

Physical and Catalytic Properties of Solids Produced from Solid-Solid Interactions between NiO and Fe₂O₃ System Doped with Ag₂O

M.A. El-Kherbawi

Department of Chemistry, Women faculty for Science, Ain Shams University, Asmaa Fahmi Street, Cairo, Egypt
magdaelkherbawi@hotmail.com

Abstract: Physicochemical properties of equimolar ratio of pure NiO/Fe₂O₃ system and that doped with 2 and 4% Ag₂O were investigated using DTA, XRD and BET. All solid mixtures were calcined at 500, 800 and 1000 °C. The catalytic activity was studied through isopropanol conversion in flow system under normal pressure. X-ray diffraction showed the formation of NiO, α-Fe₂O₃ and NiFe₂O₄. The activation energy (ΔE) of NiFe₂O₄ phase formation of pure and doped samples was determined. Ag₂O doping enhances the formation of NiFe₂O₄ and increases the catalytic conversion of *iso*-propanol to acetone and MIBK. The selectivity of sample doped with 4% Ag₂O and calcined at 400 °C towards acetone and MIBK formation was 64.26 and 13.30 % respectively. [Journal of American Science 2010;6(10):470-478]. (ISSN: 1545-1003).

Keywords: Nickel oxide; Fe₂O₃; NiFe₂O₄; Isopropanol conversion

1. Introduction:

A great deal of fundamental research has been done on mixed oxide catalysts in the field of heterogeneous catalysis¹⁻³. These mixed systems may be more active than their individual components⁴. The mixed oxide catalysts are often produced by thermal decomposition of mixed solid components of transition metals⁵. Metal nitrates (hydrates) are the most popular precursor components for the preparation of oxides and metallic materials with wide spread properties, such as high surface catalysts⁶⁻⁸. Ferrites have found wide uses in many industrial applications such as electronic inductors, transformers, electromagnets and semiconductors⁹⁻¹¹. Several preparation methods were used such as hydrothermal synthesis^{12,13}, sol-gel^{14,15} or coprecipitation¹⁶ techniques. Solid-state interactions may be formed as a result of thermal treatment depending on the prehistory of parent solids, their ratio and also by the addition of foreign oxides¹⁷⁻²³. Ferrites crystallize in three crystal types, namely, spinel, garnet and magnetoplumbite²⁴. The general chemical formula of ferrite is (MFe₂O₄)_n where M represents a metallic cation, it is often divalent but other valences are possible if the number of anions is doubled.

MIBK (methyl isobutyl ketone) is an important product used as useful solvent for paints and resin-based protective coating systems^{25, 26}, an important reagent dewaxing mineral oils²⁶ extracting agent for the production of antibiotics and commercial lubricating oils and intermediate for production of various plastics and resins²⁷. MIBK is produced by

using bifunctional catalyst, indirectly during the conversion of *iso*-propanol as follow: (i) dehydrogenation of *iso*-propanol to acetone, (ii) self-condensation of the resulting acetone to meistyle oxide (MO) and (iii) hydrogenation of MO to MIBK²⁸.

The present work reports the results of a study on the effects of calcination temperature and doping with different amounts of Ag₂O on the physical and catalytic properties of NiO/Fe₂O₃ system. The pure and doped samples were calcined at 500, 800 and 1000°C for 3 hours and characterized by DTA, XRD and BET techniques. The catalytic activity of all solids was measured by using catalytic conversion of *iso*-propanol in flow system under normal pressure.

2. Materials and Experimental:

2.1. Materials

Equimolar mixtures of ferric nitrate and nickel nitrate were dissolved in the least amount of distilled water, dried at 110°C then heated in air at temperatures 500, 800 and 1000 °C for 3 hr. Two doped mixed solid samples were obtained by treating a known mass of thermally untreated mixed solids with calculated amount of silver nitrate dissolved in the minimum amount of distilled water, dried at 110 °C, then calcined at 500, 800 and 1000°C for 3 hr. The concentrations of silver oxide were 2 and 4 mol%. All chemicals used were of analytical grade supplied by BDH.

2.2. Techniques

DTA curves for the pure and doped uncalcined samples were performed in air atmosphere using a

Shimadzu Japan50M thermal analyzer. The parent mixtures were heated from ambient up to 1000°C under a heating rate of 5°C / min.

X-ray diffractograms for the calcined samples were recorded via Philips model diffractometer type X Pert MPD at $\lambda = 1.54 \text{ cm}^{-1}$ with a source of Cu-K α radiation and gravite monochromator at 35 kV and 20mA. Data were collected over the range $4 < 2\theta < 90$ with continuous scan mode. The d-spacing were calculated for all samples and compared with relative intensities and characteristic spacing of ASTM cards²⁹.

The surface area of pure and doped samples calcined at 500, 800 and 1000°C were determined from nitrogen adsorption isotherms measured at -196°C after degassing at 250°C for 2hr to eliminate air and water vapour³⁰.

The catalytic activity was measured using a flow technique³¹. The catalyst sample was introduced into the quartz reactor, and reactivated in situ by calcinations at 500°C for 2hr in a current of dry air free from CO₂. The activated catalyst was then cooled to the required reaction temperature. The isopropyl alcohol was introduced using micro dose pump (Unipan 335A). The speed of feeding was kept constant at $7.2 \times 10^{-1} \text{ min}^{-1}$, and the reaction temperature was in the range of 250–450°C. The gaseous and liquid products were analyzed by gas – liquid chromatography (Perkin Elmer 8600) with flame ionization detector on column 5% CW1540 on CSORB (GAW-DMCS) using nitrogen as a carrier gas.

3. Results and Discussion:

3.1. Thermal behavior

Figure 1 shows the DTA curves of pure mixed solids of nickel and ferric nitrates and that doped with Ag₂O. From this figure it can be shown for the pure mixed solid three endothermic peaks located at 83, 161 and 273°C indicating the removal of physisorbed water, water of crystallization and NO₂ produced from the thermal decomposition of nitrates.

The DTA curve of 2% Ag₂O –doped mixed solid shows three endothermic peaks at 81, 161 and 266 °C. The DTA curve of 4% Ag₂O –doped mixed solid shows three endothermic peaks located at 72, 165 and 261.

The comparison of DTA curves of pure and doped solids revealed that silver –doping enhanced the removal of water and thermal decomposition of both nickel nitrate and ferric nitrate into their corresponding oxides. The endothermic peak relative to this process shifted from 273.5 to 266 and 261 °C respectively.

3.3. XRD investigation

Figures (2- 4) represent the X-ray diffractograms of pure NiO/Fe₂O₃ and various Ag₂O –doped samples calcined at 500, 800 and 1000°C. Table 2 shows the effect of Ag₂O doping and calcination temperature of the mixed oxide system on the crystal size of NiO and NiFe₂O₄ phases. It was observed that doping with Ag₂O enhancing the formation of nanosize nickel oxide and nickel ferrite crystals. The sample doped with 4% Ag₂O exhibits the lowest crystal size of 12nm. Increasing the calcination temperature increases the crystal size. At 1000 °C all samples form phases with crystal size (60-66nm). The characteristic diffraction lines of nickel ferrite of high intensity at d-spacing of 2.51Å (100%) and 1.47 Å (40%) are common between α - Fe₂O₃ and NiO, to talk about solid-solid interaction El-Shobaky et al.¹⁷ suggested that diffraction lines at d-spacing values of 2.94 and 4.81 Å are characteristic ‘key- lines’ of the NiFe₂O₄ phase. The variation of the peak heights of the characteristic diffraction lines are listed in Table 2 which indicates the formation of NiFe₂O₄ phase²³. The obtained data emphasized that: (i) pure and doped samples calcined at 500 °C consisted of diffraction lines of NiO, Fe₂O₃ and NiFe₂O₄ phases with the disappearance of any diffraction lines corresponding to silver phase in the doped samples. (ii) The peak heights and the degree of crystallinity of NiO, Fe₂O₃ and NiFe₂O₄ phases were found to decrease with silver doping at 500°C which may be attributed to the formation of amorphous silver ferrite at this low temperature. (iii) The crystal size of NiFe₂O₄ phase formed over pure and doped samples calcined at 500°C exhibit nanosize of 20, 15 and 12nm respectively. The degree of crystallinity and peak height of NiFe₂O₄ phase were decreased with increasing silver doping. (iv) The X-ray patterns of pure and variously doped solids calcined at 800 °C consisted of NiO, Fe₂O₃ and NiFe₂O₄ phases with the appearance of new diffraction lines of Ag metal. (v) Further increase in calcination temperature to 1000 °C for pure sample resulted in decrease in NiO peak’s height and disappearance of Fe₂O₃ diffraction lines accompanying with increasing of NiFe₂O₄ peak’s height. (vi) Diffractograms of doped samples calcined at 1000°C show increase in crystallinity of NiO and NiFe₂O₄ phases, the existence of the diffraction lines of Fe₂O₃ and Ag metal at this temperature emphasized the formation of Ag₂Fe₂O₄ at low temperature which decomposed at higher temperature.

Inspection of the above results indicates that: (i) Solid-solid interactions take place between NiO and Fe₂O₃ when the samples calcined at 500°C. (ii) The presence of diffraction lines of free oxides at 1000°C indicate that the complete conversion of these oxides into NiFe₂O₄ requires a prolonged heating at temperature 1000°C or higher. (iii) Doping the

investigated system with 2 and 4% Ag₂O enhanced the formation of nickel ferrite and decreased the crystal size of formed phases.

According to Arrhenius equation the activation energy of nickel ferrite formation (ΔE) for pure and doped solids can be determined by plotting the peak height of the diffraction line at d-spacing 2.94 Å versus $1/T$, a straight line is obtained its slope determines (ΔE) value²³. The computed (ΔE) values were 30, 34 and 40 kJ mol⁻¹ for pure NiO/Fe₂O₃, NiO/Fe₂O₃ + 2% Ag₂O and NiO/Fe₂O₃ + 4% Ag₂O.

3.2. BET measurements

The specific surface area (S_{BET}) conducted at -196°C of pure and doped samples calcined at 500, 800 and 1000°C was determined from nitrogen adsorption isotherms. Fig.5. represents the corresponding isotherms of the samples calcined at 500 °C, they are of type III, reflecting the very low affinity of nitrogen to the surface. Table 1 indicates very low surface area for the prepared samples which is slightly changed with Ag₂O doping %.

3.4. Catalytic measurements

The catalytic conversion of *iso*-propanol was studied using flow system under normal pressure over pure and doped NiO/Fe₂O₃ samples precalcined at 500, 800 and 1000°C.

Preliminary experiments showed significant catalytic activity and the durability of the investigated catalysts. This was done by carrying out the experiment on one and the same catalyst five times showing the same catalytic activity towards *iso*-propanol conversion. The reaction products indicate that the reaction proceeds via two processes: 1- dehydration and 2- dehydrogenation. The products are propene, diisopropyl ether and acetone which is the major product as emphasized with GLC. Another side reaction takes place which is the self-condensation of the produced acetone followed by hydrogenation to give methyl isobutyl ketone (MIBK)³². The total conversion of *iso*-propanol and catalyst selectivity towards various products was much affected by the amount of dopant, calcination temperature and reaction temperature.

Figure 6 shows the variation of the total conversion % of *iso*-propanol over pure and doped calcined samples with different temperatures, where (a) represents the un-doped sample, (b) sample doped with 2% Ag₂O and (c) that doped with 4% Ag₂O. It is obvious that the catalytic activity decreases with calcination temperature. The maximum catalytic conversion over pure and doped samples was observed at 400 °C for all samples calcined at 500 and 800°C while the samples calcined at 1000°C have the highest conversion at 450°C, generally the

sample doped with 4% Ag₂O and calcined at 500 °C is the most active one, and the catalyst doped with 2% Ag₂O is the least active one.

Figure 7 shows the variation of products % of *iso*-propanol conversion over the investigated system calcined at 500°C. Acetone is the main product and the highest yield is produced over sample doped with 4% Ag₂O, the others are propene, diisopropyl ether and methyl isobutyl ketone.

Figure 8 reveals that the order of catalytic activity is (NiO/Fe₂O₃+ 4% Ag₂O) > (NiO/Fe₂O₃) > (NiO/Fe₂O₃+ 2% Ag₂O).

Inspection of the obtained data given in Table 3 and Figs. 6-8, we can observe that; i) All the investigated solids act as dehydrogenation and dehydration catalysts and more selective towards acetone formation. ii) Dehydration process proceeds with limited quantities forming propene and diisopropylether. The latter produced in limited quantities with all investigated samples and its selectivity slightly changed with calcination temperatures, reaction temperatures and Ag₂O doping %. Propene was observed only with solid calcined at 500°C. iii) Aldol condensation takes place over doped and pure system forming (MIBK) and the maximum selectivity and yield were observed with catalyst calcined at 500°C. The yield and selectivity % increase with doping % and slightly changed with reaction temperature, 4% dopant system at 400°C gives maximum yield 7.75% and the selectivity to MIBK is 13.30%. iv) Total conversion and selectivity toward acetone formation increase with reaction temperature and Ag₂O doping %. The mixed solid system calcined at 500°C exhibit maximum total conversion for *iso*-propanol. It was 58.25% over catalyst doping with 4% Ag₂O at 400°C while maximum yield of acetone was 41.09% over the same solid at 450°C.

These results can be discussed in the light of the following: i) Pure and doped NiO/ Fe₂O₃ system showed high catalytic activity in the dehydrogenation of *iso*-propanol this is attributed to the fact that besides the one-component sites Ni⁺² or Fe⁺³ there will also be the mixed sites (Ni⁺² -Fe⁺³)⁵, in addition to the early formation of NiFe₂O₄ as detected by X-ray diffraction. ii) Doping with Ag₂O (2 and/or 4%) followed by calcination at 500°C increases the total conversion of *iso*-propanol and enhances the selectivity to acetone formation and to MIBK. This may be explained in the light of the nature of catalytic material used in MIBK synthesis from *iso*-propanol in one step. This material contains in intimate contact the metallic and acid – base sites required for consecutive reactions leading to MIBK. iii) Further increase in calcination temperature to 800 and 1000°C decreases the

catalytic activity of the investigated system this may be due to sintering effect, but the investigated catalyst still have detectable catalytic activity and selectivity to acetone formation and MIBK. This

may be attributed to the increase of concentration of NiFe_2O_4 compound.

Table 1: The variation of crystal size of nickel ferrite and nickel oxide with calcination temperature and doping % of Ag_2O

Samples	Crystal size of NiFe_2O_4 , nm			Crystal size of NiO , nm			(ΔE) of NiFe_2O_4 formation, kJ mol ⁻¹
	500	800	1000, °C	500	800	1000, °C	
$\text{NiO}/\text{Fe}_2\text{O}_3$	20	28	60	40	50	60	29.9
$\text{NiO}/\text{Fe}_2\text{O}_3+2\% \text{Ag}_2\text{O}$	15	48	60	39	55	61	34.2
$\text{NiO}/\text{Fe}_2\text{O}_3+4\% \text{Ag}_2\text{O}$	12	36	66	33	54	65	40.4

Table 2 : Effect of calcination temperature and Ag_2O -doping of $\text{NiO}/\text{Fe}_2\text{O}_3$ system on the peak height of main diffraction lines of NiO , Fe_2O_3 , NiFe_2O_4 and Ag phases

Pure and doped samples	Calcination temperature, °C	S_{BET} m ² /g	NiO (a.u.) (d=2.08) (100%)	Fe_2O_3 (a.u.) (d=2.69) (100%)	NiFe_2O_4 (d=2.94) (29%)	Ag (a.u.) (d=2.35) (100%)
$\text{NiO}/\text{Fe}_2\text{O}_3$	500	10.3	1358	263	87	----
2% Ag_2O	500	10.1	1225	217	88	----
4% Ag_2O	500	12.2	1032	175	60	----
$\text{NiO}/\text{Fe}_2\text{O}_3$	800	5.6	1527	88	259	----
2% Ag_2O	800	5.0	1417	107	521	54.7
4% Ag_2O	800	4.6	1367	34	447	28.7
$\text{NiO}/\text{Fe}_2\text{O}_3$	1000	2.4	1346	---	581	----
2% Ag_2O	1000	2.3	1642	38	654	43
4% Ag_2O	1000	2.3	1639	40	639	162

Table 3: Effect of calcination temperature and Ag_2O –doping of $\text{NiO}/\text{Fe}_2\text{O}_3$ on total conversion of isopropanol, selectivity to propene, acetone, diisopropylether and MIBK using pure and doped samples at reaction temperature 400°C

Solid($\text{NiO}/\text{Fe}_2\text{O}_3$)+dopant concentration	Calcination temperature, °C	ΔE , kJ	Total conv. %	S_{propene} %	S_{acetone} %	$S_{\text{diisopropylether}}$ %	S_{MIBK} %
Pure solid $\text{NiO}/\text{Fe}_2\text{O}_3$	500	44.38	34.45	7.02	60.26	7.07	7.58
$\text{NiO}/\text{Fe}_2\text{O}_3+2\% \text{Ag}_2\text{O}$	500	44.82	29.97	2.47	61.09	8.31	8.54
$\text{NiO}/\text{Fe}_2\text{O}_3+4\% \text{Ag}_2\text{O}$	500	43.03	58.25	1.58	64.26	13.30	8.64
Pure solid	800	49.34	32.02	7.04	63.87	4.59	5.84
$\text{NiO}/\text{Fe}_2\text{O}_3+2\% \text{Ag}_2\text{O}$	800	59.74	28.42	–	68.61	5.42	6.58
$\text{NiO}/\text{Fe}_2\text{O}_3+4\% \text{Ag}_2\text{O}$	800	51.20	44.44	–	71.49	8.55	6.82
Pure solid	1000	44.40	16.19	–	75.11	7.53	5.68
$\text{NiO}/\text{Fe}_2\text{O}_3+2\% \text{Ag}_2\text{O}$	1000	50.37	15.54	–	56.43	6.31	9.52
$\text{NiO}/\text{Fe}_2\text{O}_3+4\% \text{Ag}_2\text{O}$	1000	50.67	17.46	–	71.82	4.29	7.27

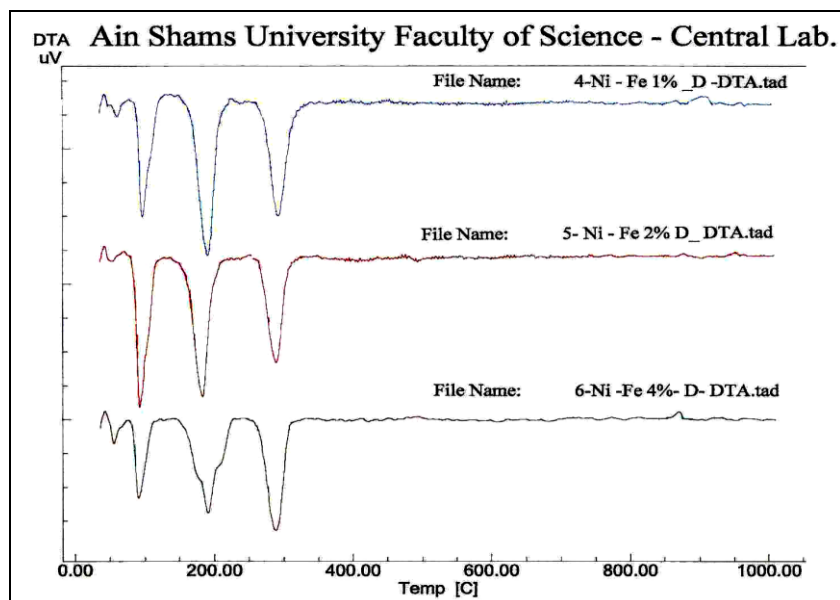


Fig.1. DTA of pure and doped mixed solids with formula $(\text{NiNO}_3 \cdot 9\text{H}_2\text{O} + 3\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} + 2\text{or } 4\% \text{AgNO}_3)$.

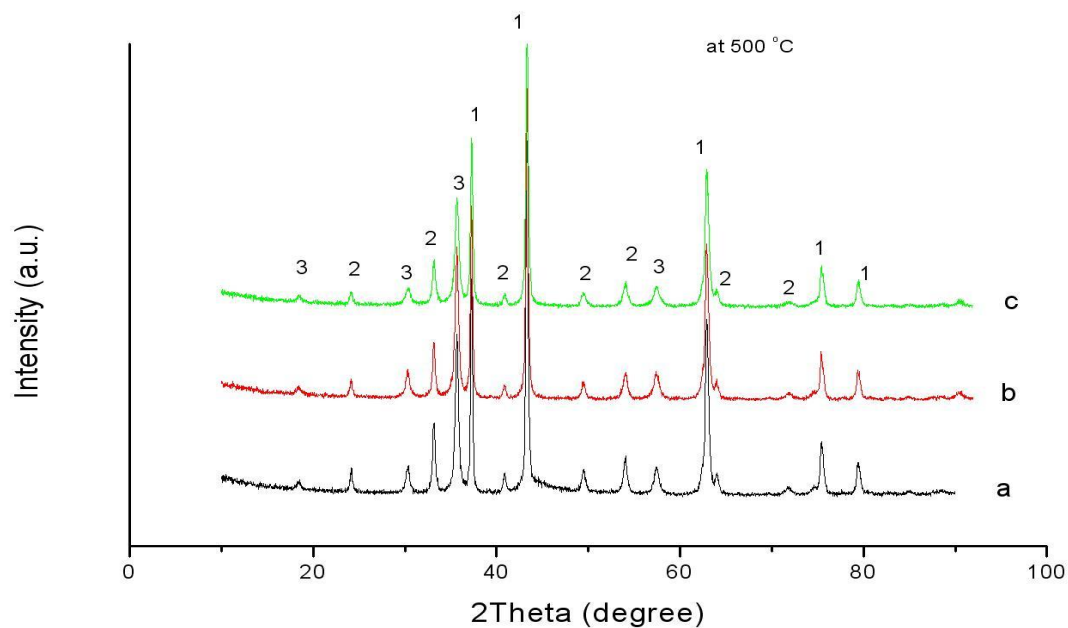


Fig.2. XRD patterns of pure and doped solids precalcined at 500 °C (a) pure, (b) doped with 2% Ag_2O and (c) doped with 4% Ag_2O [1-NiO, 2- Fe_2O_3 and 3- NiFe_2O_4].

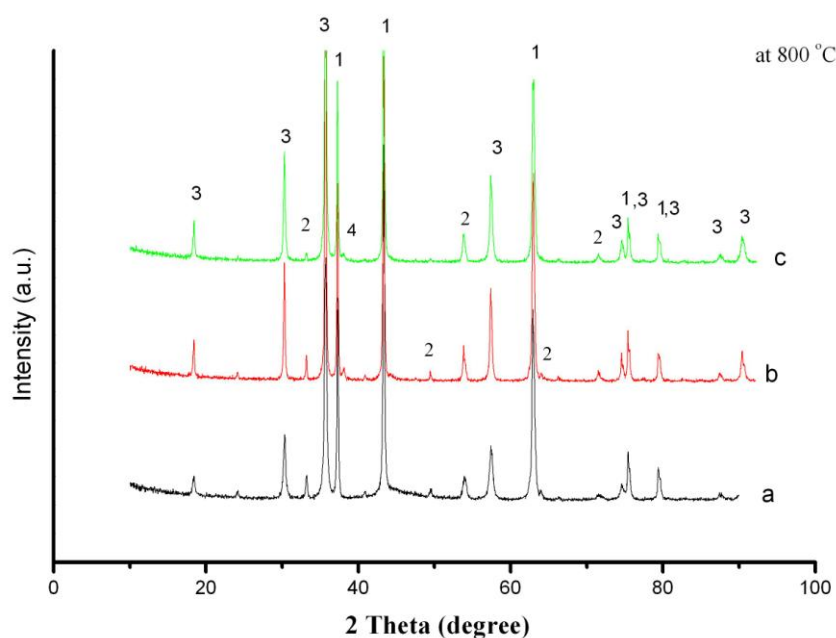


Fig.3. XRD patterns of pure and doped solids precalcined at 800 °C (a) pure, (b) doped with 2%Ag₂O and (c) doped with 4%Ag₂O [1-NiO, 2-Fe₂O₃ and 3-NiFe₂O₄].

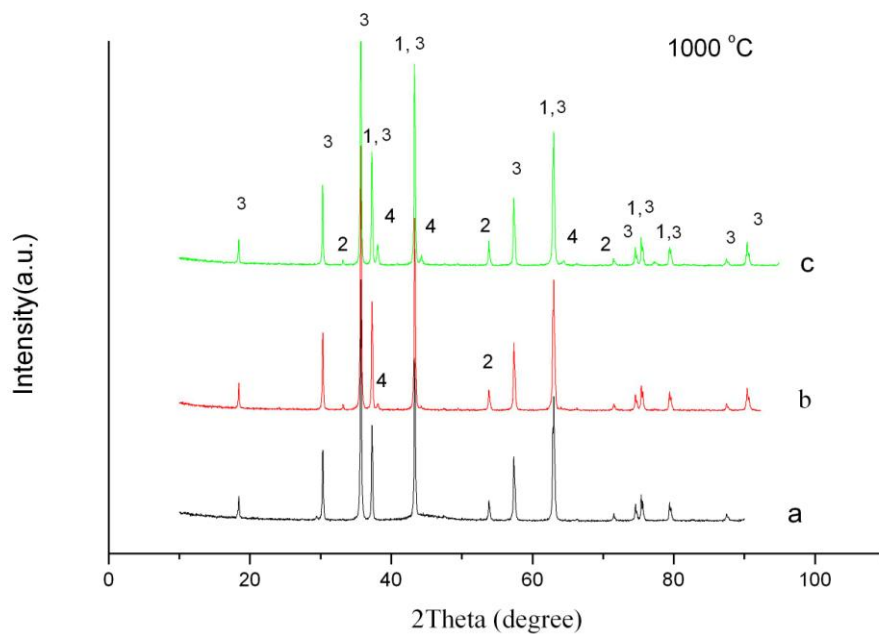


Fig.4. XRD patterns of pure and doped solids precalcined at 1000 °C a) pure, (b) doped with 2%Ag₂O and (c) doped with 4%Ag₂O [1-NiO, 2-Fe₂O₃, 3-NiFe₂O₄ and 4-Ag₂O].

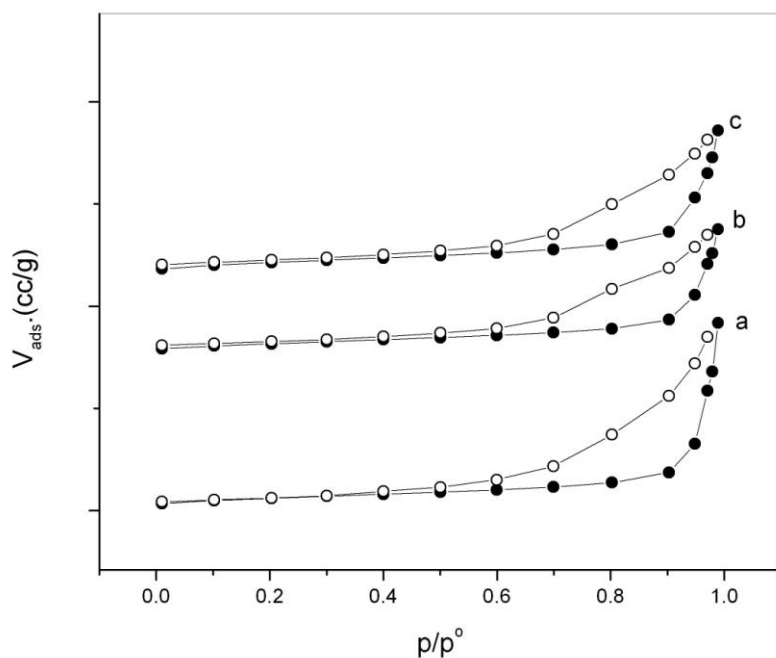


Fig.5. N₂ adsorption-desorption isotherms of pure and doped samples calcined at 500°C (a) pure, (b) doped with 2%Ag₂O and (c) doped with 4%Ag₂O.

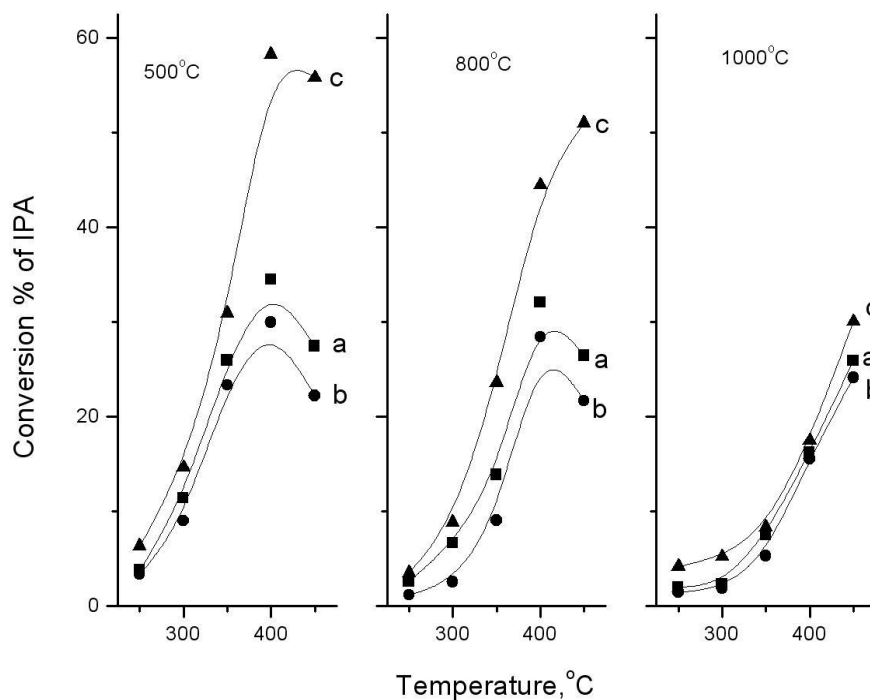


Fig.6. Catalytic conversion of *iso*-propanol on pure and doped samples calcined at 500, 800 and 1000°C.

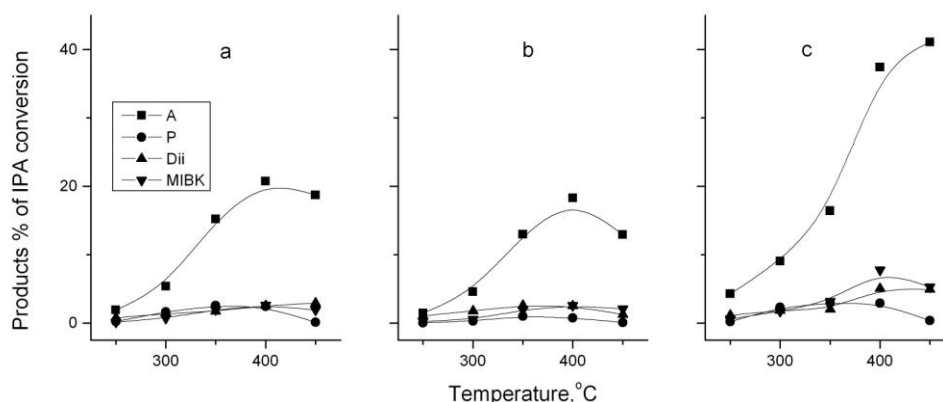


Fig.7. Products % of IPA conversion on pure and doped samples calcined at 500°C.

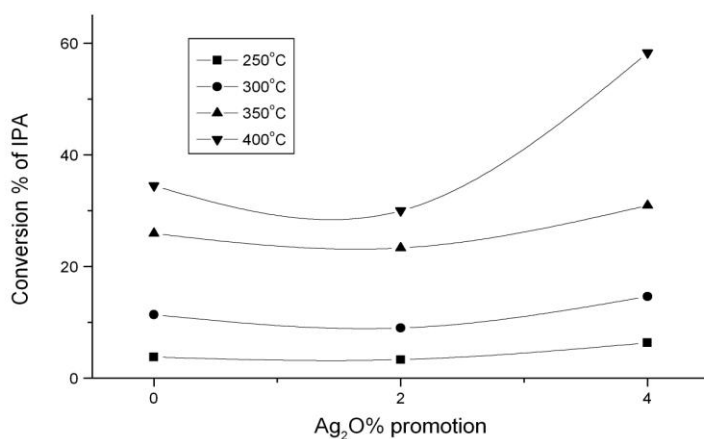


Fig.8. Effect of Ag₂O doping % on the catalytic conversion of IPA over pure and doped samples calcined at 500°C.

4. Conclusions

1. Treatment of equimolar proportions of nickel nitrate and ferric nitrate with AgNO₃ (2 and 4%) enhanced the thermal decomposition of these salts to NiO and Fe₂O₃.
2. Solid interaction between α -Fe₂O₃ and NiO occurred at temperatures starting from 500°C to produce nanocrystalline NiFe₂O₄ and NiO. This was accompanying with the formation of silver ferrite which decomposed at higher temperature yielding silver metal and ferric oxide. The activation energy of NiFe₂O₄ formation was found to be 30, 34 and 40 kJ mol⁻¹ respectively.
3. The surface area of NiO/ Fe₂O₃ system was found to be of small value with type III adsorption isotherms. Doping with a small amount of Ag₂O slightly increase the surface area ,while heating the studied samples to 800 and 1000 °C results in a sharp decreased in surface area.
4. The catalytic conversion of *iso*-propanol using pure NiO/ Fe₂O₃ and Ag₂O-doped shows that acetone is produced as the major product and another side reaction takes place which is the self-condensation of acetone to methyl isobutyl ketone (MIBK). Ag₂O-doping of NiO/ Fe₂O₃ system enhances the total conversion of *iso*-propanol and the selectivity to MIBK to 7.75 and

13.30 % respectively. This may be attributed to the presence of the pairs of active sites.

5. Catalytic activity and selectivity to MIBK did not decrease by rising the reaction temperature to 400°C with doped system which may be attributed to the fact that, Ag₂O-doping decreases coke formation.

Corresponding author

M.A. El-Kherbawi

Department of Chemistry, Women faculty for Science, Ain Shams University, Asmaa Fahmi Street, Cairo, Egypt

magdaelkherbawi@hotmail.com

5. References:

1. A. Tsyganok, P.J.E.Harlick, A. Sayari, *Catalysis Communication* 8 (5) (2007) 850.
2. S.A. El-Molla, *Appl. Catal. A* 298 (2006) 103.
3. A.A. Zahran, W.M. Shaheen, G.A. El-Shobaky, *Materials Research Bulletin* 40 (2005) 1065.
4. W.M.Shaheen, *Materials science and Engineering B* 135(1) (2006) 30.
5. W.M.Shaheen, *Materials science and Engineering A* 445-446 (2007) 113.
6. M.A.A. El-Masry, A. Gaber, E.M.H. Khater, *J. Thermal analysis*, 52(1998) 489.
7. T.Nissinen, M. Leskela, M. Gasik, J.Lamminen, *Thermochim.Acta* 427(2004) 155.
8. J.Estelle, P.Salagre, Y. Cesteros, M. Serra, F. Medina, J.E. Sueiras, *Solid State ionics* 156 (2003) 233.
9. P.R.Bandaru, C.Daraio, S.Jin, A.M.Rao, *Nat.Mater.*4 (2005) 663.
10. L.Krusin-Elbaum, D.M.Newns, H.Zeng, V.Derycke, J.Z.Sun, R.Sandstorm, *Nature (London)* 437 (2004) 672.
11. O.V.Salata, *J. Nanobiotechnol.*2 (2004)1.
12. B.Baruwati, R.K.Rana, S.V.Manorama, *J.Appl.Phys.* 101 (2007) 014302.
13. J.Wang, Y.Zhu, W.Li, Q.Chen, *Mater. Latt.* 59 (2005) 2101.
14. A.Chatterjee, D. Das, S.K. Pradhan, D.Chakravorty, *J.Magn.Magn.Mater.* 127 (1993) 214.
15. J.Azadmanjiri, S.A. Seyyed Ebrahimi, H.K. Salehani, *Ceramics International* 33 (2007) 1623.
16. S.G.Doh, E.B. Kim, B.H. Lee, J.H. Oh, *J. Magn. Magn. Mater.* 272-276 (2004) 2238.

17. G.A. El-Shobaky, G.A. Fagal, A. Abd El-Aal, A.M. Ghozza, *Thermochim. Acta* 256(1995) 429.
18. H.G. El-Shobaky, *Thermochim. Acta* 343(2000)145.
19. N.R.E.Radwan, H.G. El-Shobaky, *Thermochim. Acta* 360(2000)147.
20. G.A. El-Shobaky, N.R.E.Radwan, F.M.Radwan, *Thermochim. Acta* 380(2001) 27.
21. J.A. Toledo, M.A. Valenzuela, P. Bosch, H. Armendariz, A.Montoya, N.Nava, A. Vazquez, *Appl.Catal. A* 198(2000)235.
22. T.Konvicka, P.Mosner, Z. Solc, *J. Therm. Anal. Calorim.*60 (2000) 629.
23. H.G. El-Shobaky, N.R.E. Radwan, *Thermochimica Acta* 398 (2003) 223.
24. D. Stoppels, *J. Magnetism and Magnetic Materials* 26 (1982) 306.
25. Y.Z. Chen, C. M. Hwang, C.W. Liaw, *Appl. Catal. A* 169 (1998) 207.
26. L.M. Gandia, M. Montes, *Appl. Catal. A* 101 (1993) L1-L6.
27. W. Nicol, E.L. du Toit, *Chem. Eng. Process*, 43 (2004) 1539.
28. J.I. Dicosimo, G. Torres, C.R. Apesteguia, *J.Catal.*208 (2002) 114.
29. P.A.Webb, C.Orr, "Analytical Methods in Fine Particles Technology" *Micromeritics Instrument Corp., Norcross* (1997)55.
30. S.J.Gregg, K.S.Sing, "Adsorption, Surface Area and Porosity" 2nd ed., *Acad.Press, San Diego*, (1982).
31. E.M.Ezzo, M.A. El-Kherbawi, M.K. El-Aiashi, *Mans.Sci.Bull. (A Chem.)*31, 2(2004)13.
32. M.A.Hasan, M.I. Zaki, L.Pasupulety, *J. of Molec. Catal.* 178 (2002) 125.

7/7/2010