PART 1

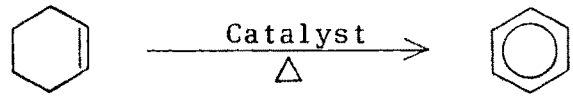
STUDIES IN DEHYDROGENATION

1. INTRODUCTION

Catalytic dehydrogenation over transition metals provides a convenient and frequently used method for synthesis of organic compounds in which hydrogen atoms are removed from the molecule. Catalytic processes enjoy the advantages over their non-catalytic counterparts of proceeding efficiently under milder conditions, thus leading to more energy-efficient processes. Furthermore, catalytic processes are generally more selective and capable of leading to optimal utilization of raw materials. Unlike the stoichiometric oxidations with traditional oxidants, such as sulphur and selenium, permanganate and dichromate, catalytic processes do not produce vast amounts of inorganic effluents which are difficult to dispose of.

The catalytic action in heterogeneous catalysis is known to occur at the interphase of two phases. The most important function of a catalyst in chemical reaction is to lower the activation energy (E*), and to enhance the rate of reaction. A catalyzed reaction is believed to involve the transitory adsorption (chemisorption) of one or more reactants onto the surface of the catalyst, rearrangement of bonding, and the desorption of the products.

Dehydrogenation reaction is reversible and liberates hydrogen; high temperature and use of sweeping gas, such as N_2, He, greatly facilitate displacement of the equilibrium in favour of dehydrogenation product. The most successful dehydrogenations involve the establishment of an aromatic system or oxidation of a particular function that offers a preferential point of attack, e.g. aromatization of cyclic hydrocarbons.



There are mainly two factors which explain, to a certain extent, the catalytic activity of transition metals.

1.1 Geometric Factor[1]

Geometric correlations in heterogeneous catalysis are based on the concept that the mutual arrangement of surface atoms must affect the formation of surface intermediates, their subsequent reactions, and therefore, their catalytic activity as well. Balandin's "multiplet theory"[2] explains it in much better way. This theory supposes that only part of a molecule undergoing catalytic conversion actually participates in the reaction. This particular group of atoms is termed as 'index group'. It further assumes that only certain atoms of the catalyst possess the necessary configuration for the reaction. These atoms are termed the 'multiplet'. According to the theory, during catalysis, the index group of a reactant molelcule is superimposed on the active atoms of the catalyst, thereby yielding an intermediate multiplet complex within which bond deformation and migration occurs.

An aspect of geometric approach of great usefulness is that the reaction selectivity may be markedly altered by the number and arrangement of sites required for competing reaction as affected by particular size, alloying, and other variables.

1.2 Electronic Factor [3]

The relationship between electronic structure and catalytic activity of metals forms the basis of electronic approach.

The band theory describes metals as consisting of a lattice of positively charged metal ions with closed electron shells in which the valence electrons have more or less free mobility, however, some of the characteristics of isolated atoms are preserved. Instead of discrete energy states there are bands of permitted values and the electrons per atom differ from the number of electrons in corresponding orbital of the isolated atom. Catalytically active transition metals characteristically have incomplete d-bands (d-holes), i.e. many of the quantum states in their d-bands are unoccupied. These neighbouring atoms of a metal crystal are assumed to be held together by covalent bonds between adjacent atoms.

However, according to Pauling[4,5] there are three types of d-orbitals associated with each atom in the solid state : bonding d-orbitals which can participate in d,s,p-hybrid orbitals, metallic d-orbitals involved in electrical conductions, and atomic d-orbitals which are non-bonding and into which electrons can be placed. According to him transition metals have some vacant atomic d-orbitals; and their cohesive energy is attributed to the formation of d,s,p-orbitals. The percentage d-character (δ) represents the extent to which d-electrons participate in d,s,p-orbitals; the higher the value of δ, the fewer the number of atomic d-orbitals there are available at each atom, i.e. δ is the measure of unavailability of electrons in the atomic d-orbitals.

Furthermore, according to Pauling's theory[6], the d-character controls the the interatomic spacing but it does not decide the precise arrangement of the active centres at a given surface. Hence this approach can embrace only the general level of activity of polycrystalline crystals and not why differences in activity between different faces on one metal with a particular d-character may be much greater than the differences in activity between two metals with significantly different d-characters.[7]

In electronic theory[8], the rate of reaction is controlled by the availability of charge carriers-electrons or holes-in the catalyst. These are visualized as being non-localized, i.e. a sea of electrons or holes is available. Chemisorption is then related to the electronic properties of the catalyst, e.g. ease or difficulty of removal or donation of an electron to or from the lattice.

2. ADSORPTION

Catalysts are chemicals which, under milder conditions, form chemical bonds of varying degrees of stability with other atoms or groups and it is the consequent perturbation of the electronic and geometric structure of the molecule which leads to the catalytic enhancement in reaction rate or in other words, the activation energy (E*) of the reaction is lowered because the activated molecules are made relatively less unstable in the presence of the catalyst. Therefore, maximum catalytic activity can be expected at some intermediate strength of chemisorption; very weak adsorption will imply too little modification of the reactant molecule for its activity to be greatly affected, while very strong adsorption will imply the formation of a stable compound which can

cover most of the catalyst surface as it happens in the case of poisons, like compounds of sulphur and nitrogen containing lone pairs of electrons which form strong donor bond to the metal surface.[9]

In chemisorption only unimolecular layer is formed on the active centres of the catalyst. The most likely explanation seems to be that first adsorbed molecules use some of the adsorption potential of atoms neighbouring those on which adsorption actually occurs; molecules arriving later can not then adsorb so strongly.[10]

Measurements of adsorption have a variety of uses and applications, but perhaps the most important is in determining surface area of the catalysts. Provided the rate of reaction is not limited by a mass-transfer process, it will be accurately proportional to the surface of the active phase of the catalyst. The activity of the catalyst is properly expressed as the rate per unit area of surface (usually per m^2).

TOTAL SURFACE AREA = (NO. OF MOLECULES) X (AREA PER MOLECULE)

Area per molecule comes either from the liquid molar volume or the collision diameter of the gas.

3. PREPARATION OF CATALYST[11]

For an industrial catalyst, the chemical composition is the most overriding consideration, but other factors, primarily of a physical nature, are also of importance, e.g. surface area, stability, and mechanical properties, which

can be controlled by the method of preparation of the catalyst.

High surface area is usually desirable for high activity per unit volume or unit weight, so most of the catalysts are made porous. However, the porous structure in the catalyst and pore size distribution may cause diffusional resistance that affect the ease of access of reactants to catalyst sites and removal of products, thereby affecting the rate and selectivity of the reaction.

Most common methods employed for the preparation of catalysts are precipitation and impregnation. Precipitation method, in general, provides more uniform mixing on a molecular scale of various catalyst ingradients, and the distribution of active species through final catalyst pellet in uniform. Also, more control may be achieved over pore size and pore size distribution.

Supported catalysts are preferred over unsupported catalysts because the active metal becomes finely dispersed, expensive metals are saved, large specific surfaces are created when pore sizes are close to the optimum, and heat resistance is increased. Active metal and support electronic interactions are also known.[12] A large number of support materials are described in literature and their structures are well confirmed, e.g. Al_2O_3, MgO, SiO_2, C, ThO_2 etc.

In impregnation method of the preparation of catalyst, a carrier, usually porous, is contacted with a solution of one or more suitable metallic compounds.

A catalyst can also be prepared conveniently by physical mixing of the support material and suitable metallic compounds.

3.1 Promoters[13]

The catalytic properties of materials are, in general, known to change considerably by the addition of small amounts (0.1-10% of the active metal component) of foreign materials. The action of a promoter can be either to inhibit the sintering of microcrystals of the active catalyst by being present in very fine particles and separating the true catalyst particles from contact with one another so they do not coalesce, thus preventing or minimizing the loss of active catalyst area during service or it may change the chemical composition of the catalyst. It may also produce lattice defects or interstitial substitution or may change the electronic structure of a catalyst, e.g. the ease of addition or removal of electrons from a metal and strength of chemisorption. Promoters are mostly high melting substances, e.g. MgO, CeO_2, Cr_2O_3, etc.

4. REFERENCES AND NOTES

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SECTION 1

DEHYDROGENATION OF ALCOHOLS TO THE CARBONYL COMPOUNDS

DEHYDROGENATION OF ALCOHOLS TO THE CARBONYL COMPOUNDS

Abstract

A catalytic process is described in which secondary alcohols are dehydrogenated to the corresponding ketones in good yields. The process consists in passing the substrate at 250°C in vapour phase under H_2 over the bed of 10% Ni-Cu/Al_2O_3 containing 0.1% CeO_2 catalyst pellets. The H_2 serves as a carrier gas and also creates reducing atmosphere. The results are summarized in the forms of tables and graphs. An apparatus is designed to carry out vapour phase catalytic dehydrogenation (Fig.9). The 2-octanol, 2-pentanol, fenchol, and menthol have been converted into corresponding ketones.

The transition metal catalysts and supports studied can be arranged in the following order : Ni > Cu > Co > Mn > Fe and Al_2O_3 > SiO_2 > MgO, respectively. The catalyst prepared by physical mixing method is more active than co-precipitation method.

Copper is either neutral (< 40 atom%) or detrimental (>40) to the activity of Ni/Al_2O_3 catalyst. Rare earth oxides promote the activity of Ni-Cu/Al_2O_3 catalyst. High temperature is superior to the low temperature reaction.

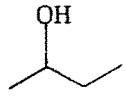
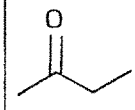
1. INTRODUCTION

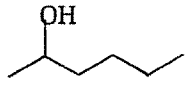
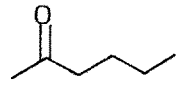
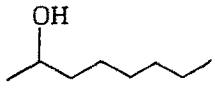
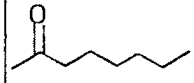
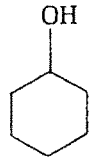
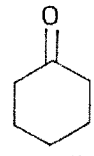
Syntheses of aldehydes and ketones are more diverse and extensive than the synthesis of any other class of compounds because they are valuable intermediates in organic syntheses. Major synthetic routes are compiled by Buehler and Pearson[1]. Most commonly such compounds are prepared by oxidation of primary and secondary alcohols. Among oxidants generally, and transition-metal oxidants in particular, chromium (VI) and manganese (VII) reagents are the most widely used. The most familiar reagent, chromic acid, is normally used in water, aqueous acetic acid, or aqueous acetone (the Jones reagent); the use of a solution in DMSO has also been described. A variety of other reagents are also available[2].

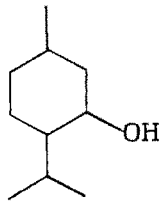
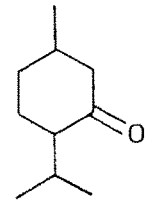
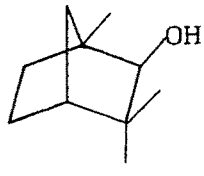
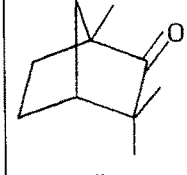
However, heterogeneous catalysis has played an important role in the synthesis of aliphatic oxygenated compounds. The dehydrogenation of alcohols was first studied by Ipatieff, who obtained the corresponding aldehydes or ketones by treatment of methyl, ethyl, isopropyl, isobutyl, and isoamyl alcohols with such catalysts as a platinum tube, zinc rods, and brass at suitable temperatures. Later on, a large number of heterogenous catalysts have been developed. Table - 1 summarizes most of the available information.

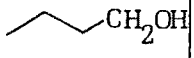
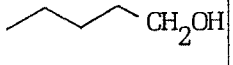
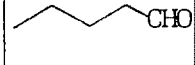
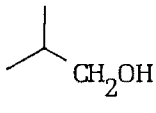
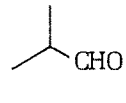
TABLE - 1

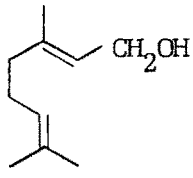
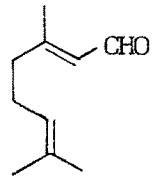
Dehydrogenation of alcohols to the corresponding aldehydes and ketones on various catalysts.

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
01.		Ir/C, 130-60° C., O		-	3
02.	"	Ru/ZnO, 250° C	"	-	4
03.	"	Ni-Cu/kieselguhr	"	94	5
04.	"	Ni-Ca-Cr_2O_3, 300-600°, steam + air	"	- 95	6
05.	"	Cu-$ZnCr_2O_4$	"	-	7
06.	"	CuO-Cr_2O_3/pumice, 270°, O	"	89	8
07.	"	Cu-CaO, K_2O, 200-300°, H	"	88-90	9
08.	"	CuO-NaF-SiO_2, 300°, N	"	96	10
09.	"	Cu/SiO_2, 220°	"	90	11
10.	"	BaO-SiO_2-Cr_2O_3,H	"	-	12
11.	"	Fe_2O_3	"	-	13
12.	"	Cu/Al_2O_3	"	90	14
13.	"	ZnO-ZrO_2, 750°F,	"	95	15
14.	"	ZnO, Na_2SiO_3	"	-	16
15.	"	Zn-Cu-Al, 220-50°	"	-	17

Sr. No.	Substrate	Catalyst, conditions	Product (%)	Yield	Literature
16.		Pt/C 600°F		91	18
17.	"	Ni-Zn,350°, H	"	92.5	19
18.	"	ZnO, Cu	"	-	20
19.		Au		-	21
20.		Pt		-	22
21.	"	Ru/C, 250-400°	"	57-67	23
22.	"	Cu-Al-Ni,K_2CO_3,350°,N	"	85	24
23.	"	Cu,200-450°,steam+N_2	"	-	25
24.	"	Raney Cu, 250-60°	"	90	26
25.	"	Cu-Co, 200-400°	"	80	27
26.	"	$CuO.Cr_2O_3$, 180-400°, steam	"	-	28
27.	"	$CuO.Cr_2O_3$,MnO,BaO	"	73	29
28.	"	Cu-Al-Zn-Cr-Co,200°	"	58	30
29.	"	Cu-Al-Cd alloy, 275°	"	73.6	31
30.	"	Raney Cu-Cu, 270-80°	"	75-80	32
31.	"	Raney Cu-Cd,	"	-	33
32.	"	$CuAl_2$ alloy, Cd, 370°	"	87	34
33.	"	Cu-BaO-RuO_2-ZnO	"	-	35
34.	"	CuO	"	80	36
35.	"	CuO - ZnO	"	-	37
36.	"	Cu/SiO_2, 170-240°	"	-	38
37.	"	Cu/pumice, 250°	"	-	39

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
38.	"	Raney Cu/SiO_2, 300°	"	89	40
39.	"	Cu/Al_2O_3, K_2O	"	-	41
40.	"	Cu/kieselguhr, Na_2CO_3, 280-300°	"	75	42
41.	"	Cu-Co/oxidised peat	"	-	43
42.	"	Cu-Zn/graphite, 394°,H	"	63	44
43.	"	$ZnO.Cr_2O_3$, 380°	"	95	45
44.	"	Zn-Cu, alloy,300-500°	"	-	46
45.	"	Zn-Fe, 310-90	"	-	47
46.	"	Fe_3O_4-CaO-ZnO-CuO/ graphite, 190-220°	"	-	48
47.	"	ZnO, 370°	"	81.5	49
48.	"	ZnO-CaO-K_2O-Na_2O/SiO_2, 400°	"	73.9	50
49.		Raney Ni, 230°		-	51
50.	"	Cu, 220°, H	"	72.8	52
51.	"	Tl, 300°	"		53
52.		Pt/Al_2O_3		-	54
53.	"	Cr_2O_3/SiO_2	"	98	55
54.	"	Fe/bentonite	"	82	56

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
55.		Cu-Ag/pumice, 350°,O		94-7	57
56.	"	CuO, Cr_2O_3/pumice, 280-340°, H.	"	87.5	58
57.	"	CuO. Cr_2O_3/Al_2O_3, 330°	"	54	59
58.	"	CuO.Cr_2O_3-C/pumice, 275-350°.	"	-	60
59.	"	Cu-Zn, 420-550°	"	-	61
60.	"	Cu-Zn-Fe-Al, 400°	"	98	62
61.	"	CuO-ZnO-Cr_2O_3-BaO/ asbestos, 250-60°	"	37-40	63
62.	"	Zn-Cr, CuO, Al_2O_3, 250-350°	"	-	64
63.	"	ZnO-Cu, 370-80°	"	27-9	65
64.		Pt/Ni-Cr wire		-	66
65.	"	CuO. Cr_2O_3/celite C-12, 320-35°	"	58	67
66.		Cu/MgO, 300-400°		77-63	68,69
67.	"	Cu-Ca	"	-	70
68.	"	CuO, ZnO, Cr_2O_3, 290-360°, H	"	-	71

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
69.	$CH_3(CH_2)_6CH_2OH$	Cu-Ba-Cr-O, 190-260°	$CH_3(CH_2)_6CHO$	60	72,73
70.	"	Fe-Cd-Zn-ZnO	"	90	74
71.	$CH_3(CH_2)_8CH_2OH$	Ru/Al_2O_3, 300°, O	$CH_3(CH_2)_8CHO$	-	75
72.	"	CuO, Cr_2O_3, BaO, K_2O	"	-	76
73		Cu, O		56	77
74.	"	Cu-Zn, 250°	"	50	78
75.	Ph-CH=CH-CH_2OH	Cu, 250°, H	Ph-CH=CH-CHO	26	79

2. PRESENT WORK

A variety of catalysts have been used in this area. Generally, noble metals or a combination of transition metals is used, although success has been reported with other catalysts, too. A comparative study of the catalysts reveals the overwhelming preference for transition metal catalysts, albeit the results were highly variable and depended critically on the substrate and reaction conditions. Both supported and unsupported catalysts have been adopted. Alumina, magnesia, silica, and graphite are the supports commonly employed. A conclusion can be reached that nickel and copper are probably the best first choice because of precedent examples and a history of success, but in case of failure, it is decidedly worthwhile to investigate other possibilities in order to make it more qualitative and quantitative. It has been the aim of present work to investigate a transition metal catalyst with high activity and selectivity for the dehydrogenation of 2-octanol and to study the effect of rare earth oxides on its activity.

To achieve this aim, a large number of supported and unsupported catalysts were prepared in different ways and evaluated for their dehydrogenation activities. The unsupported catalysts were prepared by decomposing metal carbonates at 360°C which were freshly precipitated from aqueous metal sulphate solution with sodium hydrogen carbonate. However, the supported catalysts were prepared either by physical mixing the metal carbonate and support or by co-precipitation method followed by calcination. The activity of each catalyst (10.0g) was determined at 182 ± 2°C for 8.0 hours after its reduction with hydrogen at 350°C for 2.0 hours.

Since the catalytic activities of transition metals depend upon the substrate, it was decided to compare the activities of nickel, copper, manganese, iron, and cobalt catalysts for the dehydrogenation of 2-octanol into 2-octanone.

Supported catalysts have advantages over unsupported catalysts because of low cost and relatively high specific surface area. Nickel (10% by wt.) was dispersed on alumina, silica, and magnesia supports by physical mixing to find out suitable support for the catalyst.

The effect of surface area of aluminas on the catalytic activity of Ni/ Al_2O_3 was also studied.

In order to ensure thorough and even distribution of the active metal on support, catalyst was prepared by co-precipitation method.

In the first catalyst, freshly precipitated nickel carbonate was dispersed in a solution of aluminium isopropoxide in anhydrous isopropyl alcohol and precipitated aluminium hydroxide with water at 80-85°C.

Other catalysts were prepared by precipitation of nickel carbonate with sodium hydrogen carbonate from the dispersion of alumina of different surface areas (15-20 m^2g^{-1} and 230 m^2g^{-1}) in aqueous nickel sulphate solution.

Examination of activities of such catalysts revealed low surface area alumina (15 m^2g^{-1}) as better support and catalyst preparation by physical mixing a superior method. Hence they were used in all the catalyst preparations.

It is reported that incorporation of copper (Gr. I B) with nickel reduces its hydrogenolytic activity[80], therefore, it was proposed to study the effect of copper on Ni/Al_2O_3 and Ni/MgO catalysts. The concentration of copper in these catalysts varied from 0 % to 100 %. And it was found that the catalyst containing 30% Cu (based on Ni) and supported on alumina was superior. So this catalyst was selected for studying the effect of rare earth oxides.

Rare earth oxides possess partially filled 4f subshells. They do show some activity as catalyst for the dehydrogenation of hydrocarbons, alcohols, etc.[81] Therefore, the effect of three rare earth oxides, such as lanthanum oxide, cerium oxide, and thorium oxide on the activity of $Ni-Cu/Al_2O_3$ catalyst was studied.

Effect of metal loading, pores, and reaction temperature on the activity of 10% $Ni-Cu/Al_2O_3$ catalyst containing 0.1 % by wt. CeO_2 was also studied.

The activity and selectivity of this catalyst was also checked for the dehydrogenation of 2-pentanol, fenchyl alcohol, and menthol.

Primary alcohols and allylic alcohols were also dehydrogenated using this catalyst but selectivity was very poor.

3. RESULTS AND DISCUSSION

Transition metal catalysts showed different activities for the dehydrogenation of 2-octanol into 2-octanone under the same set of conditions. Nickel catalyst was found to be more active than any other metal catalyst studied (Fig.1). The activities of the catalysts were decreased in the following order :

Ni > Cu > Co > Mn > Fe.

Table - 2 summarizes the results observed.

TABLE - 2

Dehydrogenation of 2-octanol into 2-octanone on various transition metal catalysts (10.0g) at 185°C.

Catalyst	Manganese (Mn)	Iron (Fe)	Cobalt (Co)	Nickel (Ni)	Copper (Cu)
Space velocity (v/v/sec)	0.0751	0.0751	0.0425	0.0537	0.0851
% 2-octanone	4.8	2.4	36.0	61.0	53.0

The catalytic properties of metals have often been correlated with their electronic properties without arriving, however, at direct correlation of universal validity. One of the electronic properties often used by chemists originates from the resonating valence bond theory of Pauling[82].

An actual metal surface consists of resonating configurations with various numbers of electrons in the 'atomic', 'valence', and 'metallic' orbitals. The number of electrons in the unpaired non-bonding state (denoted by δ) can be calculated for various metals. The value of δ decreases from left to right in the rows of periodic table. To a first, rough approximation, the higher the value of δ the more electron density is available for localized σ-type of bonding. Some relevant information of these metals[83,84] is summarized in Table - 3.

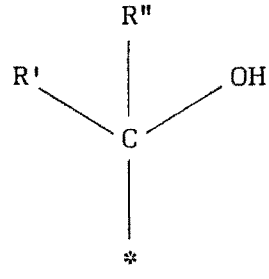
TABLE - 3

Some characteristics of transition metals.

Elements	Transition metals				
	Mn	Fe	Co	Ni	Cu
Valence electrons	7	8	9	10	11
Electronic configuration	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^9 4s^2$
Number of :					
bonding orbitals	6.56	6.56	6.56	6.56	..
bonding electrons	5.78	5.78	5.78	5.78	..
atomic orbitals	2.44	2.44	2.44	2.44	..
atomic electrons	1.22	2.22	3.22	4.22	..
No. of d-band holes per atom (δ)(spin free atomic electrons)	1.22	2.22	1.66	0.66	0.0
Atomic radius (Å)	1.18	1.28	1.26	1.24	1.28
Atomic structure	Complex	bcc	fcc	fcc	fcc

It can be noted from Table - 3 that metals which showed comparable activities possessed higher number of atomic electrons and fcc type of structure.

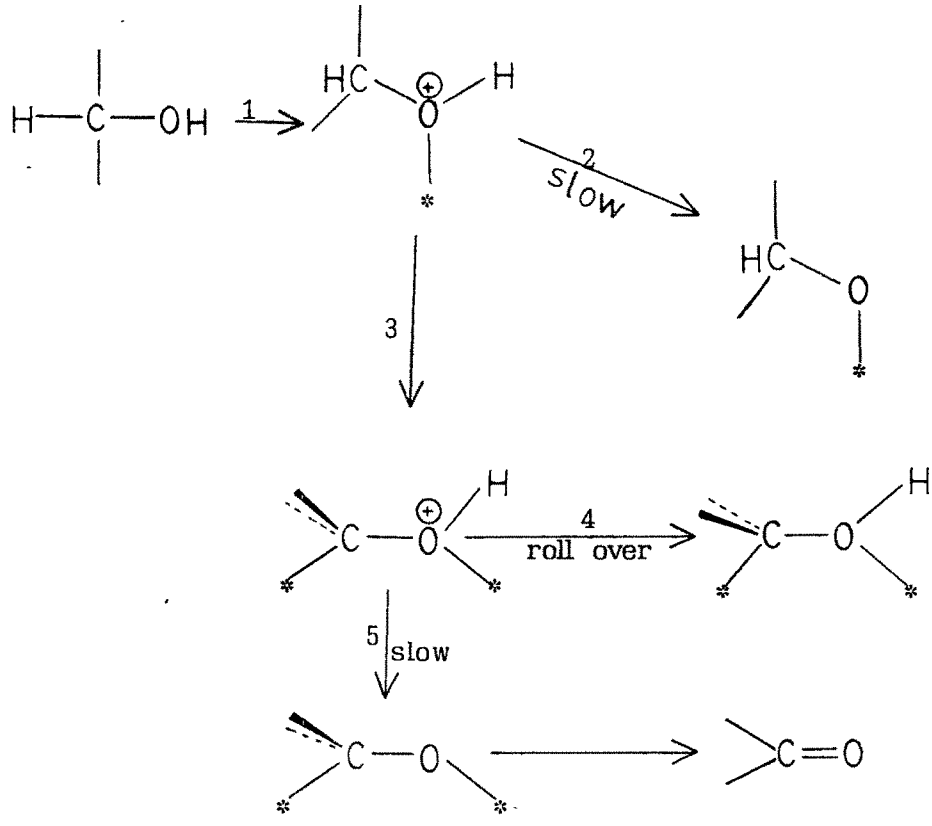
Due to practical significance of transformation, many authors have investigated the mechanism of dehydrogenation of secondary alcohols[14]. G.C. Bond[85] reviewed the previous studies and concluded that the dehydrogenation of alcohols and hydrogenation of ketones proceed via a common adsorbed surface formation of type I.



I

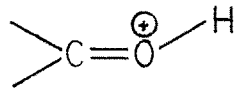
The kinetics and mechanism of dehydrogenation have been examined on Cu[86,87] Ni[88], Co, Ni-Cu[89], and Pt, Pd, and Rh. The process occurs through a carbonyl mechanism[89].

The mechanism on Cu based on deuterium exchange is proposed in which rate determining step is the cleavage of O-H bond[90] as shown in scheme - 1.



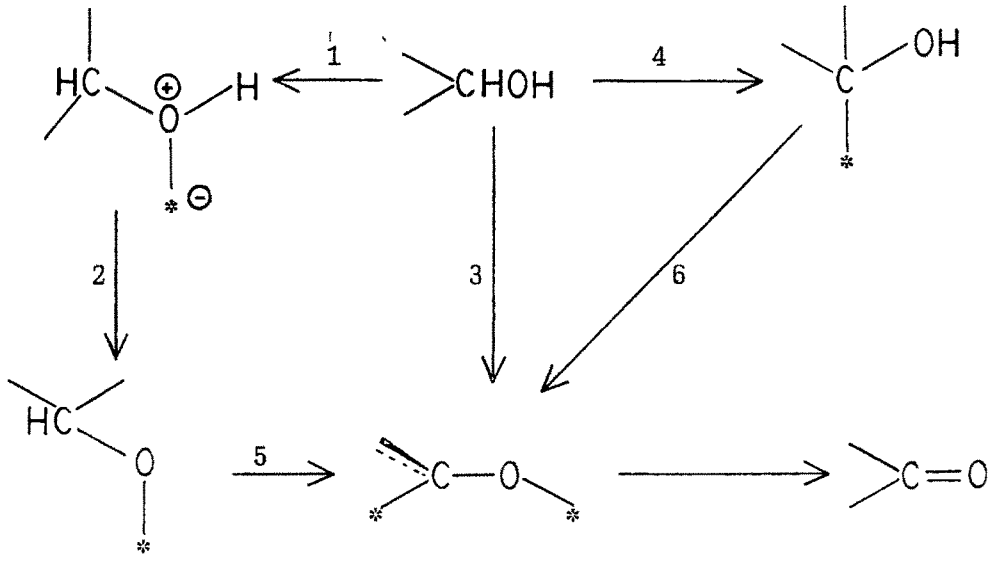
Scheme - 1 . Mechanism of dehydrogenation of sec. alcohol on Cu.

The above mechanism is supported by stereochemical studies. When optically active 2-butanol was used as starting material, a considerable amount of racemic alcohol was formed even at low conversions and the rate of recemization was same as the rate of α - C - D formation[7,90]. Reaction 4 is fast as compared to reaction 3. The roll over transition state is adsorbed so that the plane of II is perpendicular to the surface.



II

Study of the mechanism of dehydrogenation on Gr. VIII metals has led to the postulation of the mechanism[91,92] as shown in scheme - 2.



Scheme - 2 . Mechanism of dehydrogenation of sec. alcohols on Gr. VIII metals.

3.2 Effect of support on the activity of Ni catalyst.

Nickel (10% by wt.) supported on magnesia, silica, and alumina revealed distinguished effect of support on the activity of nickel catalyst (Fig. 2), but surface area of alumina did not have any effect on the activity. Table - 4 summarizes the results.

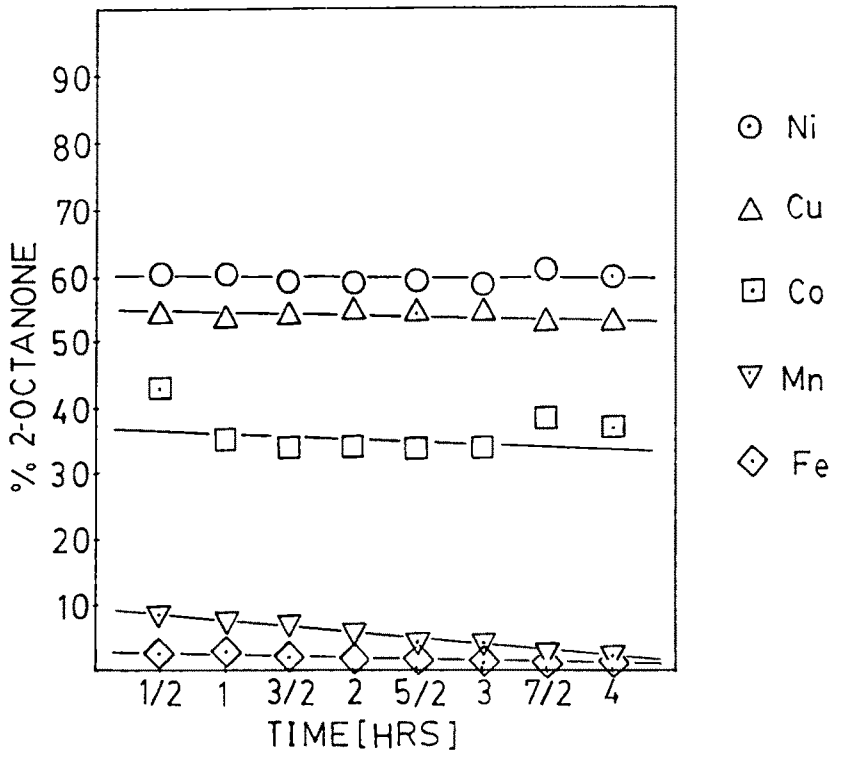


Fig. 1 - Dehydrogenation activity of transition metal catalysts.

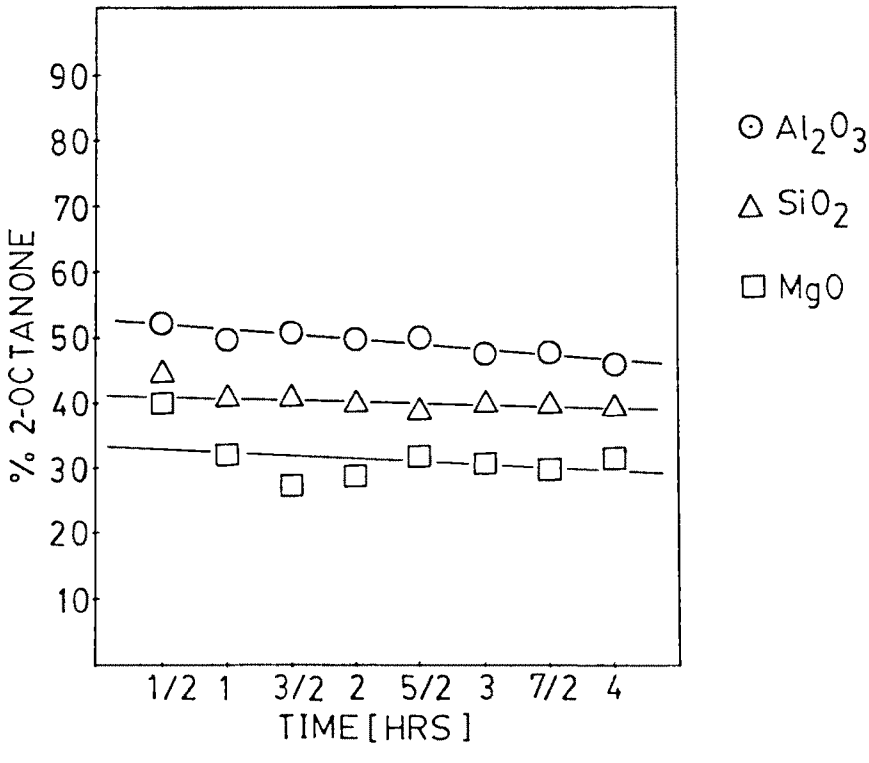


Fig. 2 - Effect of supports on the activity of Ni catalyst.

TABLE - 4

Effect of support on the dehydrogenation activity of Ni catalyst (10g) at 185°C.

Catalyst	Ni, 10 % by wt.					
	MgO	SiO_2	Al_2O_3, surface area, m^2g^{-1}			
			-	230	45-50	15-20
Space velocity (v/v/sec)	0.0851	0.0472	0.0962	0.0580	0.1277	0.0907
% 2-octanone	32.5	38.5	50.0	47.5	47.5	48.8

It can be observed from Table - 4 that supports play an important role in governing the activity of nickel catalyst. The efficiencies of the supports decrease in the following order :$Al_2O_3 > SiO_2 >$ MgO. Naturewise, alumina is slightly basic or neutral, silica towards acidic and magnesia basic. Hence neutral or slightly basic support is preferable for this reaction. Moreover, thermal stability of Ni/Al_2O_3 catalyst is also enhanced by divalent ions, such as Cu^{2+} or Ni^{2+} which occupy tetrahedral voids in spinel and retard the diffusion of Al^{3+} ions[93].

Precisely, the quantitative nature of changes which a carrier may bring in the catalyst is not yet properly understood. Yet from valance-bond theory of Pauling, there emerges a direct relationship between d-character and single bond radius of atoms in a metal crystal. The electronic factor of this type can govern the interatomic distances of metal-metal, metal-support, and support-support which will affect surface area, pore size, crystallite sites of the

active metal. It may change surface properties, too, e.g. acidic or basic sites on the surface of the catalyst. In fact, it has been proved by IR studies of dehydrogenation on supported catalysts that support affects chemisorption of the molecule, therefore, rate of reaction[94].

3.3 Effect of method of preparation on the activity of Ni/Al_2O_3 catalyst.

The catalyst prepared by co-precipitation method showed less activity compared to the catalyst prepared by physical mixing (Fig.3). The results are presented in Table - 5.

TABLE - 5

Dehydrogenation activity of 10% Ni/Al_2O_3 catalyst (10.0g) prepared by co-precipitation method at 185°C.

Catalyst	10% Ni/Al_2O_3, method of preparation			
	Physical mixing I	II*	Co-precipitation III**	IV**
Surface area of Al_2O_3 (m^2g^{-1})	15 - 20	-	230	15 - 20
Space velocity (v/v/sec)	0.0907	0.0851	0.0580	0.0962
% 2-octanone	48.8	37.0	9.0	42.8

* Al_2O_3 was co-precipitated from aluminium isopropoxide.

** $NiCO_3$ was co-precipitated with Al_2O_3.

The poor activity of catalyst II could be because of the formation of alumina coating on the surface of active metal which could affect metal ion-substrate interaction. It will cause small surface exposure of nickel for the reaction to occur. The lower activity of catalyst III could be due to restricted diffusion of reactant and product molecules caused by narrow pores. As is proved by catalyst IV where accessibility of reactant moleclules to the active sites will be easier because of bigger pores in the support.

3.4 Effect of copper on the activity of 10% Ni/Al_2O_3 and 10% Ni/MgO catalysts.

Incorporation of copper with Ni/Al_2O_3 catalyst exhibited interesting results (Fig.4). Low concentration of copper ($<50\%$) in the catalyst had slight deactivating effect while higher concentrations of copper ($>50\%$) completely diminished the activity of the catalyst. The results are presented in Table - 6.

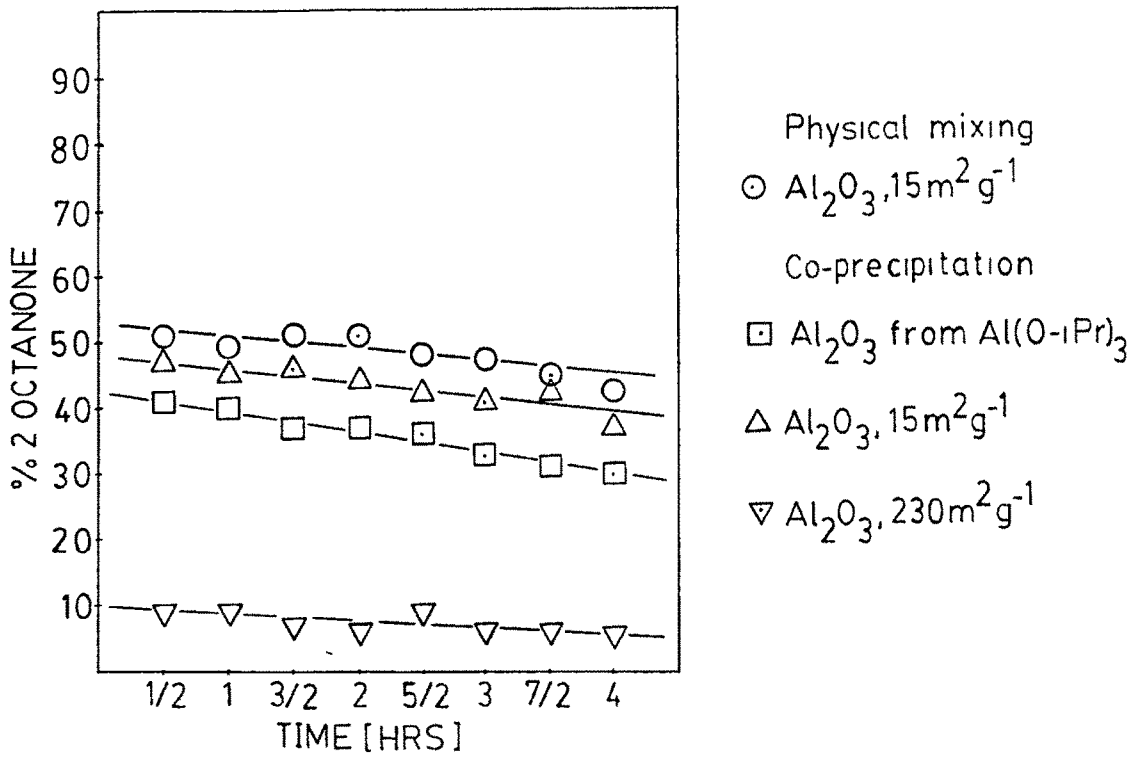


Fig. 3 - Effect of method of preparation on the activity of 10% Ni/Al_2O_3 catalyst

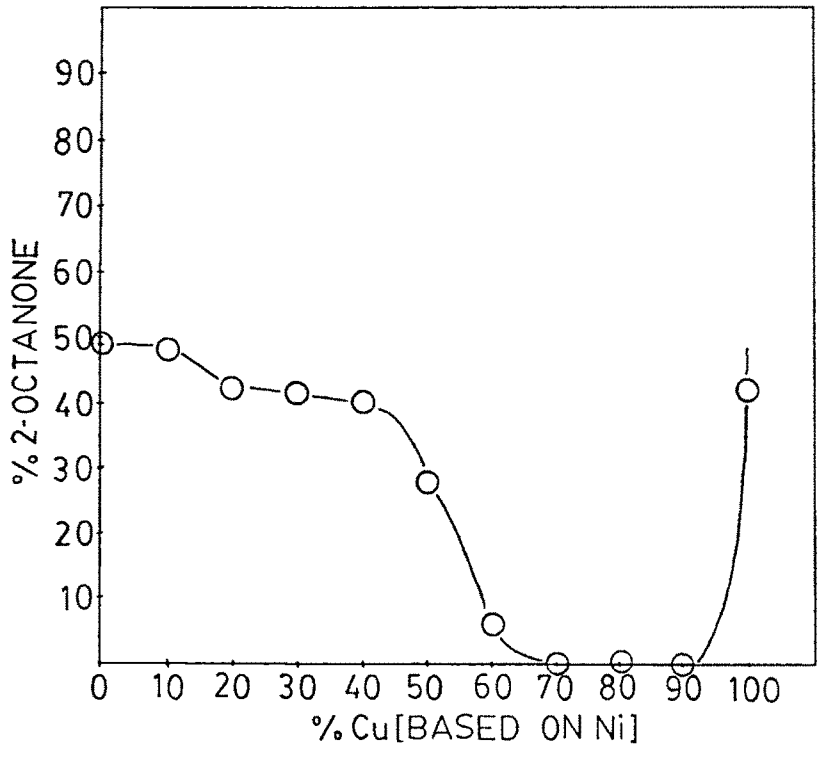


Fig. 4 - Effect of Cu on the activity of 10% Ni/Al_2O_3 catalyst.

TABLE - 6

Dehydrogenation activity of 10% Ni/Al_2O_3 and 10% Ni/MgO catalysts containing Cu in different concentrations at 185°C.

CATALYST	10 % metal loading												
		Al_2O_3 (surface area 15 - 20 m^2g^{-1})										MgO	
Cu (% by wt. based on Ni)	0	10	20	30	40	50	60	70	80	90	100	0	30
Space velocity (v/v/sec)	0.098	0.098	0.098	0.098	0.098	0.098	0.102	0.104	0.104	0.106	0.106	0.085	0.083
% 2 - octanone	48.8	48.0	42.7	42.0	40.0	28.1	6.0	0.0	0.0	0.0	42.0	32.5	26.1

It has been observed that mixed oxides of nickel and copper when reduced together with excess of hydrogen can form nickel-copper alloy[95]. And the catalytic activity of bimetallic alloys can be strongly dependent on their composition[96,97]. There are also both experimental evidence[98,99] and theoretical arguments[100] which suggest that alloy surfaces may be significantly enriched in one component of the alloy due to seggregation to the surface. This surface seggregation of an alloy has been related qualitatively to the observed composition dependence of the catalytic activity[98].

In attempting to rationalize the noticeable different effects of copper on the catalytic activity of nickel for the dehydrogenation of sec. alcohols, it is of interest to consider effects of copper on the adsorption properties of nickel. Sinfelt et al.[96] found that addition of copper to nickel decreased markedly the average strength of adsorption of hydrogen.

In general, this effect can be considered in terms of two factors, one being an electronic interaction between copper and nickel, and the other the structure or composition of the surface. The first of these factors would affect the strength of bonding of hydrogen to nickel, while the second would affect also the relative numbers of various types of sites available for adsorption, i.e. the number of surface Ni or Cu, or the number of Ni-Ni, Cu-Cu, or Ni-Cu atom pairs in the surface.

Auger spectroscopy of nickel-copper alloys containing different concentrations of copper has shown that the nickel rich alloys contained copper rich surfaces and that of copper rich alloys contained nickel rich surfaces[98].

The conclusion that one metal concentrates strongly on the surface of nickel-copper alloys of low overall copper or nickel content would imply a much greater alteration of intrinsic metallic properties in the surface region than in the bulk. Thus while the percentage d-character of the metallic bond[101] in copper-nickel alloys[103] decreases with the increase in copper content from 40 (Ni) to 36 (Cu) (Fig.5), the value of this quantity in the surface region would decline much more sharply as small amounts of copper are added to nickel because of the strong concentration of copper on the surface and vice versa (Fig.6).

The combination of the theory of seggregation[100] of one component of an alloy and reaction mechanism[102] provides a method to determine the number of atoms involved in the active site formation. In the case of dehydrogenation of secondary alcohol on Ni-Cu bimetallic catalysts, it can be assumed that formation of active site requires two or more nickel atoms[80] which, of course, will vary as the composition of two metals changes. However, it does not preclude the possibility that some copper atoms are also involved in the catalytic act.

Thus change in suitable metallic sites and percentage d-character is responsible for the observed activities of the catalysts.

3.5 Effect of rare earth oxides on the activity of 10% Ni-Cu/Al_2O_3 Catalysts (Fig.7)

Rare earth oxides exhibited promoting effect on the dehydrogenation activity of Ni-Cu/Al_2O_3 catalyst. The activating effect was nearly same irrespective

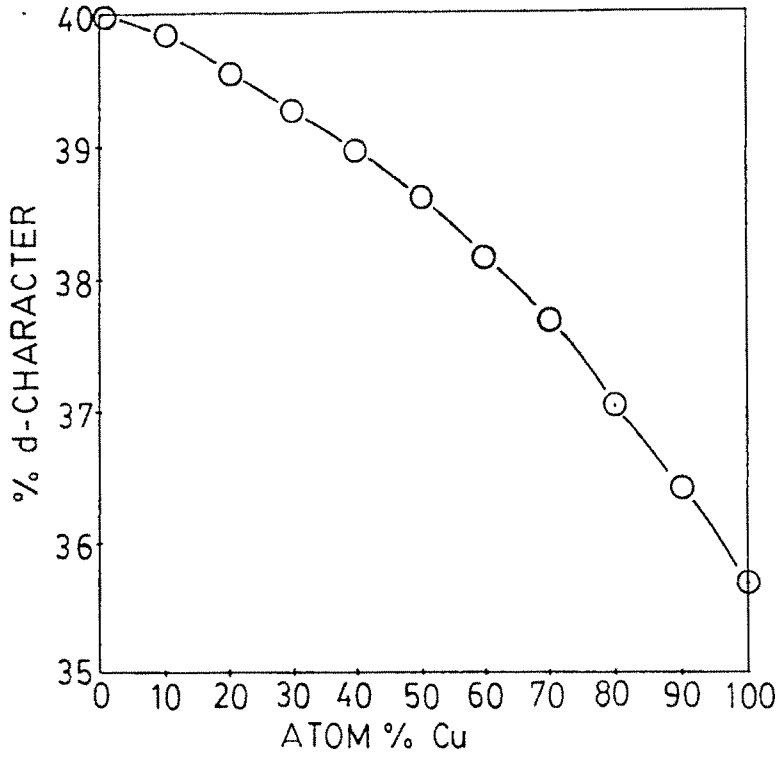


Fig. 5 - Percentage d-character of the metallic bond in Ni-Cu alloys as a function of composition.[103]

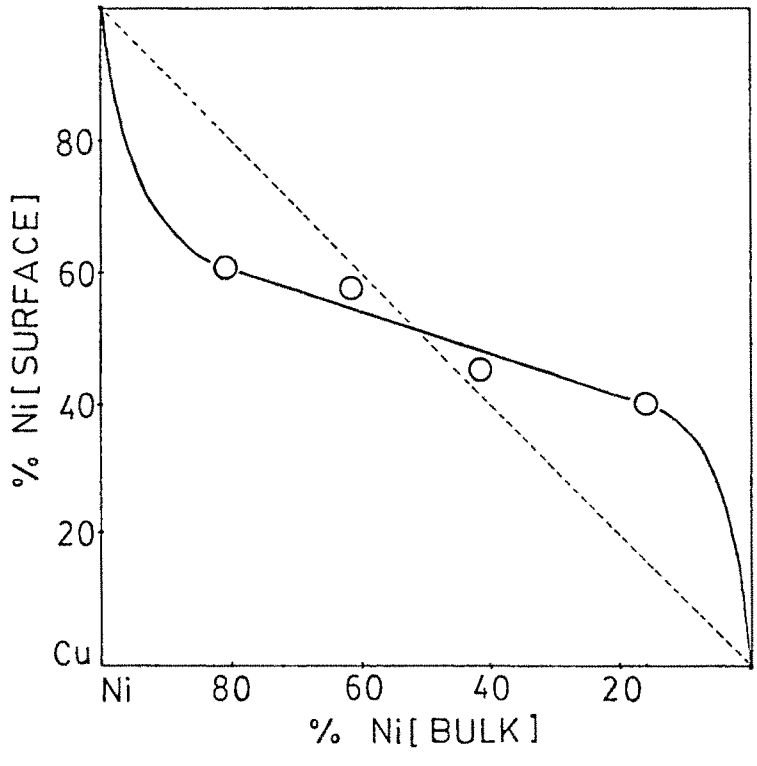


Fig. 6 - Surface composition of Ni-Cu alloys after oxidation-reduction treatment.[98]

of the concentration of rare earth oxides. The results observed are presented in Table - 7.

TABLE - 7

Effect of rare earth oxides on the dehydrogenation activity of 10% Ni-Cu/Al_2O_3 catalyst (10.0g) at 185°C.

Catalyst	10% Ni-Cu/Al_2O_3, Ni: Cu 7 : 3 (rare earth oxides, % by wt. based on Ni-Cu)								
	La_2O_3			CeO_2			ThO_2		
	0.1	1.0	5.0	0.1	1.0	5.0	0.1	1.0	5.0
Space Velocity (v/v/sec)	0.0982	0.0982	0.0982	0.0982	0.0982	0.0982	0.0982	0.0982	0.0982
% 2-octanone	52.6	53.7	54.8	54.1	54.1	50.9	51.5	51.7	55.3

As it can be seen that at low concentrations of rare earth oxides, cerium oxide had greater promoting effect on the activity of the catalyst followed by lanthanum oxide and thorium oxide, respectively. However, at higher concentrations (5.0%) the order was reverse, i.e. the activity decreased in the order $ThO_2 > La_2O_3 > CeO_2$.

The activating effect of rare earth oxides can be attributed to their electronic properties. Partial reduction of rare earth oxides can take place under the experimental conditions which through electron transfer between support or rare earth and transition-metal atoms[93] can alter the nature of active sites to favour the dehydrogenation reaction. Furthermore, geometric changes are also not ruled out in which suitable sites are created.

3.6 Effect of metal loading and CMC on the activity of Ni-Cu/Al_2O_3 catalyst containing 0.1 % CeO_2

When total metal loading was raised from 10% to 20% and bigger pores were created by adding more CMC, 10% instead of 3% , the results were not much improved.

Table - 8 summarizes the results obtained.

TABLE - 8

Effect of metal loading on the dehydrogenation activity of Ni-Cu/Al_2O_3 containing 0.1% CeO_2 as promoter (10.0g) at 185°C.

Catalyst	7:3, Ni-Cu/Al_2O_3, 0.1% CeO_2 based on Ni-Cu		
	I	II	III
Metal loading, %	10.0	20.0	20.0
CMC, %	3.0	3.0	10.0
Space velocity (v/v/sec)	0.0982	0.096	0.096
% 2-octanone	54.1	57.4	53.8

It can be inferred from the above results that aggregation of metal particles (crystallite site) as in case II does not favour the reaction to that extent. Moreover, larger number of bigger pores in the catalyst III also do not bring any effect on activity.

3.7 Effect of temperature on the activity of 10% Ni-Cu/Al_2O_3 catalyst containing 0.10% CeO_2 as promoter.

High temperature of reaction enhanced the activity of the catalyst by increasing the rate of adsorption and desorption (Fig.8). At 250° C, the activity and selectivity of the catalyst rose from 54.1% to 86.0% and 97.0% respectively.

This way a highly active and selective catalyst was developed. Other secondary alcohols, such as 2-pentanol, fenchol, and menthol were also dehydrogenated in very good to fair yields at 250°C. Table - 9 summarizes the products and their yields obtained.

The formation of fenchane (4) on dehydrogenation of fenchyl alcohol can take place either from parent alcohol or from fenchone (3)[104]. However, the formation of thymol (6) from menthol could be a product of further dehydrogenation of menthone (5).

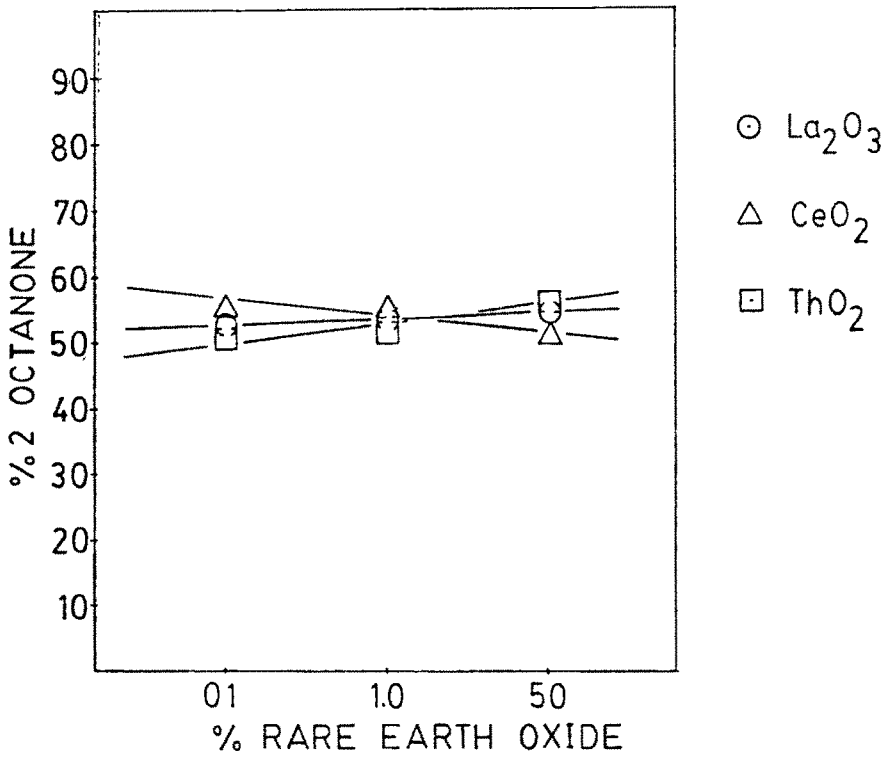


Fig. 7 - Effect of rare earth oxides on activity of 10% Ni-Cu/Al_2O_3 catalyst.

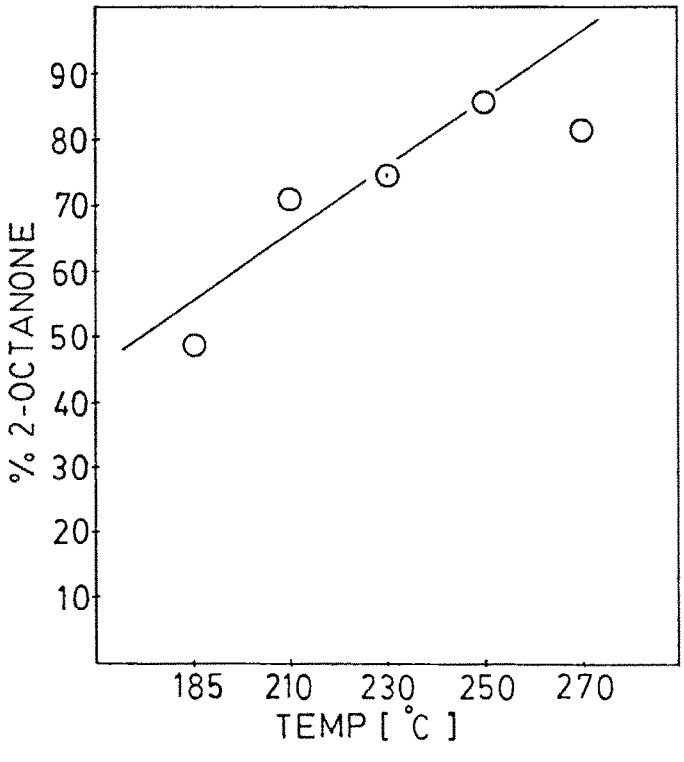
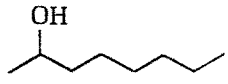
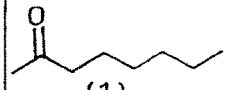
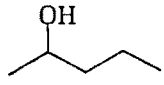
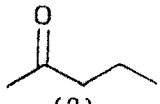
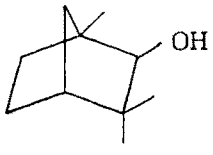
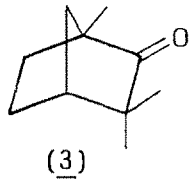
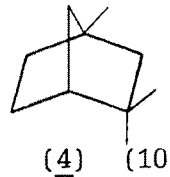
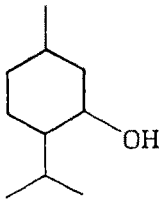
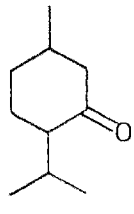
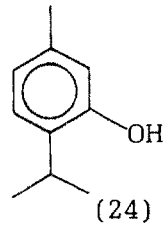
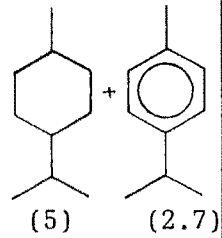


Fig. 8 - Effect of temperature on the activity of 10% Ni-Cu/Al_2O_3 catalyst containing 0.1% CeO_2.

TABLE-9

Dehydrogenation of secondary alcohols to corresponding ketones on 10% Ni-Cu/ Al_2O_3 catalyst containing 0.1% CeO_2 as promoter (10.0g) at 250°C.

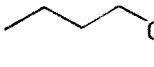
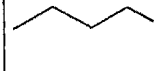
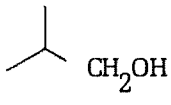
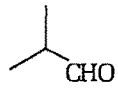
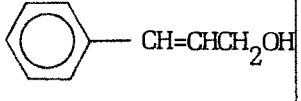
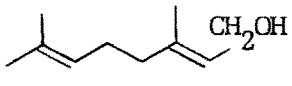
Substrate	Space velocity (v/v/sec)	Product(s)			Remarks
		Ketone	Yield %	Other products %	
	0.113	 (1)	86.0	-	11% Unreacted
	0.152	 (2)	90.0	-	10% Unreacted
	0.110	 (3)	70.0	 (4) (10)	20% Unreacted
	0.106	 (5)	48.0	 (24) (6) +  (5) (2.7)	20% Unreacted

3.8 Attempted dehydrogenation of primary alcohols on 10% Ni-Cu/Al_2O_3 catalyst containing 0.1% CeO_2 as promoter.

The dehydrogenation of primary alcohols was also attempted on 10% Ni-Cu/Al_2O_3 catalyst containing 0.1% CeO_2 but the yields of aldehydes were very poor. Table - 10 summarizes the results.

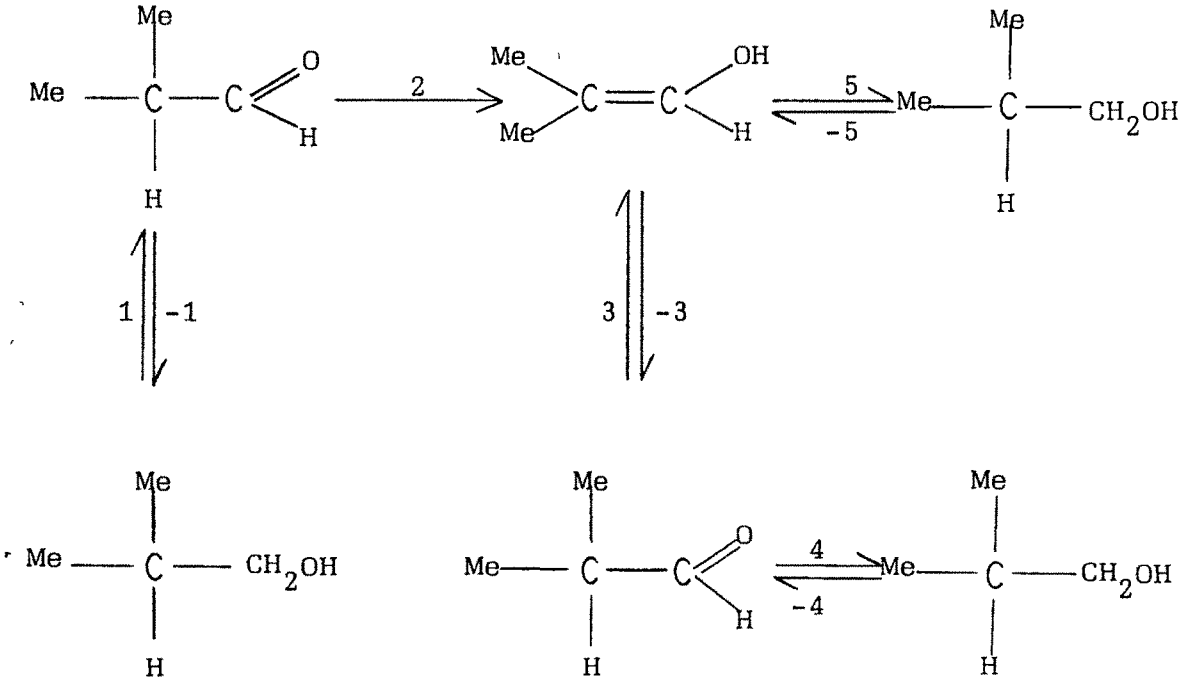
TABLE - 10

Dehydrogenation of primary alcohols on 10% Ni-Cu/Al_2O_3 catalyst containing 0.1% CeO_2 as promoter (10.0g) at 250°C.

Substrate	Space velocity (v/v/sec)	Product(s)			Remarks
		Aldehyde	Yield %	Other products %	
	0.152		3.9	-	96% Unreacted.
	0.174		4.9	-	95% Unreacted.
$CH_3(CH_2)_6CH_2OH$	0.113	$CH_3(CH_2)_6CHO$	7.4	Satd.+Unsatd. hydrocarbons (46.7)	45.8% Unreacted.
$CH_3(CH_2)_8CH_2OH$	0.099	$CH_3(CH_2)_8CHO$	2.7	Satd.+Unsatd. hydrocarbons (73.2)	25% Unreacted.
	0.132	-	-	Complex mixt.of hydrocarbons (100)	-
	0.105	-	-	Complex mixture of hydrocarbons (100)	-

The poor conversion of primary alcohols into aldehydes might have been because the resulting aldehyde could reversibly depress the activity of the catalyst[105]. The structure of the alcohols also plays an important role on bonding energy of atoms[106]. The lowering of energetic barrier of dehydrogenation of secondary alcohols in comparison with primary alcohols is caused firstly by an increase in adsorption potential and secondly by a decrease of C-H bond energy.

From the study carried on the dehydrogenation of optically active 2-methyl butanol and hydrogenation of 2-methyl butanol, it is inferred that the reaction proceeds via enol formation since there was formation of recemised product in substaintial proportion[107]. Based on this postulation, the mechanism of dehydrogenation of isobutyl alcohol is proposed as shown in scheme - 3.



Scheme 3. Dehydrogenation of isobutyl alcohol on transition metal catalyst.

4. CONCLUSIONS

From this study it can be concluded that :

(1) The dehydrogenation of secondary alcohols to ketones depends, to a greater extent, on the type of metal and its ratio of combination with other metals.

(2) A neutral or slightly basic support having low surface area is favourable for this reaction.

(3) Rare earth oxides have promoting effect on the activity of Ni-Cu/Al_2O_3 catalyst for this reaction.

(4) Primary alcohols and allylic alcohols could not be dehydrogenated using this catalyst.

(5) The catalyst [10% (7:3) Ni-Cu/Al_2O_3 containing 0.1% CeO_2] can be effectively used for the preparation of ketones from secondary alcohols in lab as well as in industry.

5. EXPERIMENTAL

All the b.ps are uncorrected.

The following instruments were used for spectral/analytical data : Perkin-Elmer infrared spectrophotometer, model 267, Perkin-Elmer model R 32 (90 MHz), NMR spectrometer; Hewlett-Packard 5712 A gas chromatograph (stainless steel column, 12', 10% CW, support 60-80 mesh chromosorb W; carrier gas H_2).

All PMR spectra were recorded with 15-20% solution in CCl_4 (unless otherwise stated) with TMS as internal reference; signals are reported in ppm (δ); while citing PMR data the following abbreviations have been used : s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

Other instruments used were : NFT-51, spinning-band teflon fractionation column (48 x 0.8 cm; theoretical plates, 80); Rajdhani moisture balance, RSMA-3 equipped with 240 V IR lamp; Cadmach rotary tablet machine, type 16 station model CMD-3.

Catalyst activity testing unit

A fixed bed type of apparatus was employed for the evaluation of catalytic activity. A glass tubular reactor, 84.0 cms in length and 2.0 cms in diameter was used. From the bottom upto the height of 36.0 cms solid glass balls (dia. 0.4-0.5 cm) were filled which acted as support and upto the height of 13.0-15.0 cms (10.0g) catalyst pellets were packed. Rest of the reactor was packed with glass balls serving as preheater zone. The reactor was

placed in a tubular furnace vertically which had the controlled heating system. The addition assembly was placed on the top of the reactor. The bottom end of the reactor rested on doubly bent tube which securely fitted in the receiver. Dry hydrogen gas which bubbled through conc. H_2SO_4 was passed through the reactor at the rate of 50-60 ml per minute. The furnace was now heated with the help of dimmerstat to a preset temperature of 350°C. During the process, initially when temperature had reached about 180°C, some water was collected in the receiver. Next, hydrogen flow was almost ceased (temp.250-280°) which after about 30 minutes became normal. The catalyst was reduced for a period of two hours when water stopped collecting. For the supported catalyst 0.25-0.30 ml and for the unsupported catalyst 1.4-1.5 ml water was collected. When reduction was complete, temperature of the reactor was lowered to 185°C and hydrogen flow was adjusted to 10-12 ml per minute. Alcohol was now added dropwise from the addition assembly at the constant rate of 15 ml per hour for a period of 8.0 hours. The receiver was kept chilled throughout the experiment. Aliquot was collected after each hour through the sampling device. A typical diagram of the apparatus is shown in Fig. 9.

General method of catalyst preparation

Unsupported Catalyst

Calculated amount of metal sulphates[108] were dissolved in water at 67-8° to a concentration of approx. 10%. Solid sodium hydrogen carbonate (2.2 g mole, purity $>$ 95%) was added in portions (~10) with vigorous stirring at 55°C to

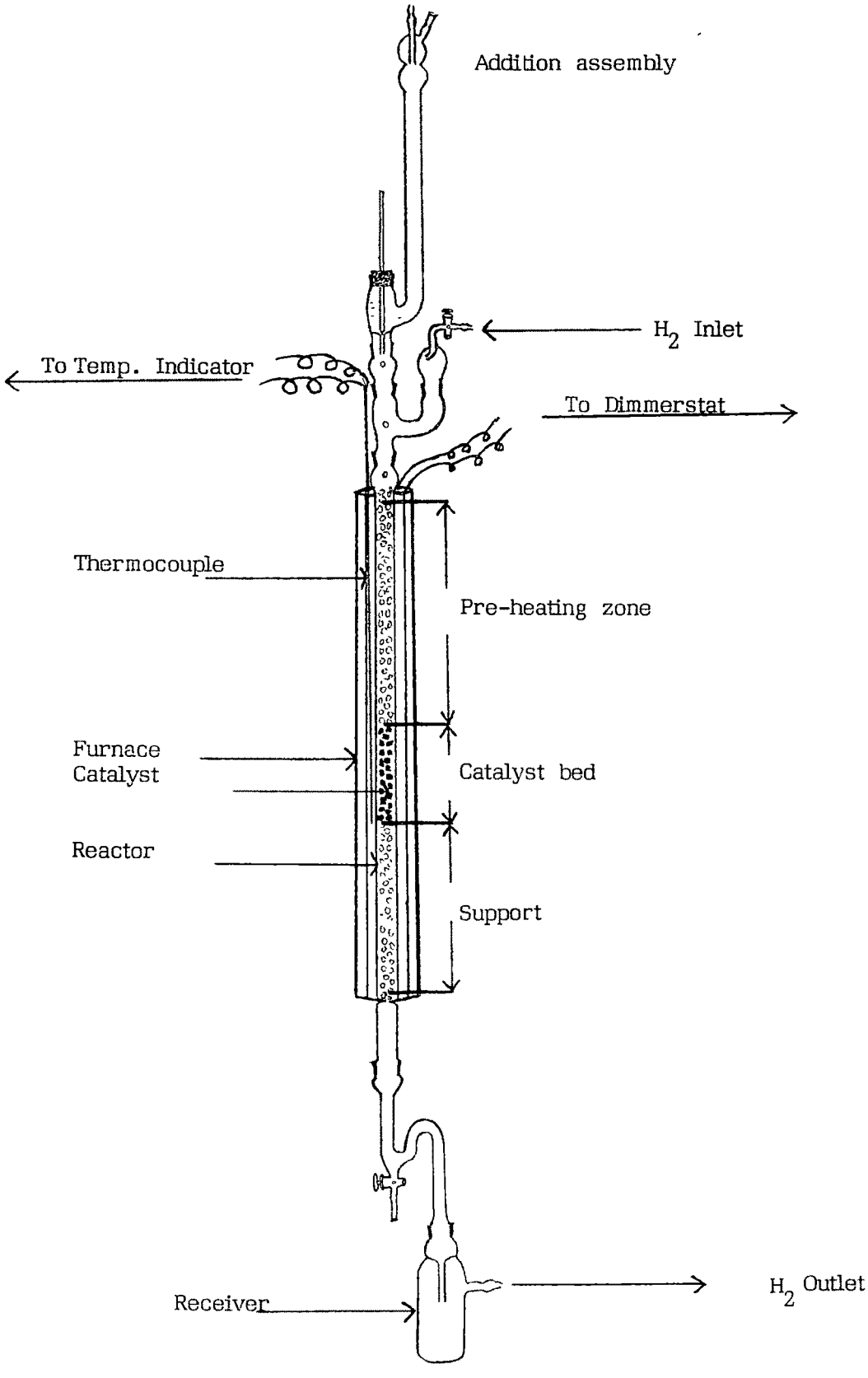


Fig. 9 - Catalyst activity testing unit.

precipitate out metal carbonates. The pH of the solution was maintained at 8.3 and it was digested for one hour at the maintained temperature. The precipitate was filtered out and washed with water several times (~14) to free it from SO_4^{2-} ions as confirmed by $BaCl_2$ test. The cake so obtained was dried over steam bath (6-8 hours) and crushed to powder. It was mixed with 3.0% CMC (pores making agent), 3.0% magnesium borate (binder), and promoter with the help of mortar and pestle. The moisture content of this powder was adjusted to 10-12%. It was then mixed with 2% graphite (lubricant) and pelleted. The pelleted catalyst was then calcined in muffle furnace at 360°C for 4 hours to convert carbonates into oxides.The colour of the pellets turned dark grey or black during this process. 10.0g of this catalyst was placed in the reactor and reduced to active metallic state before evaluation of its activity.

Supported Catalyst

Supported catalysts were prepared either by physical mixing the all ingredients or by co-precipitation method.

In physical mixing method, powdered metal carbonate was mixed with the support material[109] and other ingredients prior to pelletization.

In coprecipitation method, in one case, metal carbonate was dispersed in the solution of aluminium isopropoxide in anhydrous isopropyl alcohol at 80-5°C and precipitated alumina as aluminium hydroxide with water. It was followed by filteration, drying and pelletization.

In the other case calculated amount of alumina was dispersed in aqueous solution of metal sulphate at 68-9° C and precipitated metal carbonate with sodium hydrogen carbonate. It was followed by filteration, drying and pelletization as in the case of unsupported catalysts.

Representative exmple of catalyst preparation.

Preparation 10 % (7 : 3) Ni-Cu/Al_2O_3 catalyst containing 0.1 % CeO_2as promoter.

Nickel sulphate (6.40 g, 0.02385 mole) and copper sulphate (2.356 g, 0.00943 mole) were dissolved in 90 ml of water at 68-9°C. The solution was allowed to cool to ~ 55°C ambiently. The precipitation was then carried out by adding solid sodium hydrogen carbonate (6.15 g, 0.07323 mole) in several portions (~10) during 10-15 minutes. The temperature of the slurry at the end of addition of sodium hydrogen carbonate became ~50°C and pH 8.3. The slurry was stirred for one hour at the maintained temperature (52-5°C). The slurry was filtered and the cake so obtained was washed with warm water (52-55°C) several times (14 x 150 ml) to make it free from SO_4^{2-} ions. It was then dried and physically mixed with 18.0 g alumina (surface area 15-20 m^2/g), CMC 0.6 g, 3.0%), magnesium borate (0.6g, 3.0%), and CeO_2(0.002 g, 0.1% based on Ni-Cu) and after mixing with graphite (0.4 g, 2.0%) pelleted (dia 0.5 x 0.3 cm). The pelleted catalyst was calcined in muffle furnace at 360°C for 4.0 hours. The weight after calcination was found to be 22.0 g.

Dehydrogenation of individual alcohols.

In each experiment fresh catalyst (10.0g) was used and freshly distilled alcohol was passed at the constant rate of 15.0 ml/h for 8.0 hours at 250°C.

2-Octanol (98.2g, 120 ml) on dehydrogenation furnished 96.0g (98.9%) product which yielded 82.0g (85%) 2-octanone (b.p.89°/50 mm Hg) on fractional distillation. (Lit.[110a, 111a] NMR and IR)

2-Pentanol (97.2g, 120 ml) produced 94.0g (99%) dehydrogenated product from which 84.0g (89%) 2-pentanone was obtained by fractional distillation (b.p. 100-101°C).(Lit.[110b, 111b] NMR and IR)

Fenchyl alcohol (112.8 g, 120 ml) yielded 109g(98.0%) dehydrogenated product which on fractional distillation gave 76.0g (69.7%) fenchone (b.p. 68-9°/10 mm Hg) and 10.0g (9.1%) fenchane (b.p.85°/100 mm Hg). (Lit.[112a] NMR and IR of fenchone)

dl-Menthol (109.0g, 120 ml) afforded 105.0g (97.5%) dehydrogenated product from which 50.0g (48.0%) menthone (b.p. 89°/10 mm Hg) was separated by fractional distillation. (Lit.[112b] NMR and IR). Other products were identified to be p-menthane, p-cymene, and thymol by coinjection of authentic samples.

1-Pentanol (97.0g, 120 ml) gave 96.0g (99%) product which contained 3.9% n-valeraldehyde as identified by co-injection of authentic sample. (Lit.[110c, 111c] NMR and IR)

Isobutyl alcohol (96.0g, 120 ml) furnished 94.0g (98.0%) dehydrogenated product which was found to contain 4.9% isobutyraldehyde as identified by co-injection of authentic sample (Lit.[110d, 111d] NMR and IR)

1-Octanol (98.0g, 120 ml) afforded 91.0g (94.0%) dehydrogenated product which on fractionation yielded 6.0g (6.3%) n-octanal (b.p.88°C/50mm Hg), (Lit.[110e, 111e] NMR and IR), and 43.0g (45.7%) a mixture of hydrocarbons (b.p.125°C)

1-Decanol (99.0g, 120 ml) produced 90.0g (92%) product which contained 2.5% decanal (Lit.[110f, 111f] NMR and IR). 64.0g (71%) low boiling cut (b.p. 90°C/50 mm Hg) was obtained which was found to be mixture of n-decane, 1-decene, and 2-decene.

Cinnamyl alcohol (124.0g, 120 ml) yielded 105g (86.0%) dehydrogenated product which was found to be a complex mixture of hydrocarbons which could not be separated and identified.

Geraniol (106.0g, 120 ml) furnished 90.0g (86.0%) dehydrogenated product which was found to be a complex mixture of hydrocarbons which could not be separated and identified.

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SECTION 2

DEHYDROGENATION OF CYCLOHEXANONES TO THE PHENOLS

DEHYDROGENATION OF CYCLOHEXANONES TO THE PHENOLS

Abstract

The Ni-Cu-Mn catalyst can be conveniently prepared from their mixed carbonates, co-precipitated from aqueous sulphate salts solution with sodium hydrogen carbonate, by calcination and reduction. It has also been used to convert various substituted cyclohexanones to the corresponding phenols in high yields in vapour phase at 330°C. The results are summarized in the forms of tables and graphs.

The copper (30 atom %) induces selectivity of the Ni catalyst supported on Al_2O_3 and MgO; the former otherwise converts cyclohexanones into hydrocarbons. Higher temperature seems to be superior than low temperature reaction. In contrast to our previous results, the effect of the rare earth oxide is either neutral or diminishing on the activity of Ni-Cu/Al_2O_3 catalyst. The MgO has greater efect on the selectivity of Ni-Cu/Al_2O_3 catalyst. But Mn (41% by wt.) has still greater effect on the activity and selectivity of Ni-Cu/Al_2O_3 catalyst. Higher metal loading of Ni-Cu-Mn (7:3:7) accomplishes higher conversions.

1. INTRODUCTION

Phenol and its homologues constitute an important class of compounds. They are mainly used in the manufacture of resins, dyes, drugs, herbicides, insectisides, and as antioxidants. They are important bactericides, too.[1]

The occurrence of phenols in nature is not very common. However, some phenols like thymol is found in the oil of thyme from Thymus vulgaris and in the oils from Ptychotis ajowan and Monard punctata and carvacrol in the oils of Satureja hortensis and Origanum hiritium[2].

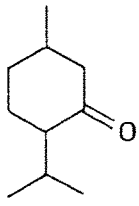
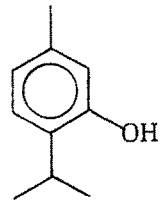
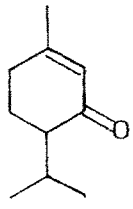
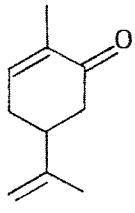
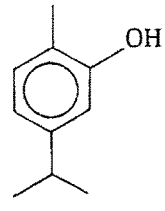
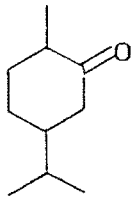
To compensate the growing demand of simple phenols, search for synthetic methods is inevitable. In general, phenols are prepared industrially by aromatic substitution. A review of the methods of industrial preparation of phenols is published by G.Szonyi[3]. However, the dehydrogenation of saturated and unsaturated ketones contained in an incipient aromatic system over transition metal catalysts has proved to be an effective, easy, economical, and industrial method for the preparation of phenols.

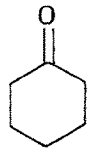
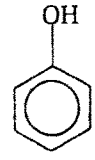
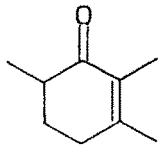
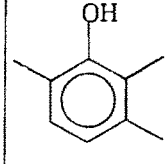
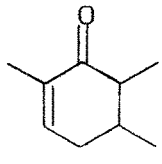
The ease of aromatization of cyclohexanones to phenols is governed mainly by two factors : (1) the relative thermodynamic stability of the two forms, and (2) the ease of transition from one form to the other[4].

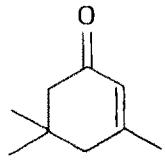
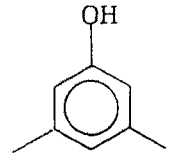
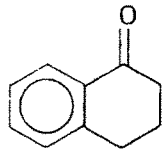
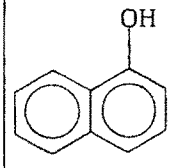
A large number of catalysts and catalyst systems have been described. Table-1 summarizes most of the available information.

T A B L E - 1

Dehydrogenation cyclohexanones to the corresponding phenols on various catalysts.

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
01.		Pd, 220°		80	5
02.	"	Ni	"	65	6
03.	"	Active C, 200°	"	-	7
04.		Pt/Charcoal, 300°, CO_2	"	quant.	8
05.	"	Porcelain-Ni, 250°	"	70	8
06.		Pd, 220°		95	5
07.	"	Pd/C, 232°	"	92	9
08.		Pt/C	"	15	5

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
09.		Pt-KOH		94	10
10.	"	Pt/C	"	74	11-13
11.	"	Pt/SiO_2, 335-54°	"	-	14
12.	"	Pt/SiO_2, K_2CO_3	"	97	15-16
13.	"	Pt/SiO_2, Na_2O	"	-	17
14.	"	Pt/Al_2O_3, KOH, 320°	"	65	18
15.	"	$Pt-Ir/SiO_2$, Na_2O	"	-	19
16.	"	Ni-CuO, Cr_2O_3, Na_2SO_4	"	97	20
17.	"	Ni-Cu-Cr/C, Na_2SO_4, 400°	"	89	21
18.	"	$Ni-Co/SiO_2$, NaOH	"	60-5	22
19.	"	$Ni-Sn/SiO_2$, 375°	"	94	23
20.	"	Cr_2O_3, 600°, steam + N_2	"	86	24
21.	"	Cu-Mn-Cr_2O_3, 350-600°	"	-	25
22.	"	Fe_3O_4-Cr_2O_3-K_2O, 260°, steam.	"	80	26
23.		Pd/SiO_2, 300°		95	27
24.	"	Pd/Mg-Al spinel, 280°, H	"	85.4	28
25.		Pd/C, 200°	"	88	29

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
26.		Cu/MgO		50	30
27.	"	Cr_2O_3/Al_2O_3,K_2O, 610-30°	"	73	31
28.	"	Fe_2O_3/Al_2O_3, 500°	"	33.6	32
29.	"	MgO/Al_2O_3	"	74-8	33
30.		Pd		46	34
31.	"	Pd/C, 160°	"	85	35
32.	"	Pt/Al_2O_3, KOH, 360°	"	92	36
33.	"	Pt/Al_2O_3, Na_2SO_4	"	89	37
34.	"	Pt/Al_2O_3, CrO_3, Na_2SO_4, Na_2CO_3.	"	93	38
35.	"	Pt-Mn, Na_2SO_4	"	48	39,40
36.	"	Ni/kieselguhr, 260-300°	"	40-65	41
37.	"	Ni/Al_2O_3, K_2SO_4, H	"	-	42
38.	"	Ni-Cr	"	-	43
39.	"	Ni-Cr, Na_2SO_4	"	93	44
40.	"	Ni-Cu-Cr, Na_2SO_4	"	60	45
41.	"	Ni-Cu-Cr/SiO_2, Na_2SO_4, 290°.	"	37	46
42.	"	$CuO \cdot Cr_2O_3$, 300°	"	76	47
43.	"	Cu/ZnO, 250°, H	"	72.1	48-50
44.	"	FeO-Mg-CaO, 450-650°	"	-	51
45.	"	CaO, 500-600°	"	-	52

2. PRESENT WORK

It can be noted from the information as summarized in Table - 1 that costly noble metal catalysts like Pt and Pd are generally employed to bring about such transformations. Although other transition metals are also used; they do not produce phenols in good yields. Impetus for intensive research stems from realization that transition metal catalysts can be further explored in order to produce phenols from cyclohexanones in high yields. It has been our main objective of present study to investigate a catalyst which could give thymol in high yield from menthone, a by-product of menthol process.

In order to achieve this aim extensive but systematic study was undertaken. A large number of supported and unsupported catalysts were prepared in the pellet shape by physical mixing the support material with metal carbonate, freshly precipitated from its aqueous sulphate salt solution with sodium hydrogen carbonate. The pelleted catalyst was then calcined to convert carbonate into oxide at 360°C for 4.0 hours in a well-ventilated furnace. The catalyst in oxide form was reduced to active metallic state in a stream of hydrogen gas. The activity of this catalyst (10.0g) was evaluated for the dehydrogenation of menthone to thymol at 250°C.

Since nickel was found to be superior dehydrogenation catalyst to copper, cobalt, iron, and manganese in our earlier experiments, it was decided to exploit nickel based catalysts for this purpose.

Supported catalysts are preferred over unsupported catalysts because of relatively high specific surface area. Nickel (10% by wt.) was despersed on alumina of low surface area (15-20 m^2g^{-1}) and magnesia separately.

It is reported that copper (Gr. I B) when incorporated with nickel catalyst, moderates activity and boosts selectivity[64]. Copper (30% by wt. based on Ni) was co-precipitated with nickel and dispersed on alumina and magnesia supports. Examination of activities of such catalysts revealed Ni-Cu/Al_2O_3 catalyst to be better than other catalysts. So the efforts were directed to promote its activity.

Rare earth oxides have 4 f and 5 f sub-shells partially filled. They were observed to promote the activity of Ni-Cu/Al_2O_3 catalyst for the dehydrogenation of alcohols. The effect of such oxides, viz. La_2O_3, CeO_2, and ThO_2 in different concentrationson the activity of Ni-Cu/Al_2O_3 catalyst for the dehydrogenation of menthone to thymol was studied.

In order to improve the activity of Ni-Cu/Al_2O_3 catalyst, metal loading was raised from 10% to 20% by wt. The effects of pores structure and period of calicination were studied, too. Dehydrogenation reaction was also tried at higher temperature.

Magnesium oxide is relatively inert catalytically. Hydrocarbons appear to undergo no reaction but there is some activity as a catalyst for alcohol dehydration and dehydrogenation[53]. It was proposed to study the effect of different concentrations of magnesium oxide on the dehydrogenation activity of Ni-Cu/Al_2O_3 catalyst at various temperatures.

Addition of manganese in the noble metal catalyst increases hydrogen adsorption and dehydrogenation activity of it. It also suppresses hydrocracking of the hydrocarbons[54]. Hence we incorporated manganese with Ni-Cu/Al_2O_3 catalyst in the concentrations of 26, 41, and 58% by weight based on Ni-Cu and studied the effect.

The effect of total metal loading on Ni-Cu-Mn/Al_2O_3 catalyst containing 41% manganese by wt. was also studied. The observations led to the complete elimination of alumina support.

In order to prove wider applicability of this catalyst (Ni-Cu-Mn), other related cyclohexanones were also dehydrogenated to their corresponding phenols.

3. RESULTS AND DISCUSSION

3.1 Effect of support on the activity of Ni

Ni/Al_2O_3 catalyst showed 37.0% activity and 33.7% selectivity (Fig.1) while Ni/MgO revealed 12.5% activity and 98.4% selectivity (Fig.2). The side products in the former catalyst were deoxygenated compounds, p-menthane and p-cymene. The results are summarized in Table - 2.

It is clear from the results that nature of support plays a major role in governing the activity and selectivity of nickel catalyst. The deoxygenation property of Ni/Al_2O_3 catalyst can be rationalized in terms of dipolar character of Al_2O_3 surface. It is generally agreed that alumina has amphoteric nature and there are both electron-donor and electron-acceptor sites on its surface and acts as an acid-base bifunctional catalyst. Some relevant information is also available about surface groups of alumina[55]. The Lewis acid site is visualized as an incompletely co-ordinated aluminium atom formed by dehydration and the weak Brønsted acid site as a Lewis site which has adsorbed moisture while the basic site is considered to be a negatively charged oxygen atom. And it has been stated that random removal of all hydroxyl groups leave the surface of variable properties. The remaining $\bar{O}H$ ions cover about 10% of alumina surface and have been grouped into five types having from four to zero nearest oxide neighbours. These five $\bar{O}H$ sites should vary in chemical properties; site having four nearest oxide neighbours is most basic and site having no oxide neighbour is most acidic[56].

On the other hand, magnesia supported catalyst does not have such sites, hence no such side reaction was observed.

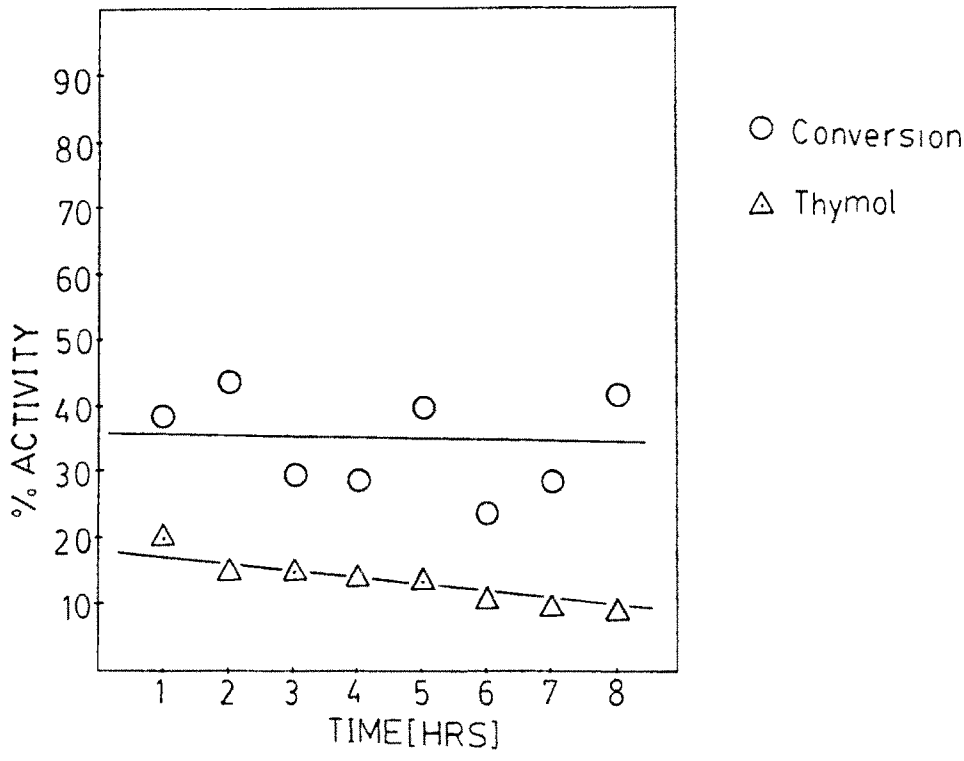


Fig. 1 - Activity of Ni/Al_2O_3 catalyst for menthone dehydrogenation.

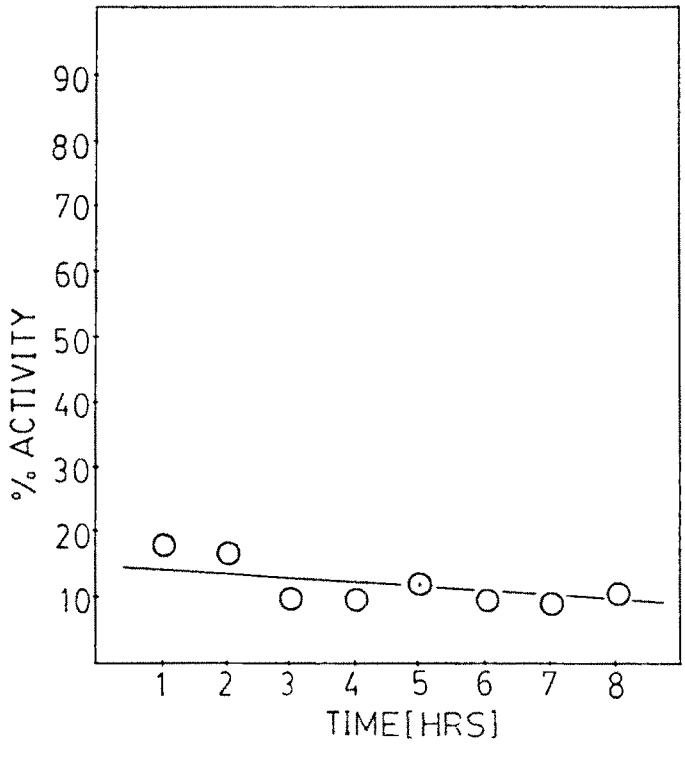
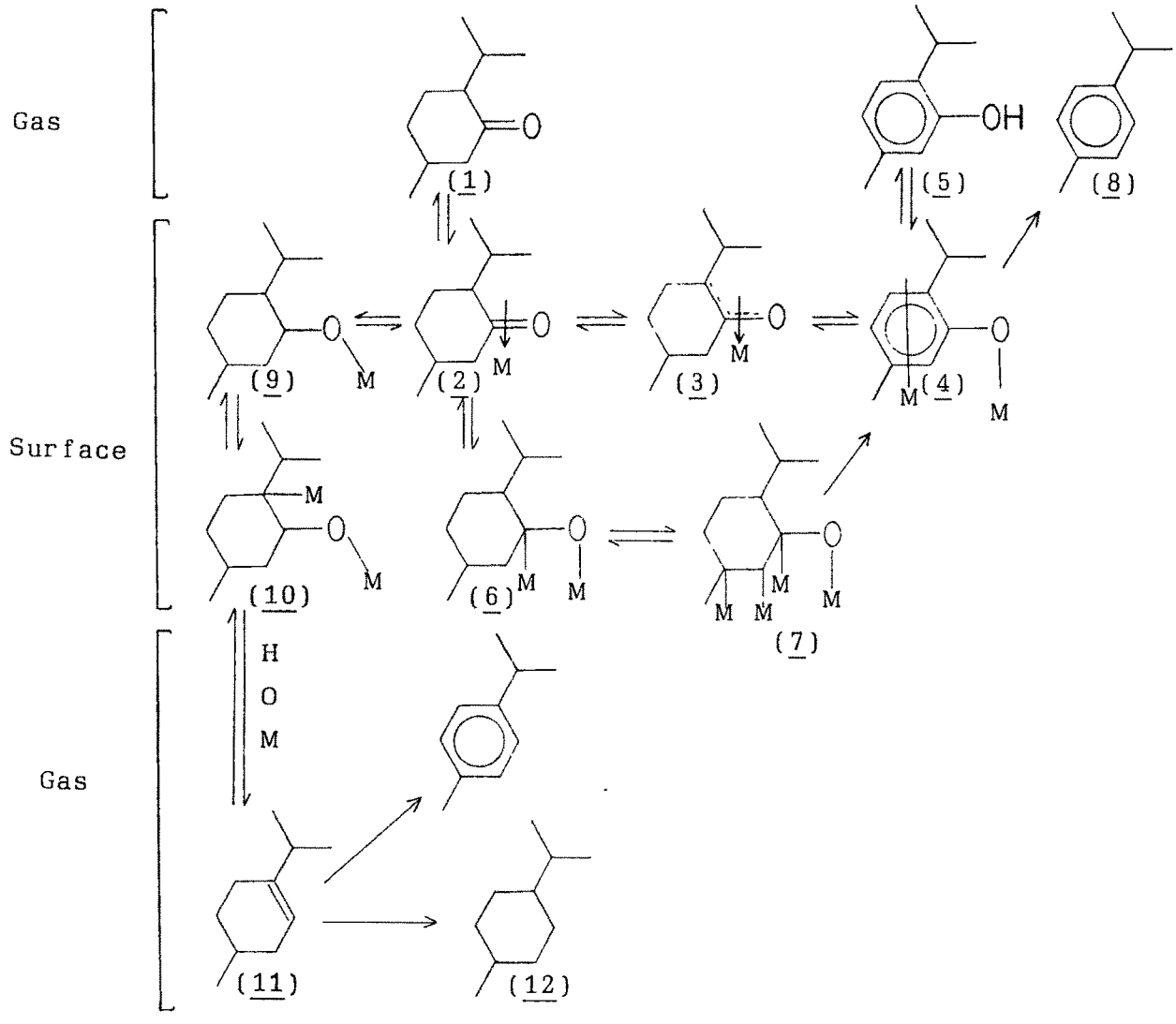


Fig. 2 - Activity of Ni/MgO catalyst for menthone dehydrogenation.

The formation of various products on the active sites of catalyst can now be pictured as shown in scheme-1. Although, the mechanism of dehydrogenation of cyclohexanones to phenols on solid surfaces is not yet well understood, but it is proposed that reaction proceeds via adsorption of carbonyl group followed by abstraction of hydrogen atoms of the ring[41]. And the abstraction of hydrogen from the more substituted α-carbon is favoured[57].



Scheme - 1 . Formation of various products from menthone.

Where M stands for the active site on catalyst surface. Adsorption of ketone group on donor site of the catalyst and subsequent addition of hydrogen to form species like 9 which on loosing one hydrogen from its α-position can lead to the formation of olefin which can either hydrogenate or dehydrogenate or disproportionate to 12 . On the other hand, reaction can proceed via 2 , 3 , or 6 , 7 to form aromatic species like 4 which on desorption can form phenol 5 or dehydroxylate to aromatic hydrocarbon 8 .

3.2 Effect of Cu on Ni/Al_2O_3 and Ni/Mgo catalysts.

Incorporation of Cu (Gr.I B) with Ni/Al_2O_3 and Ni/MgO catalysts increased activity and selectivity of the former catalyst to 42.7% and 85.9% (Fig.3) and that of latter to 21.0% and 90 % (Fig.4) respectively. The results are summarized in Table- 2.

TABLE - 2

Dehydrogenation of menthone to thymol on supported Ni and Ni-Cu catalysts (10.0g) at 250°C.

Catalyst	10% by wt. metal loading, Ni:Cu ratio 7:3			
	Ni/Al_2O_3	Ni/MgO	$Ni-Cu/Al_2O_3$	Ni-Cu/MgO
Space velocity (v/v/sec)	0.107	0.095	0.109	0.095
Conversion (%)	37.0	12.5	42.7	21.0
Thymol (%)	12.5	12.3	36.7	18.9
Other products (%)	24.5	0.2	6.0	2.1

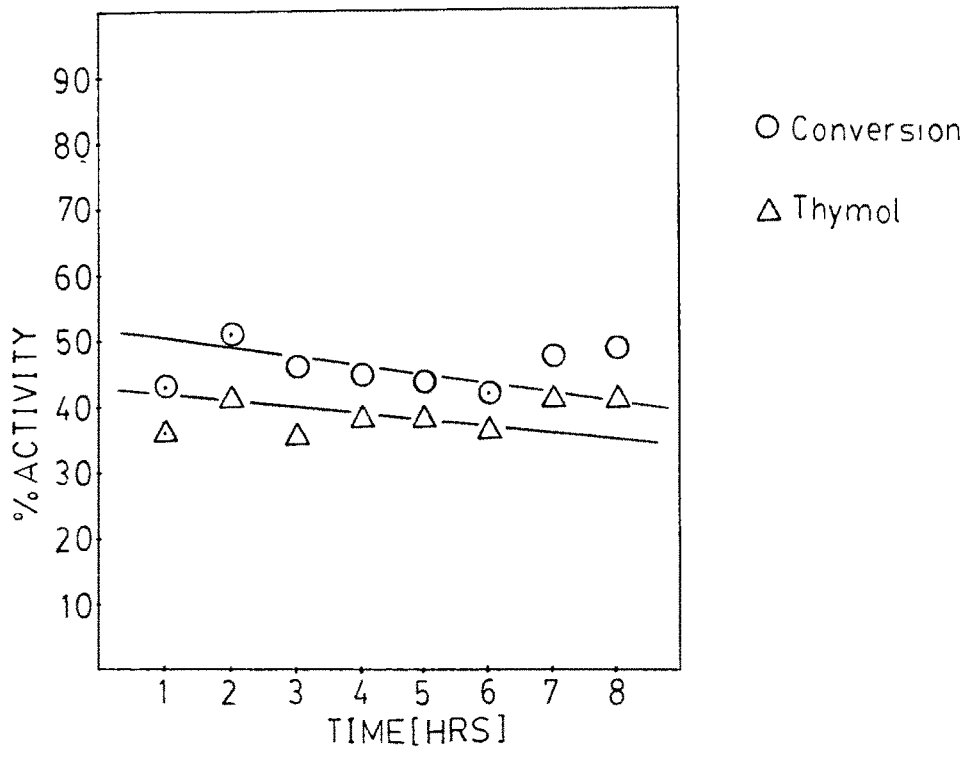


Fig. 3 - Activity of Ni-Cu/Al_2O_3 catalyst for menthone dehydrogenation.

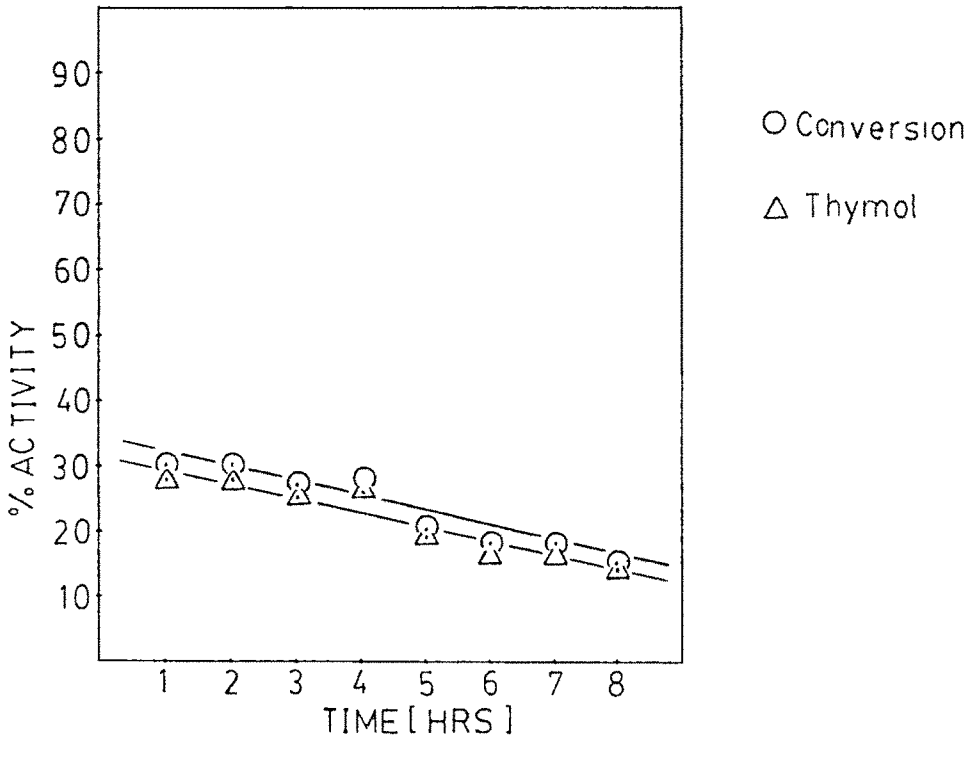


Fig. 4 - Activity of Ni-Cu/MgO catalyst for menthone dehydrogenation.

The effect of copper on nickel catalyst has been studied by many workers. A review article on bimetallic catalysts has been published by Sinfelt[58]. It has been observed that when mixed copper and nickel oxides are reduced together with excess of hydrogen at elevated temperature 350-500° form Cu-Ni alloy[59,60]. And the alloy has a tendency to clustering at high temperatures (>300°) above the miscibility gap and because the sublimation heats of copper and nickel are different and lower for copper, copper is enriched in the surface of equilibrated alloy[61]. This fact is proved by the use of Auger spectroscopy on large, flat crystals which showed that copper was seggregated onto the surface of nickel and that significantly suppressed hydrogen adsorption by the catalyst[62]. This cluster formation can affect the catalytic activity in two ways : one being an electronic interaction between copper and nickel can decrease percentage d-character of Cu-Ni metallic bond[63] much more than usual due to seggregation of Cu onto the surface (section-1) and second effect can be on the relative number of various types of sites available for adsorption, i.e. the number of surface nickel or copper atoms or the number of nickel-nickel, copper-copper, or nickel-copper atom pairs onto the surface[64].

The transformation of menthone to thymol can now be rationalized in these terms. It can be assumed that intermediates involved in dehydrogenation form bonds with more than one surface metal atom[65,66]. The concentration of such an adsorbed species would be proportional to the concentration of suitable multiple sites which, in turn, is a sensitive function of nickel content of the surface.[61,64,67]

A geometric factor of this type can account for at least part of the effect of

copper on nickel catalyst. Copper can affect the property of nickel on the surface by altering the strength of adsorption of intermediates. This refers to electronic factor. The strength of adsorption would, in turn, increase the difficulty in rupturing C-O bond. Besides, the nature of sites on alumina surface could also be modified through electronic interaction.

3.3 Effect of rare earth oxides on 10% Ni-Cu/Al_2O_3 catalyst.

The effect of rare earth oxides on the activity of Ni-Cu/Al_2O_3 catalyst has been either deactivating or nil (Fig.5). The results obtained from such catalysts are presented in Table - 3.

TABLE - 3

Effect of rare earth oxides on the activity of 10% Ni-Cu/Al_2O_3 catalyst (10.0g) at 250°C.

Catalyst	10% Ni-Cu/Al_2O_3, rare earth oxides (% by wt. of Ni-Cu)									
	-	La_2O_3 0.1	La_2O_3 1.0	La_2O_3 5.0	CeO_2 0.1	CeO_2 1.0	CeO_2 5.0	ThO_2 0.1	ThO_2 1.0	ThO_2 5.0
Space velocity (v/v/sec)	0.109	0.109	0.109	0.109	0.109	0.109	0.109	0.109	0.109	0.109
Conversion (%)	42.7	16.0	40.0	22.2	33.1	44.6	33.7	30.6	25.8	30.1
Thymol (%)	36.7	11.5	34.3	14.6	28.8	36.8	31.1	27.2	23.8	26.7
Other products (%)	6.0	4.4	5.6	7.5	4.2	7.7	2.5	3.4	2.0	3.3

The effect of rare earth oxides on Ni-Cu/Al_2O_3 catalyst can be correlated with their structural and electronic properties. The rare earth oxides have 4 f or 5 f subshells partially filled. The electronic configurations of them are as follows:

$La_{(57)} = 5\ d^1\ 4\ f^0\ 6\ s^2$

$Ce_{(58)} = 5\ d^1\ 4\ f^1\ 6\ s^2$

$Th_{(90)} = 6\ d^1\ 5\ f^1\ 7\ s^2$

Lanthanum oxide possesses rhombohed type of structure while thorium oxide and cerium oxide have cubic type of crystal lattices. The size of these molecules is also bigger than transition metals. Some other relevant information is also available.[68]

These oxides can change the degree of interactions between metal-metal and metal-support particles by being present in between them; this can lead to the change in the extent adsorption of intermediates and subsequent change in activity. Partial reduction of these oxides is also possible under the experimental conditions which through electron transfer between support or rare earth and transition-metal atom can change the nature of active sites.[69] However, no conclusion can be derived from these experiments because in some cases catalysts retained their activities.

3.4 Effect of metal loading, CMC, and period of calcination.

The amount of metal loading on alumina did not have much activating effect. Similarly, period of calcination and size of pores created by addition of more

of CMC had little effect on the activity of the catalyst (Fig.6). Table - 4 summarizes the results obtained.

TABLE - 4

Effect of metal loading, CMC, and period of calcination on dehydrogenation activity of Ni-Cu/Al_2O_3 catalyst (10.0g) at 250°.

Catalyst	Ni-Cu/Al_2O_3 (Ni-Cu ratio 7 : 3)			
	I	II	III	IV
Metal loading (% by wt.)	10.0	20.0	20.0	20.0
CMC (% by wt.)	3.0	3.0	10.0	10.0
Calcination time (Hrs.)	4.0	4.0	4.0	12.0
Space velocity (v/v/sec)	0.109	0.107	0.107	0.107
Conversion (%)	42.7	35.1	46.6	49.3
Thymol (%)	36.7	28.5	39.0	38.0
Other products (%)	6.0	6.5	7.6	10.3

Slightly low activity of catalyst II can be explained in terms of surface area of the catalyst. On higher metal loading the surface area of the catalyst will decrease for there will be aggregation of crystallite sites or metal particles. As is proved by catalyst III where large number of bigger pores can be expected formed by higher amount of CMC which can facilitate diffusion of reactant and product molecules. Since no change in catalytic activity is observed

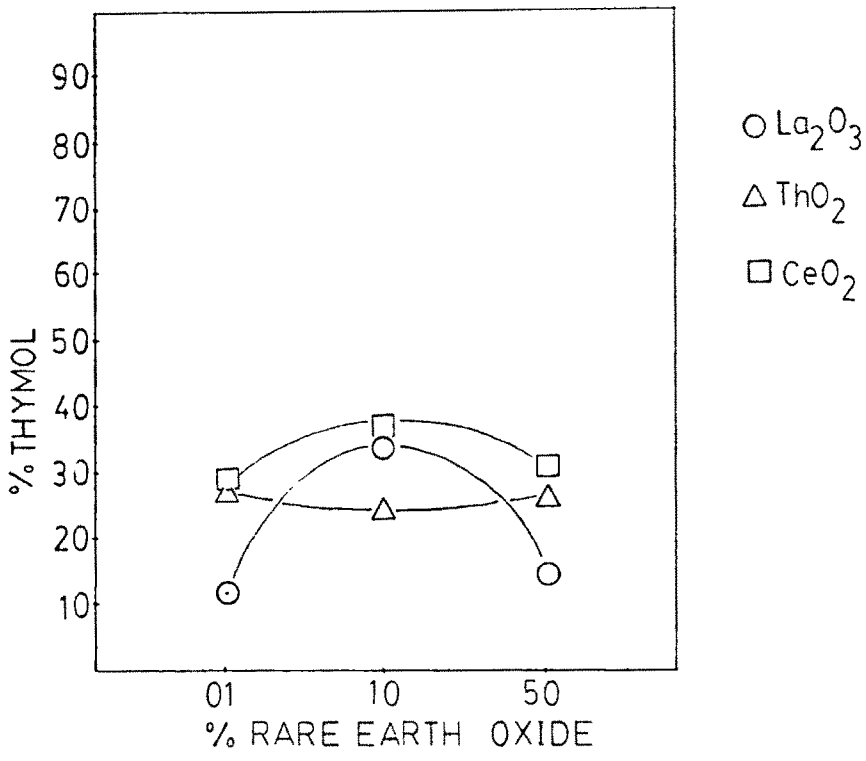


Fig. 5 - Activity of Ni-Cu/Al_2O_3 catalyst promoted with rare earth oxides.

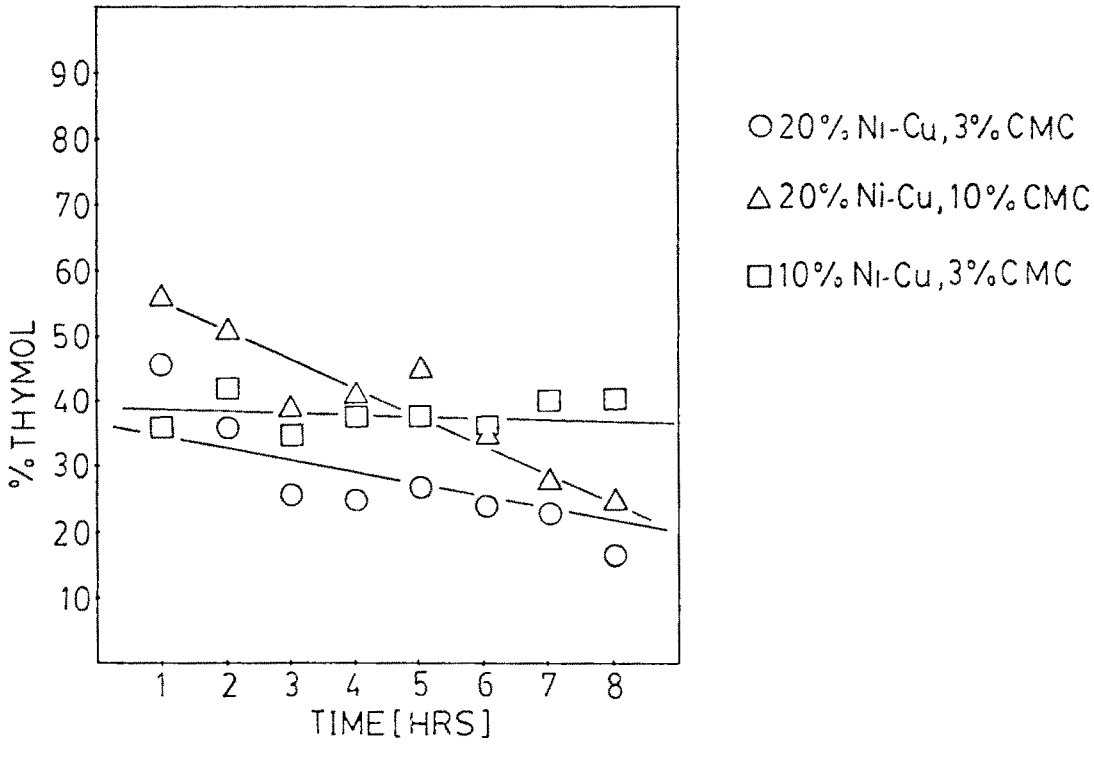


Fig. 6 - Effect of metal loading and CMC on activity of Ni-Cu/Al_2O_3 catalyst.

on longer calcination must mean that either the structural changes which occur in 4.0 hours of calcination remain same or changes do occur, but do not affect the catalytic activity.

3.5 Effect of reaction temperature on Ni - Cu/Al_2O_3 catalyst

It is generally agreed that higher temperature favours dehydrogenation reaction by making adsorption - desorption faster. As is shown in Fig. 7 the activity of the catalyst rose from 42.7% at 250° C to 70.0 % at 330° C.

3.6 Effect of magnesium oxide on 10% Ni-Cu/Al_2O_3 catalyst.

Addition of magnesium oxide in catalytic amount to the base catalyst improved activity as well selectivity of the catalyst (Fig. 8-10). The results obtained are presented in Table - 5.

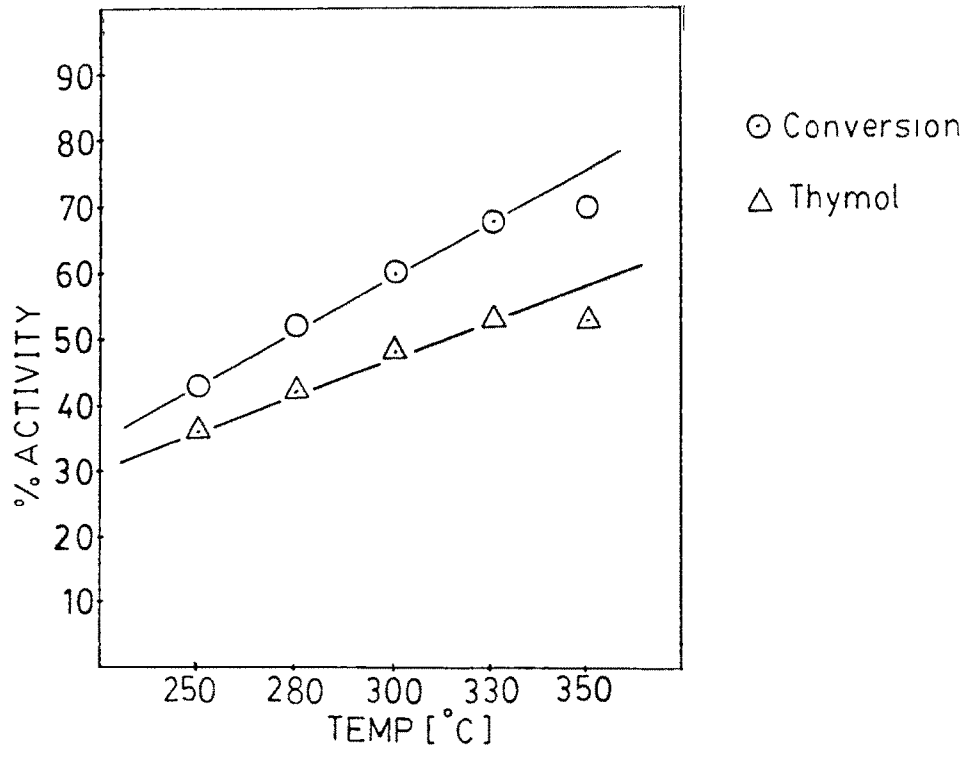


Fig. 7 - Effect of temperature on the activity of Ni-Cu/Al_2O_3 catalyst.

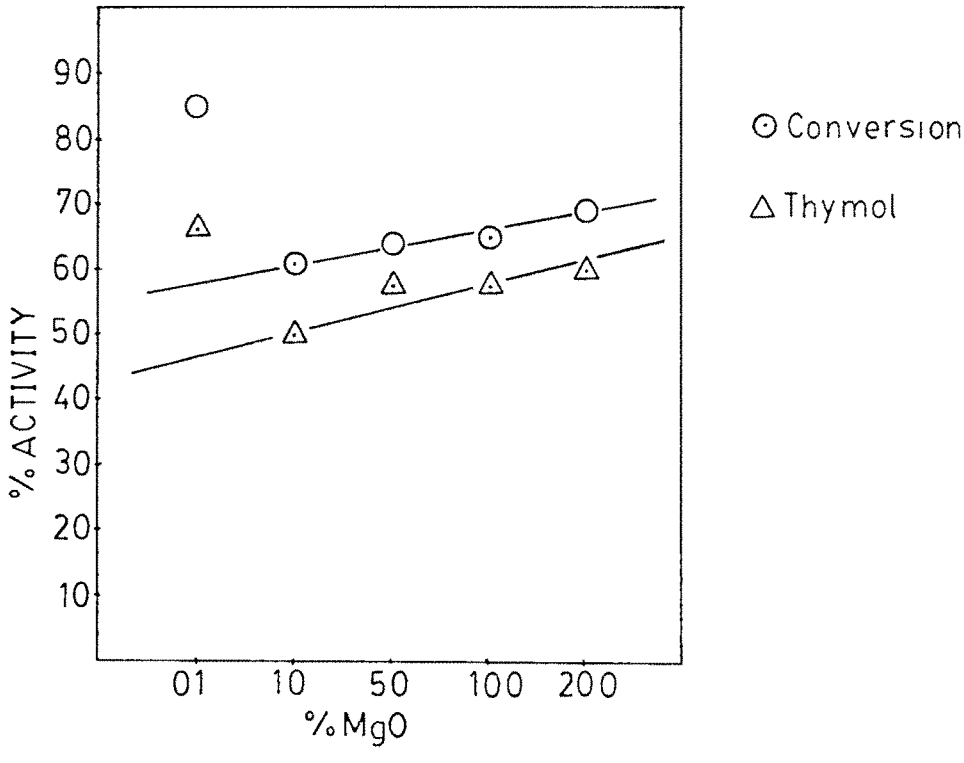


Fig. 8 - Activity of Ni-Cu/Al_2O_3 catalyst containing MgO as promoter at 280°C.

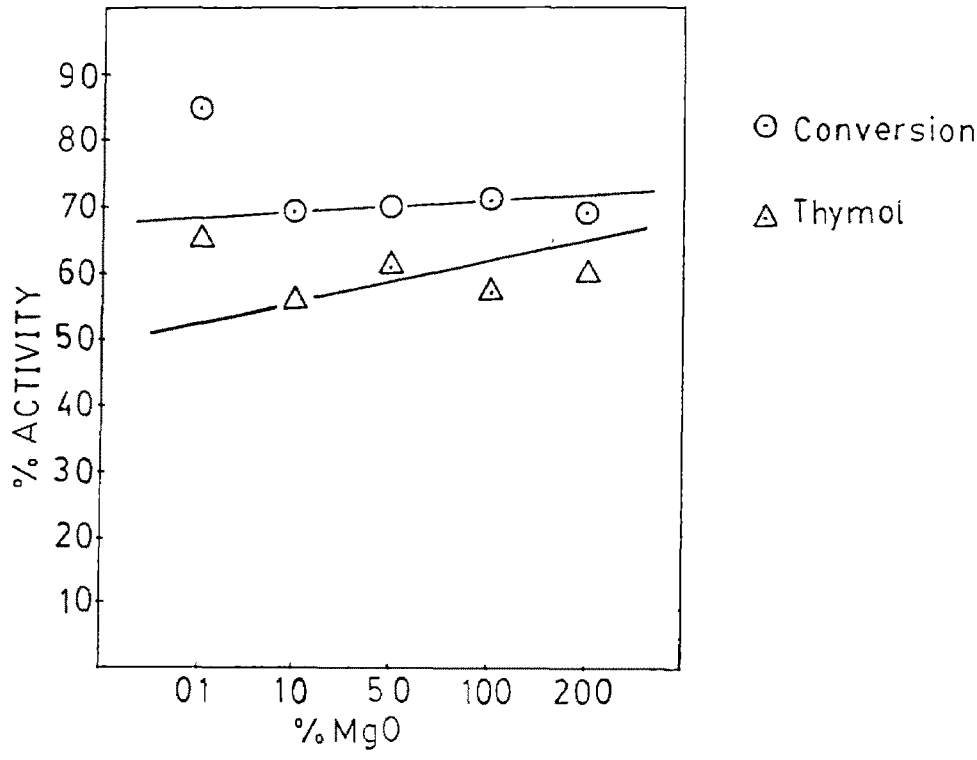


Fig. 9 - Activity of Ni-Cu/Al_2O_3 catalyst containing MgO as promoter at 300°C.

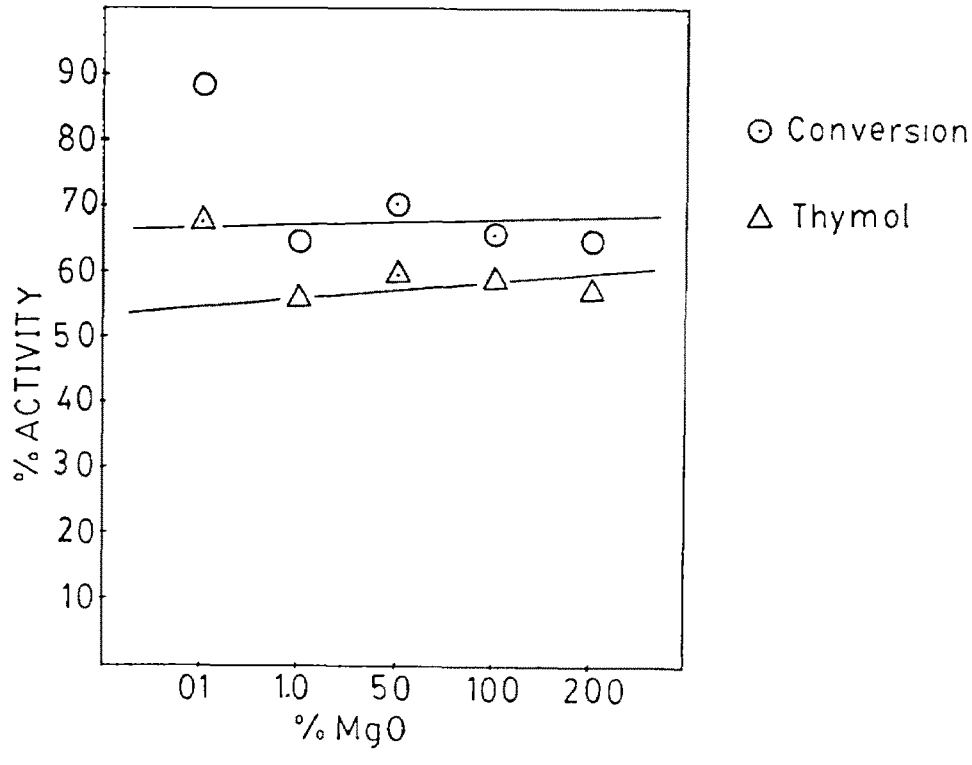


Fig. 10 - Activity of Ni-Cu/Al_2O_3 catalyst containing MgO as promoter at 330°C.

TABLE - 5

Effect of MgO on the dehydrogenation activity of 10% Ni-Cu/Al_2O_3 catalyst (10.0g) at various temperatures.

Catalyst	Ni-Cu/Al_2O_3 (10% by wt. Ni-Cu ratio, 7 : 3)														
Reaction temp (°C)	280°					300°					330°				
Magnesia (% by wt. of Ni-Cu)	0.1	1.0	5.0	10.0	20.0	0.1	1.0	5.0	10.0	20.0	0.1	1.0	5.0	10.0	20.0
Space velocity (v/v/sec)	0.116	0.116	0.116	0.116	0.116	0.120	0.120	0.120	0.120	0.120	0.126	0.126	0.126	0.126	0.126
Conversion (%)	80.6	57.6	62.0	62.9	65.7	79.1	66.1	65.2	66.2	62.9	81.4	63.2	67.7	63.0	61.2
Thymol (%)	66.2	50.0	57.6	57.3	60.0	65.3	55.3	61.2	56.8	57.4	67.7	56.1	60.2	58.3	57.6
Other products (%)	14.4	7.6	4.4	5.6	5.7	13.7	10.7	4.0	9.3	5.5	13.7	7.1	7.4	5.7	3.6

It can be noticed from the results shown in Table-5 that at high temperature the activity of individual catalyst is higher. The catalyst containing low magnesia content has higher activity than other catalysts. But as the magnesia content increases in the catalyst, selectivity raises proportionately. The selectivity of the catalysts rose from 83 % to 88, 89 and 92 % respectively, though activities were nearly same.

Since magnesium oxide is basic in nature, it can provide extra basic sites which will facilitate dehydrogenation, thus promoting effect on the activity of the catalyst. Apart from this, it can modify the nature of acidic sites in the catalyst through interaction which may be responsible for decarbonylation of menthone, thus promoting selectivity of the catalyst[33].

3.7 Effect of manganese on Ni-Cu/Al_2O_3 catalyst.

Incorporation of manganese with Ni-Cu/Al_2O_3 catalyst revealed remarkable change in the selectivity of the catalyst (Fig.11-13). The results are summarized in Table - 6.

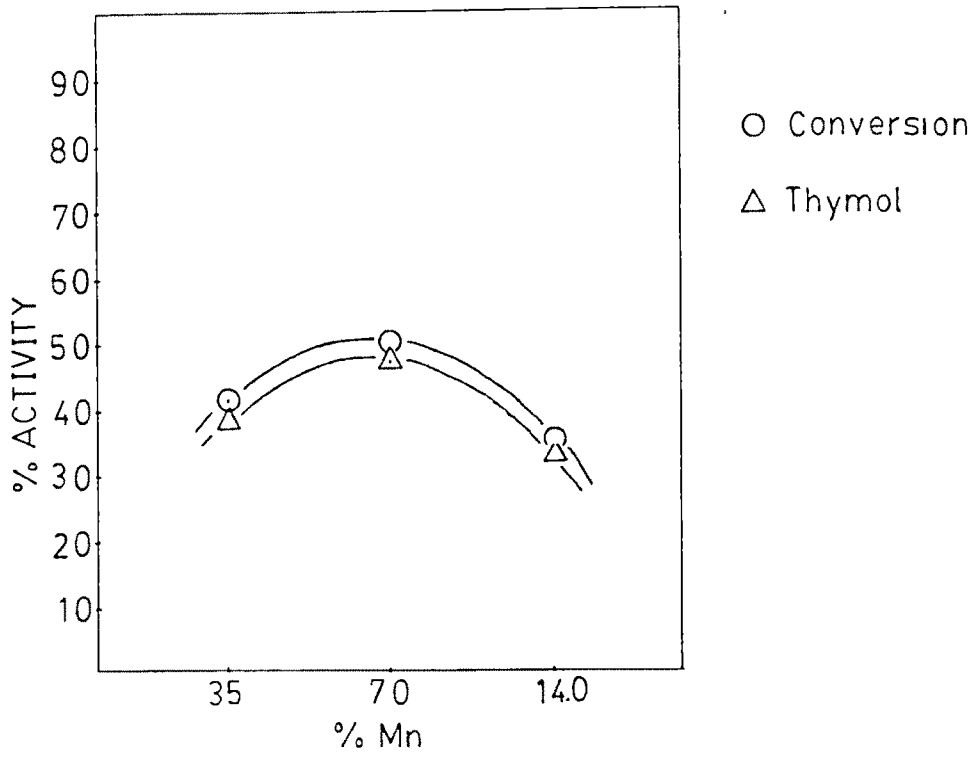


Fig. 11 - Activity of Ni-Cu/Al_2O_3 catalyst containing Mn as promoter at 280°C.

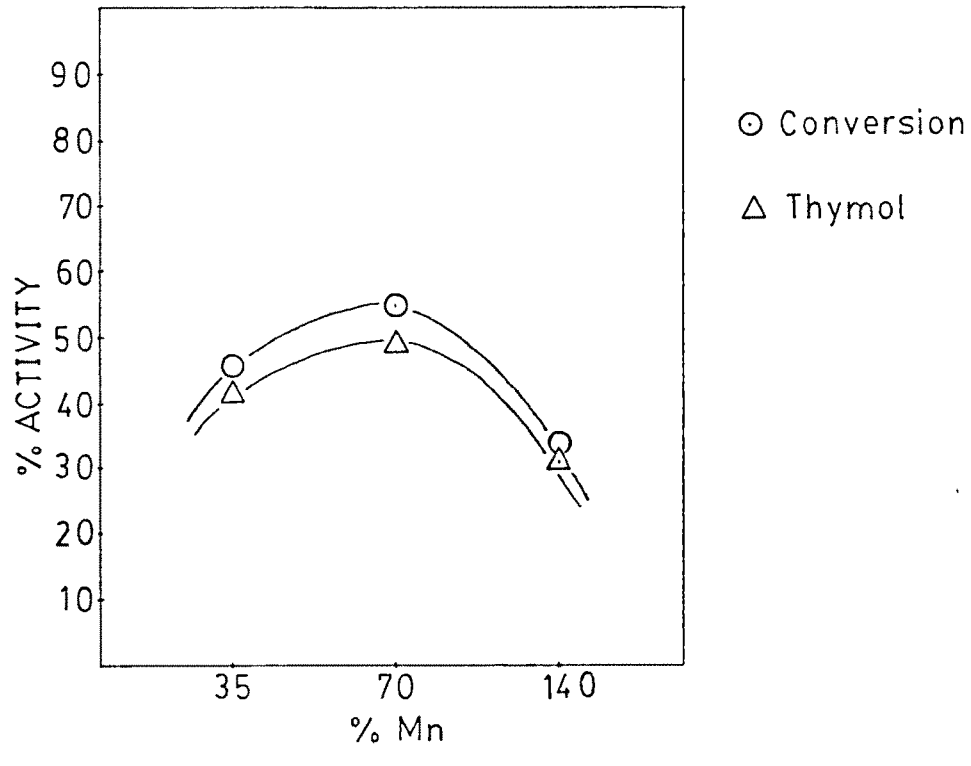


Fig. 12 - Activity of Ni-Cu/Al_2O_3 catalyst containing Mn as promoter at 300°C.

TABLE - 6

Effect of Mn on the dehydrogenation activity of Ni-Cu/Al_2O_3 catalyst (10.0g) at various temperatures.

Catalyst	Ni-Cu-Mn/Al_2O_3								
Reaction temp °C	280°			300°			330°		
Manganese (% by wt.)	3.5	7.0	14.0	3.5	7.0	14.0	3.5	7.0	14.0
Total metal loading	13.5	17.0	24.0	13.5	17.0	24.0	13.5	17.0	24.0
Space velocity (v/v/sec)	0.116	0.117	0.119	0.120	0.122	0.123	0.126	0.128	0.130
Conversion (%)	40.8	49.5	34.4	44.3	51.2	33.0	42.7	47.9	36.8
Thymol (%)	38.0	47.3	32.7	41.6	49.5	31.0	40.1	46.4	28.4
Other Products (%)	2.8	1.8	1.7	2.7	1.7	2.0	2.6	1.5	8.4

The results shown in Table-6 indicate that 7.0% by wt. manganese has greater effect on the activity as well as on the selectivity of the catalyst. And at higher temperature, 330°C, higher manganese content reduces the selectivity of the catalyst from 94.0 % to 77.0 %.

The suppression of side reaction by manganese containing catalyst can be associated with the stability of its half filled d-shell (d^5) which can form a common d-band in the miscibility range of two d-metals; this common d-band has more occupiable quantum states than the d-band of two transition metal components[70,54].

However, if we see the effect of the three metals on consecutive additions for the defunctionalization of menthone, the order follows : Ni > Cu > Mn which coincides, in general, with the order of decreasing e/r, Lewis acidity, or complex forming activity[71].

3.8 Effect of metal loading on Ni-Cu-Mn/Al_2O_3 catalyst.

The effects of higher metal loading were encouraging. The activity of the catalyst increased considerably (Fig. 14-16). The results obtained are presented in Table - 7.

TABLE - 7

Effect of metal loading on the dehydrogenation activity of Ni-Cu-Mn/Al_2O_3 catalyst (10.0g) at various temperatures.

Catalyst	Ni-Cu-Mn/Al_2O_3 (Ni:Cu:Mn ratio, 7:3:7)								
Reaction temp °C	280°			300°			330°		
Metal loading (% by wt.)	34.0	85.0	99.0	34.0	85.0	99.0	34.0	85.0	99.0
Space velocity (v/v/sec)	0.122	0.140	0.143	0.126	0.145	0.148	0.133	0.153	0.156
Conversion (%)	48.3	55.1	59.2	62.5	70.4	78.5	68.0	76.0	84.5
Thymol (%)	43.7	52.1	55.3	58.0	67.4	71.9	63.0	70.0	77.9
Ohter products (%)	4.6	3.0	3.8	4.5	3.0	6.5	5.0	6.0	6.6

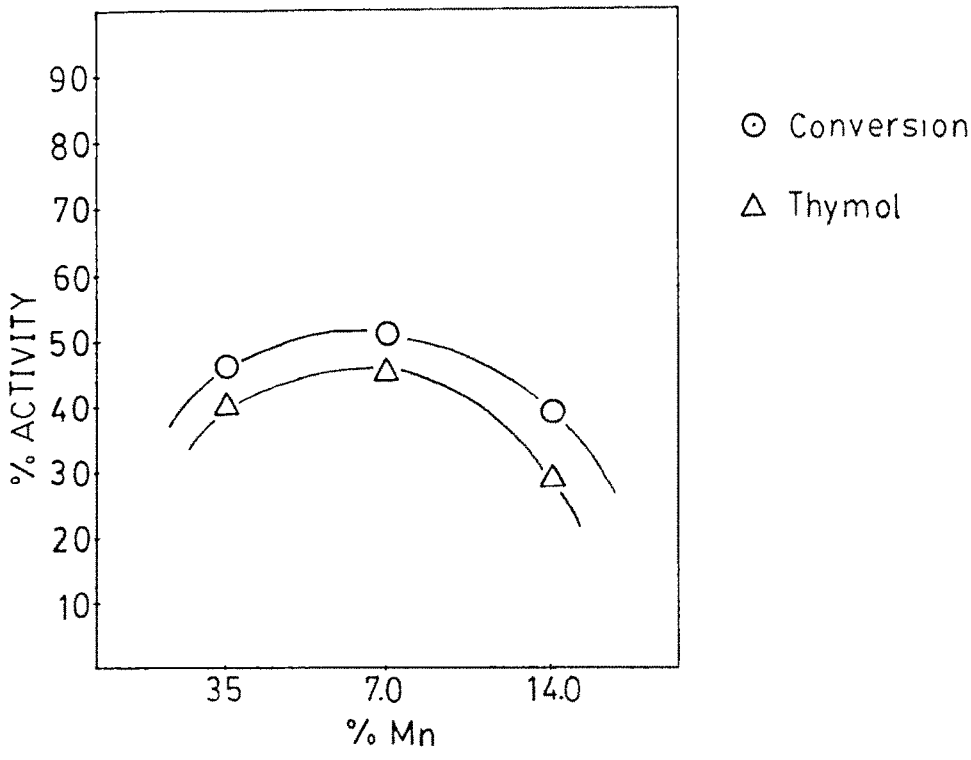


Fig. 13 - Activity of Ni-Cu/Al_2O_3 catalyst containing Mn as promoter at 330° C.

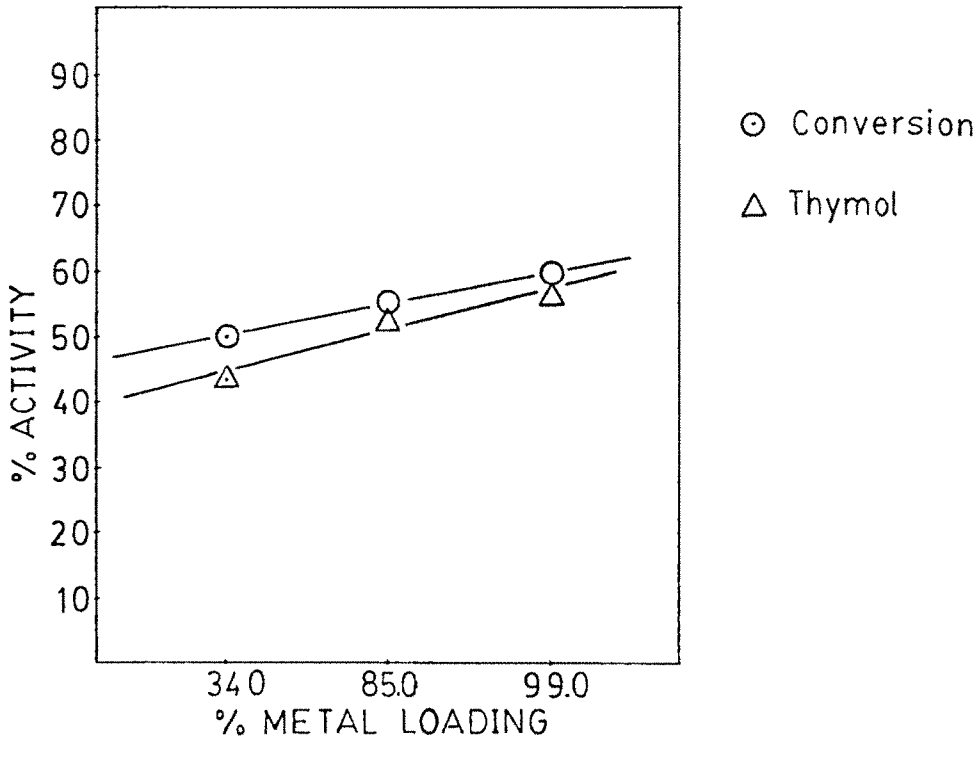


Fig. 14 - Effect of metal loading on Ni-Cu-Mn/Al_2O_3 catalyst at 280° C.

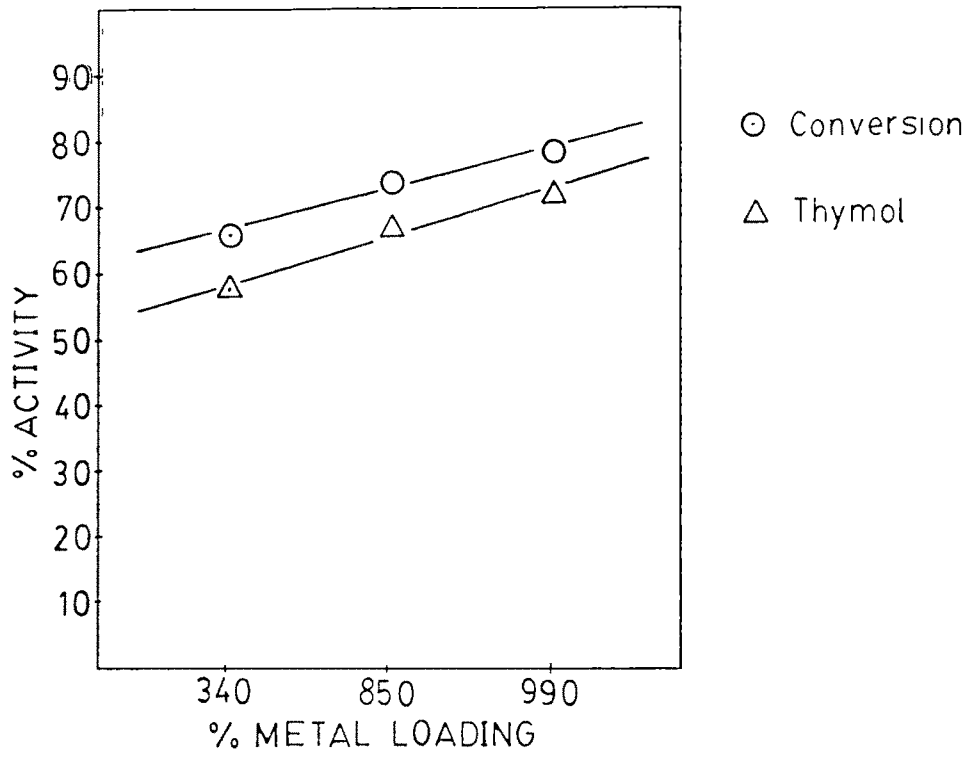


Fig. 15 - Effect of metal loading on Ni-Cu-Mn/Al_2O_3 catalyst at 300° C.

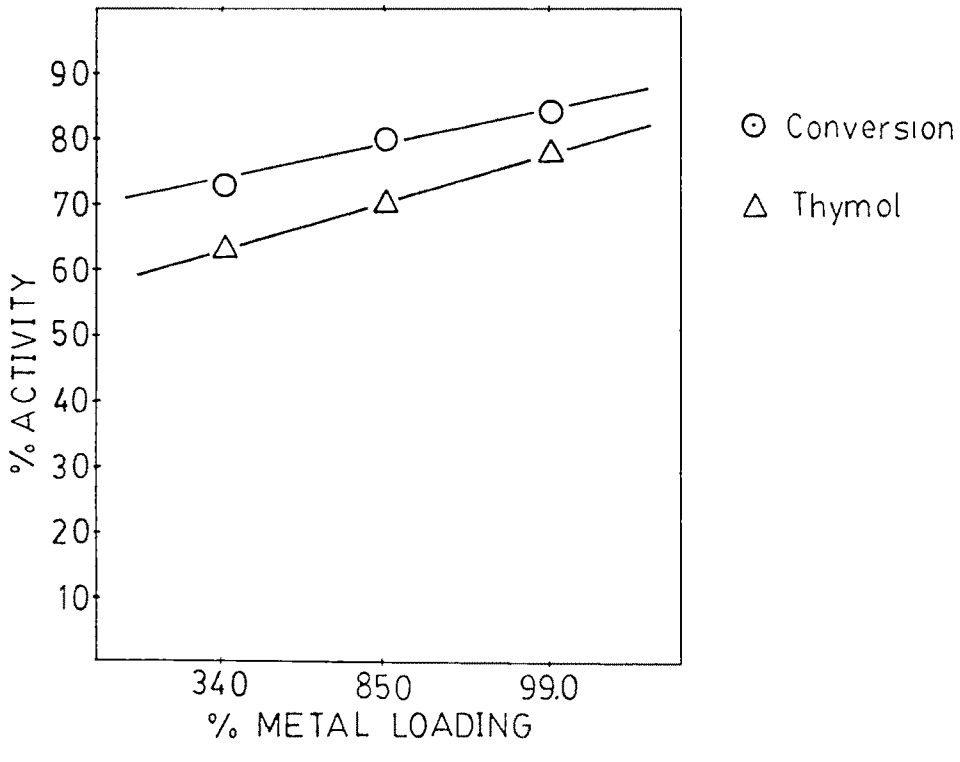


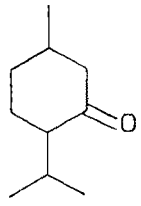
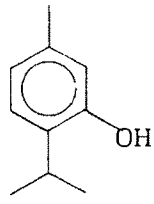
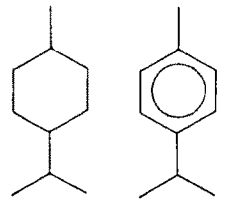
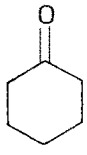
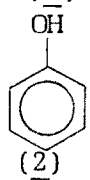
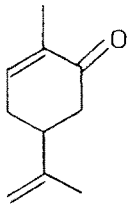
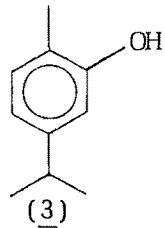
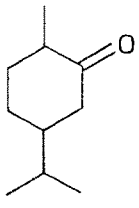
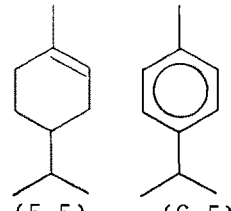
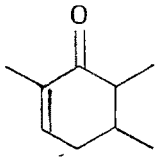
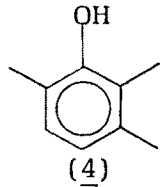
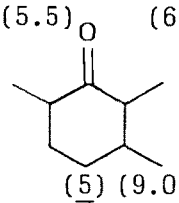
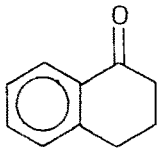
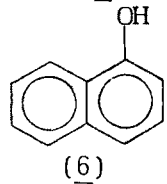
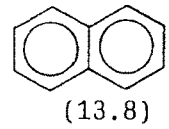
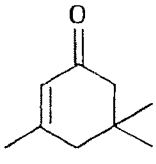
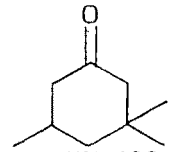
Fig. 16 - Effect of metal loading on Ni-Cu-Mn/Al_2O_3 catalyst at 330° C.

It is clear from Table-7 that higher the metal loading, higher is the activity. The complete elimination of alumina from Ni-Cu-Mn/Al_2O_3 made the catalyst highly active and selective. It gave 100% conversion with 92-4% selectivity for menthone dehydrogenation at 330°C.

This way a new catalyst containing Ni-Cu-Mn in the ratio of 7:3:7, was developed which exhibited very high activity and selectivity for the dehydrogenation of menthone. Other substituted cyclohexanones were also successfully dehydrogenated using this catalyst. Under the same set of reaction conditions different yields of phenols were obtained. Table - 8 summarizes the compounds dehydrogenated and the yields of products obtained. The difference in the reaction rates of various substrates can be attributed to their steric effects, relative stability of enols or rate of α-C-H abstraction to form enol like intermediates.

TABLE - 8

Dehydrogenation of cyclohexanones to corresponding phenols using Ni-Cu-Mn Catalyst (20.0 g) at 330°C.

Sr. No.	Substrate	Space velocity (v/v/sec)	Product	Yield (%)	Other Products (Yield %)	Remarks
01		0.060	 (1)	92	 (3.5) (4.5)	
02		0.084	 (2)	91		7% Unreacted.
03		0.062	 (3)	93		5% Unreacted 5% Unreacted.
04		0.060	"	62	 (5.5) (6.5)	26% Unreacted.
05		0.065	 (4)	75	 (5) (9.0)	16% Unreacted.
06		0.070	 (6)	66	 (13.8)	20% Unreacted.
07		0.064	-	-	 (7) (26.0)	74% Unreacted.

4. CONCLUSIONS

From this study it is concluded that :

(1) The dehydrogenation of cyclohexanones to phenols depends, to a greater extent, on the chemical composition of the catalyst.

(2) Supported catalysts are not effective catalysts for this reaction.

(3) Rare earth oxides do not have any promoting effect.

(4) The defunctionalization activity of different metals decreases in the following order : Al > Ni > Cu > Mg > Mn.

(5) NCM catalyst (Ni-Cu-Mn) could be effectively used for the preparation of phenols from cyclohexanones in lab as well as in industry.

5. EXPERIMENTAL

All m.ps and b.ps are uncorrected.

The following instruments were used for spectral/analytical data : Perkin - Elmer infrared spectrophotometer, model 267; Perkin-Elmer model R 32 (90 MHz) NMR spectrometer; Hewlett-Packard 5712 A and 7624 A gas chromatographs (stainless-steel columns, 6', 10% SE-30 and 12', 10% CW, support 60-80 mesh chromosorb W; carrier gas H_2). All PMR spectra were recorded with 15-20% solution in CCl_4(unless otherwise stated)with TMS as internal reference ; signals are reported in ppm (δ); while citing PMR data, the following abbreviation have been used : s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

Other instruments used were: NFT-51, spinning-band teflon fractionation column (48 x 0.8 cm; theoretical plates, 80); Rajdhani moisture balance, RSMA - 3 equipped with 240 V IR lamp; Cadmach rotary tablet machine, type 16 station model CMD-3.

A detailed description of catalyst activity testing unit and general method of supported and unsupported catalyst preparation has been given in section-1.

Preparation of Ni-Cu-Mn catalyst[72] (Ni,Cu,Mn, 7:3:7)

Nickel sulphate (38.22 g, 0.1422 mole), copper sulphate (14.1 g, 0.0564 mole), and manganese sulphate (25.8 g, 0.1526 mole) were dissolved in

780 ml of demineralized water at 67-8°C. The solution was allowed to cool ambiently. When temperature of solution had reached 55°C solid sodium bicarbonate (64.92 g, 0.7228 mole) was added in portions (~10) over a period of 10-15 minutes with vigorous stirring. At the end of the process, the temperature of the slurry dropped to 50 ± 2°C and pH was 8.3. It was digested for one hour at 55°C while agitation continued. Slurry was filtered and cake so obtained was washed with hot water (~55°C) several times (500 ml x 8) in order to make it free from SO_4^{2-} ions as confirmed by $BaCl_2$ test. It was dried over steam bath (3-4 hours) and physically mixed with CMC (0.6 g, 3.0%), magnesium borate (0.6 g, 3.0%) and after mixing with graphite (0.4 g, 2.0%) pelleted (0.5 x 0.3 cm). The pelleted catalyst was calcined in muffle furnace at 360°C for 4.0 hours. The colour of the pellets turned black during this process. Only after ambient cooling (~ 20 hours) of the furnace, the catalyst was taken out (23.0 g) and used for the dehydrogenation reaction.

Dehydrogenation of individual cyclohexanones

In each experiment 20.0 g fresh catalyst[73] was used and freshly distilled ketone was passed at the constant rate of 10 ml per hour for 8.0 hours at 330°C.

(1) Menthone to thymol (1).

Menthone (72.0 g, 80 ml) afforded 69.0 g (98.5%) dehydrogenated product from which 64.0 g (91.0%) thymol (mp. 50-1°C) was separated by crystallization and fractional distillation. (Lit.[74a] NMR and IR). Other products were identified to be p-menthane and p-cymene by co-injection of authentic samples.

(2) Cyclohexanone to phenol (2).

Cyclohexanone (75.0 g, 80 ml) yielded 71.0g (98.6%) dehydrogenated product from which phenol (65.0 g, 90%) was separated by fractional distillation (bp. 97-99°C/60 mm Hg) (Lit.[75a,76a] NMR and IR).

(3) Carvone to Carvacrol (3).

Carvone (77.0 g, 80 ml) furnished 75.4 g (98.4%) product on dehydrogenation from which 71.0 g (92.0%) Carvacrol was obtained by fractional distillation (b.p. 93°C/3 mm Hg) (Lit.[74b] NMR and IR).

(4) Carvomenthone to Carvacrol (3).

Carvomenthone was prepared from 1,2-epoxy-p-menthane with aq. $HClO_4$ which, in turn, was prepared from p-menth-1-ene with peroxyacetic acid[77]. p-Menth-1-ene for this reaction was obtained by partial hydrogenation of limonene with P-1 nickel catalyst[78].

Dehydrogenation of 72.0 g (80.0 ml) carvomenthone furnished 69.0 g (98.5%) product from which 40.0 g, (61.4%) Carvacrol was obtained by fractional distillation. Other products were identified to be p-menth-1-ene, and p-cymene by co-injection of authentic samples.

(5) 2,5,6-Trimethyl cyclohex-2-en -1-one to 2,3,6-trimethyl phenol (4).

2,5,6-Trimethyl cyclohex-2-ene-1-one for this reaction was prepared according to the procedure described by Wehrli et al.[29]

Dehydrogenation of 73.0 g (80.0 ml) ketone yielded 72.0 g (98.0%) product which on fractional distillation 54.0 g (75.0%) 2,3,6-trimethyl phenol. (Lit.[76b] IR).

NMR(Fig.17) : Me(9H, three singlets, 2.05, 2.1 and 2.16 ppm), CH=C (1H, d, 6.51 ppm, J=7.5 Hz ; 1H, d, 6.71 ppm, J=7.5 Hz).

2,3,6-Trimethyl cyclohexanone (5)(6.2 g, 8.6%) was also obtained (b.p. 79-80°C/20 mm Hg).

IR(neat)(Fig.18): 1712, 1220, 1170, 1110, 1030, 980, 810, 735 cm^{-1}.

NMR (Fig.19) : Me(9H, three singlets, 0.75-1.15 ppm), CH_2(4H, b, 1.11-1.8 ppm), CH(3H, b, 2.17-2.7 ppm).

(6) α -Tetralone to α -naphthol (6)

α- Tetralone was prepared according to the procedure of Olson and Bader[79].

α- Tetralone (87.0 g, 80 ml) yielded 84.0 g (98.0%) dehydrogenated product which on fractional distillation yielded 55.0 g, (65.4%) 1-naphthol (m.p. 95-96°C)(Lit.[75a,76c] NMR and IR) and 10.5 g (12.5%) naphthalene.

(7) Dehydrogenation of isophorone.

Isophorone (73.0 g, 80.0 ml) furnished 72.0 g, (98.6%) product which on fractional distillation gave 18.0 g (25.0%) 3,3,5-trimethyl cyclohexanone (7). (Lit.[76d] IR).

NMR (Fig.20) : Me(3H, s, 0.87 ppm; 6H, s, 1.04 ppm), CH_2(4H, m, 1.8-2.1 ppm).

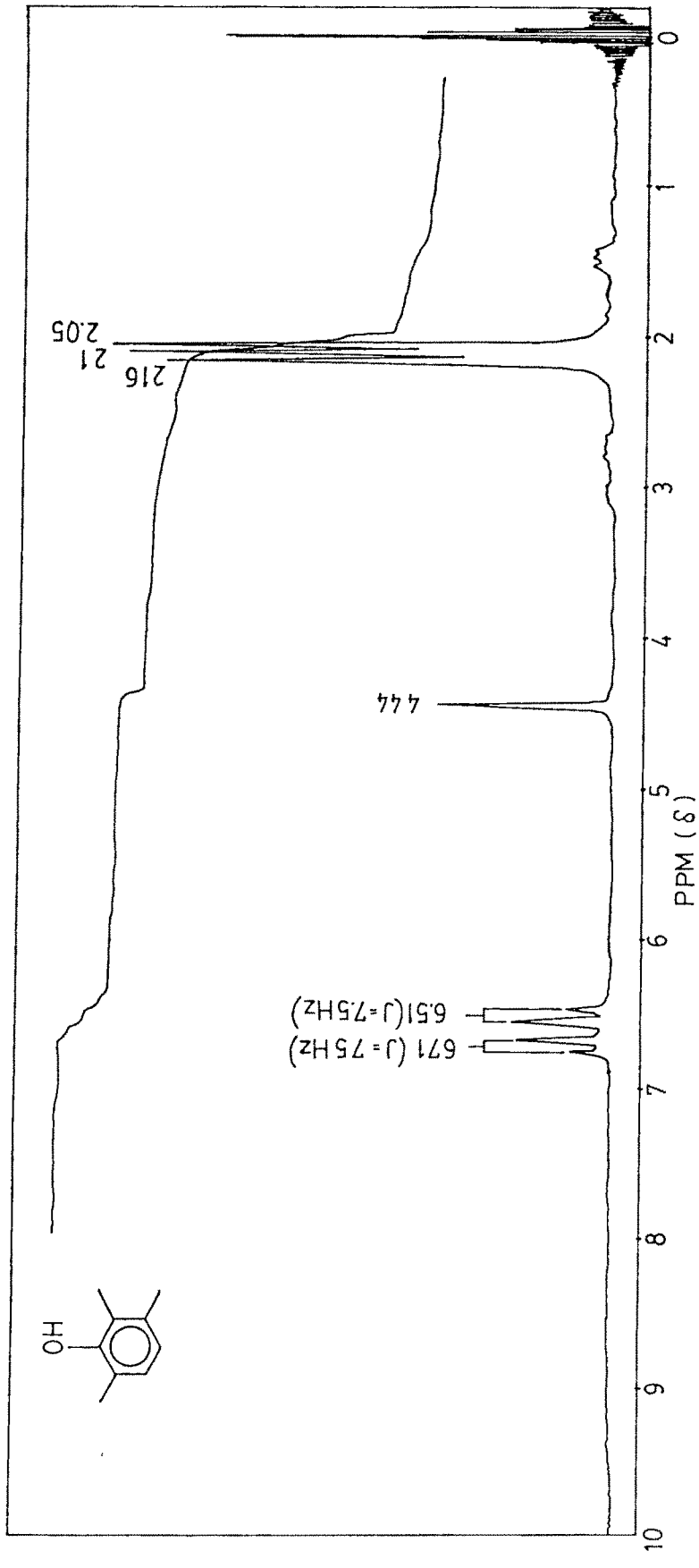


Fig. 17 - NMR spectrum of 2,3,6-trimethyl phenol.

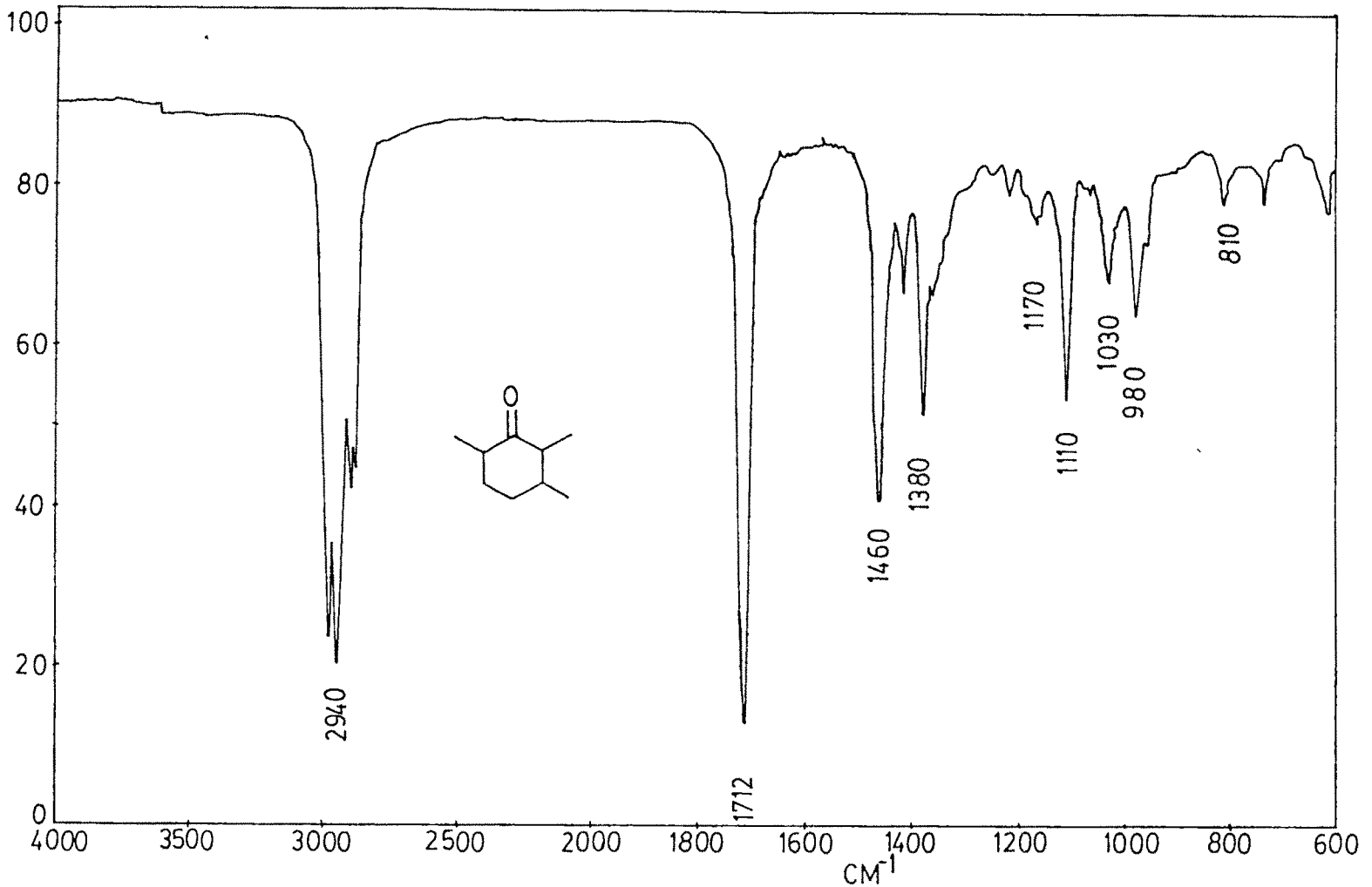


Fig. 18 - IR spectrum of 2,3,6-trimethyl cyclohexanone.

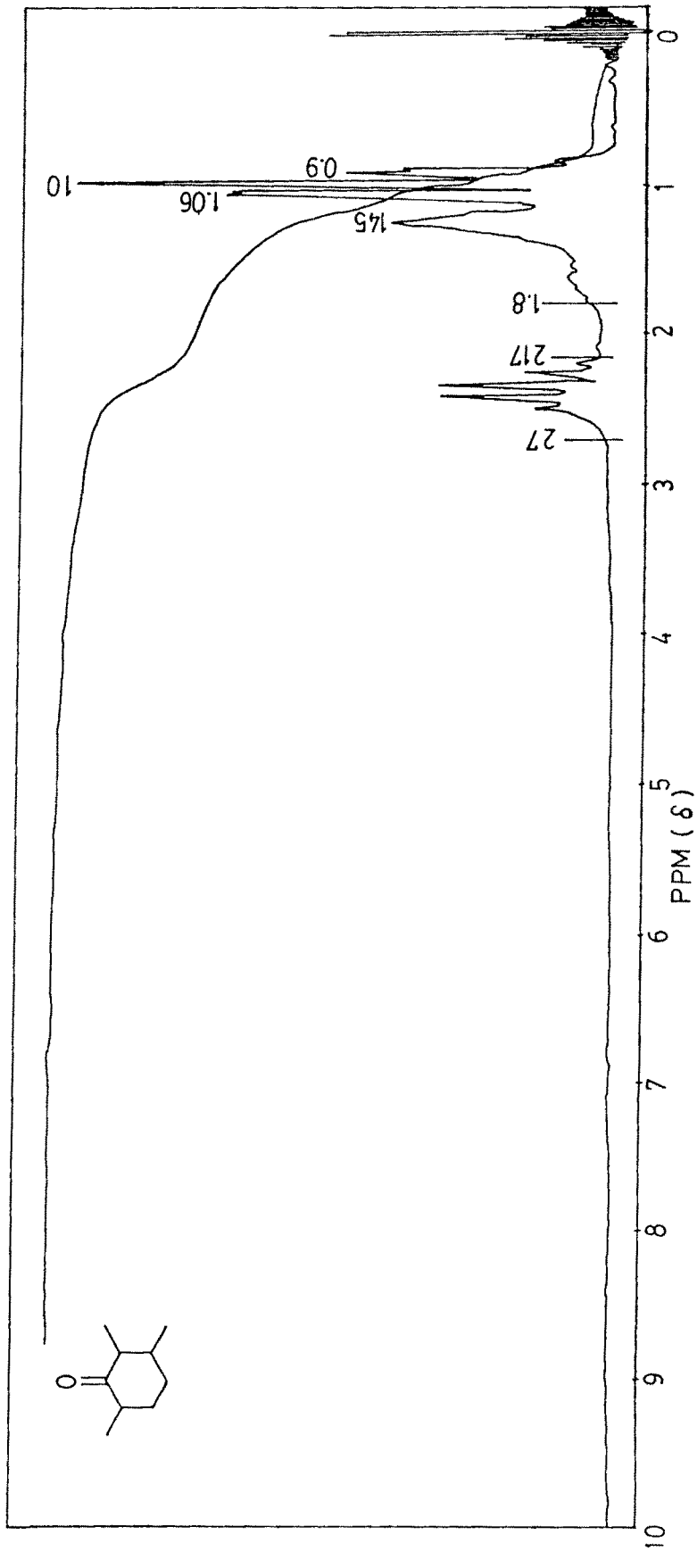


Fig. 19 - NMR spectrum of 2,3,6-trimethyl cyclohexanone.

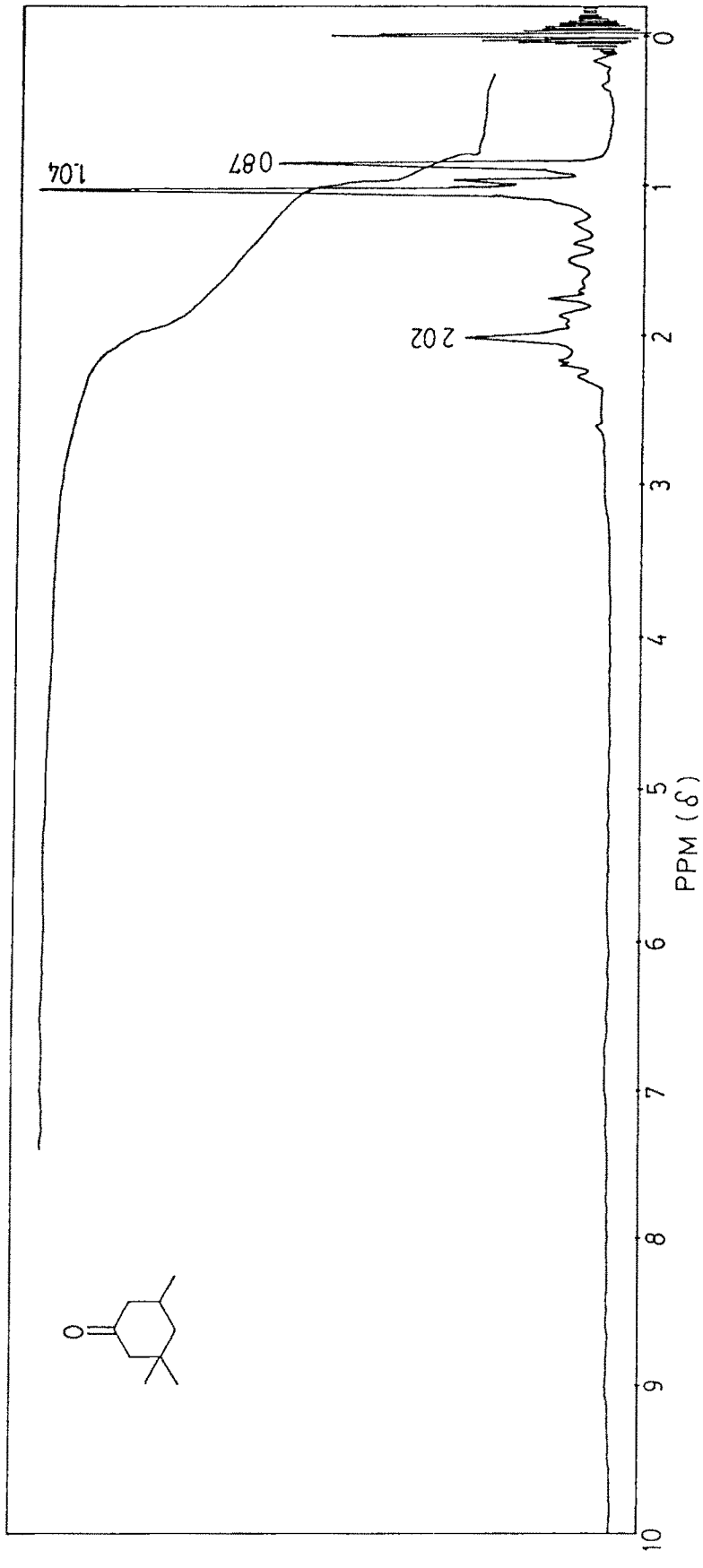


Fig. 20 - NMR spectrum of 3,3,5-trimethyl cyclohexanone.

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63. See Ref. 97 of Section 1, part 1.

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65. J.H.Sinfelt, Adv.Catalysis 23, 91 (1973).

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71. O.V.Krylov, Catalysis by Non-Metals, p. 247, Academic Press, Inc. New York (1970).

72. L.R.Grade sulphates were used for the preparation of catalysts. Purity of sodium bicarbonate was checked before use (95%).

73. Reduced catalyst was highly pyrophoric hence it should be used under inert atmosphere.

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75. (a) C.J.Pouchert and J.R.Campbell, Aldrich Library of NMR spectra, Vol. IV, entry no. 109 A (1974).

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SECTION 3

DEHYDROGENATION OF CYCLOHEXANES TO THE AROMATIC HYDROCARBONS

DEHYDROGENATION OF CYCLOHEXANES TO THE AROMATIC HYDROCARBONS.

Abstract

A catalytic process has been described to dehydrogenate substituted saturated or partially saturated cyclohexanes into aromatic hydrocarbons in high yields. The process consists in passing the substrate at 280°C in vapour phase under H_2 over the bed of Ni/MgO catalyst. The results are summarized in the forms of tables and graphs.

The MgO support is superior to Al_2O_3 for the Ni catalyst. The copper enhances hydrogenation activity of Ni supported on MgO and Al_2O_3 rather than its dehydrogenation activity. The rare earth oxides have been found to diminish the activity of Ni/MgO catalyst. Higher temperature favours higher conversions to aromatic hydrocarbons.

1. INTRODUCTION

Aromatic hydrocarbons, arenes are one of the important class of compounds because they are the main source of aromatic compounds. Aromatic hydrocarbons are generally obtained from petroleum fractions, however some, such as p-cymene is widely spread in nature and found in many essential oils, such as cumin, thyme, and chenopodium[1].

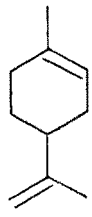
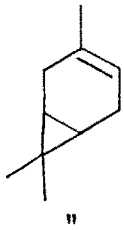
It is used in the manufacture of p-cresol[2], terephthalic acid, thymol[3], perfumery products, phantolid and tonalid[4], and as solvent. It is obtained from the oil in the waste liquors of the sulphite wood pulp process. It can be prepared by heating camphor with $ZnCl_2$ or from oil of turpentine. There are more than 300 ways of preparing it[5].

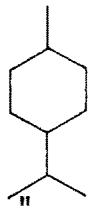
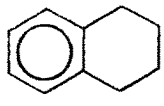
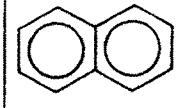
However, dehydrogenation of hydroaromatic compounds to aromatic compounds over a suitable catalyst offers an easy, economic, and industrially feasible process. The ease of aromatization is governed by relative thermodynamic stability of the aromatic system.

A large number of catalysts are available in literature to bring about such transformation. Table-1 summarizes most of the available information.

TABLE-1

Dehydrogenation of substituted cyclohexanes to corresponding aromatic hydrocarbons.

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
01.		Pd/Al_2O_3, 275°		-	6
02.	"	Pd/C, 290-310°	"	92	7
03.	"	Pt, 350°	"	65-70	8
04.	"	Cu, 280°	"	88	9
05.	"	Cr_2O_3, CuO, 375-475°	"	91	10
06.	"	Cr_2O_3/ Al_2O_3	"	81	11
07.	"	Cr_2O_3-CrO_3-SnO_2/ Al_2O_3, 415-59°	"	56.8	12
08.	"	Cr_2O_3-SnO_2/Al_2O_3, 425-525°	"	-	13
09.	"	Cr_2O_3-ZnO/clay 425-500°	"	90	14
10.	"	CoO-MoO_3, 425°	"	-	15
11.	"	V_2O_5/SiO_2	"	61	16
12.		Pt/Al_2O_3	"	65	17
13.	"	Ni-Cu	"	55-60	18

Sr. No.	Substrate	Catalyst, conditions	Product	Yield (%)	Literature
14.	"	Cr/Al_2O_3, 400-50°,H	"	80-90	19,20
15.	"	Cr_2O_3/Al_2O_3	"	80	21, 22
16.	"	Cr_2O_3/Al_2O_3, K_2O	"		23
17.	"	ZnO	"	30	24
18.	"	Fe_2O_3/gypsum	"	28	25
19.	"	SiO_2, 400°	"	opt.	26
20.	"	Al_2O_3, 500°	"	-	27
21.		Pd/C, 260-70°		91.2	28
22.	"	Pt/Al_2O_3, 300°	"	95-100	29
23.	"	Ni	"	28	30
24.		Ni/Al_2O_3		98	30
25.	"	Ni-Mo	"	-	31
26.	"	Cr	"	-	32
27.	"	Cu-Cr	"	opt.	33
28.	"	-Fe, 260-360°	"	-	34
29.	"	Fe_2O_3, 350°	"	28.6	35
30.	"	Te/MgO	"	-	36
31.	"	MoO_2, 446-543°	"	-	37
32.	"	SiO_2-Al_2O_3,ZrO_2, 400-500°	"	quant.	38

2. PRESENT WORK

Catalytic dehydrogenation of relatively saturated 6-membered hydrocarbons to aromatic hydrocarbons is generally performed with noble metal catalysts, such as Pd, Pt, etc., or with transition metal catalysis, like Ni, Cu, Cr, etc. Both supported and unsupported catalysts have been used. Alumina, silica, carbon, etc. are the supports frequently employed. It can be noted from a comparative study of dehydrogenation catalysts that chromia or chromia supported on alumina is more frequently used because acidic sites of the catalyst facilitate transition from one form to the other, but at the some time it leads to the formation of further isomerized products. Nickel catalyst also is not completely reliable because it decomposes part of the hydrocarbon with lower hydrocarbons. Hence, it is decidedly worthwhile to investigate other possibilities of such catalysts in order to get aromatic hydrocarbons in high yields. The objective of present study is to investigate transition metal catalyst for the preparation of p-cymene in high yield from dipentene, a by-product of camphor process.

In order to achieve this aim, a large number of supported and unsupported catalysts were prepared by physical mixing the support material and metal carbonate freshly precipitated from aqueous solution of metal sulphate with sodium hydrogen carbonate. The catalysts were used in the pellet shape and reduced to active metallic state with hydrogen prior to evaluation of dehydrogenation activities. The activities of the catalysts were determined for conversion of dipentene into p-cymene at 185°C.

In our earlier experiments we found nickel catalyst to be more active than other transition metals, hence it was decided to explore nickel-based catalysts.

Nickel (10% by wt.) was supported on magnesia and alumina of low surface area (15-20 m^2g^{-1}) separately, and dehydrogenation activities examined.

In order to increase activity and selectivity of the catalyst, copper (Gr. I B) was incorporated with nickel and loaded on alumina and magnesia supports. Such catalysts did not show any improvement in the activities.

Effect of rare earth oxides was studied on the activity and selectivity of Ni/MgO catalysts because it was more active than other three catalysts prepared. Lanthanum oxide, cerium oxide, and thorium oxide were mixed in different concentrations and activities examined. And it was found that these oxides reduced dehydrogenation activity of the catalyst.

Metal loading was raised from 10% to 20% by wt. in one catalyst and in the other more of the CMC (pores making agent) was added and checked for dehydrogenation activity.

Reaction was carried out at higher temperature also, and maximum conversion was achieved at 280°C.

Other related hydrocarbons, such as, isoterpinolene, p-menth-2-ene, Δ^3 -Carene, p-menthane, and tetralin were also dehydrogenated.

3. RESULTS AND DISCUSSION

3.1 Effect of supports on the activity of nickel catalyst.

Nickel (10% by wt.) supported on alumina showed lower dehydrogenation activity but Ni/MgO catalyst showed higher activity (Fig.1). The other products were saturated hydrocarbons. The results are summarized in Table-2.

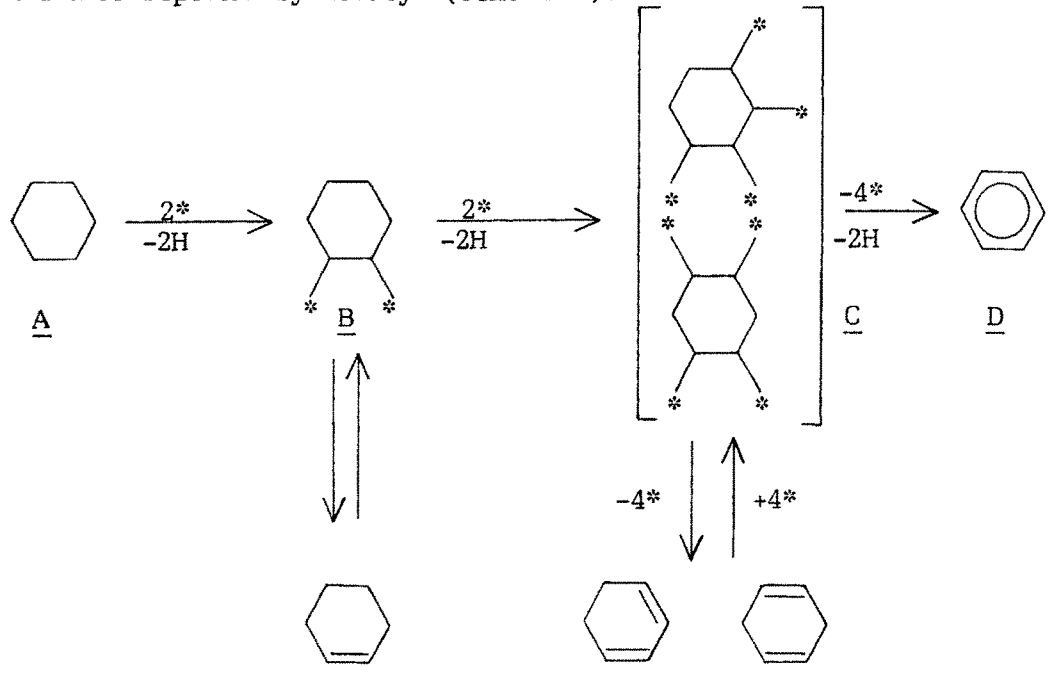
Formation of hydrogenated products can take place by disproportionation of dipentene. Since alumina contains both acidic and basic sites[39] such disproportionation might be faster. Higher dehydrogenation activity of magnesia supported catalyst could be because of relatively basic character of its surface. Other relevant information about properties of magnesia is also available[40].

Since dehydrogenation of 6-membered ring is thermodynamically more favoured, most of the studies have been carried out on cyclohexane.

The dehydrogenation of cyclohexane led Balandin[41] to put forward the first scientific theory on catalysis. In his sextet mechanism, the hydrogenation involves the planar arrangement of the 6-membered ring on the (111) faces of the metal crystallites.

Various views have been expressed for the mechanism of dehydrogenation on nickel catalysts. Tetenyi and Schachter[42] has compared the activities of catalysts in relation to their hydrogen adsorption, their mode of preparation[43], and also on the catalytic activities of different metals based on their crystalline

structure[44]. On carrier free nickel catalysts, Tetenyi and Schachter[45] considers dehydrogenation process to take place far from equilibrium, in a succession of slow stages, assuming that the adsorption of one component does not impede the adsorption of another, an assumption which seems to be contradicted by the evidence reported by Galvey[46](Scheme-1).



* Active site

Scheme-1. Stepwise route via π -bonded edgewise adsorption on Ni.

The mechanism offered by Ross and Valentine[47] involves a single slow step, probably the formation of cyclohexene on the basis of the dependence of rate on hydrogen and cyclohexane concentrations.

3.2 Effect of copper on the activity of Ni/Al_2O_3 and Ni/MgO catalysts.

Addition of 30% by wt. copper (based on nickel) in the catalysts reduced dehydrogenation activities of both the catalysts (Fig.2). The results are summarized in Table-2.

TABLE - 2

Dehydrogenation of dipentene to p-cymene on Ni and Ni-Cu supported on Al_2O_3 and MgO (10.0g each) at 185°C.

Catalyst	10% Ni / support		10% Ni-Cu / support	
	MgO	Al_2O_3	MgO	Al_2O_3
Space velocity (v/v/sec)	0.0866	0.090	0.0873	0.100
p-Cymene (%)	74.00	65.00	66.00	57.00
Other products (%)	26.00	35.00	34.00	37.00

It is well established that nickel-copper oxide form nickel-copper alloy[48] on reduction with hydrogen at high temperature and that the copper seggregates onto the surface which significantly suppreses hydrogen adsorption by the catalyst[49].

If we assume that the strength of adsorption of hydrocarbons is affected directionally in the same way as the strength of adsorption of hydrogen when copper is added to nickel; it would mean that it is adsorption rate of dipentene which is affected and not the desorption of final product. Hence it is entirely

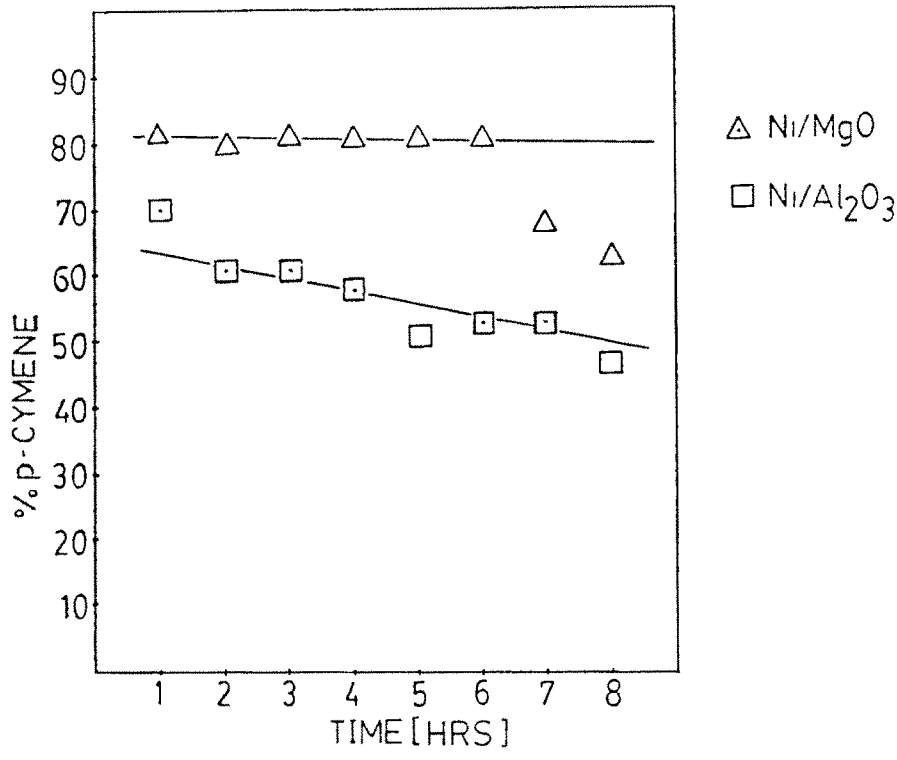


Fig. 1 - Effect of support on the activity of Ni catalyst.

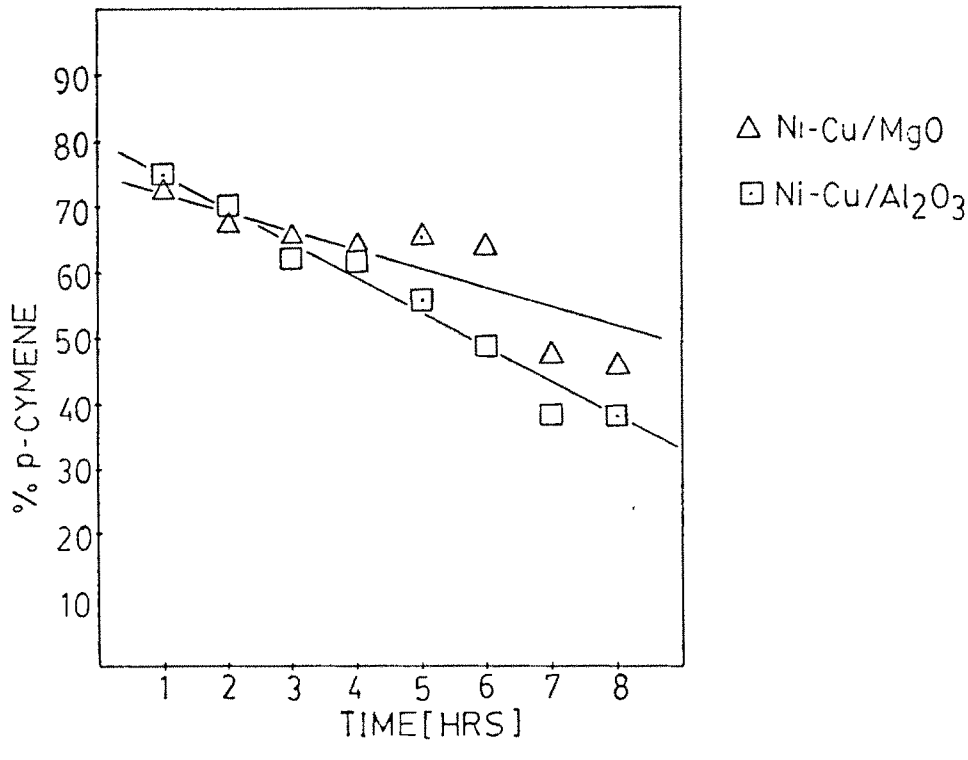


Fig. 2 - Effect of Cu on the activity of Ni/Al_2O_3 and Ni/MgO catalysts.

reasonable that the decrease in heat of adsorption of hydrocarbons on addition of copper to nickel will adversely affect the reaction rate[50].

3.3 Effect of rare earth oxides on the activity of 10% Ni/MgO catalyst.

Addition of rare earth oxides further reduced the dehydrogenation activity of the catalyst. Fully saturated and partially hydrogenated products were formed as by-products (Fig.3). Table-3 summarizes the results observed.

TABLE - 3

Effect of rare earth oxides on the activity of Ni/MgO catalyst (10.0 g) at 185°C.

Catalyst	10% Ni/MgO, rare earth oxide								
	La_2O_3 (wt. % of Ni)			CeO_2 (wt. % of Ni)			ThO_2 (wt. % of Ni)		
	0.1	1.0	5.0	0.1	1.0	5.0	0.1	1.0	5.0
Space velocity (v/v/sec)	0.086	0.086	0.086	0.086	0.086	0.086	0.086	0.086	0.086
p-Cymene (%)	54.6	60.5	67.5	45.3	52.8	66.0	55.4	60.0	52.7
Other products (%)	42.5	36.0	32.5	39.8	42.1	34.0	40.9	39.0	40.9

The catalytic behaviour of rare earth oxides have been correlated with their electronic properties.[51]. The oxides of rare earths may change the degree of interactions between metal-metal and metal-support particles by being present in between them; this may affect the extent of adsorption of reaction intermediates.

Moreover, partial reduction of these oxides can take place under the experimental conditions, which through electron transfer between support or rare earth and transition metal atoms may change adsorption strength of nickel catalyst[52]. And as a consequence, it may lead to reduction in rate of reaction.

3.4 Effect of higher metal loading and CMC on the activity of 10% Ni/MgO catalyst.

Higher metal loading and creation of bigger pores did not improve the activity and selectivity of the catalyst. Table-4 summarizes the results obtained.

TABLE - 4

Effect of metal loading and CMC on the activity of 10% Ni/MgO catalyst (10.0 g) at 185°C.

Catalyst	Ni/MgO (% metal loading)		
	10	20	20
CMC (% by wt.)	3	3	10
Space velocity (v/v/sec)	0.086	0.087	0.088
p-Cymene (%)	74	74	73
Other products (%)	26	26	27

No change in catalytic activity on higher metal loading would mean that either the number of suitable crystallite sites and effective exposed metal surface area remain same or do change but do not affect the activity[53].

3.5 Effect of temperature on the activity of 10% Ni/MgO catalyst.

As it is well known that dehydrogenation reaction is favoured at higher temperature; a maximum of 90% selectivity and 100% activity was obtained at 280° C, which did not increase further with the increase in temperature (Fig.4).

Other related hydrocarbons were also dehydrogenated successfully in very good to high yields. Table-5 summarizes the products and their yields obtained.

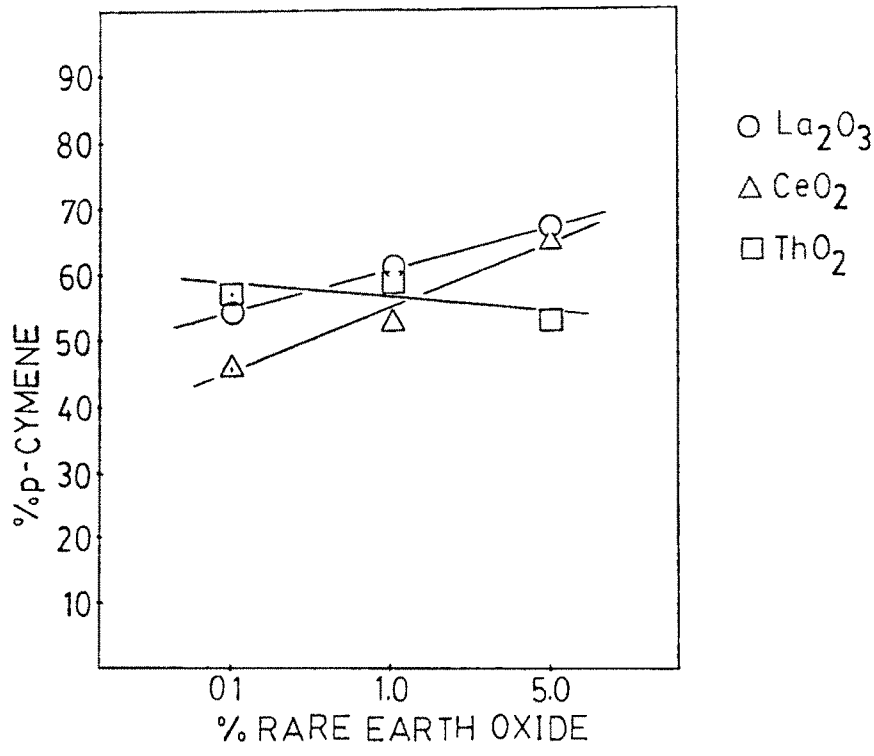


Fig. 3 - Effect of rare earth oxides on the activity of 10% Ni/MgO catalyst.

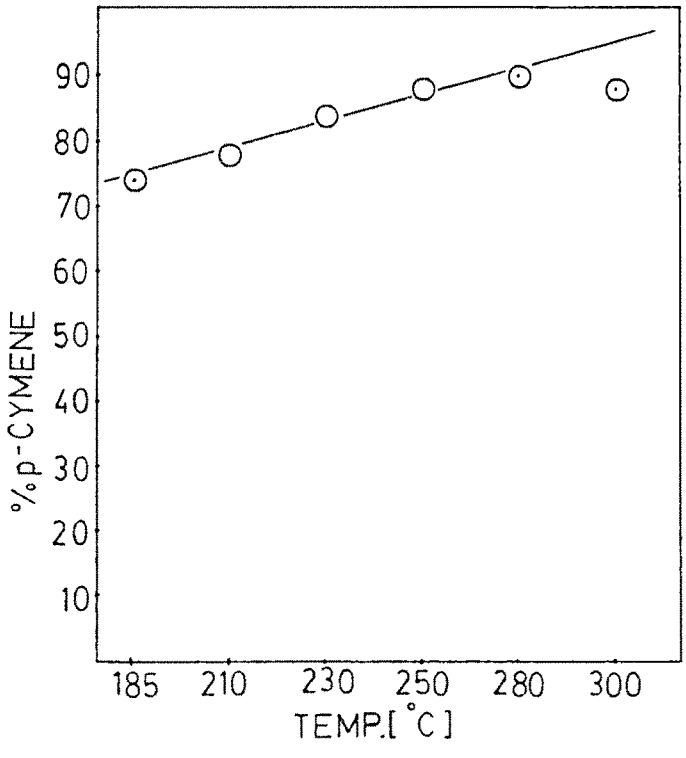
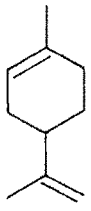
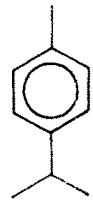
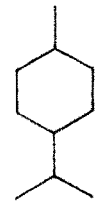
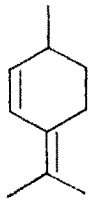
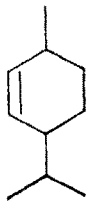
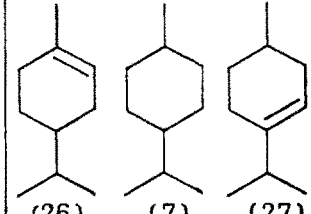
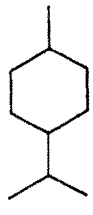
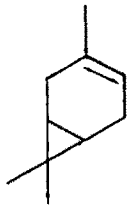
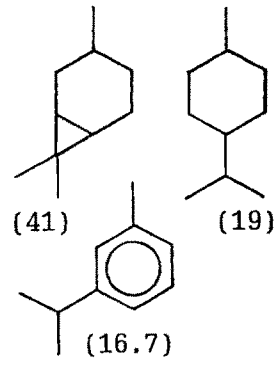
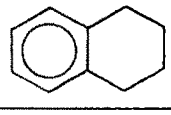
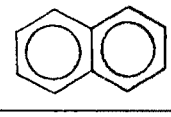


Fig. 4 - Effect of temperature on the activity of 10% Ni/MgO catalyst.

TABLE - 5

Dehydrogenation of six-membered hydrocarbons on 10% Ni/MgO catalyst (10.0 g) at 280°C.

Sr. No.	Substrate	Space velocity (v/v/sec)	Products			Remarks.
			Aromatic hydrocarbon	Yield (%)	Other products (%)	
01.		0.104		90.0	 (10)	
02.		0.104	"	88.0	" (12)	
03.		0.101	"	24.0	 (26) (7) (27)	16% Unreacted.
04.		0.100	"	9.0	-	91% Unreacted.
05.		0.104	"	20.7	 (41) (19) (16.7)	2.6% Unreacted.
06		0.120		47.0	-	53% Unreacted.

4. CONCLUSIONS

It can be concluded from this study that :

(1) The dehydrogenation of cyclohexanes depends, to a greater extent, on the metallic composition of the catalyst.

(2) A basic support is favourable for this reaction.

(3) Rare earth oxides do not have promoting effect for this particular reaction.

(4) The catalyst 10% Ni/MgO could be effectively used for the preparation of aromatic hydrocarbons in vapour phase from relatively saturated hydrocarbons in lab as well as in industry.

5. EXPERIMENTAL

All b.ps are uncorrected.

The following instruments were used for spectral/analytical data : Perkin-Elmer infrared spectrophotometer, model 267; Perkin-Elmer model R 32 (90MHz), NMR spectrometer; Hewlett Packard 7624 A gas chromatograph (stainless steel columns, 18', 10% FFAP and 6', 5% Bentone-34, support 60-80 mesh chromosorb W; carrier gas N_2) equipped with flame ionization detector. All PMR spectra were recorded with 15-20% solution in CCl_4 (unless otherwise stated) with TMS as internal reference; signals are reported in ppm (δ); while citing PMR data the following abbreviations have been used: s, singlet; d, doublet; t, triplet; m, multiplet; b, broad.

Other instruments used were : NFT-51, spinning-band teflon fractionation column (48.0 x 0.8 cm, theoretical plates, 80); Rajdhani moisture balance, RSMA-3 equipped with 240 V IR lamp; Cadmach rotary tablet machine, type 16 station, model CMD-3.

General description of catalyst activity testing unit and catalyst preparation is given in section 1.

Preparation of 10% Ni/MgO catalyst.

Nickel sulphate (9.1 g, 0.0338 mole) was dissolved in 90 ml of pure water at 68-9°C. It was allowed to cool down to 55°C ambiently and added solid sodium bicarbonate (6.25 g, 0.0743 mole) in portions ($\sim$ 8) with vigorous

stirring. The slurry was digested for one hour at the maintained temperature of 55°C while agitation was continued (pH=8.3). It was filtered and cake so obtained was washed with hot water (55°C) several times (100 ml x 10) in order to make it free from SO_4^{2-} ions. It was then dried on steam bath for 3-4 hours (wt.4.0-4.5 g) and physically mixed with 18.0 g magnesia, 0.6 g CMC (3.0%), 0.6 g magnesium borate (3.0%) with the help of mortar and pestle. After mixing with 0.4 g graphite (2.0%) it was pelleted. The pelleted catalyst was then calcined at 360°C for 4.0 hours in a well-ventilated furnace. After ambient cooling of furnace, catalyst was taken out (24.0 g) and used for dehydrogenation.

Dehydrogenation of individual hydrocarbons.

Each hydrocarbon was dehydrogenated on 10.0 g fresh catalyst, passing at the constant rate of 15 ml/hour for 8.0 hours at 280°C.

(1) Dipentene to p-cymene

Dipentene (100.0 g, 120 ml) furnished 98.0 g (99%) dehydrogenated product which contained 90% p-cymene and 10% p-menthane as identified by co-injection of authentic samples. (Lit.[54] NMR and IR).

(2) Isoterpinolene to p-cymene

Isoterpinolene (100.0 g, 120 ml) yielded 98.0 g (99.0%) product on dehydrogenation which contained 88.0% p-cymene and 12.0% p-menthane.

(3) p-Menth-2-ene to p-cymene.

p-Menth-2-ene (98.0 g, 120 ml) gave 97.0 g (99.0%) dehydrogenated product which contained 24.0% p-cymene, 27.0%. p-menth-3-ene, 26.0% p-menth-1-ene and 7.0% p-menthane as identified by coinjection of authentic samples

(4) p-Menthane to p-Cymene

p-Menthane (96.0 g, 120 ml) produced 95.0 g (99.0%) dehydrogenated product which contained only 9.0% p-cymene and rest p-menthane.

(5) Δ^3-Carene to p-Cymene.

Car-3-ene (100.0 g, 120 ml) yielded 98.0 g (99.0%) dehydrogenated product which was found to contain 20.7% p-cymene, 16.7% m-cymene, 19.0% p-menthane and 41.0% carane; rest was starting material.

NMR (Fig.5) : CH(2H, m, 0.55-0.88 ppm), Me(9H, three singlets, 0.88, 0.92, 0.95 ppm), CH_2 (7H, b, 1.6-2.1 ppm)

(6) Tetralin to naphthalene

Tetralin (116.0 g, 120 ml) afforded 112 g (98.0%) dehydrogenated product which contained 47.0% naphthalene. Balance was tetralin (Lit.[55] NMR).

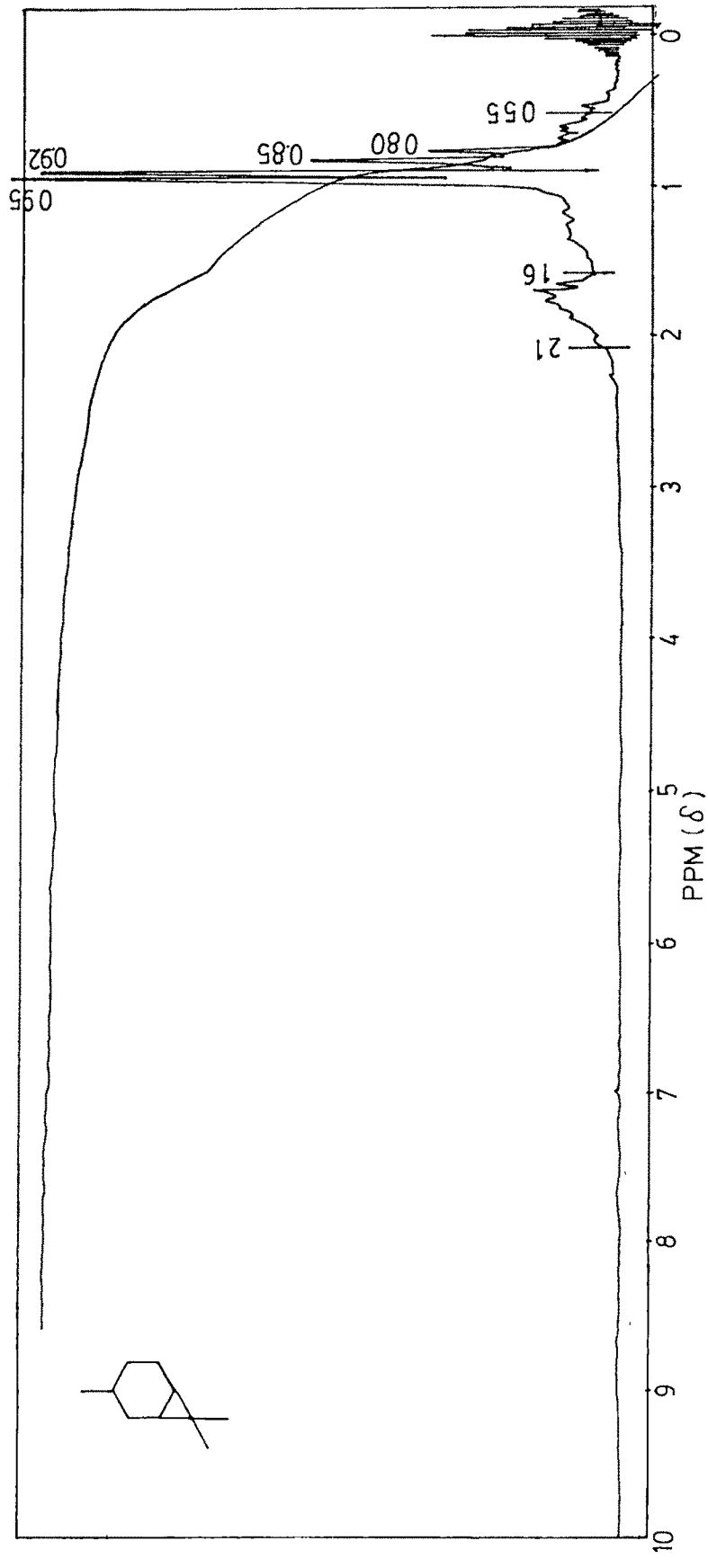


Fig. 5 - NMR spectrum of carane .

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