ACTIVITY AND SELECTIVITY OF NANO-CRYSTALLINE NIO AND NI-METAL SUPPORTED ALUMINA SYSTEM AS BEING INFLUENCED BY MOO₃ DOPING

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ABSTRACT: *The catalytic conversion of cyclohexane was carried out on NiO and Ni-metal supported on alumina doped with MoO₃. The extent of NiO loading was 13 weight % and 8 weight %, the amount of dopant was fixed at 2 weight %. Pure and doped solids were prepared by wet impregnation method using a known weight of γ-Al₂O₃ with known amount of nickel nitrate and molybdic acid dissolved in a least amount of distilled water making paste, dried, then calcined in dry air at 500 ^{0}C. Nickel alumina doped with MoO₃ were readily obtained by heating the calcined solids in a current of H₂ at 500 ^{0}C. Physicochemical surface and catalytic property of different solids investigated were characterized by XRD, N₂ adsorption at –196 ^{0}C and catalytic conversion of cyclohexane using flow system under normal pressure at a temperature range of (400 – 480) ^{0}C. The results revealed that NiO supported alumina existed as nanocrystalline Ni and aluminum oxides, and the H₂ treatment at 500 ^{0}C resulted in the formation of big sized nickel crystals. The S$_{BET}$ of NiO-alumina suffered a measurable decrease upon doping with 2 weight % of MoO₃. The concentration of MoO₃ being far below the detection limit of X-ray diffractometer and its intense existence in the diffractograms of the doped solids calcined at 500 ^{0}C suggested on effective migration of Mo- species from the bulk to the surface of the solids. The activity and selectivity of different solids were found to be dependent on Ni- content, the presence of Mo- as dopant, and the oxidation state of the nickel present. The main catalytic reaction products were, mainly, dehydrogenation products whose content are dependent on the nature of the catalyst used. The increase in Ni- content increased the catalytic activity. The co-existence of MoO₃ and NiO showed catalytic activity much bigger than those measured for the individual supported NiO and MoO₃ catalysts.*

KEYWORDS: Nano-Crystalline Nio. Ni-Metal, Alumina System, Moo3 Doping

INTRODUCTION

The subject of the two or more components in catalysts as can affect their activity and selectivity has been well known for a long time [1]. Bimetallic catalysts, however, have been of interest to workers in heterogeneous catalysis. Since bi-functional catalysts play an important part in basic petroleum refining processes such as catalytic reforming and C₈ aromatic isomerization. A major theme of the works was the investigation of the relationship between catalytic activity and the electronic structure of metals [2]. Indeed, for supported metals in particular, the support was initially perceived only to disperse the active metal, increasing and preserving its surface area. More recently [3], it has been accepted that the support can influence the activity of the metal by strong metal support interaction (SMSI) [4].

It was found that the catalytic properties of bimetallic system of group VIII metal of the periodic table (iron-cobalt-nickel) with a group IB metals (copper-silver-gold) is of interest

for hydrogenation and many conversion reactions. Owing to that the electronic structure of the group VIII metals in such that the band is only partially filled, whereas the d-band of the group 1B is completely filled. According to the early hypothesis, the addition of group 1B metals gave an alloy with a more completely filled d-band [5]. Besides, the group VIII- group 1B metal systems are still highly interesting in catalysis, since they exhibit a high degree of specificity with regard to the type of reaction being catalyzed.

The conversion of cyclohexane [6] is one of the catalytic reactions with numerous contradictory statements [4]. However, the conversion of cyclohexane was studied on Nickel/ silica catalyst at (330-350) ^{0}C by Zelinskii et al [5,6]. The products were benzene, methane, toluene, xylene, methylcyclohexane and dimethylcyclohexane. Zelinskii proposed the formation of methyl radicals among the intermediate compound. In 1984 Ostrovskii et al [7] studied the dehydrogenation of cyclohexane on Pt / Al_2O_3 catalyst. It was found that the dehydrogenation of cyclohexane to benzene over Pt / Al_2O_3 at 280-340 ^{0} C was found to be a reversible reaction and was inhibited by the benzene formed. Ni - Ag /Ai_2O_3 catalysts with different Ni:Ag ratios were used for the dehydrogenation of cyclohexane. It was observed that the reaction products contain cyclohexene , cyclohexadiene and benzene inaddition to H_2 and CH_4 gases. Both the activity and selectivity are strongly dependant on Ni : Ag ratio as well as the reaction temperature. TGA, XRD and N_2 adsorption techniques were used to explain the catalytic properties [8]. The oxidative dehydrogenation (ODH) of cyclohexane with air was studied on a 10 w/w% V_2O_5/Al_2O_3 catalyst modified by different weight percentage (wt%) cerium loadings. The catalysts employed were characterized by N_2 adsorption, O_2 chemisorption, TEM, XRD and FT-IR spectroscopy. Benzene and cyclohexene were the main components of the products, with the benzene and cyclohexene selectivities depending on the wt% cerium loading, the order of cerium and vanadium impregnation, and the reaction temperature. The best cyclohexane conversion and good benzene selectivity were obtained at 500°C using a vanadium catalyst modified by 10 wt% cerium. Different types of vanadyl species present in the system were identified by IR measurements. Thus, vanadium–oxygen clusters were detected in the V_2O_5/Al_2O_3 material, although such clusters were not found in the cerium–vanadium catalysts. Polymeric $CeVO_4$ species were detected in cerium-modified V_2O_5/Al_2O_3 catalysts by XRD. The concentration of these species depended on the wt% cerium loading and the order of cerium and vanadium impregnation on alumina. The selectivity of cerium-modified V_2O_5/Al_2O_3 catalysts towards cyclohexene was attributed mainly to the presence of such polymeric $CeVO_4$ species. Oxygen chemisorption and electronic microscopic studies attributed the marked improvement in cyclohexane conversion of the cerium–vanadium samples to the presence of relatively high-dispersed vanadium species [9]. The opening of the cyclohexane ring over metallic nanoparticles of rhodium and iridium supported on alumina is reported in this paper. HRTEM micrographs of the catalysts, prepared by simple impregnation and in situ reduction, showed metallic nanoparticles 4.4 nm (S.D ± 1.7) in size for Rh and 4.6 nm (S.D ± 1.2) for Ir. The iridium catalyst showed a higher cyclohexane conversion and better stability than the rhodium catalyst. The main products with the iridium catalyst are *n* -hexane and *n*-pentane, while with the rhodium catalyst, there is also a significant production of benzene [10].

In the present work, the heterogeneous catalytic conversion of cyclohexane was investigated over two bimetal nickel-molybdenum supported on alumina to improve the catalytic activity of nickel alumina, by flow system under normal pressure. The textural properties, thermal gravimetric analysis and X-ray diffraction for the solid samples were also studied.

Experimental

Materials

Aluminum support material was prepared by precipitation of aluminum hydroxide from aluminum nitrate solution by using 0.1N NaOH. The obtained precipitate was thoroughly washed by distilled water till free from sodium ions, dried, then calcined at 500 ^{0}C for 4 h. The catalyst samples were prepared by using wet impregnation method, taking a known weight of Al_2O_3 with calculated amounts of molybdic acid and nickel nitrate dissolved in a least amount of distilled water sufficient to make pastes. The pastes will be dried, then calcined at 500 ^{0}C for 4 hrs. The concentration of MoO_3 in different catalyst was fixed at 2 weight % and those of Ni- were 8 and 13 weight %. Two additional samples were prepared by impregnating known weight of Al_2O_3 with a calculated amount of molybdic acid (2 wt % MoO_3) and another sample by treating with a known amount of nickel nitrate (15 wt.% NiO). The prepared solids also calcined at 500 ^{0}C.

The cyclohexane reactant was obtained by refluxing a supplied sample from Prolabo Company with anhydrous magnesium sulphate for 6 hr and obtained product was distilled. The chromatographically pure fraction was collected at 83 ^{0}C.

Techniques:

X-ray powder diffractograms of various investigated samples calcined at 400, 500 and 750 ^{0}C were determined out using Burker diffractometer (Burker D8 advance target). The scan rate was fixed at 8 ^{0} in 2θ min.$^{-1}$ for phase identification and 0.8 ^{0} in 2θ min.$^{-1}$ for line broadening profile analysis. The patterns were run with Cu $K_{\alpha 1}$ with secondly monochromator (λ = 0.1545 nm) at 40 KV and 40 mA. T*he* crystallite size of crystalline phases present in different solids investigated was calculated from the line broadening of the main diffraction lines of these using Scherrer equation [11].

$$d = K \lambda \,/\, B_{1/2} \,.\, \text{Cos}\, \theta$$

where: d is the mean crystalline diameter, λ the X-ray wavelength, K the Scherre constant (0.89), $B_{1/2}$ the full-width half maximum (FWHM) of the main diffraction peak of crystalline phases and θ is the diffraction angle.

TGA and DTA investigations of uncalcined catalyst samples were carried out using a Perkin Elmer TGA thermal analyzer. A (10 mg) solid specimen was taken in each experiment. The rate of heating was kept at 10 ^{0}C min^{-1}.

The specific surface areas (S_{BET}), total pore volume and mean pore radius (r $^-$) of the various catalysts were determined from nitrogen adsorption isotherms measured at   (-196) ^{0}C using a conventional volumetric apparatus. The values of r$^-$ were determined from the equation

$$r^- = 2V_p \,/\, S_{BET} \,.\, 10^4 \, A^0$$

The chemical composition of different catalyst being calcined at 500 ^{0}C was determined using atomic absorption technique.

The catalytic activity measurements were carried out using a flow technique and the reactant was introduced by a micro–dose pump (Unipan 335 A). The rate of feeding of cyclohexane reactant was varied between 2.5 to 12.9×10^{-2} ml min^{-1}. The reaction temperature was varied between 400- 480 ^{0}C. The weight of catalyst sample was taken in order to have a volume of 1 cm^3, and was introduced into a silica tube reactor with an internal diameter of 12 mm. The gaseous and liquid products were analyzed in a programmed gas–liquid chromatography (Pye-Series104 programmed chromatography) with a heated dual flame ionization detector. Pure N_2 was used as a carrier gas.

RESULTS AND DISCUSSION

Chemical Analysis of Investigated Solid:

The concentration of Ni and Mo present in different solids calcined at 500 ^{0}C has been determined by using atomic absorption. The results obtained are given in Table (1). It is clearly shown from this table that the concentrations of both Ni and Mo in different solids were very close to the normal values indicating the purity of the used chemicals for the preparation of these solid compounds.

Table (1) The chemical analysis of the investigate solids calcined at 500 ^{0}C

Catalyst	% of Ni & Mo: % of Al_2O_3 prepared	% of Ni & Mo : % of Al_2O_3 actual
A1	13 % Ni : 2 % Mo : 85 % Al_2O_3	12.80 % Ni: 2.1 % Mo : 85 % Al_2O_3
AII	8 % Ni : 2 % Mo : 90 % Al_2O_3	7.92 % Ni: .95 % Mo : 90 % Al_2O_3

TGA and DTA investigation of uncalcined solids:

The DTA and TGA curves of uncalcined catalyst samples (not given) show the presence of a broad endothermic peak located at 140 ^{0}C, indicating removal of physo-sorbed water which accompanied by a weight loss of about 3 %. Another endothermic peak was found at 316 ^{0}C indicating the thermal decomposition of nickel nitrate yielding NiO which accompanied by a weight loss 13.1%. A third small endothermic peak appeared at 400 ^{0}C with negligibly small weight loss, characterizing the conversion of molybdic acid into MoO_3.

Surface characteristics of different adsorbents calcined at 500 ^{0}C

Different surface characteristics namely S_{BET}, S_t , V_P and r^- were determined for different solids being calcined at 500 ^{0}C using N_2 adsorption isotherm measured at (-196) ^{0}C. The computed values of surface characteristics are given in Table 2. Examination of Table (2) reveals the following:

(i)The S_{BET} and S_t values of different adsorbents are closed to each other, which justifies the correct choice of the t-curve used in pore analysis and indicates the absence of ultra-micro pores.

(ii) The coexistence of Ni and Mo in supported catalyst calcined at 500 ^{0}C led to a tremendous drop in the BET surface areas, which falls to about 1/3 its value. This decrease may be attributed to some kind of pores blocking via the produced of MoO_3.

(iii) increase in the concentration of NiO present from 8 to 13 wt % NiO much decreased the S_{BET} than catalyst A. The observed measurable decrease in the S_{BET} due to treating with different amount of NiO in presence of 2 wt % MoO_3, could also, be attributed to an effective pore widdening (about 53%). In fact r⁻, increased from 18 to 27.5 upon treating with both NiO and MoO_3.

Table (2) Some surface characteristics of diff. investigated samples calcined at 500 ^{0}C

Adsorbent	S $_{BET (m2/ g)}$	Vp (cm^3/g)	r $^-$ (A^0)	S $_t$	d^0A
Ni 0/ Al_2O_3 A	322	0.29	18.48	315.1	-
AI	138.1	0.19	21.37	135.3	48
AII	110.7	0.15	26.96	111.3	72

*XRD investigation of different solids calcined at different temperatures*

Figures (1,2) show X-ray diffractograms of two samples calcined at 400, 500 and 750 ^{0}C. The first sample consist of 2wt % MoO_3, 8 wt % NiO and 90 wt % Al_2O_3, while the second consists of 2 wt % MoO_3 ,13wt % NiO and 85 wt % Al_2O_3. Examination of Figures 1 & 2 show the following:

(i) all investigated solids calcined at 400,500 and 750^{0}C are composed of NiO as a major phase together with MoO_3 , Ni- MoO_4 , γ - alumina.

(ii) the degree of crystallinity of the phases present increases by increasing the calcinations temperature.

(iii) the appearance of all diffraction lines of MoO_3 in the diffractograms of all solids in spite of its presence in very small concentration (2 wt %) which is beyond the detection limit of the X-ray diffractometer might suggest its enriched presence in the outermost surface layers of different solids. This finding could be attributed to an effective migration of molybnia species from the bulk to the surface. This migration processes resulted the low sublimation temperature of MoO_3 which takes place at 750 ^{0}C [13]. This behavior led to vaporization of MoO_3, i.e. having a vapor pressure attaining 1 atm. However, one can not overlook the rule of alumina in dissolution of a portion of molybdina in its matrix of alumina forming solid solution. In fact it has been reported by El Shobaky et al [12] that alumina can dissolve about 40 wt % MoO_3 even by heating at 1000 ^{0}C.
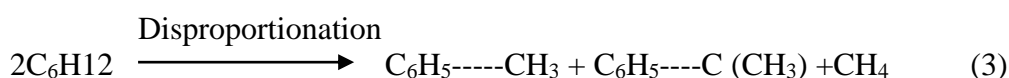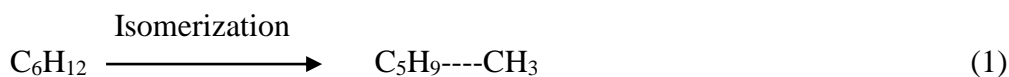
(iv) the appearance structure of the distraction lines of Ni- molybdate could be attributed to solid- solid interaction between NiO and MoO_3 according to:

$$NiO + MoO_3 \rightarrow Ni\,MoO_4$$
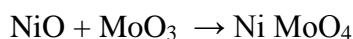
The computed value of the crystallite size of NiO phase present in the two solids containing 2 wt %molybdina together with 8 and 13wt %NiO were found to be 48 and 72A^o,respectively . These two values suggested the increase in the NiO content from 8to13 wt% much increased the crystal size of NiO phase . The percentage increase attain 50%. This finding might sudjest an effective decrease in the degree of dispersion of the nanosized NiO phase upon increasing its content from 8to13 wt%. These results seems to be logical and indicating an effective decrease in the dispersion power of Al_2O_3towards NiO.

Catalytic activity and selectivity of the investigated solids

Concerning the cnonvertion of cyclohexane on catalysts samples activated by H_2 at 500 ◦C, the activity and selectivity of these solids showed different behaviour. yclohexane converted into different producut (cyclohexene ,cyclohexadiene , benzene, metthylcyclohexane, toluene, and cumene) according to :

$$C_6H_{12} \xrightarrow{\text{Isomerization}} C_5H_9----CH_3 \tag{1}$$

$$C_6H_{12} \xrightarrow{\text{Dehydrogenation}} C_6H_{10} +H_2 \text{ or } C_6H_8 + 2H_2 \text{ or } C_6H_6 + 3H2 \tag{2}$$

$$2C_6H12 \xrightarrow{\text{Disproportionation}} C_6H_5-----CH_3 + C_6H_5----C (CH_3) +CH_4 \tag{3}$$

The process (3) of hydrogenation and dehydrogenation "disproportionation" might take place on metallic nickel, molybdynam produced from the reduction of nickel oxide, molybdynum oxide by hydrocarbons which passed over the catalysts at the initial stages of catalysis.

On the other hand, the isomerization process takes place onto acid site i.e Lewis acid or Bronsted acid site. The activation of catalysts at 500◦C increases the number of Lewis acid sites i.e tricoordinated Al [14,15]
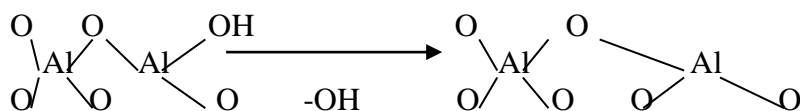

Figure (3); depicts the percent conversion of cyclohexane carried out at different temperatures over various solids calcined at 500 ^{0} C. Table (3) indicates the different reaction products of the catalyzed reaction carried out at temperature ranges from 400- 480 ^{0}C. It is clearly shown from Figures (3,4) and Table (3) that:

(i) the % conversion increases progressively as a function of temperature.

(ii) as a result of dehydrogenation reaction, benzene contributes the major portion of the products.

(iii) the increase in the amount of NiO from 8 to 13 % by weight resultes in an significant increase in catalytic activity indicating that nickel is an excellent dehydrogenated catalyst.

(iv) formation of toluene as Disproportionation product take place only in case of catalyst poor in nickel content.

(v) isomerization reaction yielding cumene takes place over all investigated solids .

(vi) both investigated solids acted as dehydrogenation catalysts and the selectivity towards benzene formation changes slightly with the reaction temperature from 400-480 ^{O}C ,while selectivity towards isomerization product was limited[16].

(vii) as the Ni −content decreased AII system , the selectivity towards dehydrogenation decreased from 74.7→41.81% ,while the selectivity towards disproportionation (toluene formation) increased from 0→53.16 % at the reaction temperature.573°K [17].

Table (3) The effect of temperature on the catalytic conversion of cyclohexane on   Ni –Mo/ Al_2O_3 catalyst calcined at 500 ^{0}C in flow system under normal pressure

| Temp. ^{0}C | Analysis of liq. Product, % | | | | | | |
| | AI Catalyst | | | AII Catalyst | | | |
	% dehyd.	% Isom.	% Unreacted	% dehyd.	% Isom.	% Disprop.	% Unreacted
400	18.60	3.42	77.92	9.14	0.85	7.00	83.01
430	20.54	3.58	78.88	9.44	1.38	9.00	80.18
450	21.66	9.80	68.54	11.41	1.40	9.22	77.97
480	24.68	8.58	66.78	12.22	1.47	15.54	70.77

The apparent activation energy of cyclohexane conversion was calculated from the values of % conversion carried out at temperature within 400-480 ^{0}C for different solids by direct application of the Arrhenius equation. The computed ΔE values were 95.7 and 115 K mol $^{-1}$ for the catalyst containing 13 and 8 weight % NiO, respectively. These two values ran parallel to the observed increase in the catalytic activity by increasing the NiO content, c.f. Figure (3). However, the difference in the ΔE values did not necessarily reflected a possible change in the mechanism of the catalyzed reaction. This conclusion comes from a measurable difference in the pre-exponential factor of the Arrhenius equation (A), which measured 2 and 2.7×10^7 sec $^{-1}$ for the two catalyst investigated.

In order to shed more light about the role of the coexistence of NiO and MoO_3 in the supported catalyst on their catalytic activity [18-20], the % of cyclohexane conversion carried on individual supported catalyst and the mixed oxide catalyst were determined and given in Figure (5). It's clearly shown from Figure (5) that a considerable synergism took place from the co-presence of NiO and MoO_3.

This conclusion is estimated by comparing the catalytic activity of the individual supported catalyst with the supported mixed oxide samples which measured catalytic activity 3-fold bigger catalytic activity as compared to those of the individual supported oxide catalysts.

CONCLUSION

The main conclusions that may be drawn from the results obtained are as follows:
1-   The investigated catalysts calcined at 5000C consisted of nanosized NiO,MoO3 and NiMoO4 phases.
2-   MoO3 – treatment of NiO/Al2O3 system calcined at 5000C much modify its surface characteristics (SBET,VP,and r') .

3-   The addition of small amount of MoO3 (2 weight%) to NiO/Al2O3 followed by calcinations at 5000C resulted in a significant decrease in SBET to about 1/3 its value. This decrease may be attributed to some kind of pores blocking via the occupation of some pores by diffusible MoO3 substrate.

4-   All the investigated catalysts acted as dehydrogenation catalysts in cyclohexane conversion .

5-   The catalytic activity increased effectively by increasing the concentration of NiO present.

6-   The selectivity of different catalyst was dependent mainly on NiO content and the temperature of the catalytic reaction.

7-   The co-existence of MoO3 and NiO in catalysts investigated much increased their activities as compared to those MoO3/ Al2O3 and NiO / Al2O3

REFERENCES

(1) Advances in catalysis, 34, volumes (1947- 1986), Acad. Press N.Y.

(2) Schwab, G.M., Trans. Far. Soc. 42, 609 (1946), Z. Electro- Chem. 60, 112, 1956. Dowden, D.A., J. Chem. Soc. 242 (1950); Dowden, D.A., and Rreynolds, Disc. Far. Soc. 8, 1950.

(3) Curts Conner, JR. W., Pajonk, G.M., and Teichner, S.J., Advances in Catalysis and Related subjects, Vol. 34, A.P. New York p. 1. 1980.

(4) Ezzo E.M., Yousef N.A., and Ali S.A., Surface Technology, 13, 379 1981.

(5) Zelinskii N D., "Sobranie Trudov", "Collective Works", I zd. Akad. Nauk. SSSR, Moscow, , 111, 26, 51, 53, 61, 114, 138, 199, 1955

(6) Zelinskii N D. and Shuiken N.E., Dokl. Akad. Nauk.SSSR, 3, 255, 1934

(7) Ostrovskii N. M., Karpova L.A., Duplyakin V.K.. Kinet. Katal., 25 (5), 1117- 23. 1984

(8) Ezzo E.M., El-Kherbawi N.A., and El Aiashi M.K. Mans. Sci. Bull. (A. Chem.) Vol. 31 (2), December 2004.

(9) Hany M. AbdelDayem, Adsorption Science and Technology, Volume 22, Number 9 , Multi-Science Publishing Co Ltd pp. 755-772(18), November 2004

(10) Geonel Rodríguez-Gattorno, Laura O. Alemán-Vázquez,* Xochitl Angeles-Franco, José Luis Cano-Domínguez, and Roberto Villagómez-Ibarra , *Energy Fuels,* 21 (2), 1122 -1126, 2007.   10.1021/ef060084i   S0887-0624(06)00084-3 Web Release Date: January 23, , American Chemical Society, 2007

(11)A.A Ibrahim and G.A.El-.Shobaky. Thermochemica Acta, 147, 1989.

(12) G.A.El-Shobaky, G.A.Fagal and N.A.Hassan. Thermochimica Acta, 311, 205-211. 1998

 (13) Carlos G. Morales-Guio and Xile Hu *, *Acc. Chem. Res.*, *47* (8), pp 2671–2681 2014,

(14) M. Nagai, A. Miyata, T. Kusagaya & S. Omi "Surface molybdenum species and acid sites on nitrided molybdena-alumina catalysts", The Chemistry of Transition Metal Carbides and Nitrides" pp 327-344, 1996.

(15) Tetsuya Tsuda, Charles L. Hussey, and Gery R. Stafford "Electrodeposition of Al-Mo Alloys from the Lewis Acidic Aluminum Chloride-1-ethyl-3-methylimidazolium Chloride Molten Salt., J. of the Electrochemical Society, V 151, 6, 379-384, 2004.

(16) Xu Zong, Zheng Xing, Hua Yu, Yang Bai, Gao Qing (Max) Lu, Lianzhou   Wang , *Journal of Catalysis, Volume 310, pp 51-56, February,2014*

(17) Zhining Kou, Shaohui Shen, Kai Liu, Guohua Xu*, Yue An, Chaohong He , international journal of hydrogen energy 38, 11930e1193. 2013

(18)M.L. Pacheco, J. Soler, A. Dejoz, J.M. Lopez Nieto, J. Hergiudo,M. Menendez, J. Santamaria, Catal. Today 61 () 101 2000.

(19) Rajesh B. Bini ,wale Nobuko Kariya, Masaru Ichikawa and Catalysis Letters Vol. 105, Nos. 1–2, November, 2005

(20) S. Mikhai and M. Riad Catalysis Communications 9, 1398–1403, 2008.

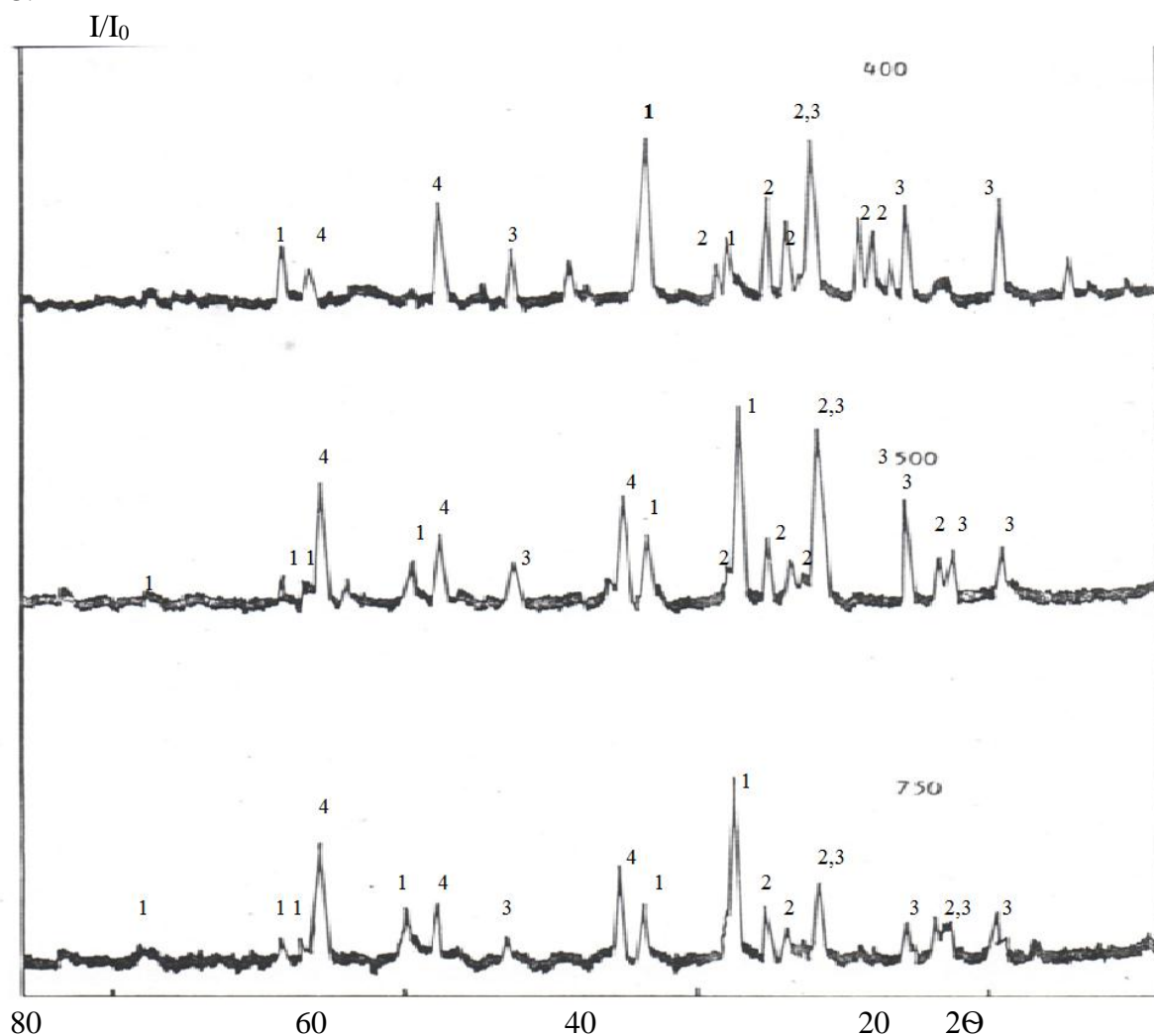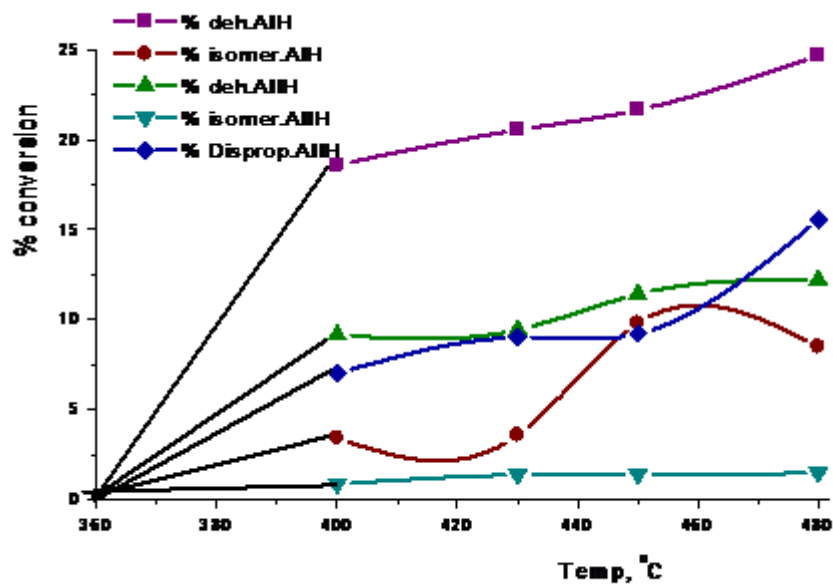**Fig (1)** : X-Ray diffraction patterns for Ni-Mo catalysts thermally treated at 400 ,500 ,700 ^{0}C.
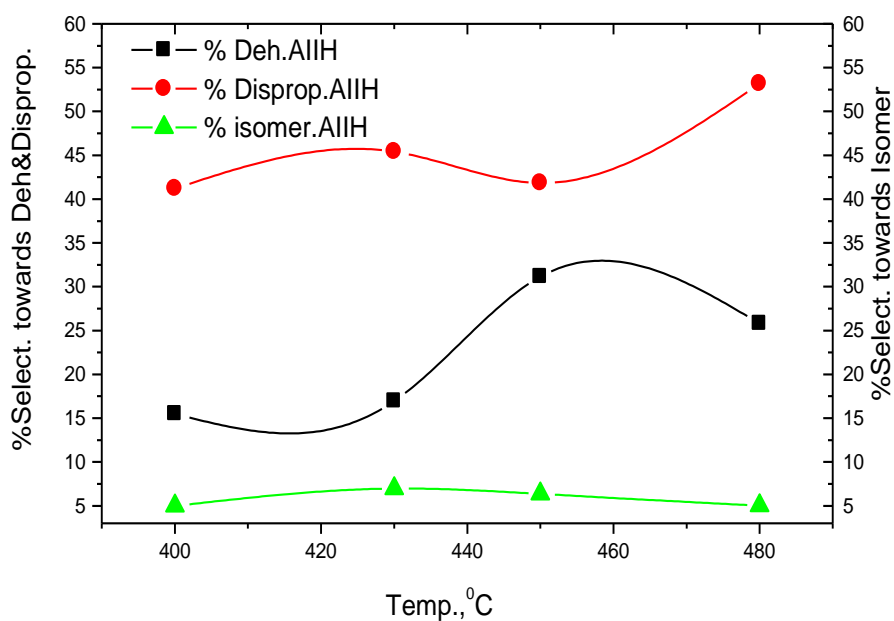

Fig (2) : X-Ray diffraction patterns for Ni-Mo catalysts thermally treated at 400 ,500 ,750 ^{0}C.

Fig(3) Effect of reaction temperature as afunction of catalytic conversion of cyclohexane over different catalysts sample calcined at 500^{0}C.

Fig(4): % Selectivity of diff. products and reaction temp . for diff. catalyst samples
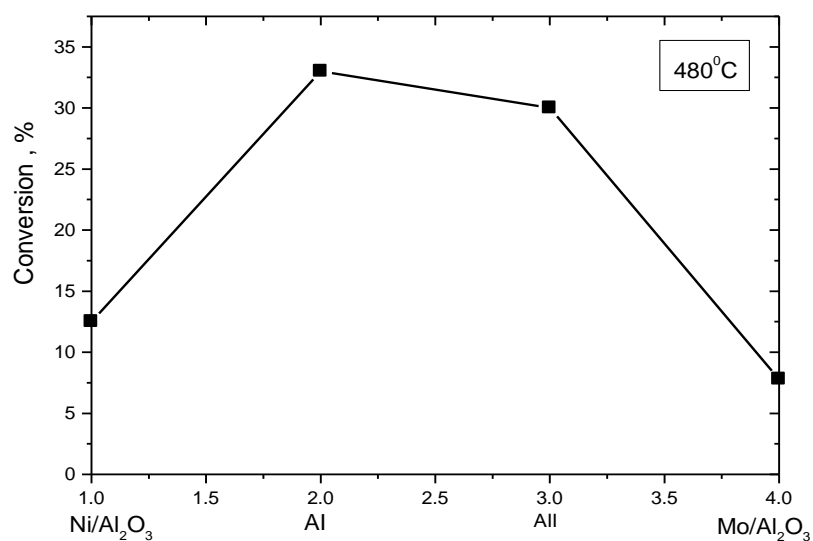
Fig (5) :Effect of dispersity on the activity and selectivity of Ni-Mo/Al$_2$O$_3$ catalysts in heterogeneous catalytisis of cyclohexane