

Physicochemical and Catalytic Conversion of Iso-propanol over NiO-doping/nanosized ZnO-Fe₂O₃ system

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Catalytic activities of solids on isopropanol conversion at 200–400 °C using flow method. Addition of NiO and increasing the heating temperature stimulated ZnFeO₄ formation. Crystallite size of ZnFeO₄ phase varied between 11.5 and 28.6 nm. The increasing of calcination temperatures and/or by increasing the amount of dopant of various solids led to decrease of their S_{BET}. The decrease of S_{BET} might be attributed due to the creation of anionic and cationic vacancies which might increase the sinterability. Isopropanol conversion of the investigated solids increased which might be attributed to the formation of cationic and anionic vacancies which accelerate reduction-oxidation cycles.

Keywords: NiO-doping, Isopropanol conversion, Zinc ferrite, Reduction-oxidation cycles.

Introduction

In the recent years, there was an increase in the volume of waste water due to the increase in industrial usage. Various industries such as pharmaceutical, cosmetic, textile, and rubber contain aliphatic organic solvents which are often flammable, malodorous and potentially toxic to aquatic organisms [1]. The common organic solvent was 2-propanol and it was important environmental issue to its removal. There were many methods in purifying wastewater containing 2-propanol: (i) Distillation is very energy intensive and the 2-propanol water separation may be complicated if the 2-propanol concentration of the wastewater approaches the azeotropic value. (ii) Wastewater biological treatment may require further disinfection via chlorination to kill harmful bacteria [2]. Acidic sites are responsible for the conversion of 2-propanol to give propene (dehydration). This process is potentially attractive because the propylene/water separation is much easier than the 2-propanol/water separation. Dehydrogenation to give acetone is catalyzed in a concerted fashion by both acidic and basic sites [3, 4].

Dehydrogenation or oxidative dehydrogenation of isopropanol has been taken as a model test for checking the catalytic potential of many catalysts [5,6]. There were three reasons for studying the catalytic dehydrogenation of isopropanol to acetone in aqueous medium; (i) to improve the water quality in terms of isopropanol contamination, (ii) testing the selectivity of the catalyst for acetone conversion and (iii) recovery of acetone as useful industrial product by fractional distillation or rotary evaporation.

Many industrial applications used ferrites which can be prepared by different methods [7-11]. Many methods of synthesis have been developed to obtain fine particles with controlled shapes and sizes [7-12]. The prehistory of parent solids, their ratio and the addition of small amounts of certain foreign oxides affected the solid-solid interaction between ferric oxides and transition metal oxides [7-13]. Treating the transition metal ferrites with small amounts of other transition metal cations modified their activity and selectivity [9, 10].

The present work discussed surface and crystalline phase of NiO-doping of ZnO/Fe₂O₃ system. The role of calcination temperatures (500

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and 700°C) and dopant concentration (0.05 – 0.15 mol% NiO) has been investigated. Isopropanol conversion at 200–400 °C using flow method was studied.

Experimental

Materials and catalyst preparation

Zinc and iron mixed oxides system having the formula $0.5 \text{ ZnO-Fe}_2\text{O}_3$ was prepared by coprecipitation method from their nitrate solutions using 1 M NaOH solution at 70 °C and pH=8. The obtained precipitate was thoroughly washed by distilled water till free from Na and nitrate ions. The obtained solid was dried at 110 °C until constant weight then heated in air at 500 and 700°C for 4 hr. The NiO-doped samples were prepared by treating a known mass of uncalcined system with definite amounts of nickel nitrate dissolved in the least amounts of distilled water sufficient to make pastes. The pastes were dried at 110 °C until constant weight then heated in air at 500 and 700 °C for 4 hr. The concentrations of NiO added were 0.05, 0.1 and 0.15 mol%. The employed chemicals were of analytical grade supplied by Fluka company [6, 8].

Techniques

X-ray powder diffractograms of variously supported solids calcined at 500 and 700 °C were determined using a Bruker diffractometer (Bruker D 8 advance target). The patterns were run with copper K_α with secondly monochromator ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 40 mA. The scanning rate was 0.2° in 2θ . min^{-1} for phase identification and line broadening profile analysis, respectively. The crystallite size of the phases present in pure and variously supported solids was determined using the Scherrer equation [15]:

$$d = K \lambda / \beta_{1/2} \cos \theta$$

where d is the mean crystalline diameter, λ is the X – ray wave length, K is the Scherrer constant (0.89), $\beta_{1/2}$ is the full width at half maximum (FWHM) of the main diffraction peaks of the crystalline phase present and θ is the diffraction angle.

The specific surface areas (S_{BET}) of various catalysts were determined from nitrogen adsorption-desorption isotherms measured at -196 °C using conventional volumetric apparatus. Before undertaking such measurements, each sample was degassed under a reduced pressure of 10^{-5} Torr for 3 hr at 200°C.

The catalytic conversion of isopropanol was carried out over various catalysts within 200–400 °C using a flow method. The reactant (pure isopropanol) was induced using a microdose pump (Unipan 335A) via pure nitrogen gas flowing at a rate varying between 7.2 and $18.7 \times 10^{-2} \text{ ml.min}^{-1}$. The catalyst sample (100 mg) was introduced into a quartz reactor and put between two silica wool beds. The catalyst sample was activated by heating at 400°C for 2 hr. in a current of dry air free from CO_2 then cooled down to the temperature of the catalytic reaction. The gaseous and liquid products of the catalytic reaction were analyzed using programmed chromatograph (Perkin-Elmer 8600) double flame ionization detector on a column 5% CW1540 on CSORB (Gaw-DMCs) which was applied for alcohols using pure nitrogen as a carrier gas[16].

Results and Discussion

XRD investigated of pure and variously doped solids

Figures 1 and 2 show the X-ray diffractograms of pure and different treated solids heated at 500 and 700 °C, respectively. The crystallite size of ZnFe_2O_4 of different investigated solids was given in Table 1.

Table 1 and Fig. 1 and 2 reveal the following:
 (i) All solids consisted of poorly crystalline ZnFe_2O_4 (22-1012 JCPDS-ICD, copyright 2001). There is no diffraction peaks of both ZnO and $\alpha\text{-Fe}_2\text{O}_3$ might suggest their entire participation in ZnFe_2O_4 formation and/or a possible presence of some of these un-reacted oxides in a very poorly crystalline state that could not be easily detected by X-ray diffractometer [6,8]. The degree of crystallinity and/or abundance of ZnFe_2O_4 formed in various solids could be measured by the peak area of the diffraction line at $d=2.52\text{\AA}$.
 (ii) ZnFe_2O_4 formation enhanced to an extent proportional to the amount of NiO added. This could be shown by the peak area of the main diffraction line of ZnFe_2O_4 ($d=2.52\text{\AA}$) which was determined and found to be 49, 66, 82 and 93 a.u. for pure and samples treated with 0.05, 0.1 and 0.15 mol% NiO, respectively for solids calcined at 500 °C. The main diffraction line of ZnFe_2O_4 for pure and those doped with 0.05, 0.1 and 0.15 mol% NiO for solids calcined at 700°C was found to be 33, 52,113 and 133 a.u., respectively.
 (iii) the crystallite size of ZnFe_2O_4 increased by increasing the NiO added to the solids calcined at 500 and 700°C.

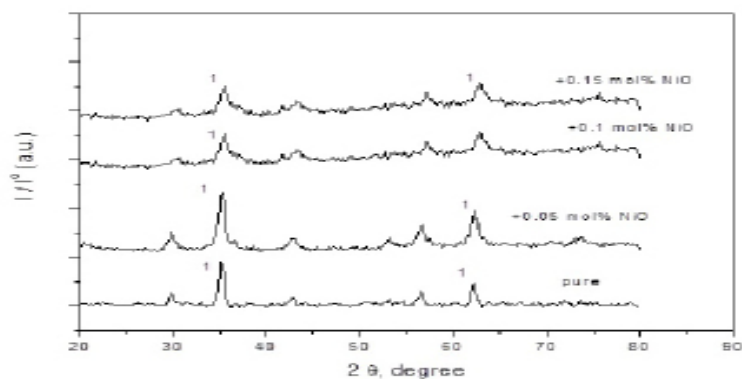


Fig. 1. XRD diffractograms of pure and NiO-doped ZnO/Fe₂O₃ solids calcined at 500 °C, 1. ZnFe₂O₄

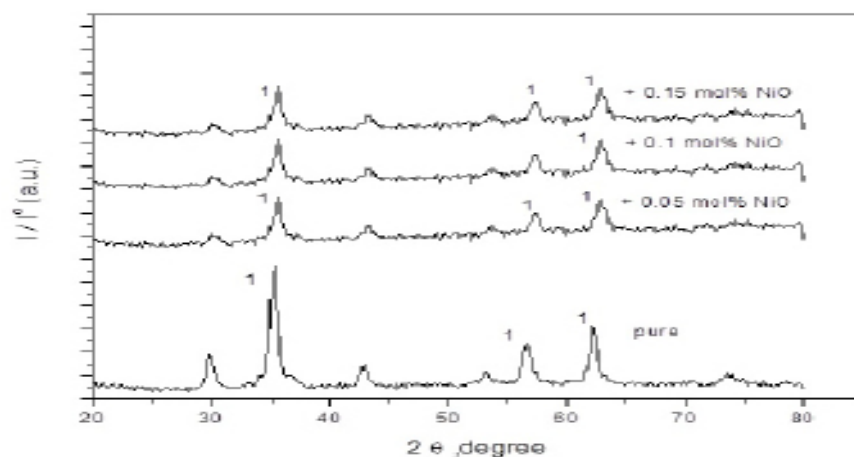
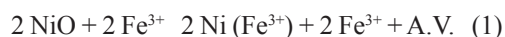


Fig. 2. XRD diffractograms of pure and NiO-doped ZnO/Fe₂O₃ solids calcined at 700 °C, 1. ZnFe₂O₄

The reason of the stimulation effect of NiO-doping might be due to increasing the mobility of reacting cations participating in the formation of ZnFe₂O₄. Mechanisms by adopting Kröger's notations [17] might clarify this speculation as follows:



The reactions followed by formation of cationic and anionic vacancies (reaction 1 and 2)

are expected to enhance the solid-solid interaction between the free oxides yielding ZnFeO₄. The formation of these cationic and anionic vacancies might be followed by a decrease in S_{BET} (*c.f.* specific surface area section).

surface areas of different investigated catalysts

The S_{BET} values are given in last column of Table 1. Table 1 shows the following: (i) A significant decrease of specific surface areas of pure and different doped solids heated at 500 to 700 °C reaching to 35%, 28%, 21% and 17%

for un-doped, 0.05, 0.1 and 0.15 mol.% NiO, respectively. (ii) A progressive decrease in the specific surface areas of the doped solids to an extent proportional to the amount of dopant added. The presence of 0.15 mol.% NiO brought about decrease of 33% and 13% in S_{BET} for solids calcined at 500 and 700 °C, respectively.

Increasing the mobility of reacting cations participated in ZnFe_2O_4 formation might be the reason of the changes observed in the S_{BET} due to the NiO-doping might be attributed to a possible via creation of cationic vacancies (*c.f.* reactions 1 and 2). The sinterability might increase by creation of such vacancies.

Catalytic conversion of isopropanol over investigated solids

Iso-propanol conversion was carried out over pure and variously doped solids heated at 500 and 700 °C. The percentage of conversion as a function of reaction temperature which varied between 200- 400 °C was investigated [15]. Figures. 3 and 4 depicted the relationship between % conversion and reaction temperature for the reaction carried out over various solids heated at 500 and 700 °C. Table 2 revealed the catalytic selectivities towards the reaction product as a function of the reaction temperature over various catalysts calcined at 500 and 700 °C, respectively. Table 2 and Fig.

3 & 4 showed the following: (i) For pure solids calcined at 500 °C, the percentage of isopropanol conversion as a function of reaction temperature increases progressively reaching a maximum limit at 325 °C then suffers a limited small decrease. (ii) For doping solids calcined at 500 °C, the percentage of isopropanol conversion increases as a function of reaction temperature and to an extent proportional to the amount of NiO-doping. (iii) Pure and doped catalysts calcined at 700 °C, the percentage of conversion increases as a function of temperature of the reaction and to an extent proportional to the amount of NiO-doping. (iv) All investigated solids have selectivities towards acetone formation. The production of acetone through dehydrogenation process [15]. Acetone formation selectivity increased with increasing the reaction temperature and NiO-doping.

The observed significant increase in isopropanol conversion of the investigated solids might be attributed to the increase of ZnFe_2O_4 formation (most catalytic constituent) [18, 19] accompanied by the formation of cationic and anionic vacancies which accelerate reduction-oxidation cycles.

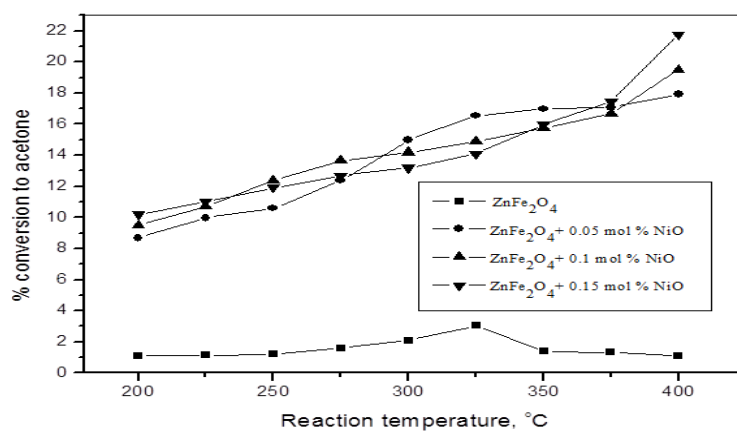
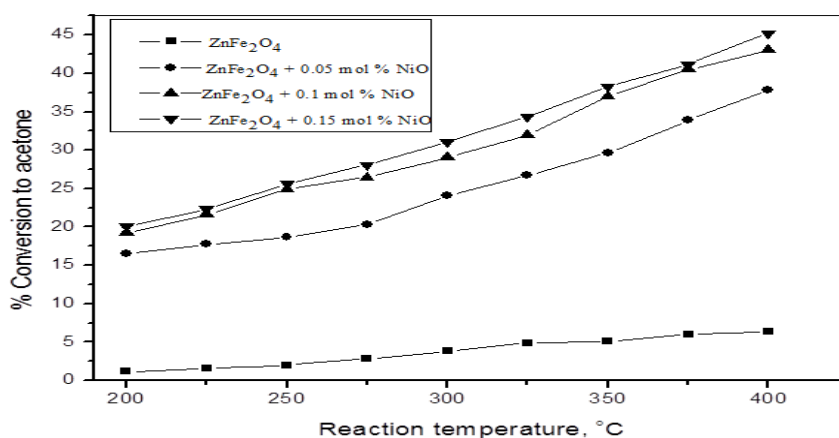
Conclusions

TABLE 1. Crystallite size of ZnFe_2O_4 for the investigated solids and Specific surface areas, $\text{m}^2\cdot\text{g}^{-1}(\pm 0.5)$, of pure and variously doped solids being calcined at 500 and 700 °C.

Solid	Calcination temperature, °C	Crystallite size (nm)	S_{BET} (m^2/g)
0.5 mol% Fe_2O_3 + 0.5 mol% ZnO	500	28.6	105.1
+ 0.05 mol% NiO	500	13.4	86.7
+ 0.1 mol% NiO	500	12.8	76.7
+ 0.15 mol% NiO	500	11.5	71.6
0.5 mol% Fe_2O_3 + 0.5 mol% ZnO	700	17.5	68.8
+ 0.05 mol% NiO	700	17.2	62
+ 0.1 mol% NiO	700	15.1	60.4
+ 0.15 mol% NiO	700	13.5	59.7

TABLE 2. Dehydrogenation selectivity of the investigated solids calcined at 500 and 700°C

Solid	% selectivity at 500 °C	% selectivity at 700 °C
0.5 mol% Fe ₂ O ₃ + 0.5 mol% ZnO	3.1	6.75
+ 0.05 mol% NiO	21.82	61.01
+ 0.1 mol% NiO	24.22	68.1
+ 0.15 mol% NiO	31.2	73.09

**Fig. 3.** Effect of reaction temperature on the catalytic conversion of isopropanol over different catalysts calcined at 500 °C.**Fig. 4.** Effect of reaction temperature on the catalytic conversion of isopropanol over different catalysts calcined at 700 °C.

Main conclusions that may be drawn from the results obtained:

1. Nano-crystalline $ZnFe_2O_4$ phase resulted from thermal treatment of zinc/ferric hydroxides prepared by coprecipitation.
2. NiO-doping enhanced the formation of $ZnFe_2O_4$ phase.
3. Crystallite size of $ZnFe_2O_4$ increased by increasing NiO-doping.
4. NiO-doping led to a progressive decrease in specific surface area.
5. All investigated solids have selectivities towards acetone formation.

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الخواص الفيزيوكيميائية والتحويل الحفزي لكحول الايزوبروبانول علي خليط من اكاسيد الحديد والكوارصين
النانوية والمشابيه باكسيد النيكل

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تم دراسة النشاطية الحفزية للعينات في تحويل كحول الايزوبروبانول عند درجات حرارة تتراوح بين 200-400 درجة مئوية بطريقة التدفق. وقد وجد ان اضافة اكسيد النيكل مع زيادة درجة الحرارة يعمل علي زيادة تكوين حديدات الكوارصين. وقد وجد ان الحجم البلوري لحديدات الكوارصين يتراوح بين 11.5 إلى 28.6 نانوميتر. ووجد ان مساحة السطح لمختلف العينات تقل اما بزيادة درجة الحرارة او بزيادة كمية الاشابة ويمكن ان يعزي النقص في مساحة السطح الي تكزين فراغات انيونية او كاتيونية والتي يمكن ان تزيد من التلبيد للعينات. وقد وجد ان تحويل الايزوبروبانول للعينات يزداد ويمكن ان يرجع ذلك الي تكوين الفراغات الانيونية والكاتيونية التي تزيد من دورات الاكسدة والاختزال.