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STUDY OF THE CATALYTIC AND SURFACE CHARACTERISTICS OF NICKEL BASED CATALYST SUPPORTED WITH METEL OXIDE FOR H/D ISOTOPIC EXCHAGE

A.M.El-Sharkawy

Chemistry department Faculty of Science, Benha University, Benha 13518, Egypt

Abstract: *Nickel catalysts supported with different metal oxides proved to be suitable for H/D isotopic exchange between hydrogen and water vapor. Ferric and aluminum oxide, proved to be suitable as promoter for nickel catalyst for such reaction* Cr_2O_3*, CoO and MnO were selected to be the second promoter for nickel catalyst in addition to* Fe_2O_3 *producing ternary catalytic systems. Accordingly,* $Ni/Fe_2O_3/AL_2O_3$*,* $Ni/Fe_2O_3/CoO$ *and* $Ni/Fe_2O_3/MnO$ *ternary catalytic systems were prepared by the Co-precipitation technique. These systems were characterized through complexometric titration, IR absorption spectroscopy, thermal analysis and x-ray analysis. The catalytic activity of the examined systems was carried out using a simple test reaction. The kinetic and thermodynamic parameters of the prepared systems were calculated and discussed followed by study the surface nature of these catalysts which characterized through specific surface area measurements, pore volume and pore radius analysis. It was concluded that not only the preparation method, but also the type of the support and its amount in the catalyst mixture are important factors which affect the surface quality of the catalyst.*

Keywords: Complexomtric analysis, x-ray analysis, IR spectra, thermal analysis, specific catalytic activities and surface catalyst nature.

INTRODUCTION

The development of catalysis has been characterized by wide applications in both industrial and nuclear technology. Scientific principles for the selection of catalysts appear to be the central problem of the development of catalysis. Nevertheless, the selection of the suitable catalysts for certain catalytic process was carried out empirically.

The scientific principles for the selection of catalysts appear to be the central problem of the development of catalysis. The crystal structure of the catalyst constituents, their melting points, their ionic radii and generally their physical characteristics must be considered in catalyst selection. The correlation between the ionic radius of the reaction constituents and of catalyst used for it is acceleration is of utmost importance. As an experimental result (1), mixed crystal formation between two substances depends mainly on the difference between their atomic radii. The difference in atomic radius does not exceed 15% of the small radius to form solid solution at room temperature. Up tell now it should be emphasized that a single theory of catalyst selection does not exist.

Metal oxides have wide applications in many fields, one of these is their use in nuclear technology (2).
Industrial catalysts are manufactured traditionally by established routes based upon empirical knowledge rather than scientific understanding of how the preparation conditions affect the catalyst performance (3).

Much is known about the behavior of catalysts, but more is required about catalyst selection, preparation, or an identification of how preparative conditions might influence its performance. Such attempts were applied on catalysts used for hydrogen - deuterium isotopic exchange reaction, which represents one of the major reactions applied for heavy water production. The present study offers a systematic study on nickel catalysts promoted with different metal oxides to produce additional binary and ternary mixed catalysts. Suitable promoters are frequently needed to get adequate performance. These may either modify the catalyst structure, so improving stability, or enhance the catalytic reactions to give better activity or selectivity.

In addition, the nature of nickel as the base catalyst material for such reaction, is always the most important factor.

The dependence of intrinsic activity on the refractory support is usually small, but there are some remarkable exceptions.

The research work on hydrogen-deuterium isotopic exchange reaction as a typical hydrogenation-dehydrogenation reaction indicated that two types of catalysts may be used one type is based on the nickel metal with the use of different metal oxides as supports, while the other type is based on platinum metal spread on porous supports such as charcoal. From these two types of catalysts, promoted nickel was preferred on platinum, according to it is low sensitivity to poisoning and low price, but is more elaborate in it is preparation.

Systematic studies (4) on catalytic H/D isotopic exchange reaction proved that aluminum oxide is the most famous promoter for nickel. Several publications were given in the literature which recommends the use of nickel/aluminum oxide, catalysts. Some of them recorded partial reduction of nickel in presence of aluminum oxide Promoter. The results given by those authors indicated that the addition of small amounts of aluminum oxide causes an increase in the catalytic activity.

Also, there are a lot of works,(5) which used chromium oxide as promoter for nickel. Chromium oxide represents a good promoter for nickel due to its high melting point. An indicating for the high efficiency of Ni/Cr_2O_3 catalyst was given by sadek and Taylor (6). The activity of this catalyst varies greatly not only according to the method of its preparation but also according to its composition. The presence of (15-20) mol% of Cr_2O_3 promoter produced an active nickel chromia catalyst for H/D exchange reaction between hydrogen and water vapor (7).
Different metal oxide promoters were used with nickel to produce a binary catalyst (8).

The idea of partial replacement of one metal oxide support by another one to produce ternary catalyst was tried (9).

The use of Al_2O_3 as second promoter for Ni/ Fe_2O_3 catalyst to give Ni/ Fe_2O_3/ Al_2O_3 ternary catalyst was based on the hypothesis, that a synergetic effect was produced which leads to an increase in the catalytic activity of such type of catalysts. This selection was based on scientific principles related to the more or less homogeneity of the physical properties of both promoters and the base nickel metal.

Cobalt oxide and Manganese oxides were also used as a second promoter with Ni/ Fe_2O_3 producing (Ni/Fe_2O_3/CoO) and (Ni/Fe_2O_3/ MnO) as ternary catalysts (10).

The selection of second promoters was based on its crystal structures and the highly melting point which are suitable to promote nickel catalyst due to the ability of such highly melting point metal oxides to hinder the partial recrystallization of nickel which leads to loss of its catalytic activity.

The specific activity of promoted nickel catalysts in the gas phase decreased to a great extent due to water condensation on it is surface. To overcome this difficulty, it is essential to search for a catalysts of high activity in both liquid and vapor phases; this is one of our aims in the present work.

EXPERIMENTAL AND DISCUSSION

1-Preparation method of ternary systems:

Nickel supported with Fe_2O_3 was promoted with Al_2O_3, CoO and MnO additional promoters to obtain ternary mixed catalysts. They were prepared by Co-precipitation of calculated amounts of the corresponding nickel, ferric, aluminum, cobalt and manganese nitrate solutions by means of sodium carbonate solution at room temperature(11). To ensure complete precipitation, one molar nitrate solutions of such elements were mixed together and added to about 1.5 molar solution of sodium carbonate under continuous mixing, the precipitate was then washed by breaking up the filter cake in a small amount of bi-distilled water and adding additional amount of about five liters bi-distilled water and stirring up the whole mass for one quarter to one half hour. The washing cycle was repeated until the catalyst becomes free from impurities.

The obtained material was then dried for twenty four hours at about 105°C calcite at 350°C - 370°C to decompose the metal carbonates into oxides, and then sieved into 0.2-0.4mm diameters grains.

Reduction of the calcite material was then made using hydrogen gas at about 320°C. The hydrogen flow rate was about 15 L/h. The obtained catalyst was stabilized before use against spontaneous oxidation in air by impregnating in bi-distilled water and allowing slow oxidation to take place while heating up to 100°C. It is advisable to refresh the catalyst before use by passing hydrogen gas at a temperature of about 160°C for two hours. the compositions of the selected catalysts under investigation are given in Table (1).

Table (1) catalyst composition of the selected systems

Catalysts	**Composition**				
	Ni	**Fe_2O_3**	**Al_2O_3**	**CoO**	**MnO**
A5	85	10	5		
A6	85	5	10		
A7	85	0	15		
A11	80	5	15		
A14	70	20	10		
B5	85	10		5	
B6	85	5		10	
B7	85	0		15	
B11	80	5		15	
B14	70	20		10	
C5	85	10			5
C6	85	5			10
C7	85	0			15
C11	80	5			15
C14	70	20			10

2-Catalyst characterization

A- Complexometric Analysis:

The real composition of the catalytic systems are investigated, their metal content was estimated by complexometric titration under the proper conditions (12)

The sample was dissolved in the least amount of 2N HCL and then evaporated to about one third of its initial volume. After cooling the solution containing the metal cation was transferred quantitatively into a measuring flask, the metal ion concent-ration was determined by EDTA. The results of some selected samples are given in table (2) they are in good agreement with the proposed tentative composition. It is found that no loss in the metal content of the catalyst mixture which does not exceed 2%.

Table (2): comlexometric Analysis of Metal percent in some selected catalysts

Catalyst	**Composition**	**Input Metal %**	**Out put metal %**
A_1	Ni Co_3	100	99.82
A_3	$Ni/Fe_2(Co_3)_3/Al_2(Co_3)_3$	90/0/10	89.53/0/10.01
A_5	$Ni/Fe_2(Co_3)_3/Al_2(Co_3)_3$	85/10/5	84/9.62/6.52
C_3	$Ni/Fe_2(Co_3)_3/MnCO_3$	90/0/10	90.21/0/10.01

B- Thermal Analysis :

The thermogravimeteric analysis (T.G.A) of some representative catalysts as well as differential thermal analysis (D.T.A) were performed by shimadzu

DT-40 apparatus in the temperature range from 25°C to up 500°C with heating rate in atmosphere of 10°C/min.

Thermal Analysis permitted the investigation of the catalyst material⁽¹³⁾. From T.G.A curves, one could calculate the percentage of metal, whereas those of D.T.A make it possible to characterize thermo graphically the process of phase transformation in the examined system. To understand the mechanism of nickel catalyst promoted with different metal oxides formation, it is of interest to observe the intermediate products formed by the calcinations process of the metal carbonate. Inspection of the D.T.A and T.G.A curves given in fig (1).

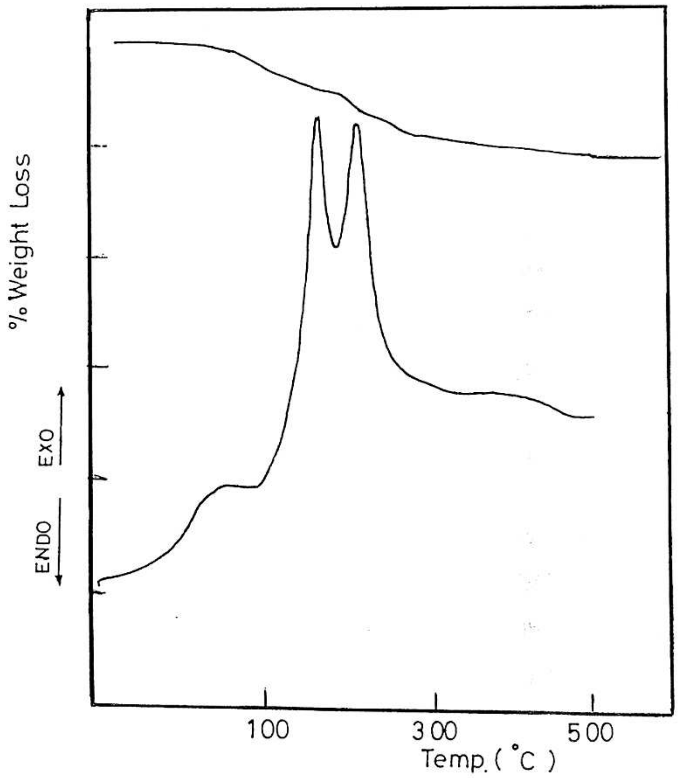


Fig. 1 DT. & TG. Curve of selected catalyst composed of (70% Ni/ 30% Fc_2O_3 /0% Al_2O_3)

For catalyst composed of (70%Ni/30% Fe_2O_3/0%Al_2O_3) show that:

(i) The weak exothermic peak on the D.T.A curve at 60 °C corresponds to phase transformation leading to the removal of humidity water molecules physically adsorbed. This peak is accompanied by an inflection on the T.G curve from which the corresponding weight loss was found to be 3%.

(ii) The D.T.A curve exhibits two strongly exothermic peak at 200°C and 250°C, due to some lattice rearrangement at the beginning of the calcinations of $Fe_2(CO_3)_3$ and $NiCO_3$ respectively leading to the formation of Fe_2O_3 and NiO as an end product, which are represented by the weak broad exothermic peak within the range 320-350°C. The relative weight loss on the T.G curve corresponds to the two peak given in fig (1) was found to be 4:3, which is actually equal to the relative percentage of carbon dioxide in $Fe_2(CO_3)_3$:$NiCo_3$.

(iii)On the basis of the percent weight loss, the thermal calcinations of this sample can be represented as following.

$$\text{Ni Co}_3\text{, Fe}_2(\text{Co}_3)_3\ (\text{H}_2\text{O})_x) \xrightarrow[-3\%]{60^\circ C} \text{NiCo}_3\text{, Fe}_2(\text{Co}_3)_3) \xrightarrow[200^\circ C]{-CO_2}$$

$$(\text{NiCO}_3\ ,\ \text{Fe}_2\text{O}_3) \xrightarrow[250\ ^\circ\text{C}]{-\ \text{CO}_2} (\text{NiO, Fe}_2\text{O}_3)$$

C) I.R Analysis :

The infrared spectra of the different selected catalysts under investigation were recorded by KBr disc technique using a perkin-Elmer 1430 double beam spectrophotometer at the examined range.

Fig (2) shows the I.R spectra of some selected catalysts and indicates that.

1) There is a broad band at 3600-3300cm^{-1} which is characteristic of the (-OH) group of the physically adsorbed water molecules. Another bond at about 1370cm^{-1} due to Fe^{3+}O^{2-} band and two bands at 590cm^{-1} and at 390cm^{-1}which may be attributed to tetrahedral and octahedral complexes of Ni- M stretching.
2) The I.R spectra of (70% Ni/ 10% Fe_2O_3/20%CoO) catalyst, show a broad band at 3600-3400cm^{-1}, characterizing the (-OH) group of the water molecules, a band at 1390 cm^{-1} which is attributed to Fe^{3+}-O^{2-} bond and three bonds at 685 cm^{-1}, 555cm^{-1}, and 405cm^{-1} which may be attributed to Ni-M and Co-M stretching bond.

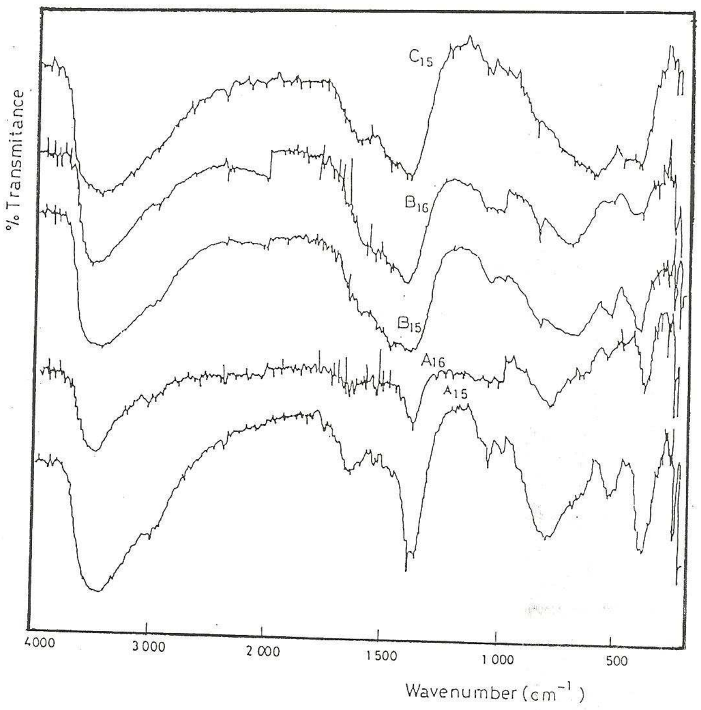


Fig.(2) IR. Spectra of catalysts A-16 (70% Ni/ 0% Fe_2O_3/ 30% Al_2O_3), B-16 (70% Ni /0% Fe_2O_3/30% CoO), A15 (70% Ni / 10% Fe_2O_3/20% Al_2O_3), B15 (70% Ni/10% Fe_2O_3/ 20%CoO), C15 (70% Ni/ 10% Fe_2O_3/ 20% MnO)

3) The infrared spectra of the 70% Ni/ 10% Fe_2O_3/ 20% Al_2O_3 catalyst show a broad band at 3600- 3300cm^{-1} characterizes the OH group present in the hydrated metal oxides.

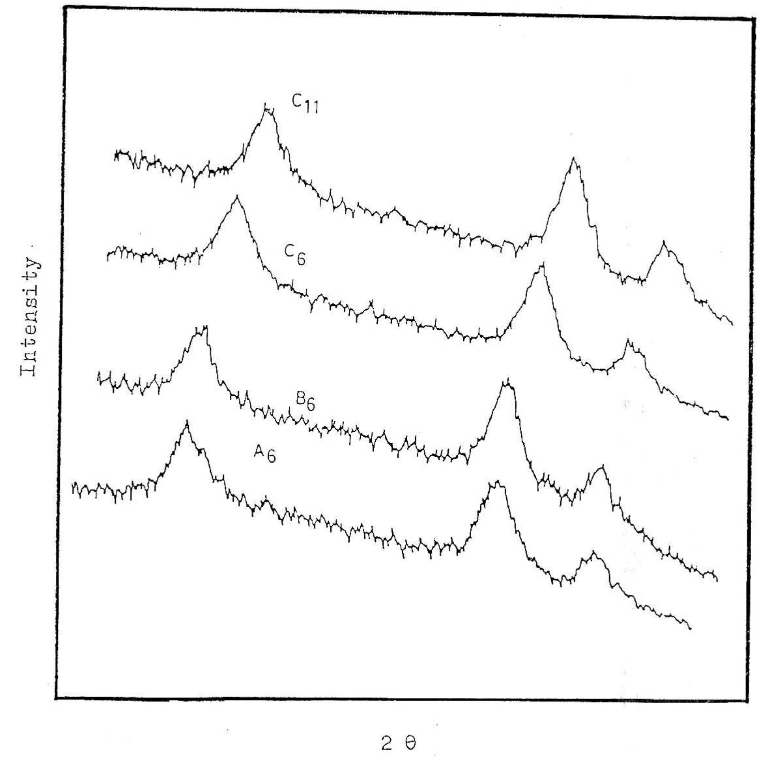
D) X- Ray Analysis :

X-ray spectroscopy represents one of the most powerful tool available for rapid determination of the feature of mixed oxide catalysts.

Examination of Nickel based catalysts promoted with different metal oxides was carried out using on X-ray diffract meter of the following specifications:

1- X-ray generator type Pw 1120/00/60.
2- Vertical type diffract meter of type Pw 1050/70.
3- Proportional detector type Pw 1965/50.
4- Vertical chromium lamp of wavelength 2290.9 Å

Fig (3) show the x-ray pattern of some selected catalysts which permits to study the structural properties of their bulk of catalysts (14)



Fig(3) X- ray diffraction pattern of catalysts A6(85%Ni/ 5% Fe_2O_3/10% Al_2O_3),

B6 (85% Ni/5% Fe_2O_3/ 10% CoO), C6 (85%Ni/ 5%Fe_2O_3/10%MnO), Cll(80%Ni/5%Fe_2O_3/15%MnO

The x-ray diffraction lines for samples composed of Ni/Fe_2O_3/ CoO correspond to d values of 2.475Å characterizing Fe_2O_3, 2.03Å and 1.76Å due to NiO and 1.497Å for CoO. These lines indicate the presence of NiO, Fe_2O_3 and CoO. The x-ray diffraction patterns for Ni/Fe_2O_3/MnO show small shift in the lines of x-ray diffraction which may be due to the presence of different types of metal oxides. The above sample produced lines having d-value of 2.436Å corresponding to Fe_2O_3, 2.113Å due to NiO and 1.486 Å attributed to MnO.
The presence of NiO in the catalyst mixture ensures partial reduction of nickel throughout it's thermal treatment

3- Specific Catalytic Activity measurement:

The specific catalytic activity of nickel catalysts promoted with different metal oxides in the liquid phase reaction was performed using the thermal decomposition of hydrogen peroxide as a simple test reaction by using gasometrical apparatus. .

In a kinetic experiment about 50mg of the sample was placed in the samplers tube at the selected temperature 0.5ml of 24M hydrogen peroxide was added. The volume of oxygen collected at S.T.P was obtained at different intervals until complete decomposition was reached. The kinetic experiments were carried out at 30°C, 40 °C and 50 °C.

Then, the specific catalytic activity AH_2O_2 could be calculated for certain amount of catalyst (weigh) by knowing the volume of oxygen (Vo_2) at ($t_{1/2}$) where $t_{1/2}$ is (the time taken for half the amount of H_2O_2 decomposition) using the following equation (15). As shown in table (4)

$$A_{H2O2}= 9\times10^{-17}\frac{Vo2}{t1/2} \cdot \frac{1}{w} \text{ moles } H_2O_2.\ Sec^{-1}.g^{-1}$$

The obtained results showed that the reaction follows first-order kinetics in all cases. The slopes of the first-order plots allow ready determination of the reaction rate constant (K) measured at a given temperature over a selected catalyst sample and the specific catalytic
activity are included in Tables (3-5).

Table (3): Catalyst A6 (85% Ni/ 5% Fe_2O_3/ 10% Al_2O_3)

t (min)	30 °C			t (min)	40 °C		
	X (m1)	(a-x)	In a/a-x X10^3		X (m1)	(a-x)	In a/a-x X10^3
5	4.8	235.2	0.0202	5	6.8	113.8	0.0530
14	6.9	233.1	0.0291	15	8.9	111.4	0.0743
20	8.0	232.0	0.0339	21	10	110.0	0.0870
30	12.1	230.9	0.0389	30	14.1	109.0	0.0961
60	12.5	227.5	0.0534	40	14.5	107.6	0.1090

90	14.8	225.2	0.0636	50	16.8	106.0	0.1240
120	16.4	223.6	0.0707	60	18.4	105.2	0.1316
∞	240	--	--	∞	120	--	--

t (min)	50 ^{o}C		
	X (m1)	(a-x)	In a/a-x $X10^3$
5	8.8	50.0	0.1823
20	10.9	47.6	0.2315
40	12	44.6	0.2966
60	16.1	42.6	0.3425
80	16.5	41.0	0.3807
120	18.8	37.2	0.4780
140	20.4	35.4	0.5276
∞	60	--	--

The Examination of the specific activity of the these selected catalytic systems for the liquid phase hydrogen peroxide decomposition are given in table (4)

Table (4): Liquid phase activity of ternary Nickel catalysts

Catalyst	**Composition %**	**(Specific activity) moles H_2O_2/S.g 10^{-17}**		
	Ni/Fe_2O_3/Al_2O_3	**30 °C**	**40 °C**	**50 °C**
A5	85/10/5	0.5	0.6	1.2
A6	85/5/10	0.1	0.3	0.7
A7	85/0/15	0.1	0.1	0.3
A11	80/5/15	0.2	0.4	0.7
A14	70/20/10	0.2	0.4	0.6
	Ni/Fe_2O_3/ CoO			
B5	85/10/5	0.1	2.2	3.2
B6	85/5/10	0.9	1.1	1.3
B7	85/0/15	0.1	0.2	1.4
B11	80/5/15	1.2	2.02	2.4
B14	70/20/10	1.4	1.7	2.1
	Ni/Fe_2O_3/ MnO			
C5	85/10/5	0.1	0.6	1.3
C6	85/5/10	0.5	0.6	0.8
C7	85/0/15	0.1	0.2	0.8
C11	80/5/15	0.8	0.9	1.6
C14	70/20/10	0.4	0.6	0.9

1) Examination of the catalyst B5 and C5 composed of 85% Ni/10%Fe2O3 and 5% CoO and MnO respectively shows that CoO is more suitable as second promoters producing an active catalyst composed of (85%Ni/10% Fe2O3/5% CoO).

2) Examination of the catalysts A6, B6 and and C6 composed of (85% Ni/5% Fe2O3 and 10% Al2O3, CoO and MnO respectively shows that the catalyst B6 (85% Ni/5% Fe2O3/10% CoO exhibits higher catalytic activity.
3) Examination of the catalysts All, Bll and C11 shows that the catalyst B11 composed of (80% Ni/5% Fe2O3 /15% CoO) has a relatively higher catalytic activity, indicating that CoO is more suitable promoters for the Binary system composed of (80%Ni/5% Fe2O3 producing active ternary catalyst of (80%Ni/5% Fe2O3/15%CoO).
4) Examination of the catalysts A14, B14 and C14 composed of (70%Ni/ 20% Fe2O3 and 10% of Al2O3, CoO and MnO respectively shows that the catalyst B14 composed of (70%Ni/ 20% Fe2O3 10% CoO) has a relatively high catalytic activity.
5) Generally, catalysts B5 and B11 composed of (80%Ni/ 5% Fe2O3/ 15% CoO) and (85% Ni/10% Fe2O3/ 5% CoO) have a relatively high activity for the Liquid phase decomposition of hydrogen peroxide as a simple test reaction.

4- Kinetic and thermodynamic Behaviors:

The kinetic study of the liquid phase reaction demonstrates that the decomposition of hydrogen peroxide over the surface of the examined catalysts is a first order reaction. The obtained result of the liquid phase reaction on the surface of different catalytic systems regarding rate constant, enthalpy, free energy of activation, entropy of activation and the activation energy as shown also in Table (5) were calculated using the following equations:

$$\Delta G^* = 2.303\ RT\ (\log \frac{R}{N} - \text{Log}\ h) - (\text{Log}\ K - \text{Log}\ T)$$

Where $\frac{R}{N} = 0.3298 \times 10^{-23}$ cal. deg^{-1}

R= 1.9871 cal . deg $^{-1}$. mole $^{-1}$

h= 1.5822×10^{-34} cal sec.

$$\Delta S^* = \frac{\Delta H^* - \Delta G^*}{T}$$

$$\Delta H^* = \Delta E^* - RT$$

Table (5) Rate constant K, enthalpy ΔH*, Free energy activation ΔG*, entropy of activation ΔS* and activation energy Ea for the thermal decomposition of H_2O_2 on ternary promoted nickel catalysts.

Catalyst	Temp °C	K Sec $^{-1}$	K.cal mol^{-1}			E_a
			ΔH^*	ΔG^*	ΔS^*	
B5	30 40 50	1.3×10^{-5} 1.4×10^{-5} 2.1×10^{-5}	8.5 5.7 5.7	17.7 18.2 18.5	- 39 - 40 - 39	6.4
B6	30 40 50	6.4×10^{-6} 7.2×10^{-6} 8.3×10^{-6}	2.4 2.4 2.3	18.1 18.6 19.1	-67 -52 -52	3

B11	30	6.7×10^{-6}	6.5	18 - 38	7
	40	1.3×10^{-5}	6.5	18 -38	
	50	1.6×10^{-5}	6.5	19 -38	
B14	30	9.1×10^{-6}	3.4	18 -40	4
	40	1.1×10^{-5}	3.4	18 -38	
	50	1.3×10^{-5}	3.3	19 -52	

The positive value of ∆G* means that the reaction does not proceed spontaneously, and the positive ∆H*value refers to heat evolution during the reaction and the positive value of the ∆S* means that the activated complex has more entropy than the reactants which is unimolcular dissociation, but the negative value of ∆S* indicates that the activated complex has less entropy than the reactant

5-Surface Area Measurements:

a- Adsorption – desorption isotherm:

Adsorption – desorption behavior of nitrogen gas on the surface of the prepared catalytic system at liquid nitrogen temperature were measured by quanta chrome Autosorb – 6 BET apparatus, the results were tabulated for selected catalyst as shown in table (6)

Table (6): Adsorption – Desorption Isotherm of Nitrogen Gas at 77k on Ternary Promoted Nickel catalysts,(85%Ni/5%Fe_2O_3/10%Al_2O_3)

P/PO	**S CC./g**	**P/PO**	**S CC./g**
0.006	**1.98**	**0.636**	**7.64**
0.012	**1.04**	**0.600**	**7.58**
0.018	**1.10**	**0.536**	**7.52**
0.024	**1.16**	**0.500**	**6.78**
0.030	**1.22**	**0.500**	**6.42**
0.036	**1.28**	**0.472**	**5.12**
0.042	**1.83**	**0.472**	**4.09**
0.100	**2.07**	**0.424**	**3.97**
0.142	**2.43**	**0.400**	**3.79**
0.200	**2.75**	**0.342**	**3.29**
0.236	**2.93**	**0.300**	**3.11**
0.242	**2.99**		
0.300	**3.17**		
0.342	**3.22**		
0.400	**3.91**		
0.424	**3.91**		
0.454	**4.03**		
0.500	**4.58**		
0.536	**4.82**		
0.600	**5.39**		

0.636	**5.80**		
0.700	**6.60**		
0.742	**6.96**		
0.800	**7.64**		
0.842	**7.82**		
0.900	**7.88**		
0.936	**8.25**		
0.978	**9.17**		
0.900	**8.06**		
0.830	**7.88**		
0.800	**7.76**		
0.742	**7.36**		
0.700	**7.70**		

The first theoretical equation relating the quantity of adsorbed gas to the equilibrium pressure of the gas was proposed by Langmuir(16). In his model, adsorption is limited to a monolayer adsorption. One basic assumption in deriving the Langmuir equation is that the energy of adsorption is constant.

The most important step in the study of adsorption came with a derivation by Brunauer, Emmet and Teller(17), for a multilayer adsorption of gases on solid surfaces such as catalysis. This multilayer adsorption theory has occupied a central position in gas adsorption studies and surface area measurements.

b-Multi point BET measurement:

The adsorption desorption data were recorded relating the volume and the relative vapor pressure (PIP°) of the adsorbate. All isotherms seem to be belong to types of Brunauer's classification(18) and form closed hysteresis loops in all cases as shown in Fig (4)

The specific surface area (S_{BET}) of catalysts were derived from the so called multi point B.E.T curves, deduced from the corresponding adsorption – desorption isotherm up to p/po= 0.35. The values of the SBET were calculated and included in table (7)

c-V_I-t Surface Area measurements:

The so called t- plots (19) relating the volume of gas adsorbed and the Deboar statistical thickness of adsorbate in angstroms (Å) were recoded and shown in Fig (5) this permit calculation of specific surface area of catalysts (St) to be compared with those obtained from the derived multi point BET plots (S_{BET}). Table (7) also summarizes the experimental data of surface area (St) in comparison with that of (S_{BET}) for the ternary promoted nickel catalysts.

d-Pore volume and pore radius measurements:

The BET measurements (20) permitted calculation of the corresponding total and commutative pore volume of the examined catalytic systems in addition to pore radius.

The results, are inclucled in table (7) too, their presence in the same table with the values of S_{BET} and St permits the choice of the suitable catalyst composition to be used for H/D isotopic exchange which is the aim of the present work.

Table (7). Surface area, Pore volume, and Pore radius of Different Selected Catalysts.

Cat	**Composition% $Ni/Fe_2O_3/Al_2O_3/CoO/MnO$**	**Surface area m2/g**		**Pore volume (c.c/g)**			**Pore radius** (Å)
		S_{BET}	**S_T**	**V total**	**Ads Vcum**	**Des Vcum**	
A5	85%Ni/10%Fe_2O_3/5% Al_2O_3	1.03	1.03	1.42	9.9	1.2	2.8
A11	80/5/15	5.9	6.6	1.6	7.5	8.8	5.2
A14	70/20/10	1.7	1.7	1.8	1.1	1.3	2.2
B5	85%Ni/10%Fe_2O_3/5% Al_2O_3	1.7	1.7	2.8	1.2	1.2	3.3
B11	80/5/15	1.4	1.4	2.8	2.1	2.2	4
B14	70/20/10	1.8	6.7	1.3	4.4	5.2	1.5
C5	85%Ni/10%Fe_2O_3/5% Al_2O_3	1.6	1.3	2.5	1.4	1.7	3.1
C11	80/5/15	1.3	1.1	3.8	2.3	3.1	6
C14	70/20/10	1.8	6.7	1.2	4.3	5.2	2

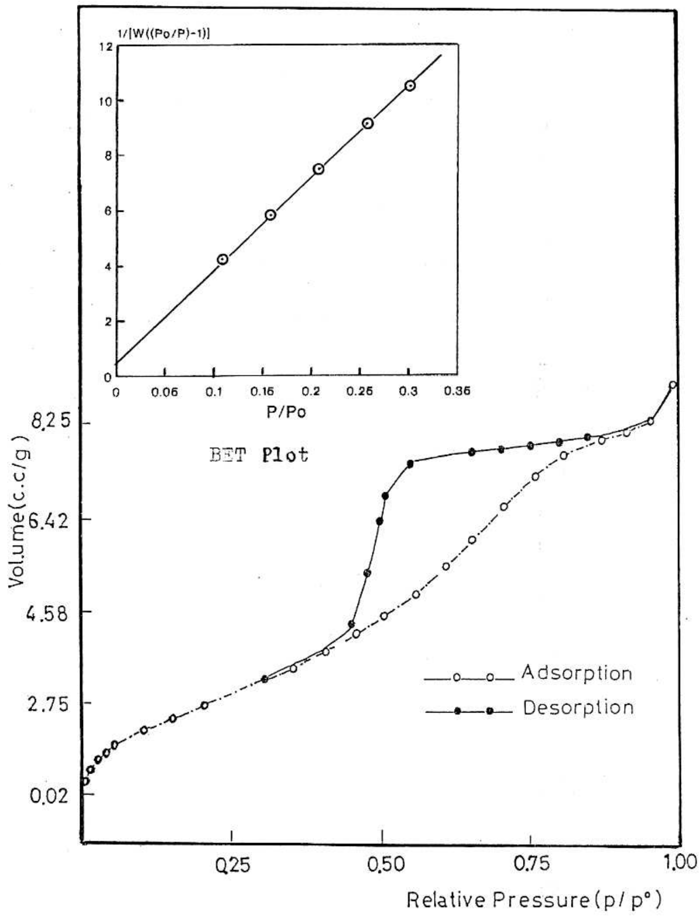


Fig (4) Adsorption – Desorption isotherm of N_2 at 77K on catalyst A-6 (85%Ni/ 5%/ Fe_2O_3/ 10% Al_2O_3)

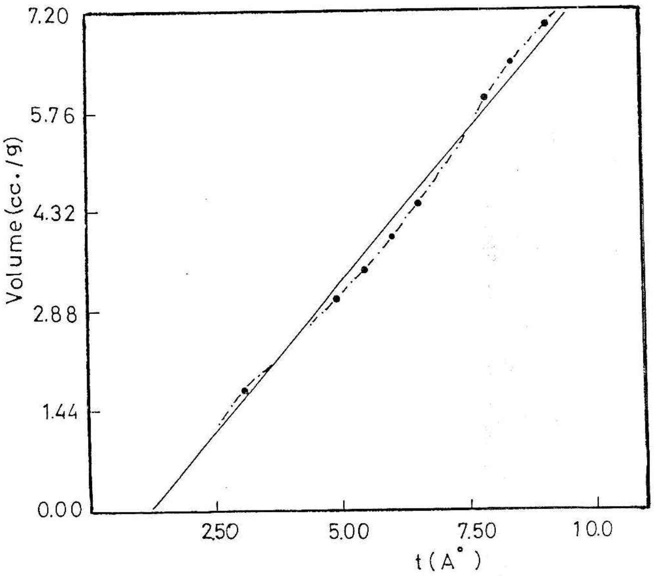


Fig (5) VL- t plots of N2 adsorption on catalyst A6 (85%Ni /5% Fe2O3/ 10% Al2O3)

6) Catalysts B5 and C5 composed of (85%Ni / 10% Fe2O3) and 5% of CoO and MnO respectively have almost the same surface area.
7) Catalysts A11, B11 and C11 composed of (80%Ni /5% Fe2O3) and 15% Al2O3, CoO and MnO respectively show higher surface area for the catalyst A11, indicating that the Al2O3 as second promoter is more suitable regarding surface extension.
8) Catalysts A14, and C14 composed of (70%Ni /20% Fe2O3) and 10% Al2O3 and MnO respectively have almost the same surface area, indicating that both Al2O3 and MnO supports have the same effect on such type of catalysts.
9) The small pores most remote the surface of the particle (21-25) will have little chance to play their parts in helping to catalyses the reaction. Consequently, unless the two catalysts being compared have two identical pore distributions and pore sizes, they would not be expected to have activities proportional to areas even if the activity per unit accessible area happened to the same. Furthermore, the very small pores probably are not participating in the catalytic reaction According the existence of such very small pores is still another reason for the lack of proportionality between catalytic reaction rate and the surface area of porous solids.
10) In general, one will not expect to find the activity(26) of a catalyst to be proportional to its surface area for a number of reasons:
11) In the first place, there is a good evidence that in many instances at least catalytic action is limited to certain active spots or active regions on the surface of the catalyst(27) these active regions may constitute only a small fraction of the total surface area arises from the fact that in porous solids frequently only the more easily accessible pores are available for the reaction that is being catalyzed.
12) The overall view on the surface area measurements (28) shows that the amount of nickel must be between (80-85% mol), and that of Fe2O3 between (0-5% mol) while these of Al2O3, CoO and MnO must be between (5-15 mol %) to obtain catalytic systems in high surface extended form and suitable for H/D isotopic exchange for heavy water production.

Conclusions

The results obtained from the present investigations are of industrials importance. The choice of metal oxides promoter suitable to support nickel is based on theoretical and experimental aspects.

Nickel based catalyst promoted with ferric oxide proved to be suitable for hydrogenation-dehydrogenation process.

-Several catalysts of different composition were prepared by Co-precipitation technique.
Nitrates were used as the most suitable starting materials.

Three catalytic systems are prepared namely: Ni/Fe2O3/Al2O3, Ni/ Fe2O3/CoO and Ni/ Fe2O3/MnO.

The nature and characteristics of other different catalysts were studied by complexometric analysis, infrared spectroscopic analysis, differential and thermogravimetric analysis and x-ray diffraction pattern, which emphases that nickel present in crystalline form, but other metal oxides promoters in amorphous character.

Surface characteristics of the prepared catalysts including the specific surface area, Pore volume and radius were performed, which shows that the amount of nickel must be between (80-85%mol), and that of Fe2O3 between (0-5% mol), while these of third promoters of Al2O3, CoO and MnO must be between (5-15% mol) to obtain catalytic systems in high surface area and suitable for H/D isotopic exchange reaction for heavy water production.

Catalytic activity measurements permitted the searching for the catalysts resisting water condensation on their surfaces and exhibiting highly catalytic activity in both liquid and vapor phase.

The performance of the reactions at different temperatures allowed the study of both kinetic and thermodynamic parameters.

1- The present work does not lay claim to creation of a theory founded on the bases of some criteria, but it tries to use some principles to produce new catalysts suitable for hydrogenation-dehydrogenation processes on scientific bases as a typical reaction of H/D isotopic exchange.

References

1).V.M.Gold Schmidt," An introduction to crystal chemistry by R.C.Evans" Cambridge university. (1948).
2) M.V.Twigg," catalyst Hand book " wolfe publishing Ltd.,(1989).
3) T.Khalil,M.Sc.Thesis,Faculty of science, Ain Shams University.,(1988).
4) P.Margineau,A.Olariu,J.Catalysis., 8,359,(1967).
5) United Kingdom Atomic energy Authority,London,patent specification800,730,sep.,(1958).
6) H.Sadek,H.S.Taylor,Am.J.Chem.Soc.,72,1168,(1973).
7) H.S.Taylor,H.Sadek,(A.J.C.S).,72,1168,(1950).
8) E.Hallaba.F.H.Abo-ElNour,E.M.Abdel Wahabe,Arab Journal of Nuclear Science and application.,6,133,(1973).
9) F.H.Abo-ElNour,H.Shutze,Isotopenpraxis.,10,391,(1972).
10) F.H.Abo-ElNour,Isotoppraxis,Bd.,16,370,(1980).
11) H.Shutze,K.Watzel,patents Shrift No 87562,Amt Four Erfindugs und patent-wesen,DDR.,(1972).
12) G.W.Frank"The Analatical uses of EDTA" D.Van-Nostrend Company Inc,Princeton New Gersy.,118,(1961).
13) D.A.Skoog,"principlesof industriaanalysis"3rd edition,saunders golden sun bnrst serio, saunder college publishing.,(1985).
14) A.Al-Suhaybani,S.Al-Khowaiter,Isotopenpraxis,18,223,(1982)
15) H.A.Ali,M.Sc.Thesis,Faculty of Science Ain Shams University.,(1976).
16) I. Longmuir, J. Am chem. Soc., 39, 1848, (1917).
17) S.Brunauer,P.H.Emmet,E.Teller,J.Chem.Soc.,60,309,(1938).
18) S.Brunauer,P.H.Emmet,E.Teller,J.Chem.Soc.,27,1745,(1955).

19) B.C.Lippens,B.G.Linsen,J.H.De-boer ,J.Catal.,3,32,(1964).
20) R.Sh.Michail,S.Brunauer,E.E.Bodor,J.Colloid and enterface Sci.,26,45,(1968).
21) M.M.Abdel-Khalik,M.M.Abdel-Badi,Isotopenpraxis., 926,336,(1990).
22) A. Khan, T. Sukonket, B. Saha, and R. Idem, Energy & Fuels, (26), 365-379, (2012)
23) T. Sukonket, A.Khan, B. Saha, and R. Idem, Energy & Fuels, (25), 864-877, (2011).
24) D. P. Debecker, V. Hulea, and P.H. Mutin, Applied catalysis A:General, (2012).
25) R. Alvarez, A. Toffolo, V. Perez and C. F. Linares, Catalysis Letters, 137, 3-4, (2010).
26) M. B. Gawade, R.K. Pandey, and R.V. Jayaram, catalysis Science and Technology, (2), 1113-1125, (2012).
27) O.F. Louis, B.K. Minsker, and A. Cecile, Applied catalysis A: General, (392), 36-44, (2011).
28) E. Fumoto, S.Sato, and T. Tokanohashi, American Chemical Society, (1092), 75-85, (2012).