydrothermal is an environmental and economic technique, because of its closed system and energy efficiency [32].

Catalytic decomposition of H_2O_2 is an oxidation-reduction reaction; one of its applications is its using as a green fuel/propellant in spaceflight at certain conditions [31]. H_2O_2 is used as an oxidizer in many fuel cells [33]. The waste water treatment by oxidative removal of natural organic pollutants takes place by H_2O_2 [34]. H_2O_2 decomposition in presence of catalysts is considered as a model reaction for measuring the redox activity of both heterogeneous [5] and homogeneous catalysts [35]. The catalytic activities of metal oxides may be described in some redox reactions [31]. This paper aimed at studying the role of both preparation method and calcination temperature on the physicochemical properties of Fe_2O_3 /magnesia. The obtained solids were characterized by using XRD, EDX, S_{BET} and decomposition of H_2O_2 in aqueous solution at 25-35°C in presence of these samples.

Experimental

Materials and Preparation Methods: Three Fe_2O_3 /MgO catalyst samples with composition 0.065 Fe_2O_3 /MgO were prepared by three different techniques:

Impregnation Method: Incipient wet impregnation method in which a sample of a known mass of $Mg(OH)_2$ is impregnated with a known mass of iron nitrate dissolved in smallest possible volume of double-distilled water. The solid thus obtained was dried at 110°C.

Co-precipitation Method: Co-precipitation of the previous amounts of iron and magnesium nitrates with 0.2mol/l NH_4OH solution at 25 °C and pH 8 were carried out. After filtration and washing with double-distilled water, the precipitate was dried at 110°C.

Hydrothermal Method: Hydrothermal method in which the catalyst was prepared from a mixture of iron and magnesium hydroxides, obtained at 25 °C prepared by co-precipitation method. The suspension from the precipitate and 30 ml doubled-distilled water was placed into a 45 ml Teflon-lined autoclave and then heated at 200°C for 1 h. The temperature of the autoclave was decreased to 25°C and the obtained hydroxides were heated at 50°C for drying [24]. All the prepared samples were heated in air at 500°C for 4 h.

Characterization Techniques

X-Ray: The calcined solids were characterized by means of X-ray powder diffraction employing a (BRUKER Advance diffractometer model AxsD8, Germany).

Scherrer equation is applied to calculate the average crystallite size (D) of the present phases [36], with the aid of TOPAZ2.Inc program.

EDX: The surface molar composition of the catalysts was determined by (EDX) i.e. Energy dispersive X-ray analysis. EDX was performed on (Hitachi S-800 Japan) electron microscope with an attached kevelex Delta system.

S_{BET} : The surface characteristics for the obtained catalysts were determined using an automated gas sorbometer (Quantachrome NOVA2000 model 7.11(USA).

Catalytic Properties: The catalytic properties of the prepared catalysts were determined by using redox reaction as H_2O_2 decomposition. The catalytic reaction was carried out using 0.45 mol/l H_2O_2 diluted to 20 ml with distilled water in presence of 100 mg catalyst at 25-35°C. The kinetics was determined by measuring the amount of oxygen collected at different time intervals until no further O_2 liberated.

RESULTS AND DISCUSSION

EDX of Fe_2O_3 /MgO System: The surface concentration of Fe, Mg and O atomic species in the calcined catalysts at 500, 700 and 900°C were readily determined from EDX measurements. The bulk concentrations of the present species in the prepared solids are readily calculated considering the catalyst formula as 0.065 Fe_2O_3 /MgO. Table 1 includes surface and bulk concentrations of the species present in different solids. Examination of Table1 shows the following: (i) The surface concentration of Fe species is much bigger than that in bulk of the catalysts prepared by coprecipitation and hydrothermal methods and calcined at 500°C. The difference attained 167 and 69%, respectively. On the other hand, the sample prepared by impregnation and being calcined at 500°C has Fe species with surface concentration is smaller than that present in the bulk. Also, it is shown that the sample prepared by impregnation has surface concentration of Fe species smaller than that prepared by coprecipitation and hydrothermal methods. (ii) Raising the calcination temperature of the solid prepared by coprecipitation from 500 to 700 °C decreased the Fe-surface concentration. This decrease may be due to concentration gradients or inward migration of Fe species to the bulk. While in case of the solids prepared by hydrothermal, increasing the heating temperature to 700°C didn't much affect

Table 1: Surface molar composition determined by EDX for Fe₂O₃/MgO System prepared by different methods

| Method of Preparation | T_{calc} °C | Element | Atomic abundance (atom%) | |
|-----------------------|----------------------|---------|--------------------------|-----------------|
| | | | Calculated (Bulk) | Found (Surface) |
| Coprecipitation | 500 | Fe | 5.59 | 14.93 |
| | | Mg | 43.01 | 44.92 |
| | | O | 51.40 | 41.88 |
| | 700 | Fe | 5.59 | 9.08 |
| | | Mg | 43.01 | 50.12 |
| | | O | 51.40 | 40.80 |
| | 900 | Fe | 5.59 | 5.55 |
| | | Mg | 43.01 | 35.37 |
| | | O | 51.40 | 59.08 |
| Hydrothermal | 500 | Fe | 5.59 | 9.46 |
| | | Mg | 43.01 | 33.47 |
| | | O | 51.4 | 57.07 |
| | 700 | Fe | 5.59 | 10.88 |
| | | Mg | 43.01 | 39.09 |
| | | O | 51.40 | 50.03 |
| | 900 | Fe | 5.59 | 6.88 |
| | | Mg | 43.01 | 32.44 |
| | | O | 51.40 | 60.69 |
| Impregnation | 500 | Fe | 5.59 | 4.10 |
| | | Mg | 43.01 | 45.30 |
| | | O | 51.40 | 50.60 |
| | 700 | Fe | 5.59 | 5.89 |
| | | Mg | 43.01 | 46.03 |
| | | O | 51.40 | 48.08 |
| | 900 | Fe | 5.59 | 3.87 |
| | | Mg | 43.01 | 38.48 |
| | | O | 51.40 | 57.69 |

Table 2: Intensity counts of main diffraction peaks of XRD, crystallite sizes of various phases and lattice parameter constant of MgO measured for all investigated solids

| | | Intensity count | | Crystallite size | | |
|---|-----------------------------|-------------------|----------------------------------|------------------|----------------------------------|---------------------------|
| | | MgO | MgFe ₂ O ₄ | MgO | MgFe ₂ O ₄ | |
| Solids prepared by | <i>T</i> _{calc} °C | ----- a. u. ----- | | ----- nm ----- | | <i>A</i> _{MgO} Å |
| Coprecipitation hydrothermal | 500 | 95.0 | -- | 18.7 | -- | 4.215 |
| | | 10.4 | 5.5 | 9.8 | 3.9 | 4.212 |
| | | 7.8 | 18.5 | 7.9 | 3.0 | 4.206 |
| Impregnation coprecipitation hydrothermal | 700 | 117.0 | 11.4 | 26.9 | 7.7 | 4.214 |
| | | 23.6 | 17.0 | 25.9 | 13.2 | 4.217 |
| | | 16.7 | 10.2 | 23.4 | 14.7 | 4.216 |
| Impregnation coprecipitation hydrothermal | 900 | 140.0 | 41.8 | 55.1 | 54.1 | 4.213 |
| | | 71.3 | 52.7 | 54.6 | 67.4 | 4.208 |
| | | 3.0 | 53.5 | 44.4 | 40.4 | 4.210 |

^a The standard lattice constant of MgO is =4.213 Å

the surface concentration of Fe species. On the other hand in the solids prepared by impregnation, the Fe species concentration present on the surface increased by increasing the calcination temperature from 500 to 700°C which may be due to Fe-movement towards the sample surface. (iii) By increasing the heating temperature of all solids from 700 to 900°C resulted in an observable

decrease in the Fe-surface concentration. The decrease was 39, 37 and 34% for the solids prepared by coprecipitation, hydrothermal and impregnation, respectively. The surface and bulk concentration of Fe in the solids prepared by these employed methods as being influenced by calcination temperature within 500-900°C are governed by migration of Fe species from surface to

bulk and vice versa depending on the Fe-concentration gradient. The migration process took place from higher concentration to lower concentration. So, the method of preparation and calcination temperature play a decisive role in determining the active sites concentration (i.e. Fe species) for H_2O_2 decomposition carried out in this work. One might expect that the samples having higher surface concentration of Fe will devoted with higher catalytic activity and vice versa.

XRD of Fe_2O_3 /MgO System: X-ray diffractograms of Fe_2O_3 /MgO prepared by wet impregnation, coprecipitation and hydrothermal methods precalcined at 500-900°C were determined. (Fig. 1 and 2) showed XRD of various solids heated at 500 and 900°C, respectively. The different structural characteristics namely degree of ordering, crystallite sizes of the crystalline phases present and lattice parameter constant of MgO support material were calculated from x-ray diffraction data. The results are

present in Table 2. Inspection of Fig.1 and Table 2 shows the following:

- The mixed oxides catalyst calcined at 500°C consisted of nanosized MgO phase. This phase showed the highest degree of ordering and crystallite size in the system prepared by impregnation. The MgO phase measured the smallest degree of ordering and crystallite size in the system prepared by hydrothermal. The structural characteristics of various solids calcined at 700°C (whose diffractograms are not given) including the crystalline phases present and the degree of ordering and crystallite size were determined and illustrated in Table 2. Inspection of Table 2, Fe_2O_3 interacted entirely with MgO yielding nanosized $MgFe_2O_4$ measuring crystallite size between (17-94 nm) depending on the mode of preparation. Increasing the calcination temperature to 900°C increased the degree of ordering of the ferrite produced with

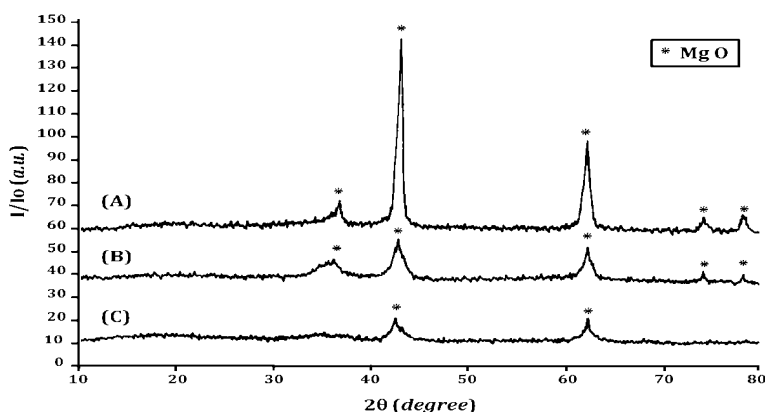


Fig. 1: X-ray diffractograms of different solids heated at 500 °C. (A) Solid prepared by impregnation, (B) Solid prepared by hydrothermal, (C) Solid prepared by coprecipitation.

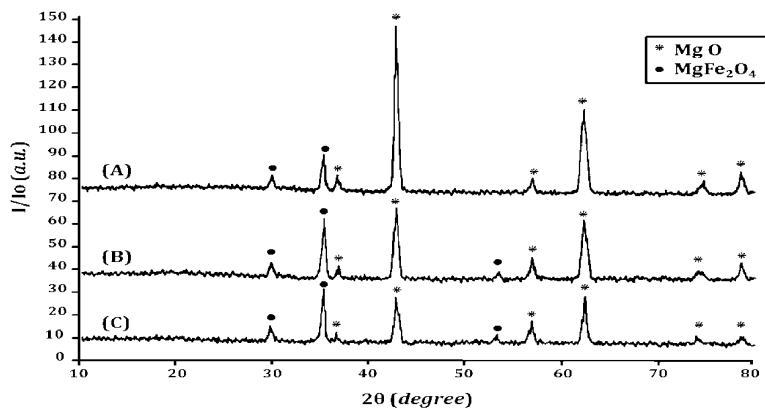


Fig. 2: X-ray diffractograms of different solids calcined at 900 °C. (A) Solid prepared by impregnation, (B) Solid prepared by hydrothermal, (C) Solid prepared by coprecipitation.

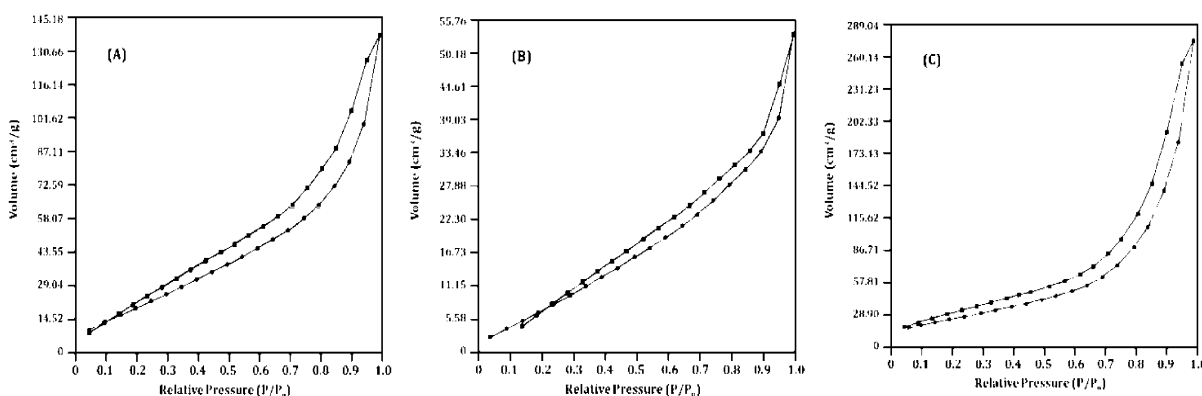


Fig. 3: Adsorption-desorption isotherms for different solids calcined at 500°C. (A) Solid prepared by impregnation, (B) Solid prepared by hydrothermal, (C) Solid prepared by coprecipitation.

subsequent increasing in its crystallite size which remained in the nanosize range (c.f. Table 2). (ii) The calculated lattice parameter "a" of MgO in different solids depends on the mode of preparation and calcination temperature (Table 2). The calculated values of the lattice parameter of MgO phase are different from the standard a-value [37]. The a-value of MgO in the solid prepared by the hydrothermal is smaller than that of the standard value. Opposite finding was found for the solid prepared by impregnation. The relatively big value of "a" constant of MgO phase in the solid prepared by impregnation could be tentatively attributed to the possible presence of Fe^{2+} ions dissolved in the MgO lattice. In fact the ionic radii of Mg^{2+} and Fe^{2+} are 0.66 and 0.78 Å, respectively [37]. The a-value of MgO phase for the system prepared by impregnation and calcined at 500°C measured the biggest value might suggest that this particular sample dissolved biggest portion of Fe_2O_3 present. So, the smallest portion could remain on the uppermost surface layers. This conclusion could be confirmed from EDX measurements (Table 1) which showed that surface concentration of Fe in this particular sample measured the smallest value. The increase in the calcination temperature of various solids above 500°C resulted in fluctuation in the lattice constant of MgO depending on the preparation route.

Surface Properties: The different surface parameters of $\text{Fe}_2\text{O}_3/\text{MgO}$ solids calcined at 500°C were determined from adsorption-desorption nitrogen isotherms carried out over various solids. These parameters are specific surface area S_{BET} , total pore volume V_p and mean pore radius \bar{r} . The computed surface parameters are given in (Table 3 and Fig. 3). Fig. 3 depicts representative adsorption-desorption isotherms for some investigated adsorbents.

Table 3: Some Surface characteristics of variously prepared $\text{Fe}_2\text{O}_3/\text{MgO}$ adsorbents calcined at 500°C

| | \bar{r} | V_p | S_{BET} |
|--------------------|-----------|--------------------|----------------------------|
| Preparation method | Å | mL g^{-1} | $\text{m}^2 \text{g}^{-1}$ |
| Impregnation | 35.8 | 0.0494 | 68 |
| Coprecipitation | 38.02 | 0.0818 | 98 |
| Hydrothermal | 86.8 | 0.4248 | 43 |

Table 4: Activation energy ΔE , ΔE^* and frequency factor for H_2O_2 decomposition in presence of various $\text{Fe}_2\text{O}_3/\text{MgO}$ solids

| | ΔE | $\ln A$ | ΔE^* |
|--------------------|----------------------|---------|----------------------|
| Preparation method | kJ mol^{-1} | | kJ mol^{-1} |
| Impregnation | 41.8 | 13.1 | 41.8 |
| Coprecipitation | 29.7 | 8.6 | 40.9 |
| Hydrothermal | 31.5 | 9.9 | 39.4 |

All the isotherms of the examined solids belong to Brunauer's classification (type II) [38] having hysteresis loops at p/p_0 about 0.4.

Inspection of Table 3 the sample prepared by coprecipitation has the highest value of surface area and that prepared by hydrothermal measured the smallest surface area value and biggest pore radius. The observed significant changes in the texture, structural, surface composition and specific surface area of the examined samples prepared by various methods are expected to be accompanied by changes in their catalytic behaviors towards H_2O_2 decomposition.

Catalytic Activity of the Prepared Catalysts Calcined at 500°C: MgO acted as a catalyst support for the investigated system where it showed no catalytic activity towards H_2O_2 decomposition. The reaction kinetics obeyed First-order for all investigated catalysts.

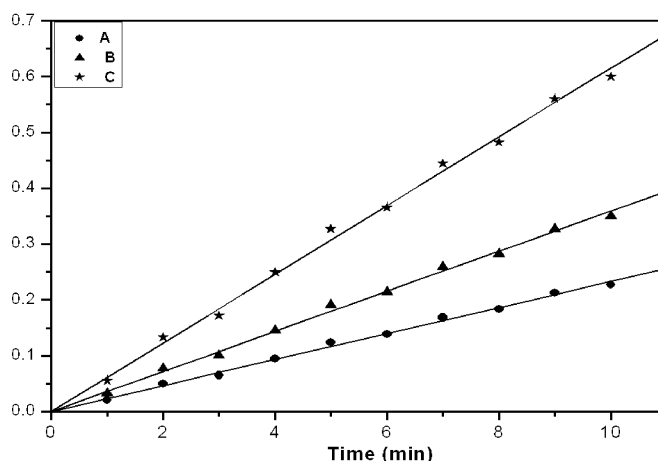


Fig. 4: First order plots for H_2O_2 decomposition, at 25°C , over prepared solids calcined at 500°C . (A) Solid prepared by impregnation, (B) Solid prepared by coprecipitation, (C) Solid prepared by hydrothermal.

The values of reaction rate constant (k/min) are determined from the obtained first-order lines slopes. Also preliminary experiments showed absence diffusion effect of the liberated oxygen resulting from the catalytic reaction. From control experiment the selected mass of the catalyst was 100 mg in all catalytic measurements. Fig. 4 depicts representative first-order plots for the catalyzed reaction conducted at 25°C over the solids prepared by various methods.

The calculated values of the reaction rate constant carried out at various temperatures over different catalysts permitted us to calculate the apparent activation energy of the investigated reaction. The calculated k per gram catalyst at 25°C measured 23×10^{-2} , 36×10^{-2} and $62 \times 10^{-2} / \text{min/g}$ for the catalysts prepared by impregnation, coprecipitation and hydrothermal, respectively. (k) is a reaction rate constant per unit surface area is calculated at 25°C for the examined catalysts and measured 33.8×10^{-2} , 36.7×10^{-2} and $144 \times 10^{-2} / \text{min/m}^2$, respectively. The fact that MgO exhibited no measurable catalytic activity in decomposition of H_2O_2 might suggest that the active sites in the investigated catalysts are the Fe_2O_3 present in top surface layer of the surface. The catalytic activity of the solids prepared by impregnation is the smallest one simply because the surface concentration of iron in this particular sample measured the smallest value (Table 1). The fact that Fe -surface concentration in the solids prepared by coprecipitation measured the highest value and exhibited a catalytic activity smaller than that measured for the solids prepared hydrothermal method might suggest that a portion of surface Fe_2O_3 contributed directly in the catalytic reaction and the other portion has no an effective role. This finding could be due to the fact that the reactive portion of Fe_2O_3 is higher in case of the

solid prepared by hydrothermal. Decomposition of hydrogen peroxide over the investigated system takes place on the following ion pairs $\text{Fe}^{3+}\text{-Fe}^{2+}$, $\text{Mg}^{2+}\text{-Fe}^{2+}$, $\text{Mg}^{2+}\text{-Fe}^{3+}$. It is well-known that hematite includes trace amounts of divalent iron [39] and the substitution of some of Fe^{3+} , in Fe_2O_3 lattice, by a portion of Fe^{2+} is the main active site for peroxide decomposition. The observed increase in the catalytic activity of $\text{Fe}_2\text{O}_3/\text{MgO}$ system due to changing the preparation method can be explained in the light of an effective increase in the concentration of active sites necessary in catalysis of H_2O_2 decomposition.

Activation Energy of Various Prepared $\text{Fe}_2\text{O}_3/\text{MgO}$ Solids:

The possible changes in the mechanism of the catalyzed reaction as a result of changing preparation method of the examined catalyst can be deduced from calculation the apparent activation energy of the catalyzed reaction. The values of reaction rate constant (k) measured at 25, 30 and 35°C over the examined samples have used to calculate ΔE through using *Arrhenius* equation. The ΔE values are listed in Table 4. Frequency factor i.e. ($\ln A$) is also calculated for the investigated catalysts and listed in Table 4. The data of Table 4 shows the following: (i) changing preparation method of $\text{Fe}_2\text{O}_3/\text{MgO}$ solid from impregnation to coprecipitation decreased the ΔE value. This result ran parallel with that obtained from the observed increase in the catalytic activities of the examined samples due to preparation method variation. Some fluctuations are observed in case of hydrothermal and coprecipitation method. (ii) $\ln A$ showed some fluctuations indicating a surface heterogeneity of these catalysts. This result justifies the calculation of ΔE^* values of different examined samples adopting the $\ln A$ values of the catalyst sample prepared

by impregnation to the other prepared samples by other two methods and calcined at the same temperature. ΔE^* values are given also in Table 4. Comparing ΔE^* values for various prepared samples calcined at 500 °C are nearly the same in the range of the experimental error. This finding showed that the preparation method of $\text{Fe}_2\text{O}_3/\text{MgO}$ system did not change the reaction mechanism. The activity depends mainly on the surface concentration of Fe species.

CONCLUSIONS

Conclusions of this work show that nano-sized $\text{Fe}_2\text{O}_3/\text{MgO}$ system was prepared by impregnation, coprecipitation and hydrothermal methods. The solids obtained were calcined at 500-900°C. The obtained solids were characterized by using XRD, EDX, N_2 -adsorption and catalysis of H_2O_2 decomposition. The results revealed that MgO phase was only detected in the diffractogram of all solids calcined at 500°C. The system prepared by impregnation measured highest degree of ordering and crystallite size. The surface compositions of various solids investigated were found to be different from each other depending on both of calcination temperature and preparation method. The Fe-species present in the top surface layers of the solids prepared by hydrothermal and coprecipitation measured the highest value. The interaction between MgO and Fe_2O_3 yielding MgFeO_4 took place at temperature starting from 700°C whose degree of ordering increases with increasing the calcination temperature to 900°C. The lattice constant "a" of MgO lattice in $\text{Fe}_2\text{O}_3/\text{MgO}$ system is dependent on the preparation method and calcination temperature. S_{BET} of the solids calcined at 500°C and prepared by coprecipitation measured the highest value and those prepared by hydrothermal measured the smallest value. The catalytic activity towards H_2O_2 decomposition was directly correlated with surface concentration of Fe. The solids having highest surface concentration of Fe measured the highest catalytic activity. The preparation method of $\text{Fe}_2\text{O}_3/\text{MgO}$ system did not affect the reaction mechanism but verified the active sites concentration necessary to catalyze the reaction.

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