

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

C E R T I F I C A T E

This is to certify that the thesis entitled **SURFACE ACIDITY/
BASICITY OF RARE EARTH METAL-ALUMINIUM MIXED OXIDE
CATALYSTS** is an authentic record of the research work carried out by **Smt. Mariamma Cherian**, under my supervision in partial fulfilment of the requirements for the award of the degree of the Doctor of Philosophy in Chemistry of the University of Calicut. This work or part thereof has not been presented before for the award of any other degree.

Calicut University,
19.08.2002.



Dr. T. Ganga Devi
(Supervising Teacher)
Professor
Department of Chemistry
University of Calicut.

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

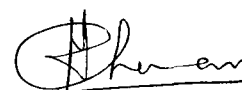
**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

D E C L A R A T I O N

Certified that the thesis bound herewith is an authentic record of the research work on SURFACE ACIDITY/BASICITY OF RARE EARTH METAL-ALUMINIUM MIXED OXIDE CATALYSTS, carried out by me under the supervision of Dr. T. Ganga Devi, Professor, Department of Chemistry, University of Calicut in partial fulfilment of the requirements for the award of the degree of the Doctor of Philosophy in Chemistry of the University of Calicut, and further that no part thereof has been presented before for any other degree.

Calicut University,
19.08.2002.



Mariamma Cherian

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

Acknowledgement

I am happy to place on record a deep sense of gratitude to Dr. T. Ganga Devi, Professor, Department of Chemistry, University of Calicut, for her patient encouragement, suggestions, discussions and guidance during the course of this work.

I wish to express my gratefulness to Dr. M.P. Kannan, Professor and Head of the Department of Chemistry, University of Calicut for providing the necessary facilities to complete the research work.

I would like to note a word of thanks to all other teaching staff, non teaching staff and students of the Department of Chemistry for their advice and assistance.

I cannot conceal my deep sense of love and thanks to Mr. Prathap K., Ms.Lasitha B.C. and Dr. (Ms.) Sheeba P.S., former research students of this department for their unaccountable help and support.

Thanks are due to Indian Rare Earth Ltd., Eloor, RCSI, Lucknow; RRL Thiruvananthapuram; CUSAT, Cochin; Sud-Chemi India Ltd., Cochin; and USIC, University of Calicut for providing the various analytical data and relevant services without which this work could not be completed.

I deeply remember my parents, family and friends for their prayers and moral support.

Finally to God, the Almighty for giving me the strength to endure the difficulties and to complete this work successfully.

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

C O N T E N T S

CHAPTER I INTRODUCTION AND REVIEW

1	Introduction	1
1.1	Bronsted and Lewis Concept of acids and bases	2
1.2	Catalysis	3
	1.2.1 Homogenous catalysis	3
	1.2.2 Heterogenous catalysis	4
1.3	Metal oxides as heterogenous catalysts	6
1.4	Acid/base sites of alumina	7
1.5	Generation of basic sites on metal oxides	9
1.6	Rare earth metal oxides	10
1.7	Determination of acid/base properties	12
	1.7.1 Calculation of acid/base strength of a solid surface	12
	1.7.2 Basic strength	13
1.8	Relation between acid/base strength and acidity/basicity of the surface	15
1.9	Methods to determine the acid/base strength and acidity/basicity of the surface	16
	1.9.1 Visual colour change method	16
	1.9.2 Titration method	17
	1.9.3 Amine titration for coloured samples	20
	1.9.4 Spectrophotometric method	21
	1.9.5 Spectroscopic method	21
	1.9.6 Adsorption and Temperature Programmed Desorption of base or acid molecules	22
	1.9.7 X-ray photoelectron spectroscopy	24
	1.9.8 Nuclear magnetic resonance method	24
1.10	Pre-compressed state of solids	25
1.11	Mixed oxides	27

1.12	Acid/base properties and catalytic activity	29
1.13	MPV reduction	29
1.14	Review	32
1.15	Present work	55
1.16	Objectives	56
CHAPTER II MATERIALS AND METHODS		
2.1	Materials	57
2.2	Experimental methods	58
2.2.1	Preparation of alumina	58
2.2.2	Preparation of Lanthanum oxide catalyst	58
2.2.3	Preparation of lanthanum-aluminium binary oxides	59
2.2.4	Preparation of gadolinium oxide catalyst	60
2.2.5	Preparation of gadolinium-aluminium binary oxides	60
2.2.6	Preparation of dysprosium oxide catalyst	60
2.2.7	Preparation of binary oxides of dysprosium and aluminium	61
2.3	Purification of solvents	61
2.3.1	Purification of benzene	61
2.3.2	Purification of propan-2-ol	62
2.4	Pretreatment techniques	62
2.4.1	Preparation of thermally activated samples	63
2.4.2	Preparation of precompressed samples	63
2.5	Determination of surface acidity/basicity	63
2.5.1	Determination of surface acidity	64
2.5.2	Determination of basicity	64
2.5.3	Gravimetric estimation of chemisorbed carbondioxide	65
2.6	Study of catalytic activity	65
2.6.1	Reduction of benzophenone	65

	2.6.2	Isolation of benzhydrol	66
	2.6.3	UV-Visible spectroscopy	67
2.7		Catalyst characterisation	68
	2.7.1	Surface area measurement	69
	2.7.2	X-ray diffraction	70
CHAPTER III		RESULTS AND DISCUSSION	71
3.1		Single oxides activated at different temperatures	73
3.2		Precompressed single oxides	81
3.3		Mixed oxide systems	90
	3.3.1	Lanthana-alumina mixed oxide system	92
	3.3.2	Gadolina-alumina mixed oxide system	94
	3.3.3	Dyprosia-alumina mixed oxide system	113
	3.3.4	Effect of precompression on binary oxides	120
3.4		Gravimetric estimation of adsorbed carbondioxide	137
3.5		Catalytic reduction of benzophenone	142
3.6		Conclusion	150
		REFERENCES	153

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

P R E F A C E

Metal oxides exhibit surface acidic and basic properties. Solid acids and bases are valuable substitutes for the toxic and corrosive acids and bases, as heterogenous catalysts in many industries. Rare earth metal oxides, in particular, have certain characteristics which promote their use in automotive exhaust treatment and in cracking industries. They are also used as catalyst supporters and promoters and also to produce thermal stability of γ -alumina, when used at high temperatures. The rare earth metal oxides are normally basic in nature and the surface characteristics can be changed by incorporating other elements in suitable proportions.

In this work, the surface characteristics of oxides of lanthanum (${}_{57}\text{La}^{139}$), gadolinium (${}_{64}\text{Gd}^{157}$), dysprosium (${}_{66}\text{Dy}^{162.5}$) and their binary oxides with aluminium are studied. Variations in surface properties are observed according to the composition and pre-treatment techniques. The activation was carried out by thermal heating and pre-compression. The thermally activated samples exhibited favourable changes in the surface properties, whereas the pre-compressed samples do not. The MPV reduction of benzophenone was carried out as a test reaction in presence of propanol-2 and the oxide catalysts.

A country cannot attain economic prosperity without proper development of its industry, but a pure environment is very essential for the survival of its people. To reduce pollution of any kind, the use of suitable heterogenous catalysts and appropriate technology is to be practised. This study comprises the possible use of such heterogenous catalysts.

The paper entitled "Acid/Base Properties of Binary Oxide Catalysts of Alumina-Gadolinium Oxides" had been presented in the National Conference on Materials for the New Millennium held at the Department of Applied Chemistry, CUSAT, Cochin from 1.3.01 to 3.3.01.

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002



Chapter I



INTRODUCTION

The surface properties of solid metal oxides are a topic of interest for the scientists at all times. The applications in the field of catalysis have demanded much attention on their surface acidic and basic properties. The acid/base sites on the surface of catalysts are assumed to be either Bronsted or Lewis acid sites. Different methods have been proposed to evaluate these properties and the parameters that can change these properties generally include temperature, composition, precompression, irradiation, etc.

Solid acids and bases are important heterogenous catalysts [1]. A number of chemical reactions have been understood in terms of acid-base interactions. Chemical reactions which are initiated by acid-base interactions followed by catalysis are called acid-base catalysed reactions. They include acid catalysed and base catalysed reactions. The largely studied solid acids were clay minerals and the bases were alkaline earth metal oxides.

Rare earth oxides have been studied as solid base catalysts for reactions including oxidation, hydrogenation, dehydrogenation of hydrocarbons, dehydration and dehydrogenation of alcohols, olefin isomerization, paraffin cracking and conversion of nitrogen oxides [2].

In recent years, much attention has been given to rare earth oxides as catalysts for methane oxidative coupling and related reactions [3]. Rare earth exchanged zeolites are widely used as cracking catalysts in petrochemical reactions.

1.1. Bronsted and Lewis Concept of Acids and Bases

Bronsted [4] suggested a general definition of acids and bases according to which an acid is defined as a substance which has a tendency to donate a proton [H⁺] to any other substance and base as a substance which has a tendency to accept a proton from any other substance. In other words an acid is a proton donor and base is a proton acceptor. This concept is applied to aqueous as well as non-aqueous solvents. An acid and a base are said to be conjugate pair when they are related by the equation



G. N. Lewis [5] put forth a more general definition of acids and bases. According to him an acid is a species that is capable of accepting a pair of electrons and base is a species that is capable of donating a pair of electrons. This definition attributed acidity/basicity to unique electron arrangement and not to any particular element.

Thus according to Bronsted, a solid acid is one which contains a proton or H⁺ ion on the surface for donation and base is the one which can accept it. The

electron deficient atom on the surface account for the Lewis type of acid and vice versa.

1.2. Catalysis

A catalyst is a substance that accelerates the rate of the chemical reaction without itself undergoing any chemical change during the process. A catalyst forms an intermediate complex and is finally regenerated. Catalyst generally lowers the free energy of activation and thus increases the rate of the reaction.

A catalytic reaction can be classified into homogenous and heterogenous. When the catalyst and reactants are in a single phase, the catalysis is called homogenous catalysis and when the reactants and catalysts form separate phases, it is called heterogenous catalysis.

1.2.1. Homogenous Catalysis

Catalytic reactions in which the reactants and the catalyst mix together homogeneously to form a single phase are called homogenous catalytic reactions. The homogenous catalyst shows high efficiency and selectivity, good control over its preparation and needs comparatively mild reaction conditions and has uniform nature of catalytically active sites. However the homogenous catalysts have some serious problems. It is difficult to separate the catalyst and products. A large amount of catalyst is usually required, and catalytic waste, which is

significant, causes environmental hazards. Also the cost of the process of installation and maintenance is high, since the liquid acids are highly corrosive.

1.2.2. Heterogenous Catalysis

Heterogenous catalysis is one of the most important phenomenon closely related with surface properties of solids. Commonly the catalyst is a solid and the reactants are gases or liquids. The catalytic activity is frequently attributed to some specific sites on the surfaces. The reaction involves the chemisorption of the substrates on the surface of the catalyst followed by reactions between them. The product molecules diffuse away from the active sites of the catalyst [6].

The use of solid acids and bases in place of the conventional acids and bases, which are highly corrosive and polluting is a significant step towards clean technology. Thus heterogenous catalysis has received great recognition from researchers and a number of works have been reported. The largely studied heterogenous acid catalytic reaction is cracking process in petroleum refining. Cracking catalysts are essentially acidic in nature. Activated clay and synthetic silica-alumina are the widely used cracking catalysts which are proved to possess strong acid centers [7-9].

Very few studies have been reported on base catalysts. The first study was reported by Pines et al [10]. Sodium metal dispersed on alumina acts as an effective catalyst for double bond migration of alkenes. Later Kokes et al [11]

reported that hydrogen molecules adsorbed on zinc oxide act as an intermediate for alkene hydrogenation. The heterolytically dissociated hydrogen (hydride ion) act as base. The basic nature of calcium and magnesium oxide on pretreatment under high temperature and high vacuum was reported by Hattori et al [12].

In fact, in view of the environmental concern, there is a global effort to replace the conventional acid and base catalysts by eco-friendly solid acids and bases. Nowadays, more of the industrial applications are based on heterogenous catalysis, also because of the easy separation of the products from the catalyst and recyclability.

A large number of technologically important chemical reactions employ solid catalysts. A wide variety of solids are used as catalysts. Metals, alloys, metal oxides and sulphides, metal salts, mounted acids and bases, mixed oxides, various kinds of zeolites, etc., are some examples. They have specific activity and selectivity.

The essential requirements of an effective heterogenous catalyst are high surface area, good porosity and mechanical strength. Heterogenous catalysis can be classified into two types.

(a) Oxidation-reduction Catalysis (electronic)

These reactants are catalysed by solids possessing free or easily excited electrons. Electrons are transferred in the elementary act of catalysis from the reacting substrate to the catalyst or vice versa.

(b) Acid-Base Catalysis (Ionic):

These reactions are accelerated under the influence of acids or bases. For such reactions, the elementary act of catalysis involves the transfer of proton or production of heteropolar donor-acceptor pair. Acid-base property of the heterogenous catalyst determines the catalytic efficiency for this type of reactions. A variety of solid acids and bases find their application as heterogenous catalyst in many of the important industries.

Solid acids and bases are characterised by the amount, strength and nature of acid and base sites. These characteristics depend on purity of material, method of preparation, heat treatment, etc.

1.3. Metal oxides as Heterogenous Catalysts

Metal oxides have a significant role in catalysis. They are used as catalysts in both redox and acid-base catalysed reactions [13]. This is due to their ability to exchange electrons, protons, or oxide ions with the reactants. The cations and anions on the surface can be considered as acid-base pair sites [14, 15].

A Lewis site on the oxide surface is considered as a metal ion (M^{n+}) formed by dehydration. A Bronsted site arises when a water molecule is adsorbed on the Lewis site. The negatively charged oxygen atom on the surface is considered to be the basic site [16]. The cations and anions present on the surface have fewer number of nearest neighbours than the corresponding ions in the bulk. Hence they are co-ordinatively unsaturated. The co-ordinatively unsaturated sites on the surface are principally responsible for adsorptive and catalytic properties of metal oxides.

The co-ordinatively unsaturated nature of the surface can be intensified by further dehydroxylation or by removing the surface lattice oxygen by reduction. The oxygen vacancies created on the site adsorb oxygen in the gas phase and activate them for participation in catalysis.

1.4. Acid/Base Sites of Alumina

γ -Alumina is widely used as an industrial catalyst and catalyst support. It possesses intrinsic acid and basic sites and catalyses many kinds of acid-base reactions, such as dehydrohalogenation, hydration, deamination, alcohol condensation and so forth. [17]. The catalytic activity is assumed to be closely related to certain acid sites developed when chemisorbed water is removed from the surface. Studies on alumina catalyst revealed that the catalyst prepared from

sodium aluminate was only weakly acidic while alumina prepared from aluminium isopropoxide was strongly acidic [18].

The Lewis and Bronsted acid and basic sites created on alumina surface by dehydration at high temperature are shown below [19]. A water molecule is removed from two hydroxyl groups attached to aluminium atom to form Al-O-Al linkages, the distortion of which is responsible for the acid strength. (Fig. 1.1) The Bronsted and Lewis acid sites can be estimated separately by IR spectral studies of ammonia (20) or pyridine [21].

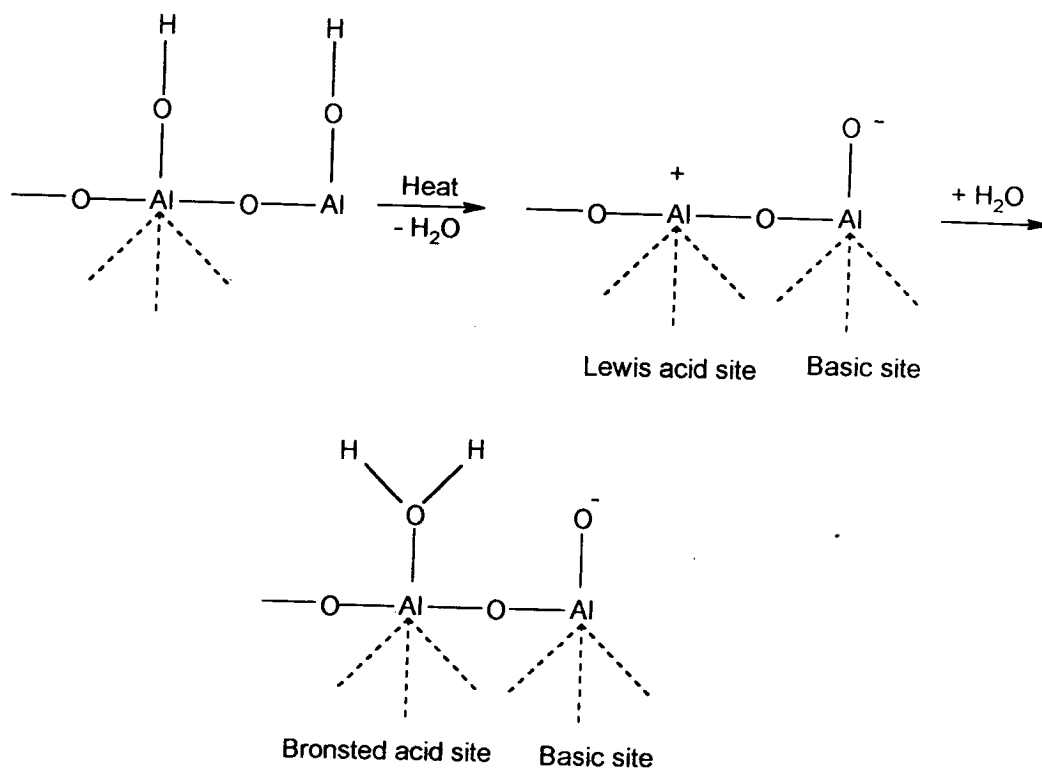


Fig. 1.1. Lewis and Bronsted acid and basic sites of alumina

The phase transformation from the γ to α phase and the decrease of its surface area, so called sintering, are serious problems for a practical use of these catalysts, without deactivation at high temperature. The addition of lanthanoid and alkaline earth elements to alumina enhance its thermal stability and the sintering effect can be reduced to some extent [22].

1.5. Generation of basic sites on metal oxides

The generation of basic sites on a metal oxide requires pretreatment at very high temperature to remove the already adsorbed carbon dioxide, water and oxygen molecules in some cases. The catalytic activity varies with the nature of basic sites which, in turn is dependent on the severity of pretreatment temperature [23]. Some kind of rearrangement of the surface and bulk atoms also occur which is supported by a decrease in the surface area with an increase in pretreatment temperature.

Coluccia and Tench [24] proposed a surface model for MgO in which several Mg-O ion pairs of different co-ordination number exist at corners, edges, or high miller index surfaces of the 100 planes. Different basic sites correspond to the ion pairs of different co-ordination numbers. The ion pairs of three fold Mg^{2+} and three fold O^{2-} ions are the most reactive and the most unstable. They tend to rearrange at high temperature. Other metal oxides also behave in a similar manner.

Alkali, alkaline earth, rare earth and certain transition metal oxides are identified as basic catalysts.

1.6. Rare Earth metal Oxides

Rare earth metal oxides are now extensively used in a number of chemical reactions, which have potential commercial applications. One of the most important of these is the use of cerium in catalysis for automobile exhaust emission control.

The rare earth oxides have a number of distinguishing properties important in catalytic applications. The gradual filling of 4f orbitals causes a decrease in their atomic and ionic sizes, increase in their surface charge and density, which provide a wide range of energy states needed for different applications [25, 26]. They are basic compared to alumina, La_2O_3 being the most basic, and the basicity decreased from La and Lu. The lattice O^{2-} ions are responsible for the basic sites on the surface of these oxides.

These metal oxides have good thermal stability [27], because of their high melting point and enhanced oxygen storage capacity [28] which are valuable characteristics in most industrial applications. Catalysts having an enhanced oxygen storage capacity are prepared under patent and widely used in the treatment of automotive engine exhaust. Other important potential catalytic

applications include ammonia synthesis, hydrogenation and dehydrogenation, polymerisation, isomerisation, oxidation-reduction, etc.

Oxides like La_2O_3 , Y_2O_3 , Sm_2O_3 , Gd_2O_3 or Dy_2O_3 are used for catalytic combustion [29] for stabilizing alumina [30] and other metallic oxides like MgO , SiO_2 , MnO_2 and Fe_3O_4 [31].

Minachev et al [32] suggested that catalytic activity of rare earth oxides depends on the binding energy of oxygen with the surface in the oxidation of hydrogen and propylene. They studied variation in catalytic activity of rare earth oxides in ethylene hydrogenation as a function of pretreatment temperature. The oxides showed catalytic activity after pretreatment at 600°C . Lanthanum oxide showed highest activity and it decreased from La to Lu. This was correlated to decrease in their basicity.

The surface sites generated on rare-earth oxides do not seem to vary much in nature with pretreatment temperature as in other metal oxides. Variations of the activities of La_2O_3 as a function of pretreatment temperature for 1-butene isomerisation, 1, 3, butadiene hydrogenation and methane D_2 exchange were reported [33-35]. For all the above reactions the maximum activity is for the catalyst at 923 K.

1.7. Determination of Acid/Base Properties of Solid Surfaces

According to Walling [8] the basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed electrically neutral acid to its conjugate base or it is the ability of the surface to donate an electron pair to an adsorbed acid. Similarly acid strength of a solid surface is the ability of the surface to convert an adsorbed neutral base to its conjugate acid. The amount of acid or acidity of solid is usually expressed as the number of millimoles of acid sites per unit weight of the catalyst or per unit surface area of the solid and is obtained by measuring the amount of a base which reacts with the solid acid. Similarly basicity is determined by the amount of acid molecules that can react with the basic sites on the surface.

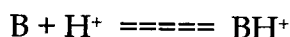
1.7.1. Calculation of Acid/Base Strength of a Solid Surface

If the surface exhibits Bronsted type acidity, the strength of the acid site is expressed quantitatively by Hammett function H_0 [36]. Hammett acidity function

H_0

$$H_0 = -\log \frac{a_{H^+} \times f_B}{f_{BH^+}}$$

When the solid acts as Bronsted acid



$$H_o = pK_a + \log (B/BH^+)$$

$$pK_a = H_o - \log (B/BH^+)$$

Where,

a_{H^+} = activity of Bronsted acid on the surface

f_B = activity co-efficient of neutral base B

f_{BH^+} = activity co-efficient of conjugate acid

$[B]$ = concentration of neutral base

$[BH^+]$ = concentration of conjugate acid

If the reaction takes place by electron pair transfer from the adsorbate to the surface

$$H_0 = -\log \frac{a_A \times f_B}{f_{AB}}$$

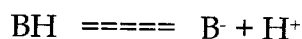


$$H_o = pK_a + \log [B] / [AB]$$

Where a_A is the activity of the Lewis acid or electron pair acceptor.

1.7.2. Basic Strength

The basic strength or the proton accepting ability of the solid surface is expressed by Hammett and Deyrup function H_0 [16,37,38].



$$\text{H}_0 = \frac{(\log a_{\text{H}^+} \times f_{\text{B}})}{f_{\text{BH}}}$$

$$\text{H}_0 = \text{pK}_{\text{BH}} - \log [\text{BH}]/[\text{B}]$$

$$\text{H}_0 = \text{pK}_{\text{BH}} + \log [\text{B}]/[\text{BH}]$$

Where

a_{H^+} = activity of Bronsted acid on the surface

f_{B} = activity co-efficient of conjugate base

f_{BH} = activity co-efficient of conjugate acid

$[\text{BH}^+]$ = concentration of the acid

$[\text{B}]$ = concentration of conjugate base

The first perceptible change in the colour of an acid indicator occurs when about 10 percent of the adsorbed layer of the indicator is in the basic form, i.e., when the ratio $[\text{B}] / [\text{BH}] = 10/90 \approx .1$. Further increase in the intensity of the colour is only perceptible to the naked eye when about 90 percent of the indicator is in the basic form, i.e., when $[\text{B}] / [\text{BH}] = 0.9 / 0.1 \approx 10$. Thus the initial colour change and the subsequent change in intensity are observed at values of H_0 equal to (pK_a-1) and (pK_a+1) respectively. If we assume that the intermediate colour appears when the basic form reaches 50 percent, i.e., when $[\text{B}] / [\text{BH}] = 1$, we have $\text{H}_0 = \text{pK}_a$. According to this assumption, the approximate values of the basic

strength of the surface is given by the pKa value of the adsorbed indicator, at which the intermediate colour appears [40].

1.8. Relation between Acid/Base Strength and Acidity/Basicity of the Surface

The strength of an acidic or basic site can be expressed in terms of Hammett acidity function. It is measured by using a series of Hammett indicators that are adsorbed on the solid surface. If an acid site of $H_0 \leq pK_a$ of the indicator exists on the surface, the colour of the indicator changes to that of the conjugate acid. Similarly when a neutral indicator is adsorbed on a basic site where the strength of conjugate acid $H_0 \geq pK_a$ of the indicator, the colour of the indicator changes to that of its conjugate base. Both acidity and basicity are measured on a common scale H_0 [41]. The strength of acid sites were expressed by H_0 as usual and that of basic sites by the H_0 of their conjugate acids. The strongest H_0 value of the acid sites was found to be approximately equal to the strongest H_0 value of basic sites. The equal strongest H_0 value was termed H_{0max} . The acid base strength distribution curves intersect at a point on the abscissa. The point of intersection is defined as H_{0max} , when acidity = basicity = 0 [42].

H_{0max} can be regarded as a practical parameter to represent acid-base properties of solids which is sensitive to the surface structure. It is known that a solid with a large negative H_{0max} value has strong acidic sites, and a solid with a large positive H_{0max} value has strong basic sites. The strongest H_0 value of the

acid sites can be found to be approximately equal to that of the strongest H_0 value of the basic site.

1.9. Methods to Determine the Acid/Base Strength and Acidity/Basicity of the solid Surface

A number of methods are in practice for determining the acid/base strength and the amount of acid/base sites in a solid.

1.9.1. Visual Colour Change Method

This method was originally suggested by Walling [8]. It is still in practice to get an idea about the relative acid strength.

A suitable indicator is allowed to adsorb on the solid surface and the colour of the indicator on the solid surface is a measure of the acid strength, $H_0 \leq pK_a$. If the sample is coloured, the method is modified by mixing a white substance of known acidity. A list of Hammett indicators is given in Table 1.

TABLE 1
List of Indicators

Sl. No.	Name of indicator	Colour		pKa
		Base form	Acid form	
1.	2,4-dinitroaniline	Violet	Yellow	15.0
2.	2,4,6-trinitroaniline	Orange	Yellow	12.2
3.	Bromothymol blue	Green	Yellow	7.2
4.	Neutral red	Yellow	Red	6.8
5.	Methyl red	Yellow	Red	4.8
6.	Phenyl azonaphthylamine	Yellow	Red	4.0
7.	p-dimethylaminoazobenzene (Dimethyl yellow or Butter yellow)	Yellow	Red	3.3
8.	2-amino-5-azotoluene	Yellow	Red	2.0
9.	Benzene azodiphenyl amine	Yellow	Purple	1.5
10.	4-Dimethylamino azo-1-naphthalene	Yellow	Red	1.2
11.	Crystal violet	Blue	Yellow	0.8
12.	Dicinnamal acetone	Yellow	Red	-3.0
13.	Benzalacetophenone	Colourless	Yellow	-5.6
14.	Anthraquinone	Colourless	Yellow	-8.2

1.9.2. Titration Method

The acid strength of a solid catalyst is determined by observing which members of a series of Hammett indicators (Table 1) are adsorbed in the acid form

[8]. Those indicators are chosen whose acid colours are intense enough to mask their basic colour [38].

Each of a series of Hammett indicators in benzene solution is added to a solution of the solid suspended in benzene. If the acid colour of the indicator develops, then the H_0 function of the surface is same or lower than the pK_a of the conjugate acid of the indicator ($H_0 \leq pK_a$). The lower the pK_a value of the indicator, the greater is the acid strength of the surface. The amount of acid sites are measured by titration with n-butyl amine solution in benzene [16, 42, 43]. This method was first reported by Tamele [9]. Use of various indicators with different pK_a values enables the determination of the acidity at various acid strength.

The basic strength and the amount of basic sites of the solid surface can also be determined [41] by using a suitable indicator and titration with a solution of trichloro acetic acid (TCA) in benzene. If the basic colour is developed on the surface of the solid, the strength of the surface is greater than or equal to pK_a of the indicator ($H_0 \geq pK_a$). The basicity at different basic strengths H_0 can be determined by using various indicators of different pK_a .

Reproducible values are available by controlling variables such as titration time, volume of the added indicator, pore size and moisture [45]. The sum of Bronsted and Lewis acid sites are obtained in this method.

Kikuchi et al [46] determined the acid-base strength distribution of certain oxides by titration of solids suspended in cyclohexane with benzoic acid using Hammett indicators.

The method was first reported by Tamele [9] using p-dimethyl amino azo benzene as an indicator. The yellow basic form of the indicator changes to red acidic form, when adsorbed on the solid. The titres of n-butyl amine required to restore the yellow colour give a measure of the number of acid sites on the surface. Since the adsorbed indicator is replaced by the titrating base, the basicity of the latter should be the stronger of the two.

Both the Lewis acid or Bronsted acid sites of the solid react with either the electron pair ($-N:=$) of the indicator or that of the amine ($\equiv N:$) to form a co-ordinate bond.

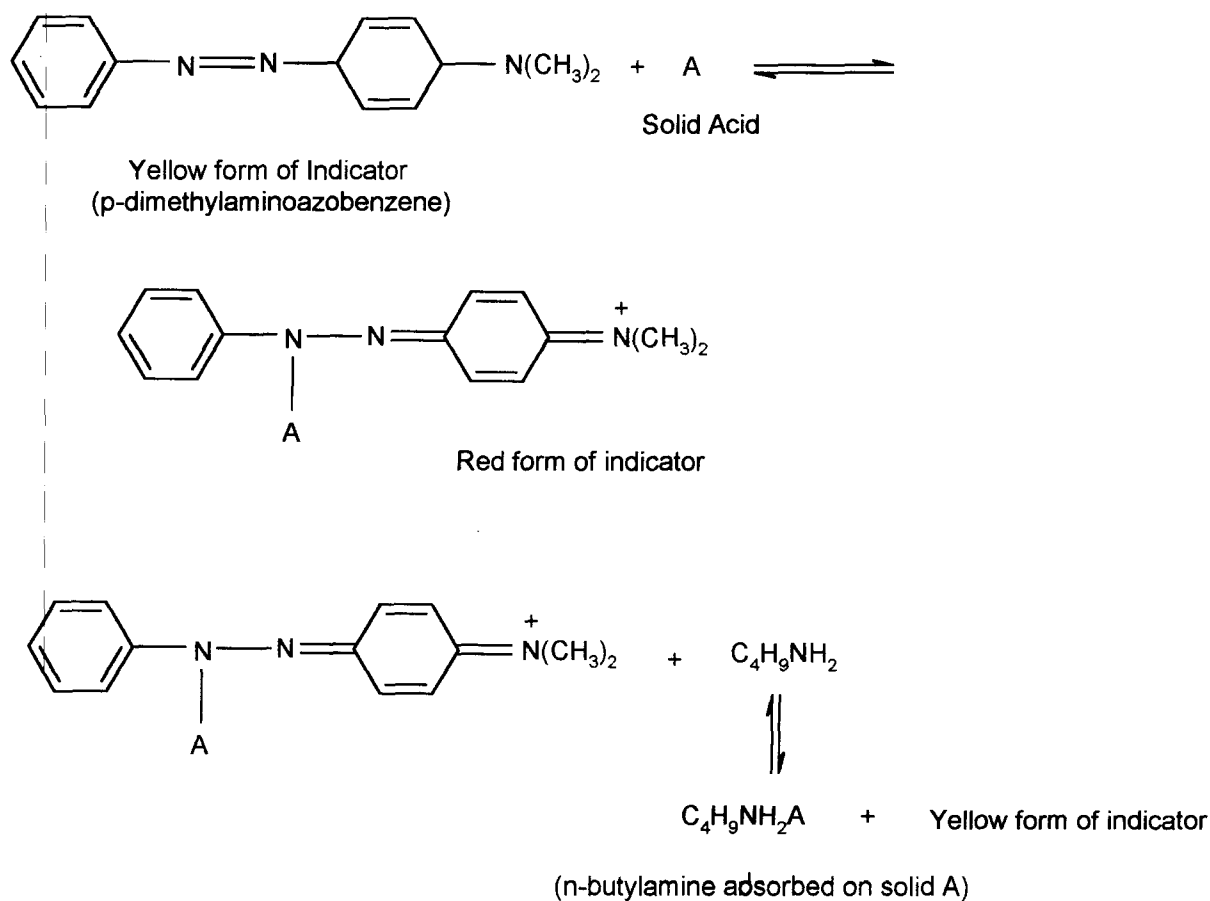


Fig. 1.2. Titration of solid acid by n-butylamine in presence of p-dimethyl amino azo benzene indicator

1.9.3. Amine Titration for Coloured Samples

The above method is restricted to white or light coloured surfaces. Titrations of dark coloured solids can be done by adding a small known amount of white solid [47]. The end point of the titration is taken when the colour change is observed on the white solid and a correction is made for the amount of n-butyl amine used for the added white material.

Colorimetric titration using n-butyl amine, ethyl acetate or dioxane can be used in this regard. This was further developed by Tanabe and Yamaguchi [48].

1.9.4. Spectrophotometric Method

The characteristic adsorption spectra of dyes adsorbed on solid acids are studied [49, 50]. The Hammett indicators were adsorbed from benzene on to thin plates of optically transparent materials. Those indicators, whose pK_a values are equal to or greater than the H₀ of the surface, are adsorbed in their acid form. Comparison of the curves, where wavelengths are plotted against absorbance, reveals the acid nature of the solid.

1.9.5. Spectroscopic Method

IR and Raman Spectroscopy have been used to determine acidity of solid catalysts by studying adsorbed probe molecules [51-56]. Basic molecules like ammonia, pyridine, substituted pyridine and less basic diazines and quinolines are used as probe molecules. IR spectral studies of adsorbed pyridine are helpful to determine the concentration of Bronsted and Lewis acid sites, in combination with thermal desorption studies [57, 58].

The basic sites are determined by IR of pyrrole [59] and adsorbed CO₂ on the surface. Carbon dioxide interacts with the basic sites of a heterogenous catalyst. The adsorption happens in different forms, bidentate and unidentate carbonate and bicarbonate forms [60, 61]. The adsorbed form varies with the

coverage of the adsorbed carbon dioxide on the solid surface. Bidentate carbonate dominates at low coverage whereas unidentate at high coverage. For CaO, it is adsorbed in the form of bidentate carbonate regardless of the coverage.

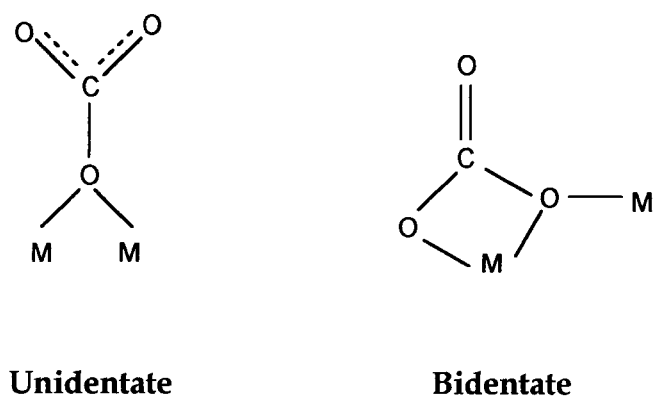


Fig. 1.3. Adsorbed forms of carbon dioxide gas on metal oxides.

In unidentate adsorption only surface oxygen atoms are involved whereas in bidentate carbonate both metal and surface oxygen atoms are used.

1.9.6. Adsorption and Temperature Programmed Desorption (TPD) of Base or Acid Molecules

The study of adsorption of volatile amines on the solid surface and their desorption at various temperatures can lead to the determination of acid strength. The solid substance is allowed to adsorb the base in excess where it is considered to be physically adsorbed which is then removed by prolonged evacuation. The

left out is accounted for chemically adsorbed and it measures the total amount of acid site.

The acid strength distribution can be calculated by direct calorimetric measurements of the heat of adsorption at different base coverages or by thermal desorption (TPD) of the preadsorbed base. The adsorbed base evacuated at different temperatures is calculated [62-68]. The relationship between temperature of peak maximum T_m and activation energy of the chemisorbed E_d , is given by the following equation.

$$2 \log T_m - \log \beta = \frac{E_d}{2.303 RT_m} + \frac{\log E_d A_m}{RK_0}$$

where β is the linear heating rate, A_m is the amount of base adsorbed at saturation, K_0 is the pre-exponential factor in the desorption rate expression and R is gas constant. There is a relation between acid strength H_0 and T_m (Temperature of peak maximum) $H_0 = \alpha + \beta/T_m$, where α and β are constants specific for the acid solid.

The strength and number of basic sites are measured by the TPD of CO_2 . The strength and amount of basic sites are reflected in the desorption temperature and the peak area in a TPD slot. The basic strength of alkaline earth metal oxide determined by this method was in the order $\text{MgO} < \text{CaO} < \text{SrO} < \text{BaO}$ and the number of basic sites per unit weight was $\text{BaO} < \text{SrO} < \text{MgO} < \text{CaO}$ [69].

1.9.7. X-ray Photo-electron Spectroscopy (XPS)

The XPS binding energy of N_{1s} lines arising from chemisorbed pyridine is used to characterise the acid sites. Both Bronsted and Lewis acidity can be determined by studying the two N_{1s} lines, one arising from protonated pyridine and the other from pyridine co-ordinated to Lewis acid site.

The XPS binding energy for oxygen reflects the basic strength of the oxygen. As the O_{1s} binding energy decreases the electron pair donation becomes stronger. In other words, the binding energy of O_{1s} band changes with the basic strength of oxygen [70].

In this technique, the kinetic energy of the photoelectron emitted from the core levels of surface atoms are measured when they are irradiated with X-rays. It is useful to characterise surface acid sites or basic sites in combination with suitable probe molecule.

1.9.8. Nuclear Magnetic Resonance Methods

NMR is another powerful technique to study solid acid catalysts [71-73]. Advanced NMR methods such as cross polarisation (CP) magic angle spinning (MASNMR) of solids, high resolution and pulse field gradient magnetic resonance, multimeter spectroscopy and variable temperature MASNMR [74] have increased the capability of this technique to study acid sites in solid catalysts. The total number of acid sites and their relative strength can be

measured by proton MASNMR technique in samples of solid acids containing as low as 10^{18} protons [75-77].

^2H MASNMR and echo fourier ^{27}Al NMR have been applied to investigate Bronsted acid sites in zeolites [78].

The interaction with probe molecules such as pyridine can also be used to characterise solid acid catalysts provided the NMR spectra of the protonated and unprotonated forms are different [79]. Phosphorous containing probe molecules (Trialkylphospherines and trialkyl phosphine oxides) have been used to quantify the number of Bronsted and Lewis sites in zeolites by means of ^{32}P MASNMR. This is a widely used technique in zeolite catalysis [80-82]. ^{13}C NMR can also measure acidities from interaction of acid sites with weak bases such as alcohols, acetone and aceto nitrile [155].

In brief, indicators can give an idea about the acid base strength distribution of a given solid catalyst. When used with titration techniques, the number of acid/base sites with different strength could be determined. The results can be correlated to catalytic activity. It can be combined with other techniques also.

1.10. Pre-compressed State of Solids

Most catalysts require some type of pretreatment before use in reactions. This is to remove extraneous adsorbed materials such as water, carbon dioxide,

etc., and in some cases to produce major chemical changes. The pretreatment steps are important since they may have a large effect on catalytic behaviour and the reproducibility of samples of the same material. Temperature, pressure, composition and irradiation are the parameters that can bring about such changes in their catalytic behaviour.

The reactivity of a solid depends on the defect structure of the solid [83].

According to Hedvall [84] the factors affecting the reactivity of a solid are:

- (1) deviations from normal crystallographic structures leading to imperfections
- (2) difference in phases, and,
- (3) changes in electronic and magnetic states.

Among them the influence of imperfections is the field that has attracted much interest. Dience and Damask [85] discussed the role of different types of defects, dislocations, stacking faults, etc., on the thermal decomposition of different solids. Due to the discontinuity in the periodic field the surface of a solid itself is a major defect. It has been shown by Tamm [86] that band levels can exist at the surface which can act as electron traps, there by influencing the reactivity of solids. Garner and Tanner [87] have shown that deliberate introduction of damage by cutting, crushing and grinding the crystals, facilitates the formation of product nuclei.

Compression can cause some changes in the volume of the crystal and in the M-O-M bond of certain metal oxides. But this change is not uniform on different crystals [88]. Different bonds and angles change by different extents.

1.11. Mixed Oxides

Changes in composition cause variations in electronic structure due to changes in the inter-atomic distance between the original and substituting atoms [89]. It causes variations in electron density. Two metal oxides when mixed together, may form a new compound or a solid solution by the reaction between two phases or by mutual contamination of the two oxides.

Acid/base sites on metal oxides are believed to be due to surface hydroxyl groups or a charge imbalance localised on the surface. Deficiency of electrons created on the surface results in a local imbalance between the positive and negative charges of the constituents and it acts as a Lewis acid for catalytic reactions. Solid oxide surfaces of new acid/base sites can be designed by doping or by mixing with other metal oxides [90, 91]. The charge imbalance is associated with the $M_1\text{-O-M}_2$ bond where M_1 is the host metal ion and M_2 the doped or mixed metal ion [92] and it is due to the surface imperfections in small crystallites [95]. The typical imperfections are due to metal or oxygen vacancies.

The vacant sites or holes facilitate the diffusion of an ion from an occupied site to an unoccupied site. One convenient way of changing the number of vacant sites in the latter is to substitute the lattice with ions of different valency.

The number, strength and type of acid-base sites generated are affected by the composition of the metal oxides, pretreatment and also by the preparation methods [94, 95]. The character of the supporting or mixing oxide also is a deciding factor in the preparation of mixed oxides. It should be acidic or at least not strongly basic, to develop a desired acidic oxide. Doping basic MgO with iron oxide does not generate new acidic sites [96], but with SiO₂ it creates new acid sites.

Nakabayshi et al [97] studied the acid properties of anatase having different crystalline sizes. The strength of the acid sites was found to be increased with a decrease in crystalline size. The strong acid sites over the surface of the crystallites were explained in terms of electronic properties, which is widely different from that of the bulk. The positive holes formed in the valence band act as Lewis acid sites during catalysis. Silicate minerals when mixed with other cations, some local deformations were observed [98].

The advantage of mixed oxide is that it is possible to develop oxides of definite oxygen sorption property [27] by choosing a particular metal component, so as to crystallise in a definite structural system. The reactivity of oxygen

depends on the neighbouring metal cations as well as on metal oxygen bond distance and bond length.

1.12. Acid-Base Properties and Catalytic Activity

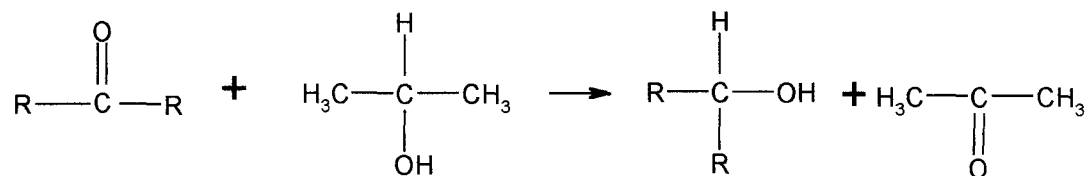
In acid catalysed reactions, reactants act as bases towards catalysts which behave as acids. In base catalysed reactions, the reactants act as acids towards catalysts which behave as bases. The catalytic activity is related to the acid-base strength, acid-base amounts, the nature of acid-base sites, etc. The correlation between catalytic activity and the acid-base property can be explained by the strength of acid-base interactions between the reacting molecules and the catalytic surface [99]. If the reactants are basic, the reactivity is increased by the acidity of the catalyst or vice versa.

1.13. MPV Reduction

A mild and specific method of reducing carbonyl compounds introduced by Meerwin and Verley and modified by Ponderoff in 1926 is known as MPV reduction. It is used successfully in a variety of aldehydes and ketones [100].

The reaction is considered to take place through hydrogen transfer mechanisms when an organic molecule, in particular, an alcohol acts as a source of hydrogen [101]. Aldehydes and ketones react with these alcohols to produce corresponding alcohols. Aluminium isopropoxide has been found to be the best

reagent for this reaction. But it required the addition of 100-200 percent excess of aluminium isopropoxide and strong acid (HCl) to neutralise the excess alkali.



Other catalysts used for this purpose included complexes of cobalt, iridium, rhodium, ruthenium, molybdenum and zirconium [102-106].

Heterogenous catalysts are also successfully employed for the reduction. Oxides of aluminium, silicon, alkaline earth metal oxides [108], certain transition metal oxides and oxides of lanthanoid group [109] are useful as catalysts. Such heterogenous catalytic reactions have several advantages in the isolation of products. Neutralisation using acids is not required and this helps to collect the product in almost pure form.

The reduction of various kinds of aldehydes and ketones in the temperature range [273-473 K] was carried out by Shibagaki et al [110].

They found hydrous zirconium oxide as a highly active catalyst for the reaction. 2-propanol was used as a hydrogen source. It was established that the rate determining step is the hydride transfer from the adsorbed 2-propanol to adsorbed carbonyl compounds.

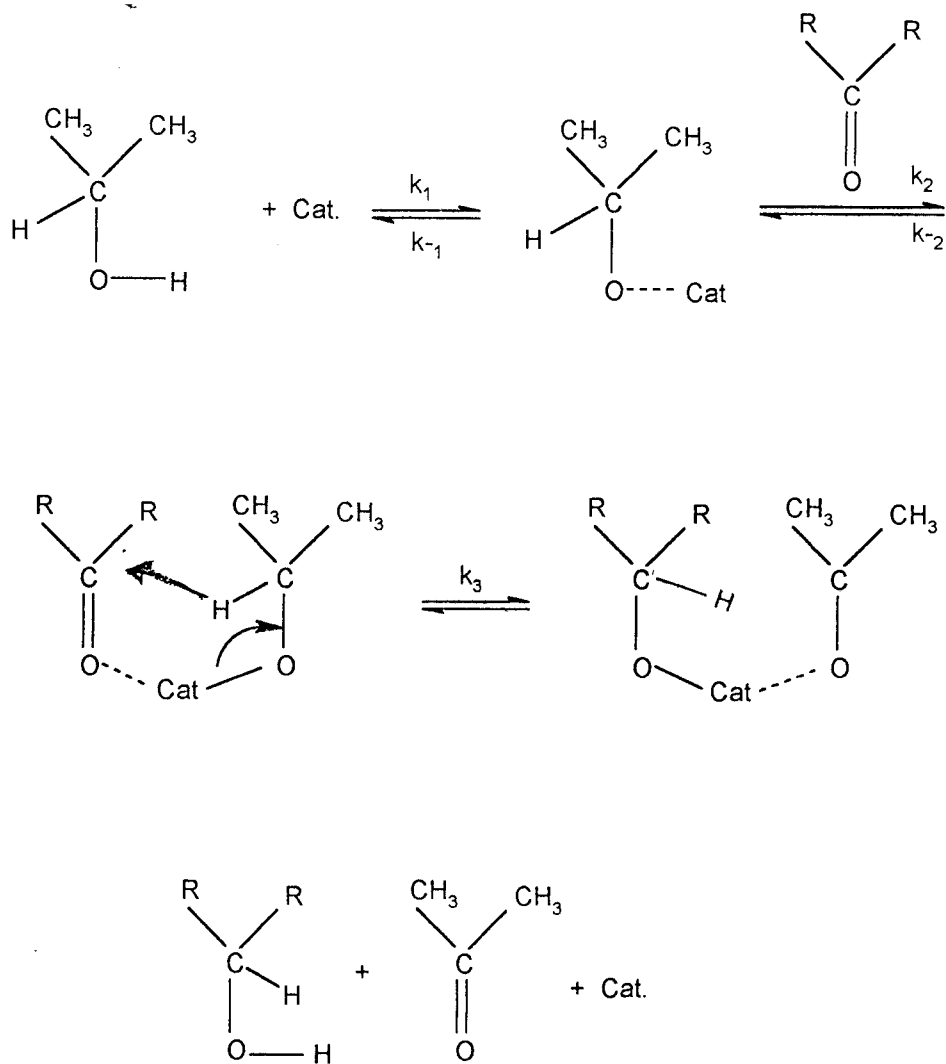


Fig. 1.4. Hydrogen transfer from 2-propanol to ketones

Y. Ishi et al [111] synthesised bi-(cyclo penta dienyl) zirconium dihydride (CP_2ZrH_2) and it was allowed to react in the presence of both ketone and alcohol. The hydrogen transfer from the alcohol to the ketone occurred (MPV reduction). They were able to reduce a number of ketones in good yield using excess of 2-

propanol (5 times the ketone) and 0.2 equivalent of the catalyst. The products were isolated without hydrolysis using acid.

1.14. Review

The interaction between alkali metal, alkaline earth and rare earth metal oxides in catalytic oxidative coupling of methane was studied by X-iangguang et al [112]. Catalytic properties of calcium oxide doped lanthanum oxide and lanthanum oxide doped calcium oxide were studied. CaO-La₂O₃ catalyst prepared by co-precipitation possess higher activity and better selectively for C₂ hydrocarbons.

N. Hideo et al [113] carried out the oxidative decomposition of chloro penta fluoro ethane in presence of butane with various metal oxides supported on alumina-zirconia. Tungsten(VI) oxide alone had a positive effect on the activity among all metal oxides. It was concluded that the active sites of the tungsten(VI) oxide catalyst supported on alumina-zirconia might be the acid sites formed by the interaction between tungsten(VI) oxide and tetragonal zirconia. This catalyst was found to be the most active of all the catalysts which have so far been examined.

The oxidation of n-butane to maleic anhydride was investigated over a series of model supported vanadia catalysts by W. Israel [114]. The vanadia phase was present as a two dimensional metal oxide over layers on the different oxide

supports (TiO_2 , ZrO_2 , CeO_2 , Nb_2O_3 , Al_2O_3 and SiO_2). No correlation was found between the properties of the terminal $\text{V} = \text{O}$ bond and the butane oxidative turn over frequency (TOF).

Uphade B. S. et al [115] investigated the influence of La-promoted CaO catalysts in the oxidative coupling of methane to ethane/ethylene. Deposition of La-CaO catalysts directly on the supports containing Al_2O_3 or SiO_2 caused an appreciable decrease in the catalytic activity/selectivity for the oxidative coupling of methane. This is attributed to strong chemical interaction between the CaO and reactive components of the support during the high temperature calcination or pretreatment of the catalysts.

Cr-Ln and Cr-Zn oxide systems are used as catalysts for the removal of industrial gases like oxides of nitrogen, carbon monoxide, etc. Leginov A. Yu et al [116] conducted this study. It elucidated the development of active surface for the transition metal promoted rare-earth catalysts.

Brunner et al [117] described the generation of catalytically relevant metal and metal oxide compounds, supported on SiO_2 fibres. They studied different transition metal oxide and rare earth metal oxide catalysts. Various analytical methods revealed differently crystallised rough surfaces.

The simultaneous oxidation-reduction reaction between CO and NO over LaMnO_3 and LaCoO_3 catalyst has been studied by H.V. Kheer *et al.* [166]. They

investigated the kinetics of oxidation-reduction reaction between CO and NO over perovskite catalysts LaMnO_3 and LaCoO_3 prepared by ceramic and wet methods in the temperature range 473-1000 K. Results have been discussed in the light of X-ray powder diffraction, atomic absorption spectrometry, gas chromatography, electrical conductivity and surface area measurements. The rate controlling step in the catalytic reduction of NO by CO is the active site reduction process. The use of perovskite type oxides containing La, Mn, Fe, Co, etc. has been proposed as a possible substitute for the costly noble metal catalysts like palladium and platinum alloys in the automotive exhaust catalytic converters.

A catalyst suitable for automotive emission control was developed by Li Shi-yao et al [118]. Cordierite honey comb catalysts supported on rare earth transition metal oxides were used to simultaneous removal of three major pollutants namely CO, hydrocarbons and NO_2 . This has improved three way performances.

An extremely active and novel lanthanide containing catalyst systems were proposed by Imamura et al [119]. The rare earth metals were dissolved in liquid ammonia to form a homogenous solution containing solvated electron. The dissolved lanthanide metal reacted readily with various transition metals or oxides to form the catalysts.

The catalytic activity of Ln-Pt ion exchanged mordenite for the nitric oxide reduction with propane was studied by Cakamolo et al [120] in a wide range of temperature. The amount of N_2O which is a by-product in the catalytic reduction of nitric oxide differs largely with the type of rare earth ions.

Investigations are carried out by C.G.R. Nair *et al.* [175] to have a systematic comparison of the acidic properties and catalytic activities of single oxides TiO_2 , SiO_2 , Al_2O_3 , their binary oxides and the ternary oxide $TiO_2-SiO_2-Al_2O_3$. The acidity distributions are measured by using n-butylamine titration technique and the test reactions selected for the catalytic activity measurements are alkylation of 2-propanol. The single oxides have only low acid strength and are not at all active in catalysing the alkylation reaction, but are marginally active in the dehydration of 2-propanol. However the binary oxides are found to contain very strong acid sites and are highly active catalysts in both the test reactions. But $TiO_2-SiO_2-Al_2O_3$ of 10 % by weight of TiO_2 showed the highest acid amount and the highest activity in the alkylation and dehydration reactions compared to the binary oxides. The acid amount and the catalytic activity of the ternary oxide increased with the increase of TiO_2 content upto 50 mol% of TiO_2 and then decreased. The increase of TiO_2 content does not affect the selectivity.

A novel ruthenium catalyst was prepared for ammonia synthesis by W. Guang et al [121]. The catalyst potassium promoted ruthenium supported on fullerene (K. Ru/ $C_{60/70}$) was prepared and evaluated. It was found that

K-Ru C_{60/70} was the most active catalyst for ammonia synthesis of atmospheric pressure and 623 K compared with other support materials.

Sohier M. P. et al [122] prepared several hydrogenation catalysts based on nickel and rare earth oxides by different routes. The calcined solids consisted mainly of NiO-La₂O₃. It was established that co-precipitation route, produced compounds with highest catalytic performances.

A review edited by Hou Xianglin [123] described typical cases of application of rare earth oxides in different types of catalysts, including transition metals, their oxides and composite metallic oxides. The rare earth oxides improved their catalytic performance by the dispersion of the active component in catalysts. These oxides are considered to act as structural as well as electronic promoter in modifying the behaviour of solid catalysts.

Jiang Zhichang et al [124] studied the lanthana-based catalyst for the oxidative coupling of methane. XPS study of La₂O₃-MgO catalyst gives evidence for the formation of super oxide ions (O₂²⁻) on the La₂O₃ surface as the result of adsorption of an oxygen atom on oxygen depleted surface of La₂O₃ at elevated temperatures.

The acidic properties and stability of sulphate promoted metal oxides were a topic of study to Waquif [125] and co-workers. The acidic properties were determined by IR spectroscopy. It allowed a comparison of the acidity of pure

and sulfated metal oxides such as ZrO_2 , TiO_2 anatase, rutile and Al_2O_3 . Sulphation enhanced the weakest Lewis acid sites but poisoned the strongest. It also created Bronsted acidity in the case of highly loaded samples. This explains the high activity of presulphated TiO_2 and ZrO_2 samples; But sulphation decreased the very high activity of Al_2O_3 . The dehydration of MeOH is used as a test reaction.

Lavelley J. C. [126] published a review on IR Spectra analysis of species formed by acid probe adsorption on divided metal oxides and alk-zeolite to study surface basicity, particularly the nature and strength of basic sites. No probe can be used universally. It depends on the nature and other characteristics of the metal oxides. Both ammonia and pyridine (probes for the measure of the acidity of the catalysts) also adsorb on basic oxides via dissociation chemisorption.

Datka and Co-workers [127] applied chemisorption of pyridine as a method for studying the acidic properties of niobium pentoxide supported on silica, magnesia, alumina, titania and zirconia. The IR of adsorbed pyridine were used to evaluate the concentration and the relative strength of Bronsted and Lewis acid sites. Lewis acidity was found in all supported Nb_2O_5 systems, while Bronsted acid sites were only detected for niobia supported on Al_2O_3 and SiO_2 supports.

The electron donating properties of ceria activated at 300, 500 and 800°C and its mixed oxides with Al_2O_3 were reported by Sugunan S. et al [128]. They studied the adsorption of electron acceptors of different electron affinities. The surface acidity/basicity of the oxides was determined by a titration method and H_{Omax} values were calculated. The limit of electron transfer from the oxide surface is depicted in terms of electron affinity of the electron acceptors. Ceria promotes the electron donating ability of Al_2O_3 without changing the limit for electron transfer.

Gervasini et al [129] used microcalorimetry of ammonia and sulphur dioxide adsorption to study the effects of adding small amounts of ions on the acid/base properties of Al_2O_3 , silica or magnesia surfaces. The modification of the oxides with the ions affected their surface properties and the catalytic conversion of isopropyl alcohol. The acidity of the catalysts correlates with the charge/radius ratio and with the generalised electronegativity of the doping ions. The basicity correlates with the partial charge of the oxygen of the corresponding oxides.

Gervasini et al [130] continued the above investigation by quantifying the number of acid/base sites by volumetric measurements and expressed them in terms of ion specific effect. They correlated the properties using the Tanabe and the Seiyamma hypothesis concerning the acidity of mixed oxides.

The distribution of acid/base strength of Y_2O_3 and its mixed oxides with alumina catalyst, was studied by Sugunan et al [131], using Hammett acidity function scale. The basicity of Y_2O_3 increases with increasing activation temperature and for the mixed oxides, the basicity increases with an increasing concentration of Y_2O_3 catalyst.

The IR spectroscopic characterisation of the acid properties of metal oxide catalysts were briefly reviewed by B. Guido [132]. The use of different basic probe molecules, whose IR spectra are sensitive to protonation and/or to the strength of Lewis acid base interaction is described. The results obtained for the characterisation of the Lewis acid strength of a number of binary and ternary mixed oxides are interpreted on the basis of the different polarising powers of the involved cations. The characterisation of the Bronsted acidity of several oxides and zeolites is also described.

The structure of silica supported ytterbium oxide catalyst was characterised by X-ray diffraction and X-ray absorption studies by Y. Yamamoto et al [133]. The spectra of all the catalysts were quite similar to each other but different from those of the Yb_2O_3 . The local structure around Yb was not affected by the loading amounts of Yb and the thermal treatment up to 84 m mol/g of SiO_2 and 1273 K respectively. The presence of Yb-Si linkage and the absence of Yb-O-Yb were confirmed in all of Yb- SiO_2 catalysts. Yb atoms were supported on SiO_2 in a lightly dispersed form.

The acidic properties of (0.5 and 1.0 wt %) iron supported on silica were probed by adsorption of pyridine by gravimetric and infrared spectroscopy measurements by J. A. Dumesic et al [134]. The state of iron on silica was monitored by Mossbauer spectroscopy. Addition of iron to the silica generated Lewis acid sites on the surface, while little or no acidity existed on the silica surface alone. The new acid sites were shown to be iron cations in sites of low coordination. Measurements showed that the trivalent iron cations were stronger Lewis acids than divalent iron cations. The strength differences of the different oxidation states are explained on the basis of electronegativity differences.

J.A. Dumesic et al [135] studied the number strength and type of acid/base sites of europium oxide supported on γ -Al₂O₃ and SiO₂ by microcalorimeter and infrared spectroscopic studies of ammonia and carbondioxide adsorption. Different methods were used to characterise the structure bonding and valence of the europium atoms. Europium oxide neutralises acid sites on γ -Al₂O₃ and increases the number and strength of base sites on γ -Al₂O₃. Both Lewis acid and Bronsted acid sites exist on Eu₂O₃/Al₂O₃ samples with Lewis acid sites in domain. The surface hydroxyl groups and oxygen anions are responsible for base sites on the Eu₂O₃/Al₂O₃ sample. The addition of Eu₂O₃ to SiO₂ increases the number and strength of acid sites and it shows few basic sites. Luminiscence spectra show that Eu³⁺ ions occupy a range of dissimilar bonding sites on both supports particularly at low concentrations. At higher concentrations, Eu³⁺ ions occupy more well

defined sites having a weaker interaction with the support. The acid/base properties of these supported europium oxide can be related to the electronegativities of these samples with higher electronegativity enhancing acidic properties and suppressing basic properties.

T. Onishi et al [136] carried out carbon monoxide hydrogenation reaction over mixed oxides of Y_2O_3 and La_2O_3 , CeO_2 and ZrO_2 with Al_2O_3 , Ga_2O_3 and In_2O_3 . The addition of Ga_2O_3 or In_2O_3 to Y_2O_3 , La_2O_3 and CeO_2 enhances the formation of light alkanes. An In_2O_3 - CeO_2 catalyst shows the highest selectivity for ethene with the lowest selectivity for ethane in total hydrocarbons produced. The addition of In_2O_3 to CeO_2 results in an increase in activity for the CO hydrogenation reaction. The high selectivity for alkene formation is due to a suppression of alkene hydrogenation by the addition of In_2O_3 . Indium in cerium oxide is highly dispersed while keeping an oxidation state of +1 or +3 under the reaction conditions.

The role of the metal during NO_2 reduction by C_3H_6 over alumina and silica supported catalysts was reported by Bamwenda et al. The role of the metal during reduction of NO_2 by propylene in oxygen over Al_2O_3 and SiO_2 supported Au, Rh and Pt was studied. Three parallel reactions occur, that is NO_2 reduction to N_2 and N_2O ; NO_2 reduction to NO and oxidation of propylene. For Rh and Pt catalysts, the reaction may proceed entirely to metallic sites and that the Al_2O_3 and SiO_2 supports do not play a critical role in determining the catalytic activity

for NO₂ reduction. For Au catalysts, the reaction seems to involve a combination of metal and support catalysed processes. It was noted that the selectivity towards N₂ formation seems to be primarily affected by the nature of the result.

Z. Leihang et al [138] studied the decomposition of methanol on MgO, Al₂O₃, ZrO₂, La₂O₃, CeO₂, Nd₂O₃, and Y₂O₃. The profile of the decomposition products was related to the acid/base active centres of the oxides determined by TPD-MS and IR methods. CO was obtained when methanol was decomposed on strong acidity oxides. They suggested that methanol can be used as probe molecule to assay catalytic acidity/basicity.

The acid properties of anatase having different crystalline sizes were determined by measuring the temperature programmed desorption (TPD) of ammonia as well as IR spectrum of dissolved pyridine at elevated temperature. Nakayashi et al [97] prepared size controlled anatase by hydrolysis of the titanium tetra isopropoxide dissolved in propyl alcohol, using various amounts of distilled water. The acid properties of anatase were confirmed to be strongly affected by the crystalline size, the strength being increased by a decrease in crystalline size.

The acid properties of aluminium supported rare earth oxides were investigated by T. Yamamoto et al [139]. They used TPD and FTIR techniques. α -pinene isomerisation and 2-butanol decomposition reaction were used to

evaluate catalytic activity. The differences in catalysis, acid base properties and structure of catalysts were discussed in terms of loaded elements and amounts.

V. R. Chaudhary et al [140] compared the acid base strength distribution of rare earth metal oxides { La_2O_3 , CeO_2 , Sm_2O_3 , Eu_2O_3 and Yb_2O_3) by stepwise thermal desorption of CO_2 from 323 to 1173 K and TPD of ammonia from 323 to 1233 K. Their catalytic activity to oxidative coupling of methane C_2 hydrocarbons was compared. The catalytic activity and selectivity showed dependence on both the surface acidity and basicity, but the relationship is not straight forward, stronger acid sites are found to be harmful for selectivity.

C. S. Narayanan and J. Jayasree [141] prepared various binary oxides of alumina with rare earth oxides like europium, samarium, prasodymium, neodymium and yttrium by co-precipitation method. The catalysts were found to be amorphous and Al showed tetrahedral and octahedral co-ordination in its lattice. Catalysts showed weak to moderate acidity and basicity.

N. Miki et al [142] studied the generation of new acid sites by silica deposition on group IV 'B' metal oxides. An ultra thin SiO_2 layer was prepared by chemical vapour deposition of $\text{SiO}(\text{OCH}_3)_4$ on to TiO_2 and ZrO_2 . The relation between surface structure and acidity was studied by measurement of coverage, IR spectroscopy of probe molecules and test reactions. SiO_2 was supposed to form 1:1 complex with the oxide cation ($\text{M}_1\text{-O-Si}$) until 90 % of the monolayer

coverage was obtained. The SiO₂ overlayer showed weak Bronsted acidity only sufficient to catalyse the isomerisation of 1-butene and the dehydration of t-butyl alcohol. The acidity could not be correlated with the differences in co-ordination number or valence of cations, but seemed to correlate with the interaction between SiO₂ and metal oxides.

Nakabayashi H. [143] reported the properties of acid sites on titania-silica and titania-alumina mixed oxides by IR spectroscopy. Both Lewis and Bronsted acid sites were found on the surface of TiO₂-Al₂O₃ mixed oxide, though no Bronsted acid sites were detected on the surface of pure TiO₂ and SiO₂. TiO₂-Al₂O₃ mixed oxide also showed no Bronsted acid sites. The rate of isomerisation of 1-butane was enhanced by the Bronsted acid sites formed on the TiO₂-SiO₂ mixed oxide.

Hess A. and Kemnitz E. [144] modified ZrO₂ and TiO₂ with NH₄F, SF₄, HCl, CHClF₂, (NH₄)₂SO₄, (NH₄)₃PO₄ and H₃PO₄ and their surface acidity and catalytic behaviour were studied. The nature of acid sites was determined by IR spectra of pyridine adsorption complexes. Gas phase alkylation of 1-butene with isobutane, the double bond isomerisation of 1-butene and the disproportionation of CCl₂.2F₂ was taken as the test reactions. Samples based on TiO₂ exhibited overall lower catalytic activity.

The effect of alkali and rare earth metal oxides on the thermal stability and carbon deposition over NiO/Al₂O₃ catalyst was studied by Liu Shang-Lini Mian Qing et al [145]. The NiO-Al₂O₃ catalyst was modified by alkali metal oxide and rare earth metal oxide in order to improve the thermal stability of carbon deposition resistance during the partial oxidation of methane to syn gas at high temperature. The reaction performance, thermal stability, dispersity of nickel and carbon-deposition of the modified NiO/Al₂O₃ catalyst and unmodified NiO/Al₂O₃ were investigated. The results indicated that the modified catalysts improved the dispersion of active component nickel and the activity for the partial oxidation of methane.

A catalyst suitable for the treatment of engine exhaust and having an enhanced oxygen storage capacity was described and obtained a patent by Wu. Joseph Hui-Sha et al [28]. The catalytic decomposition contains a catalytic material such as one or more of platinum, rhodium and palladium dispersed on an activated alumina support, an oxygen storage component (OSC) which is an ultimately mixed oxide of ceria and praseodymia having a Pr:Ce atomic mass ratio in the range of about 2 : 100 to 100 : 100 and optionally containing one or more rare earth metal oxides.

The acidic properties of a SiO₂-Al₂O₃ mono layer catalyst by ³¹P NMR of adsorbed tricyclohexyl phosphine and triphenyl phosphine was reported by Bing Hu and Ian D. Gay [146]. These large probe molecules permit the assessment of

steric effects by comparison with triethyl phosphine and reveal differences in acid strength of surface sites. They found that there are significant constraints to accessing Lewis sites, but not Bronsted sites. The concentration of strong Bronsted sites is slightly less than half of the concentration of the total Bronsted sites.

A study of the surface acidity of several fresh synthetic silica-alumina cracking catalysts was made by R. L. Richardson and S. W. Benson [147]. The surface acidities were measured by estimating the quantities of permanently bound basic gas adsorbed at a temperature range of 20-300°C. Both pyridine and trimethyl amine were used as adsorbates and kinetic measurements were made with a high temperature adsorption balance containing a quartz helix. The permanently bound fraction is considered as a measure of the surface acidity. The acidity measurements were affected by (1) particle size (2) trace water in catalyst and (3) temperature. Other kinetic aspects like calorimetric measurements are also reported.

Harrison Philip G. [148] described the potential of a variety of physical techniques in catalyst characterisation and especially in the understanding of the types of changes which may occur on calcination using Sn-P-O and Ln doped CeO₂ catalyst systems. Sn-P-O catalysts prepared by co-precipitation were examined by transmission electron microscopy, diffuse reflectance, IR, XRD, MASNMR, and Mossbauer spectrometers. The freshly prepared catalyst comprise

uniform nanosized particles of tin (IV) oxide and isolated orthophosphates ($-\text{PO}_4$) group. Progressive calcination results in the formation of tin phosphate phase. XPS was used to show that trivalent cations in the lanthanide-doped ceria catalysts segregate to the surface on calcination, giving a surface coverage of upto two monolayers after ageing at 1450°C for 24 hrs. Materials prepared by coprecipitation undergo segregation at relatively low temperature, while materials produced via sol-gel techniques are much more thermally robust. The former catalysts undergo segregation by macro defects while the latter by bulk diffusion.

Lunsford et al [149] worked on the oxidative dimerisation of methane over lanthanum oxide. They found that under oxygen limiting conditions, La_2O_3 is a reasonably selective catalyst for the conversion of methane to ethane and ethylene. At 725°C a selectivity to C_2 compound of 47 % was achieved at a CH_4 conversion of 9.4%. Although La_2O_3 is very effective in the generation of gas phase CH_3 -radicals, which are believed to be intermediate in the oxidative dimerisation, the catalyst also is active for complete oxidation of C_2H_6 under the reaction conditions. Higher reaction temperature favours C_2H_4 which may be formed from C_2H_6 via gas phase reactions.

Thermal stabilisation of transition alumina [150] is achieved by nucleating a cubic LnAlO_3 structure ($\text{Ln} = \text{La}, \text{Pr}, \text{Nd}$) on the surface of the alumina support. Structural transmission to corundum is inhibited by strong surface interactions

between the thermally stable cubic perovskite compound LnAlO_3 and alumina. A model is proposed to interpret the influence of the doping oxide. The thermal stabilization is related to the presence of LaAlO_3 , microdomains in the corundum nucleation sites. The strength of the interaction is a result of structural analogues exhibited by the two components of the support. LnAlO_3 and Al_2O_3 , both related to fcc oxygen packing.

Partial oxidation of benzyl alcohol carried out on $\text{BaPb}_{(1-x)}\text{Bi}_x\text{O}_3$ ($x = 0.1$) type perovskite oxides was studied by Viswanathan et al [151]. Benzaldehyde and toluene are obtained as the major products, when the reaction is carried out in the absence of oxygen. When the reaction is carried out in the presence of gas phase oxygen, small amounts of benzoic acid and benzyl benzoate are also obtained. Catalysts have been characterised by XRD. After the reaction, catalysts undergo partial decomposition when the reaction is carried out in the absence of gas phase oxygen. Extent of reduction of catalyst depends upon the partial pressure of oxygen. XPS studies reveal that bismuth rich compounds are more basic. High activity and selectivity of bismuth rich systems have been attributed to their high basicity.

Normand et al [152] studied the influence of the support on the reactivity of Pd/rare earth oxides catalysts (La_2O_3 , Pr_6O_{11} , Nd_2O_3 , Tb_4O_7). They are characterised by BET surface area chemisorption, temperature programmed reduction and oxidation, X-ray diffraction and X-ray photoemission. These oxide

catalysts are classified as three groups according to their ability to create anion vacancies. (1) oxides of Re_2O_3 which are unreducible, (2) CeO_2 where anion vacancies can be created extrinsically by the reduction process and (3) Pr_6O_{11} , Tb_4O_7 where anion vacancies exist due to the non-stoichiometric nature of these oxides. Concerning the catalytic activity, the active site is purely metallic in methyl cyclopentane hydrogenolysis, with small selectivity changes on fluorite oxides as compared to $\text{Pd}/\text{Al}_2\text{O}_3$ catalysts due to some electronic interaction with the support. In syn gas conversion, production of high alcohol occurs at the metal-support interface and is favoured by the presence of intrinsic anion vacancies on Pr_6O_{11} and Tb_4O_7 supports. A correlation is found between the density of anion vacancies on these supports and the chain growth.

George Dan [153] obtained patent for the preparation of an active acid type catalyst from metal supports manufactured from Al, Co, Ni, Mg, Zn, Mn and rare earth metals. The metal support is oxidised to form an oxide surface layer, followed by halogenation to form the active sites having Lewis acidity. The oxide surface layer on the metal support is preferably reacted with chloro carbons of fluorochloro carbons. The catalyst is optionally manufactured in a single stage by reacting the Al support with $\text{SO}_3\text{-CCl}_4$ gas mixture for oxidation as well as chlorination. The resulting catalysts are stable and suitable for alkylation of aromatic compounds with olefins as well as for isomerisation of paraffins.

The adsorption of probe molecules such as NH_3 and CO_2 was used by Auroux et al [154] to determine the number and character of basic and acidic surface sites of about 20 metallic oxides by microcalorimetry. It allowed a simultaneous determination of the strength and energy distribution of the adsorption sites. The adsorption isotherm, the differential heats, the integral heats and the energetic histograms are given for NH_3 and CO_2 adsorptions. Relationships between the average adsorption heats of NH_3 and CO_2 have been found as a function of the ionic character percentage and of the charge/radius ratio.

R.J. Gorte and co-workers [155] used ^{13}C NMR spectroscopy to characterise intermediates formed by the adsorption of 2-methyl, 2-propanol, on a H-ZSM-5 zeolite. Previous adsorption studies had shown that, upon exposure of H-ZSM-5 to this alcohol and subsequent evacuation at 295 K, an adsorption complex could be formed, which had a coverage of one alcohol molecule/Al atom in the zeolite and had carbenium-ion like properties. By the NMR studies, it is shown that the adsorbed species can best be described as a silyl ether, with the alkyl group covalently bonded to the zeolite framework oxygen. Furthermore, the adsorption and evaporation conditions used for preparing the samples are found to be very important, since these silyl ether intermediates are highly reactive. The ^{13}C NMR spectrum obtained shows two prominent features, one at 77 ppm from TMS which is assigned to carbon that is bonded to the oxygen, and a second at 29 ppm,

which is due to aliphatic carbons formed in secondary reactions. No spectral features were observed in the region expected for carbenium ions, which implies that the steady-state concentration of carbenium ions in H - ZSM-5 is low or that the life time of these species is short.

Minachev et al. [156] studied the variation in catalytic activity of rare earth oxides and their analysis, scandia and yttria in ethylene hydrogenation between -120 and 20°C has been studied as a function of the temperature of pretreatment. Thermal analysis has been used to study the decomposition of hydroxides from which the oxides were prepared. The oxides show catalytic activity at 600°C. When dehydration, decarboxylation and denitroxilation have gone to completion, and in addition when partial dehydroxylation of the surface has also taken place, sesqui oxides showed high activity, where as dioxides were of low activity. A decrease in hydrogenating activity in the series of oxides from lanthana to lutecia correlates with a decrease in their basicity,. As was shown by means of thermodesorption, hydrogen and ethylene are chemisorbed in two forms. With dysprosia ethylene hydrogenation proceeds by involving loosely bound forms of hydrogen and ethylene via a semi-hydrogenated complex. Associatively adsorbed ethylene is involved in the reaction, and hydrogen activation is likely to be the limiting step.

Connell and Dumesic [157] have studied the generation of new acid sites on a solid silica surface by the addition of several kinds of dopant cations. There

seems to be a common idea in these works that the generation of new acid sites is ascribed to the charge imbalance at locally formed $M_1\text{-O-}M_2$ bondings, where M_1 is the host metal ions and M_2 the doped and/or mixed metal ions.

A more recent method for preparing silica-alumina catalyst has been introduced by Katada et al [158]. The silica-alumina catalyst prepared by the traditional co-precipitation method contain both H^+ (Bronsted and Lewis) sites. Both may be catalytically active depending on the reaction. The alternative method, which has more recently been explored is the deposition of SiO_2 on an Al_2O_3 substrate in amounts of the order of one mono layer of SiO_2 . By adjusting the amount of SiO_2 deposited, this method permits the preparation of catalysts with controlled amounts, surface acidity, and to some degree permits the ratio of Bronsted to Lewis sites to be adjusted.

Studies of Gates B. C. et al [159] have concluded that the description of sulphate promoted ZrO_2 as superacids based on their catalytic behaviour is incorrect. They found that $SO_x\text{-}ZrO_2$ and the more active $SO_x\text{-}ZrO_2$ promoted with Fe or Mn contain acid sites of moderate strength. But the presence of redox sites can initiate low temperature reactions of alkanes by initially forming the required alkene intermediates. $SO_x\text{-}ZrO_2$ catalyst deactivates rapidly during many reactions and tend to reach H_2S and SO_x during H_2 and air treatments respectively and H_2SO_4 in the presence of H_2O . These processes cause irreversible loss of catalytic activity and also downstream containment and corrosion issues.

Iglesia *et al.* [160] have found that WO_x domains supported on ZrO_2 also behave as solid acids, and they are stable at high temperature in hydrogen, oxygen and water atmospheres. $\text{WO}_x\text{-ZrO}_2$ catalyses the isomerisation of butane at 323 K and of pentane at 303 K after treatment in air at 1073 K, but the selectivity to undesired cracking products is very high.

Shabati J. *et al.* [161] proposed a mechanism for the MPV reduction of ketones or aldehydes with 2-propanol over X-Zeolites ion exchanged with Cs^+ and Rb^+ . The reaction is initiated by abstraction of an H^+ from 2-propanol by the basic sites of the catalyst. In addition to the basic sites, exchanged cations play a role of stabilising the ketone by the hydride transferring from adsorbed 2-propanol to the ketone.

Shibagaki *et al.* [110] studied the reduction of aldehydes with 2-propanol and they found that the reaction proceeded efficiently by catalysis with hydrous zirconium oxide to give the corresponding alcohols. Most ketones were also reduced efficiently, but conjugated or sterically hindered ketones resisted the reduction. The reduction was carried out with primary, secondary or tertiary alcohols, and only secondary alcohols served as hydrogen donors. Kinetic experiments have indicated that the reaction rate is of first order dependence on each of the concentration of the carbonyl compounds, 2-propanol, and the catalyst. An observation of the primary isotope effect has suggested that the step

of hydride transfer from adsorbed 2-propanol to adsorbed carbonyl compound constitutes the rate determining step for the reduction.

Meerwin Ponderoff Verley and Oppenauer reactions catalysed by heterogenous catalysts were studied by Creighton T.J. et al. [162]. MPVO reactions are catalysed by metal oxides which possess surface basicity or Lewis acidity. Recent developments include the application of basic alkali or alkaline earth exchanged X-type zeolites and the Lewis acid zeolites BEA and (Ti) BEA. The BEA catalysts show high stereoselectivity, as a result of restricted transition state selectivity, in the MPV reduction of substituted alkyl cyclo hexanones with isopropanol.

Brawn Eric; L. Antone; and T. Joel [163] synthesised optically pure ortho substituted benzhydrols by asymmetric reduction of the corresponding benzophenones. Previously treated LiAlH_4 can reduce orthosubstituted benzophenones to the corresponding optically active benzhydrols with 100% enantiomeric excesses.

A very efficient synthesis of chiral benzhydrols from substituted benzophenones is described by S. Wenchung et al [164]. The asymmetric reductions of ortho substituted benzophenones with S-chlorodiisopropiono camphyl borane is used.

Reduction of benzophenone and substituted benzophenone with sodium borohydride to the corresponding alcohols was studied by Epple M. and Ebbinghans S. [165]. This reaction can be carried out without the need for a solvent, leading to pure alcohols without side products. Heating may be necessary to achieve short reaction time. This is used as a preparative organic reaction that avoids a solvent.

1.5. Present Work

A lot of work had been reported on rare earth oxides and their binary oxides with alumina. The rare earth oxides are classified as basic catalysts and find use as catalysts in a number of base catalysed reactions. But comparatively less work is reported on dysprosium, gadolinium oxides and their binary oxides with alumina. The present work is concerned with the preparation and characterisation by surface studies and catalytic activity of La_2O_3 , Gd_2O_3 , Dy_2O_3 , Al_2O_3 and their binary oxides.

The single oxides and binary oxides are prepared by precipitation methods. They are activated suitably and characterised by determining the strength and amount of surface acid/base sites by titration with n-butyl amine or trichloro acetic acid. The activation is done by preheating to different temperatures and precompression to various pressures. They are further characterised by XRD and surface area measurements.

The catalytic activity is studied by selecting the MPV reduction of benzophenone as a test reaction.

1.16. Objectives

1. To prepare lanthanum, gadolinium, dysprosium and aluminium oxides by precipitation methods.
2. To prepare their binary oxides with alumina having different composition by co-precipitation method.
3. To characterise the oxides by XRD, BET surface area, and by acidity/basicity determination.
4. To determine the surface acidity/basicity of the oxides when they are pre-heated to different temperatures and pre-compressed to various pressures.
5. To compare the acid/base properties using Hammett indicators.
6. To study the reduction of benzophenone to benzhydrol in presence of isopropyl alcohol and the catalysts.

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

Chapter II

CHAPTER II

MATERIALS AND METHODS

2.1. Materials

The following were the materials used for the study.

1. Aluminium nitrate nonahydrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, used for the preparation of alumina, was obtained from E.Merck (India) Ltd.
2. Rare earth nitrates, lanthanum nitrate hexahydrate $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ gadolinium nitrate hexahydrate $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and dysprosium nitrate pentahydrate $\text{Dy}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, were supplied by Indian Rare Earth Ltd. They are of 99.9% purity.
3. Different Hammett indicators used were the following:
 - (i) p-Dimethyl aminoazobenzene (Dimethyl yellow)
 - (ii) Methyl red
 - (iii) Neutral red
 - (iv) Bromothymol blue
4.
 - (i) Trichloro acetic acid (TCA) SQ grade from Qualigens fine chemicals Pvt. Ltd.
 - (ii) n-Butyl amine. SQ grade from Qualigens fine chemicals Pvt. Ltd.

5. (i) Benzene supplied by E. Merck
(ii) Isopropyl alcohol from E Merck
6. Benzophenone Merck KGaA. Germany.

2.2. EXPERIMENTAL METHODS

2.2.1. Preparation of Alumina

Aluminium nitrate was dissolved in distilled water to get 4-5% dilute solution. It is heated to boiling and to the boiling solution added 1:1 ammonia solution with constant stirring, the precipitate of aluminium hydroxide formed was coagulated by boiling for five minutes and was kept aside for 24 hrs. It was then filtered through a Whatman No.1 filter paper, washed free of nitrate ions using distilled water and dried at 120°C overnight. The hydroxide obtained was calcined at 500°C for 3 hrs, to get the oxide. It was then powdered to get particle size of 106-125 micron.

2.2.2. Preparation of Lanthanum Oxide

The lanthanum oxide was prepared by the calcination of $\text{La}(\text{OH})_3$ which was formed as a gelatinous precipitate, from the hot dilute solution of rare earth nitrate solution by the addition of ammonia [167-169].

The lanthanum nitrate was dissolved in distilled water to get a 5% dilute solution. Heated the solution to boiling and to the boiling solution added 1:1

ammonia solution with stirring. The precipitated lanthanum hydroxide was boiled to coagulate the precipitate and was aged for 24 hrs. The precipitate was filtered using a Whatman No.1 filter paper, washed free of nitrate ions using distilled water and was dried at 120°C overnight. The dried sample was calcined at 500°C for 3 hrs to get the oxide. It was powdered to get particle size of 106-125 microns.

2.2.3. Preparation of Lanthana-Alumina Binary Oxides

Binary oxides with different composition of lanthana and alumina were prepared by co-precipitation method [170]. Accurately weighed quantities of lanthanum nitrate and aluminium nitrate were dissolved separately in distilled water to get a dilute solution. Two solutions were mixed together and boiled. 1:1 ammonia solution was added to the boiling solution with constant stirring, the precipitated hydroxide was coagulated by boiling and aged for 24 hours. It is filtered, washed free of nitrate ions and dried at 120°C overnight. The product obtained was calcined at 500°C for three hours to get the binary oxide.

Binary oxides containing 20, 40, 60 and 80 percent by weight of lanthanum oxide were prepared using calculated amounts of lanthanum nitrate and aluminium nitrate by the co-precipitation method described above. The oxides obtained were powdered to get particles of size 106-125 microns.

2.2.4. Preparation of Oxide Catalyst of Gadolinium

Single oxide Gd_2O_3 was prepared by the calcination of gadolinium hydroxide which was precipitated from gadolinium nitrate solution. The hydroxide obtained by the addition of ammonia to a hot dilute solution was coagulated by boiling and aged for 24 hours. Filtration, washing and calcination were carried out as before. The oxide obtained was powdered to get particles of size 106-125 microns.

2.2.5. Preparation of Binary oxides of Gadolinium and Aluminium

Binary oxides containing 20, 40, 60 and 80 percent by weight of gadolinium oxide were prepared by coprecipitation method [170]. Calculated amount of gadolinium nitrate and aluminium nitrate were dissolved separately in distilled water. The two solutions were mixed and the hydroxides were precipitated by adding 1:1 ammonia solution. Coagulation, ageing and filtration were done as described earlier. The precipitate was kept overnight at $120^\circ C$ and finally calcined at $500^\circ C$ for 3 hours. Powdered oxide of particle size 106-125 microns were accepted.

2.2.6. Preparation of Dysprosium Oxide Catalysis

Single oxide catalyst of Dy_2O_3 was obtained by adopting the procedure given before. The precipitation as hydroxide was done by adding 1:1 ammonia solution to the hot dilute solution of dysprosium nitrate. The precipitate was

dried at 120°C overnight and calcined at 500°C for 3 hours to get the oxide Dy₂O₃. Powdered sample of particle size 106-125 microns were collected.

2.2.7. Preparation of Binary Oxides of Dysprosium and Aluminium

Binary oxides of same compositions as mentioned in the other two catalysts were prepared by coprecipitation method from dysprosium nitrate and aluminium nitrate solutions. Calculated amounts of the two were dissolved in distilled water and the hydroxides were precipitated as described before. The precipitate of hydroxides were coagulated, aged for 24 hours, washed and dried at 120°C overnight. Calcination was carried out at 500°C for 3 hours. The mixed oxide formed was powdered and the particles of size 106-125 microns was used for characterisation and catalytic studies.

2.3. Purification of Solvents

2.3.1. Purification of Benzene

Benzene was purified [171] by shaking with about 15% of its volume of conc. H₂SO₄ in a separating funnel whereby the main impurity thiophene dissolved in it yielding an yellow solution. The process was repeated till no yellow colour was developed. It was then washed thoroughly with distilled water, 10% sodium carbonate solution and again with distilled water. The organic layer was collected and it was dried with anhydrous calcium chloride and

distilled. The distillate was then thoroughly dried by keeping over sodium wire overnight and again distilled. The fraction boiling at 80°C was collected.

2.3.2. Purification of propan -2-ol

This may contain peroxide as impurity which if present must be removed before purification [172]. The following test was conducted for the presence of peroxide. 0.5 ml of propan-2-ol was shaken with 1 ml of 10% potassium iodide solution and 0.5 ml of dilute hydrochloric acid (1:5) and a few drops of starch solution. If a blue or bluish black colour appeared in one minute, the sample contained peroxide which has to be removed.

Peroxide is removed by the following treatment. Refluxed 1000 ml of propan-2-ol with 10-15 g of solid tin(II) chloride for half an hour. Tested a portion of this solution for peroxide. If the test was positive added further 5 g portion of tin(II) chloride and heated under reflux for half an hour. Repeated until the test was negative. Added about 20 g calcium oxide and heated under reflux for four hours and then distilled. The distillate was allowed to stand over calcium metal or Type 5A molecular sieve for several days followed by further fractionation. Anhydrous propan-2-ol was collected at 82°C.

2.4. Pre-treatment of Catalysts

The pre-treatment of the catalyst was done by two methods. They are:

1. Preparation of thermally activated samples and
2. Preparation of pre-compressed samples

2.4.1. Preparation of thermally activated samples

Prior to the experiment, the catalyst of suitable particle size was activated by heating to a definite temperature for a definite period. The samples were activated by heating to 500, 600 and 700°C for three hours and kept in a desiccator.

2.4.2. Preparation of Precompressed samples

The single oxides as well as binary oxides of particle size 106-125 microns were compressed at different pressures in a hydraulic press [173]. About 1 gm of the powdered sample was taken in the steel die of the hydraulic press (Specackent, England) and pressed to known pressures, indicated by a pressure gauge and kept at the pressure for one minute. The pellet formed was again broken gently to get the desired particle size and was used immediately to avoid further ageing. The pelletising pressure employed were 2×10^3 , 5×10^3 , 8×10^3 and $11 \times 10^3 \text{ Nm}^{-2}$.

2.5. Determination of Surface acidity/basicity

The surface acidity/basicity of the oxides at different acid/base strength was determined by titration method using different indicators [16, 41, 47, 174,

175]. The indicators used were (1) dimethyl yellow $pK_a = 3.3$ (2) methyl red $pK_a = 4.8$ (3) neutral red ($pK_a = 6.8$) and (4) bromothymol blue ($pK_a = 7.2$)

2.5.1. Determination of Surface acidity

0.1 g of the activated sample of the catalyst was placed in a 50 ml stoppered bottle and added 5 ml of benzene and two drops of the indicator solution in benzene (0.1%). The dye was adsorbed on the solid catalyst to form the conjugate acid of the indicator and is kept for 30 minutes to attain equilibrium. A .01 N solution of n-butyl amine in benzene was added dropwise from a micro burette, with constant shaking. The neutralisation was followed by the gradual disappearance of the acid colour of the solid and at the end point the acid colour completely disappeared. The volume of n-butyl amine added was determined. The neutralisation was a slow process and it was observed that the results obtained after 24 hours is the same as that obtained after 2 hrs. So in all titrations the time limit taken was 2 hrs. The experiment was repeated with samples of pre compressed oxides also.

2.5.2. Determination of basicity

0.1 g of the activated sample was suspended in 5 ml benzene as before. Two drops of the indicator solution (0.1%) in benzene were added and allowed to attain equilibrium. The indicator get adsorbed on the solid and it developed the basic colour. 0.01 N trichloroacetic acid was used as titrant. The basic colour

slowly disappeared and the acid colour developed at the neutralisation point. The titration was carried out very slowly with time limit of 2 hrs. The same procedure was adopted for the pre compressed samples also.

2.5.3. Gravimetric Estimation of Chemisorbed Carbondioxide

Another method employed to determine the surface acidity/basicity was to determine gravimetrically the amount of CO₂ gas adsorbed on the surface of the solid [176] using an electronic balance.

Acid-free dry carbondioxide was prepared using Kipp's apparatus. Accurately weighed amount of the activated catalyst was placed in a desiccator which was evacuated. Dry carbon dioxide gas was admitted into it very slowly and allowed to attain equilibrium for half an hour. The excess carbon dioxide and almost all of the physisorbed gas was removed by evacuation. The increase in weight of the catalyst was studied using a Shimadzu Ay 220 electronic balance which was considered as the amount of CO₂ chemisorbed on the basic sites.

2.6. Study of Catalytic Activity

2.6.1. Reduction of Benzophenone

The catalytic activity towards the reduction of benzophenone [197] was studied in a 25 cm³ round bottomed flask equipped with a reflux condensor. About 3 mmol benzophenone, 20 ml isopropyl alcohol and 500 mg catalyst were

heated under reflux at about 80°C for a period of 2 hrs [39,110]. The contents were transferred quantitatively into a 25 ml standard flask and the amount of unreacted benzophenone were determined using UV-Vis spectrophotometer (UV 1601, Shimadzu) by noting the absorbance of the reaction mixture at 333.5 nm. The initial amount of benzophenone were also noted using UV-Vis spectrophotometer. The activity was reported as the first order rate constant per sec per g of the catalyst. The product formed was confirmed by TLC analysis and by comparison of IR spectrum.

2.6.2. Isolation of Benzhydrol

The catalytic reduction of benzophenone was carried out using higher quantities of benzophenone, with an equivalent hike in the amount of catalyst and propanol-2. The reduction was carried out by refluxing the contents at 80°C in a round bottomed flask for two hours, as before. The reaction mixture was distilled under reduced pressure to remove excess of 2 propanol, the catalyst remaining was removed by filtration. It is then poured into water containing ice with constant stirring. The solution was cooled by placing in a freezing mixture. Crystals of benzhydrol separated out. It was collected and further purified by fractional crystallisation using rectified spirit. The crystals were collected and its melting point, IR spectrum etc. are noted.

2.6.3. UV-visible spectroscopy

UV-visible spectroscopy is used to measure the multiple bond or aromatic conjugation within the molecules. The wavelength region of common uv-spectrophotometer is 200-750nm, which includes the visible range also.

On passing electro magnetic radiation in the uv and visible region, through a solution of the compound, with multiple bond, a portion of the radiation is normally absorbed by the compound. The amount of absorption depends on the wavelength of the radiation and the structure of the compound.

UV spectrum records the wavelength of an absorption maximum in λ_{\max} and the strength of absorption. According to combined Beer Lambert law.

$$\frac{\log I_0}{I} = \frac{\epsilon xc}{l} \quad \text{or}$$

$$\frac{\log I_0}{I} = A = \frac{\epsilon xc}{2.303 \times l} = kxc \quad \text{or}$$

$$A = kxc. \text{ where}$$

$$I_0 = \text{intensity of the incident radiation}$$

$$I = \text{intensity of the transmitted radiation}$$

$$\frac{\log I_0}{I} = A, \text{ absorbance of the solution}$$

ϵ = the molar absorptivity which is a constant for an organic compound at a given wave length

l = path length of the sample in cm. For a given cell it is a constant.

C = the concentration of the solute in mol dm^{-3}

"k" is calculated by least square or graphic method, using which the concentration of an unknown solution can be determined.

The intensity of the radiation is measured by double beam process to eliminate error due to extraneous factors like fluctuation of the intensity of radiation, scattering effects and solvent effects. The radiation is passed through the cells containing the solution and solvent alternatively and repeatedly. The two rays are then combined and the difference in intensities is measured.

2.7. Catalyst Characterisation

The characterisation of the catalyst was done by surface area measurements and XRD studies.

2.7.1. Surface area measurement

The specific surface area was determined by BET method using conventional low temperature nitrogen adsorption. The volume of nitrogen adsorbed at liquid nitrogen temperature by the given weight of the sample is measured at varying pressures. The volume of nitrogen adsorbed in a monolayer V_m is calculated from the BET equation

$$\frac{P}{V_a(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)P}{V_m C P_0}$$

where

P = Nitrogen pressure

P_0 = Vapour pressure of nitrogen at the temp. of the adsorption experiments

V_a = Volume of nitrogen adsorbed at pressure P and temp. of the liquid nitrogen calculated at STP

C = Constant related to the difference between the heat of liquefaction of the adsorbate

A plot of $[(P/V_a(P_0-P))]$ against P/P_0 will give a slope of $(C-1)/V_m C$ and an intercept of $(1/V_m C)$. From this V_m can be calculated. Knowing the value of V_m , surface area can be calculated by using the relation

$$S = \frac{NAV_m}{V_M W}$$

where

N = Avagadro number

A = Area occupied by one nitrogen molecule in the liquid Nitrogen state ($16.3 \times 10^{-20} \text{ m}^2$)

V_M = Gram molar volume

W = Weight of the sample in gram

2.7.2. X-Ray Diffraction

X-Ray patterns of samples were recorded using Ni filtered CuK radiation.

In the XRD pattern the intensity of the reflected X-rays was plotted against 2θ values. The d-spacing was calculated using the Bragg's equation

$$n\lambda = 2d \sin\theta$$

where

λ = Wave length of monochromatic X-rays

d = Spacing between two similar planes

θ = the angle at which X-ray falls on the sample

n = order of diffraction

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

Chapter III

CHAPTER III

RESULTS AND DISCUSSION

Rare earth oxides have been used as promoters and supporters in many catalytic reactions and the catalytic properties of rare earth oxides have been correlated with their basicities.. Although investigations on the catalytic properties of rare earth sesqui oxides have multiplied in recent years, the primary mode of surface interactions on the materials still remain undefined. Details of adsorption/desorption process, the nature of adsorbed species on these metal oxide surfaces etc are only partly investigated. The acid/base properties of the metal oxides are generally considered to play an important role in determining their adsorption and catalytic properties. More over it has been found that the acidic/basic properties of mixed metal oxides are particularly important, since the number, strength and nature of the acid sites can be controlled by varying the composition and pre-treatment of the sample. The mixed oxides prepared by coprecipitation procedure display almost the same properties, and they have complex structures. This has made it difficult to relate the observed acidic/basic properties to the structure of the catalyst. The surface sites generated by pre treatment are rather homogenous in nature and that the same surface sites are

relevant to all the reactions. The results of the present work are analysed accordingly.

The various single oxides and their mixed oxides with aluminium were prepared by precipitation method. They were calcined at a temperature of 500°C and powdered to get samples of required particle size. The samples were activated at different temperatures and precompressed to various pressures. The amount and strength of acid/base sites were measured by using indicators adsorbed on the solid surface [42, 177]. The strength of acid/base sites were expressed as Hammett acidity function H_0 and their amount by titration method. If the acid sites with H_0 value lower than or equal to the pK_a of the indicator exist on the solid surfaces, the colour of the indicator changes to that of its conjugate acid. If a neutral indicator is adsorbed on the solid surface and the colour of the indicator changes to that of its conjugate base; then the solid has significantly high basic strength. The acid/base strength were described on a common scale H_0 . The acidity is measured with acid sites whose strength $H_0 \leq pK_a$ of the indicator, where as basicity shows the number of basic sites whose basic strength $H_0 \geq pK_a$ of the indicator. The acid/base distribution curves meet at a point on the abscissa where acidity = basicity = 0. It is taken as H_{0max} value which represented the acid/base properties of solids which is sensitive to the surface structure. It is a parameter used to compare the acid/base strength of the sites of different solid catalysts. A solid with large positive H_{0max} has strong basic sites and weak acidic

sites whereas low $H_{0 \max}$ value indicated weak basic sites and strong acid sites. A unique $H_{0 \max}$ is found for every solid. The $H_{0 \max}$ value of a solid is the strongest H_0 value of the acid sites as well as equally strongest H_0 value of the basic sites.

3.1. Single oxides activated at different temperatures

The acidity - basicity values and the $H_{0 \max}$ of single oxide catalysts activated at different temperature were given in Table 3.1. The corresponding plots, to determine the $H_{0 \max}$ were given in Fig. 3.1 to 3.4. The acidity - basicity values were plotted against acid - base strength H_0 and extrapolated to get $H_{0 \max}$.

For single oxides the acidity and basicity values are attributed to the cation M^{n+} and anion O^{2-} respectively, exposed on the surface of the catalyst. The acid strength or electron pair acceptor strength (EPA) of the surface sites is expected to be dependent upon the effective positive charge on the metal cation and on their co-ordination on the catalyst surface. Similarly the base strength or electron pair donor (EPD) strength of the surface sites is also expected to vary depending up on the effective negative charge on the anions and on their co-ordination on the surface [178]. Lower co-ordinataion sites are responsible for strong acid-base sites. Thus the electron population around the cation or anion on the surface is responsible for the acid/base properties of the oxide. Different acid/base sites generated by different pre-treatment temperatures appear to correspond to the ion pairs of different co-ordination number [133, 179]. The method of preparation

TABLE 3. 1

Surface Acidity/basicity of single oxides activated to various temperatures, at different acid/base strength

Particle size 106-125 microns

Sl. No.	Oxides	Activation temp. °C	Surface area m ² g ⁻¹	Basicity mmol g ⁻¹				Acidity mmol g ⁻¹		H _{0max}
				H ₀ 3.3	H ₀ 4.8	H ₀ 6.8	H ₀ 7.2	H ₀ 6.8	H ₀ 7.2	
1.	La ₂ O ₃	500	14,591	0.1404	0.1085	0.0753	0.0603			9.6
		600		0.1594	0.1473	0.0985	0.0845			10.5
		700		0.1050	0.0781	0.0562	0.04338			9.0
2.	Gd ₂ O ₃	500	11.7	0.0420	0.0271	0.00141	--	----	0.0212	6.9
		600		0.0473	0.0182	0.0060	--	----	0.0218	6.9
		700		0.0527	0.0254	0.0054	--	---	.02800	6.8
3.	Dy ₂ O ₃	500	42.3	0.1346	0.0560	0.0150	0.005			7.3
		600		0.1322	0.0496	0.01680	0.0063			7.4
		700		0.1084	0.0484	0.0128	0.0024			7.4
4.	Al ₂ O ₃	500	220.0	0.0483	0.0297	--	----	0.0387	0.0484	5.7
		600		0.0501	0.0275	--	----	0.0343	0.0387	5.7
		700		0.0523	0.0340	---	----	0.0368	0.0412	5.7

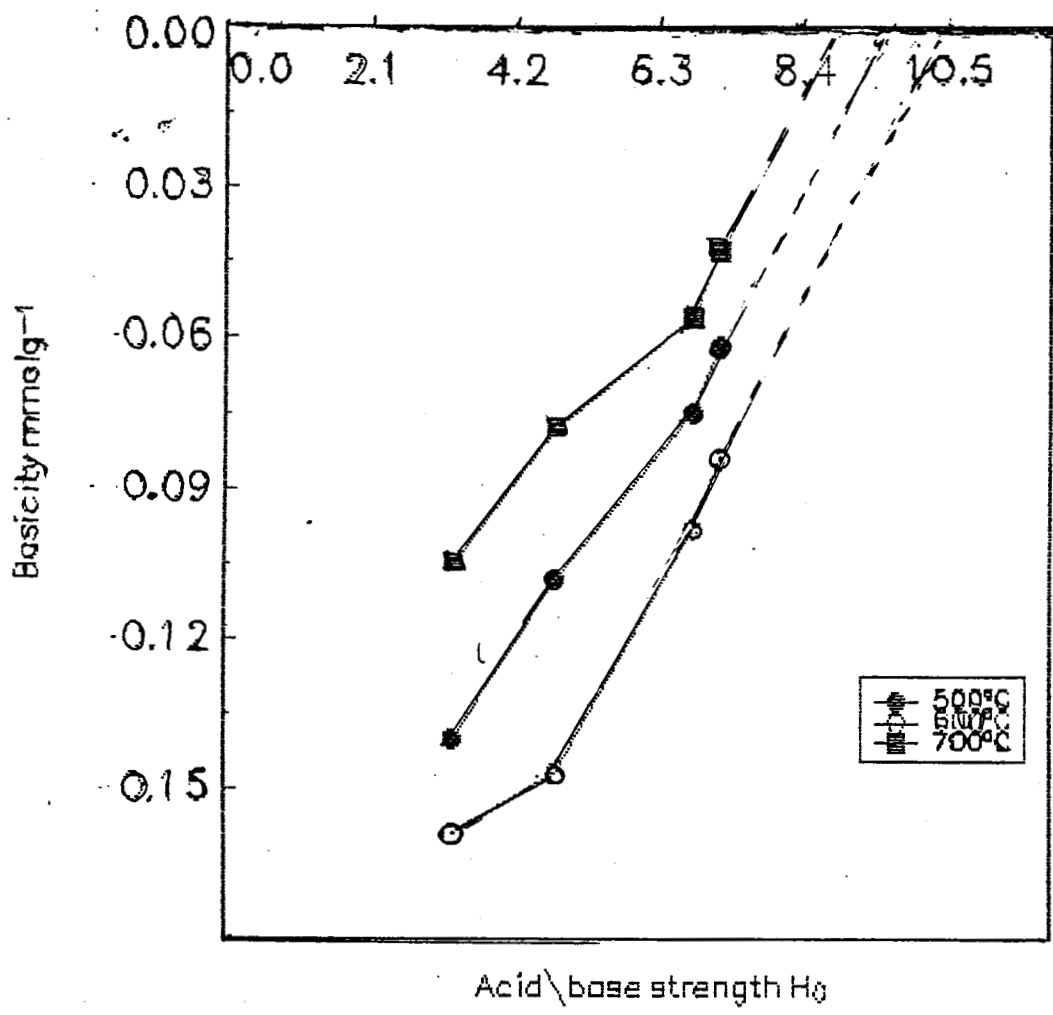


Fig. 3.1. Surface acidity/basicity of La₂O₃

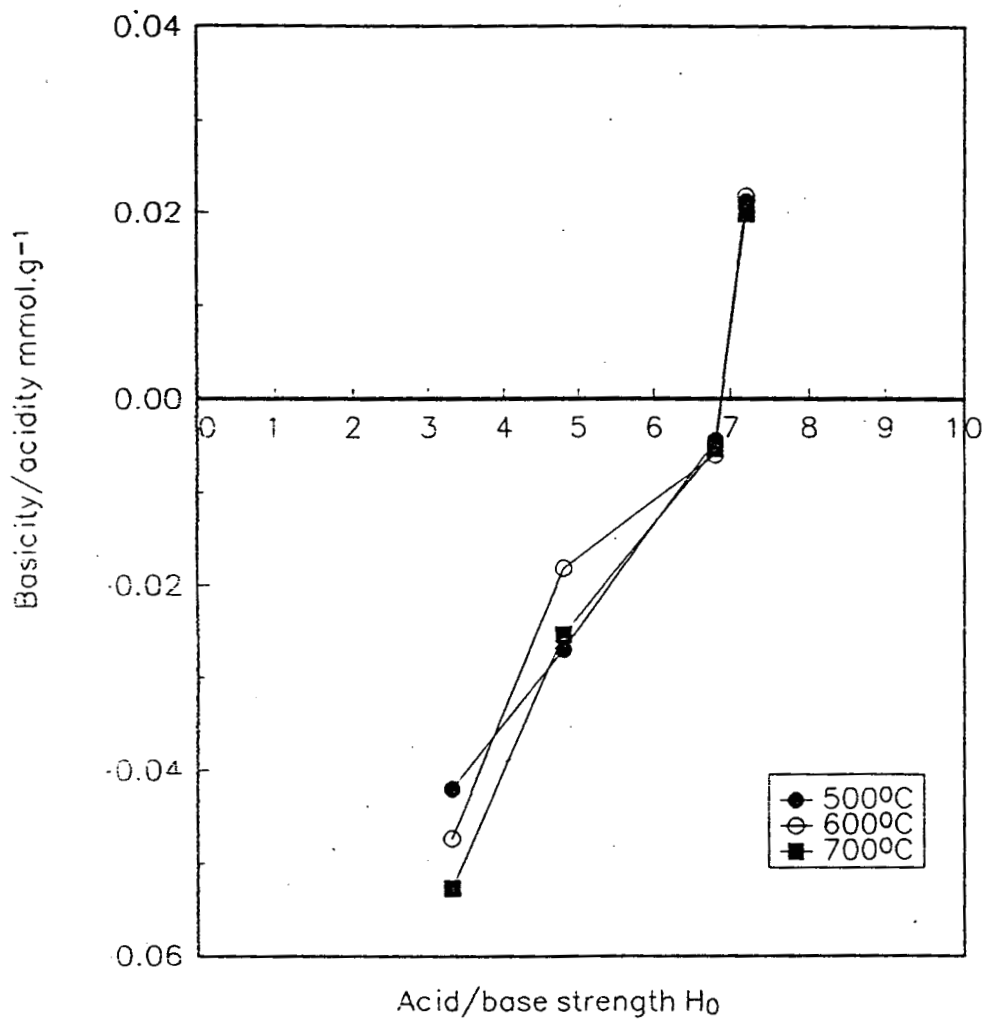


Fig. 3.2. Surface acidity/basicity of Gd₂O₃

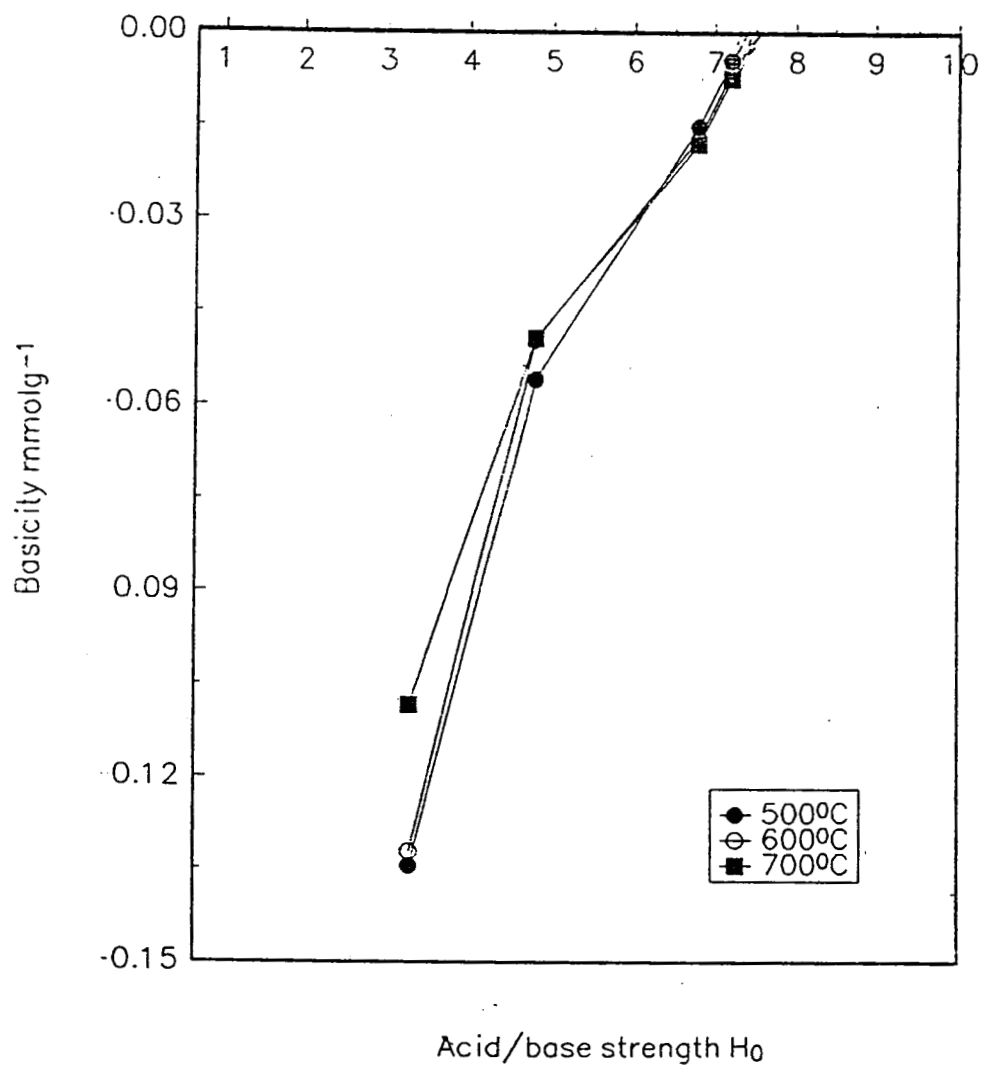


Fig. 3.3. Surface acidity/basicity of Dy₂O₃

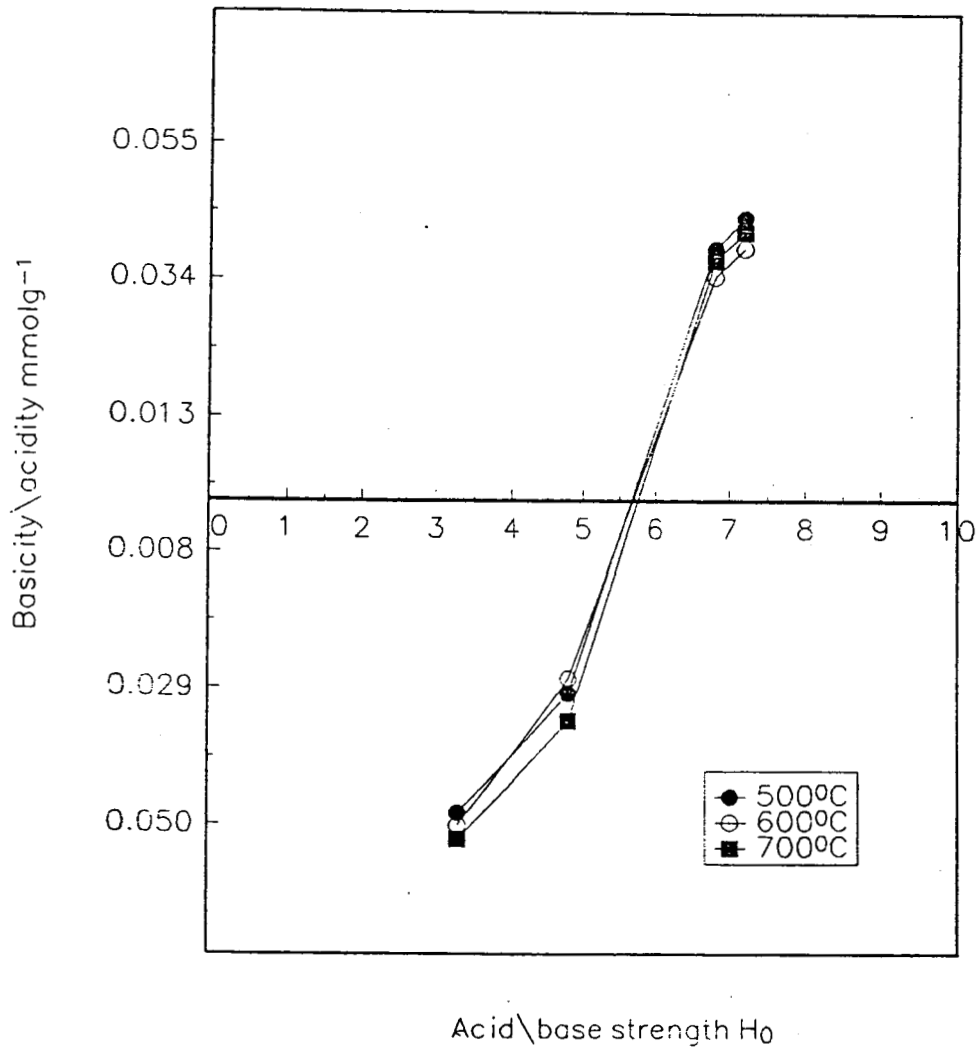


Fig. 3.4. Surface acidity/basicity of Al₂O₃

also had some influence on the acidity - basicity and H_{0max} of a solid surface. More than one kind of acid - base sites, which differ in strength of acidic and basic properties are present on metal oxide surfaces. If the surface of a solid oxide has a regular structure, the base strength would be uniform. However actual basic oxides have irregular surface structures possessing many kinds of defects, which are more prevalent in oxides of high melting points, than those of low melting point. The surface hydroxyl group also has some effect on basic character. Combined oxygen anions in such irregular surfaces are expected to have a non-uniform negative charge depending on their environment. The oxygen would be more negative in a low-coordinated metal cation environment and vice versa. Similarly a metal cation is more electron deficient in a low-co-ordinate anion environment [181].

Thus two types of electron sources are responsible for the basicity of metal oxides [182]. They are surface hydroxyl groups and the basic O^{2-} ions in the normal sites or trapped electrons at intrinsic defect sites in the lattice [148]. The concentration of surface hydroxyl ions decrease with rise in temperature. So the trapped electron or the normal O^{2-} ions must be responsible for the increase in basicity of the oxides with increase in temperature. The surface imperfections such as kinks, corners, etc. provide sites for ions of low co-ordination M^{n+}_{LC} and O^{2-}_{LC} . These sites are responsible for the presence of sites of different acid-base strength [185].

Among the single oxides, La_2O_3 showed sites of higher basicity and basic strength. Dysprosium oxide and gadolinium oxide were intermediate in basic strength, Dy_2O_3 being more basic. The outer electronic configuration of Gd^{3+} and Dy^{3+} are $4f^7 5d^{10} 6s^0$ and $4f^9 5d^{10} 6s^0$ respectively. The ionic radii of the ions Li^{3+} , Gd^{3+} , Dy^{3+} and Al^{3+} are 1.07, 0.94, 1.07 and 0.54\AA respectively [184a]. It is the stable $4f^7$ configuration of Gd^{3+} that is responsible for the slight decrease in basicity and ionic radius. The maximum basic strength of 10.5 was shown when lanthanum oxide La_2O_3 was activated at a temperature of 600°C . Alumina prepared by the same methods showed comparatively less surface basicity and basic strength. It had some acidic sites also.

The electronegativity values of oxides calculated by Sanderson method were the following:

TABLE 3.1.2.

Name of oxide	Sanderson electronegativity	Partial charge
La_2O_3	2.55	0.5600
Gd_2O_3	2.644	0.5402
Dy_2O_3	2.659	0.5369
Al_2O_3	2.723	0.5200

A combined oxygen anion in an oxide surface acts as an electron donor and its capacity is expected to be related to its effective negative charge on the atom

[179]. The higher the negative charge, the stronger the donor or base property. The partial negative charge on a combined oxygen anion has been estimated from the electronegativity equalisation principle as 0.5600, 0.5402, 0.5369 and 0.5200 respectively [184]. Accordingly the basic strength of oxides is expected to decrease in the order of La_2O_3 , Gd_2O_3 , Dy_2O_3 and Al_2O_3 . The slight discrepancy in the basic property of Gd_2O_3 and Dy_2O_3 may be attributed to the stable electronic configuration of Gd^{3+} . Single oxides of rare earth metals were shown to be crystalline by XRD measurements whereas pure Al_2O_3 is amorphous (Fig. 3.5 to 3.7).

3.2. Precompressed Single oxides

The determination of surface acidity and basicity of the pre-compressed samples reveal some interesting results. All the rare earth oxides exhibit acidic surfaces with considerable acid strength. But alumina showed basic sites of intermediate strength. This is clear from Table 3.2. and Fig. 3.8 to 3.11. The change can be explained in two ways. They are

- (a) due to the absence of the effects of thermal activation.
- (b) compression produced surface changes which increased electron pair acceptor strength.

Z01788.RAW

A 2

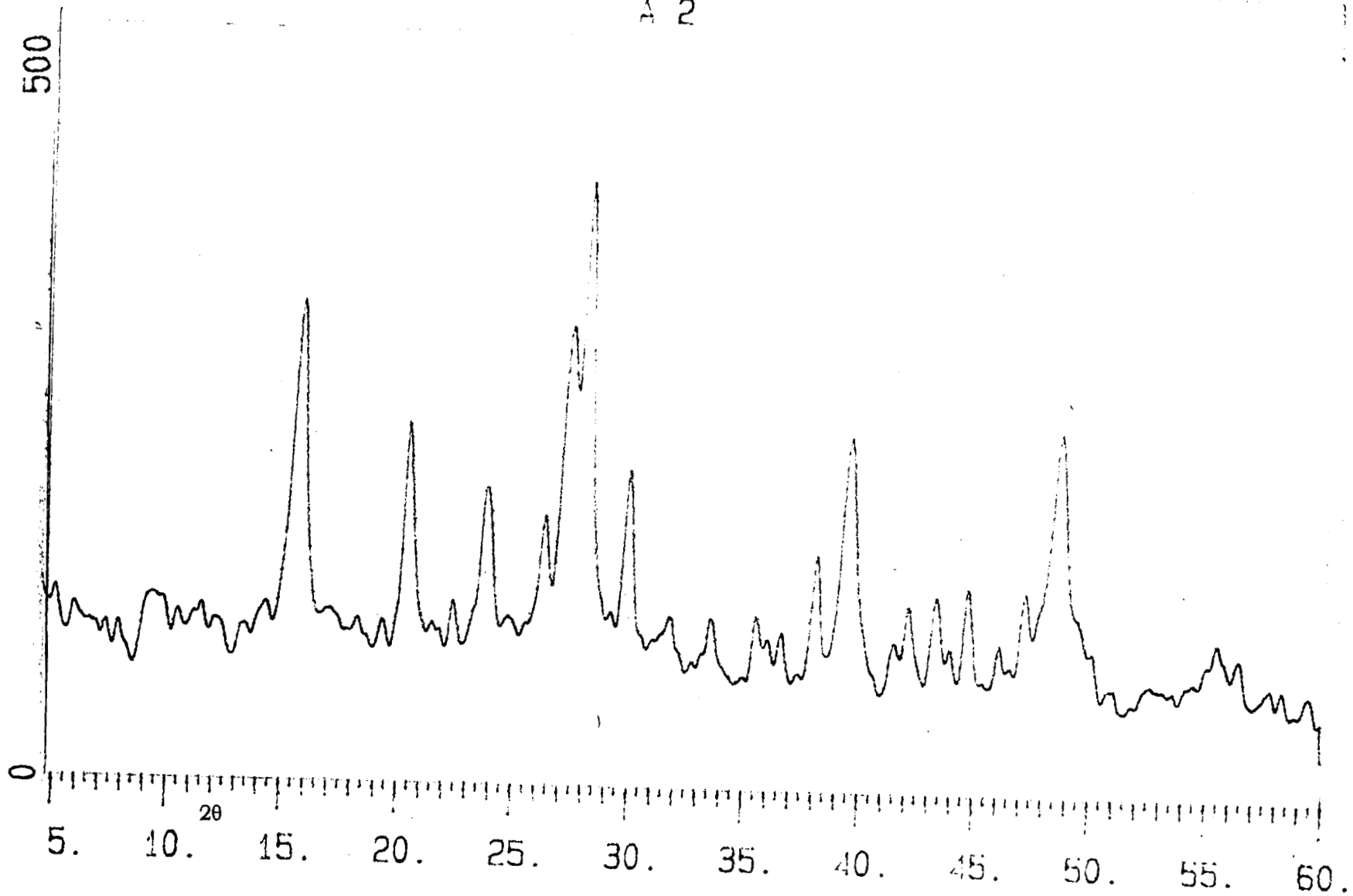


Fig. 3.5. XRD of Lanthanum oxide
(temp. of activ. 500°C; p.s. 106-125 microns)

701608.RAW

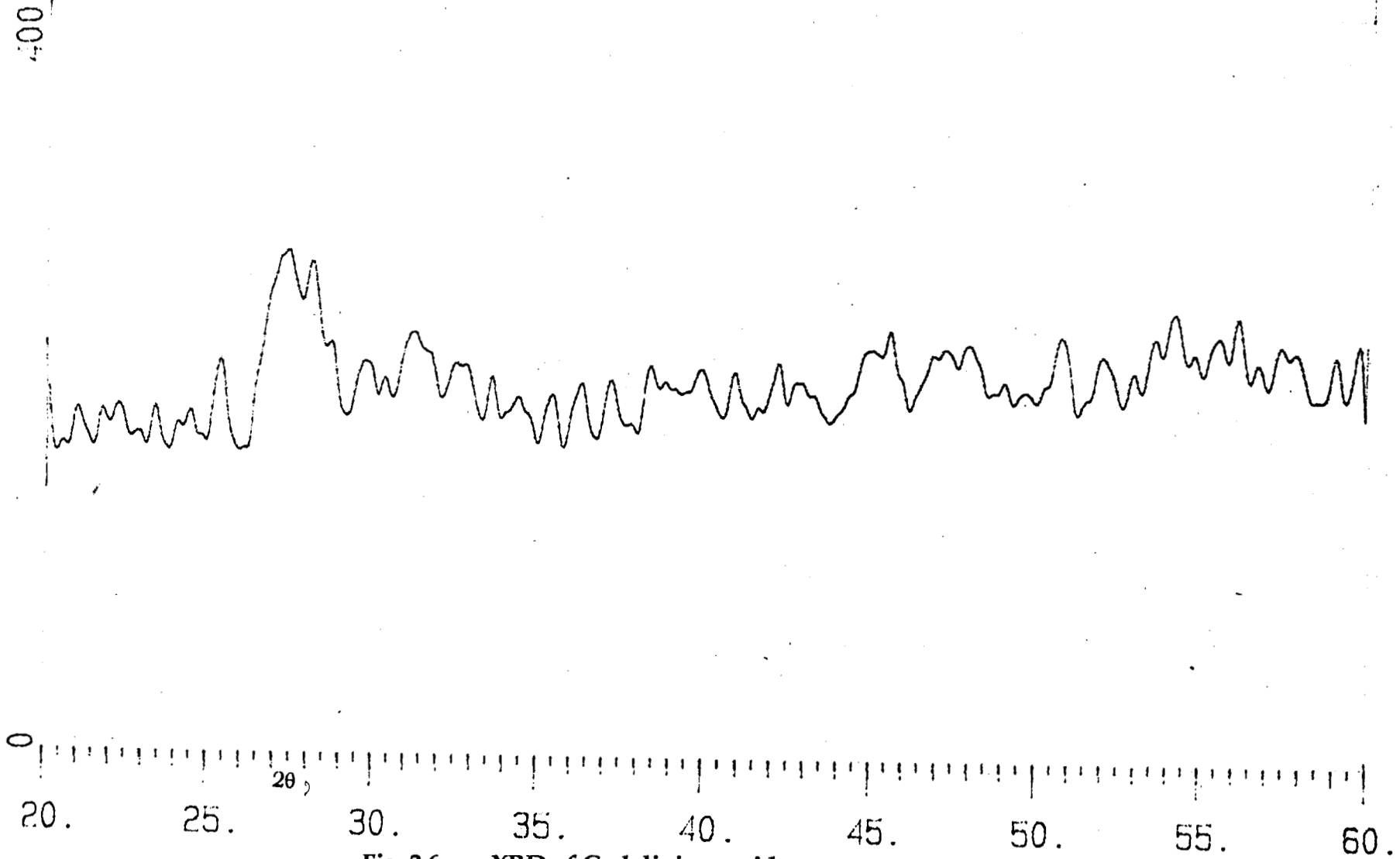


Fig. 3.6. XRD of Gadolinium oxide
(temp. of activ. 500°C; p.s. 106-125 microns)

Z01787.RAW

A 1

700

0

5. 10. 15. 20. 25. 30. 35. 40. 45. 50. 55. 60.

2θ

Fig. 3.7. XRD of Aluminium oxide
(temp. of activ. 500°C; p.s. 106-125 microns)

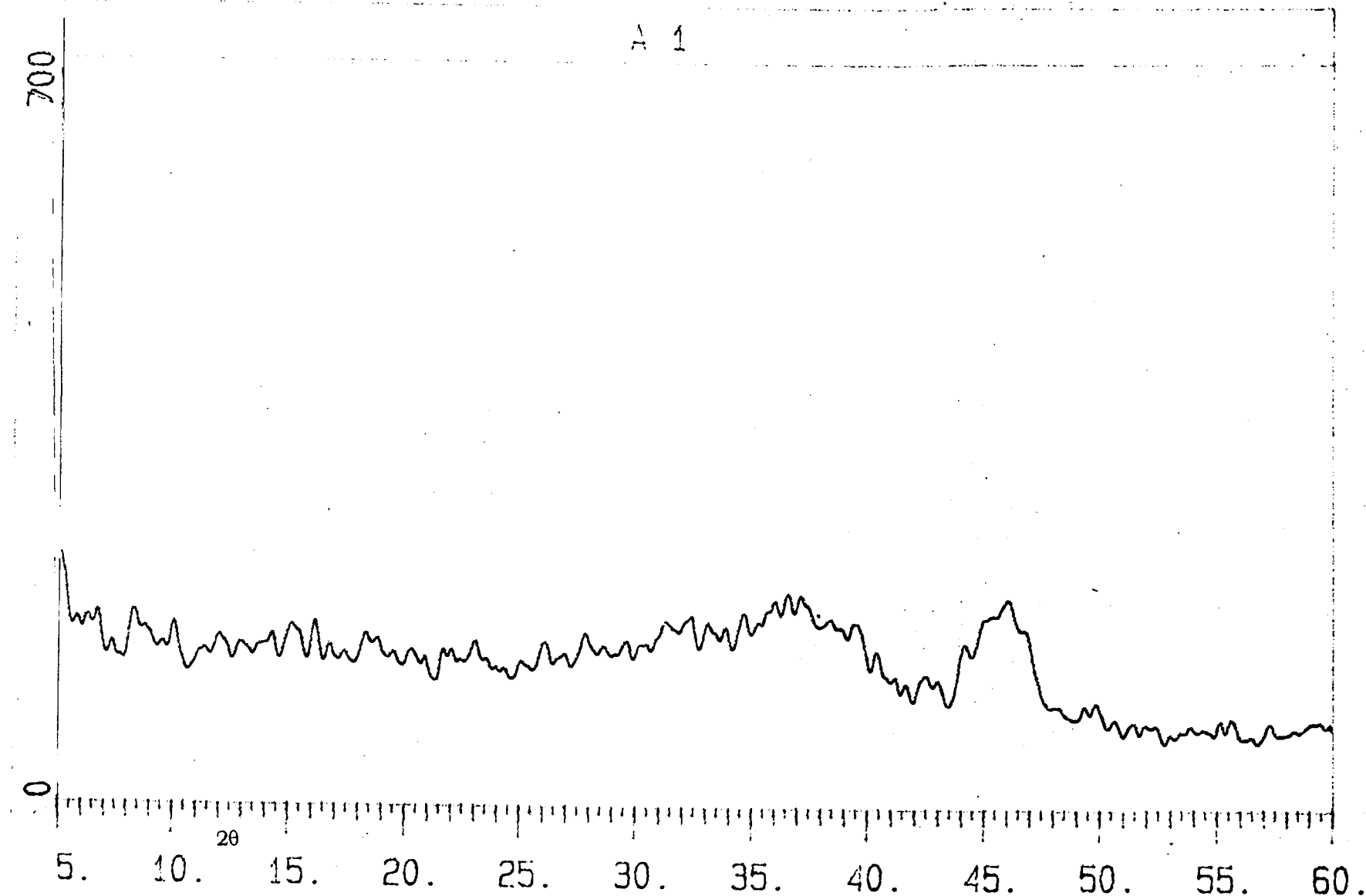


TABLE 3.2

Surface Acidity/basicity of single oxides precompressed to various pressures, at different acid/base strength

Particle size 106-125 microns

| Sl. No. | Oxides | Precompression pressures Nm^{-2} | Basicity mmol g^{-1} | | | | Acidity mmol g^{-1} | | | $H_{0\text{max}}$ |
|---------|-------------------------|---|-------------------------------|--------------|--------------|--------------|------------------------------|--------------|--------------|-------------------|
| | | | H_0
3.3 | H_0
4.8 | H_0
6.8 | H_0
7.2 | H_0
4.8 | H_0
6.8 | H_0
7.2 | |
| 1. | La_2O_3 | 2×10^3 | 0.0955 | | | | 0.0212 | 0.0412 | 0.0544 | 4.5 |
| | | 5×10^3 | 0.0694 | | | | 0.0223 | 0.0465 | 0.0562 | 4.7 |
| | | 8×10^3 | 0.0604 | | | | 0.0257 | 0.0493 | 0.0742 | 4.2 |
| | | 11×10^3 | 0.0583 | | | | 0.0300 | 0.0521 | 0.0771 | 4.2 |
| 2. | Gd_2O_3 | 2×10^3 | 0.0455 | | | | 0.0174 | 0.0441 | 0.0455 | 4.3 |
| | | 5×10^3 | 0.0399 | | | | 0.0155 | 0.0355 | 0.0502 | 4.3 |
| | | 8×10^3 | 0.0356 | | | | 0.0162 | 0.0370 | 0.0635 | 4.2 |
| | | 11×10^3 | 0.0290 | | | | 0.0181 | 0.0510 | 0.0893 | 4.2 |
| 3. | Dy_2O_3 | 2×10^3 | 0.0996 | | | | 0.0239 | 0.0651 | 0.0700 | 4.5 |
| | | 5×10^3 | 0.0874 | | | | 0.0258 | 0.0563 | 0.0665 | 4.4 |
| | | 8×10^3 | 0.0638 | | | | 0.0284 | 0.0437 | 0.0470 | 4.3 |
| | | 11×10^3 | 0.0484 | | | | 0.0312 | 0.0546 | 0.0623 | 4.2 |
| 4. | Al_2O_3 | 2×10^3 | 0.1106 | 0.0969 | 0.0187 | 0.0174 | | | | 8.0 |
| | | 5×10^3 | 0.0832 | 0.0551 | 0.0190 | 0.0172 | | | | 8.0 |
| | | 8×10^3 | 0.0801 | 0.0621 | 0.0200 | 0.0165 | | | | 7.9 |
| | | 11×10^3 | 0.0841 | 0.0581 | 0.0170 | 0.0101 | | | | 7.8 |

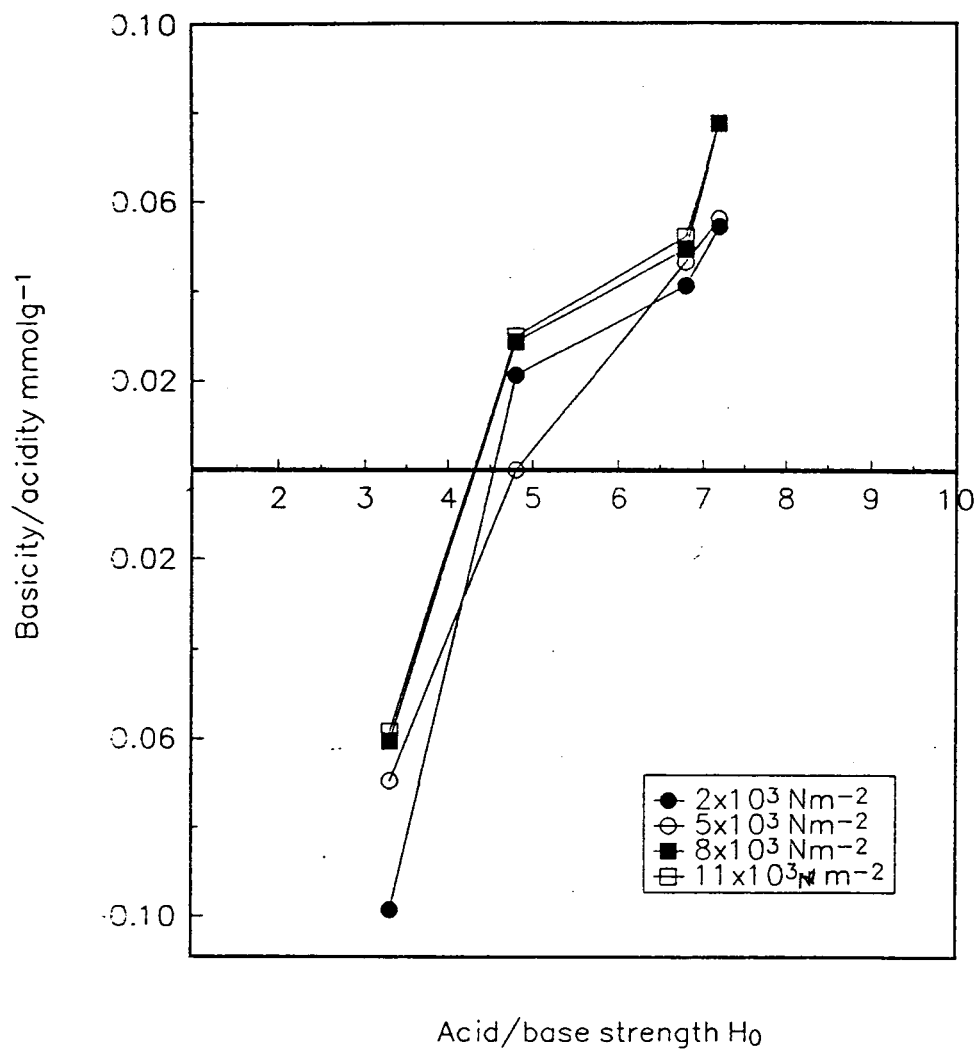


Fig. 3.8. Surface acidity/basicity of La₂O₃

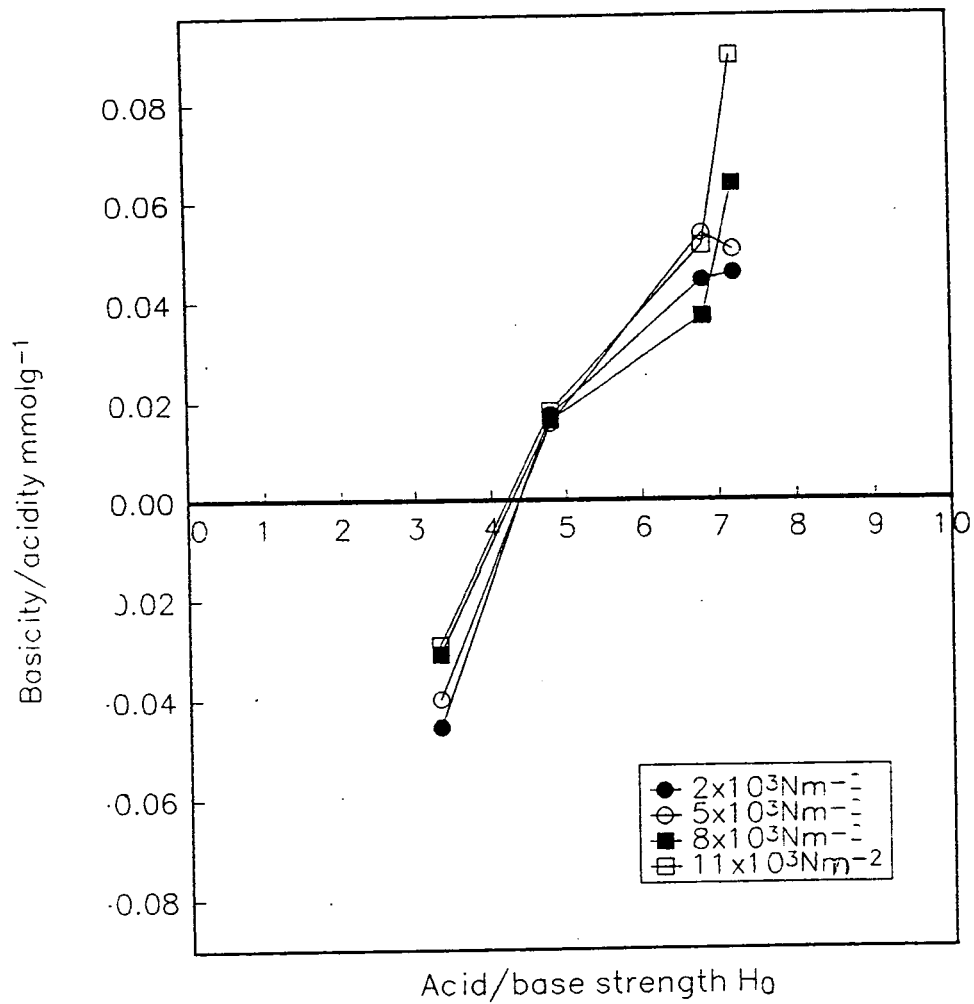


Fig. 3.9. Surface acidity/basicity of Gd₂O₃

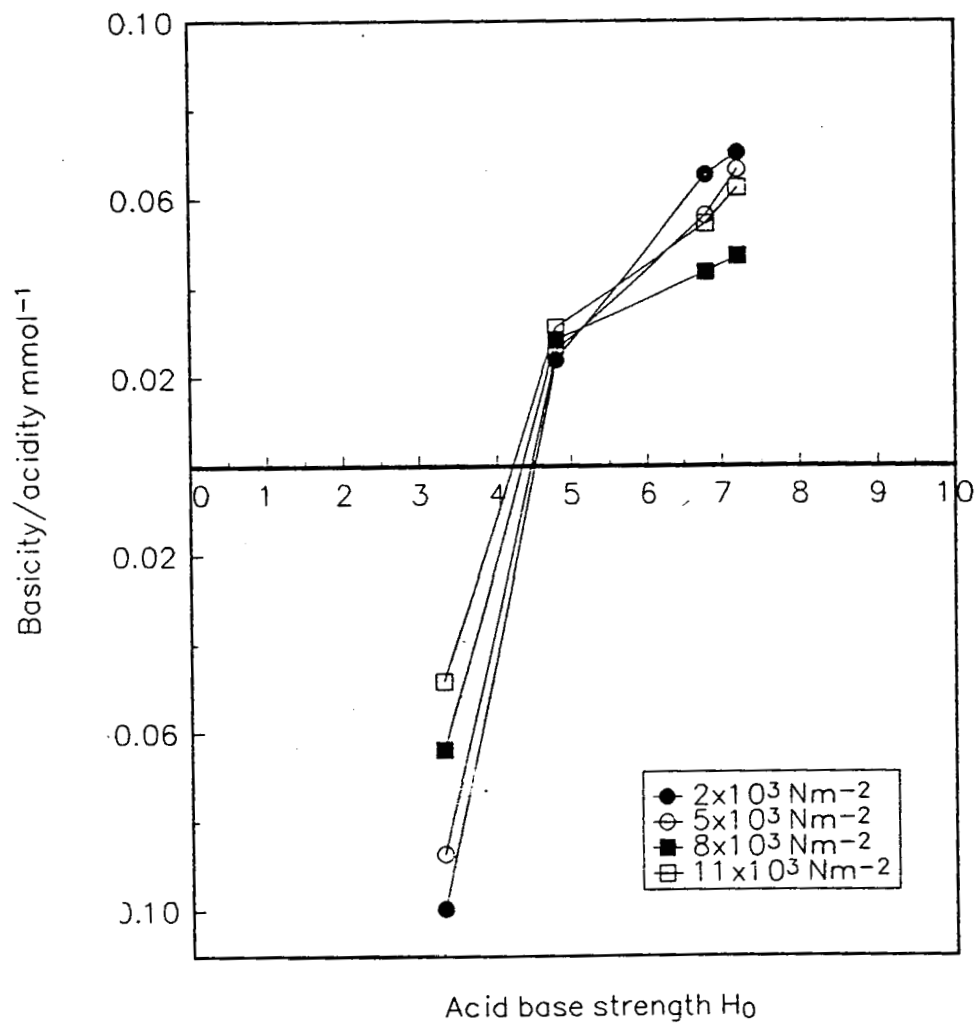


Fig. 3.10. Surface acidity/basicity of Dy₂O₃

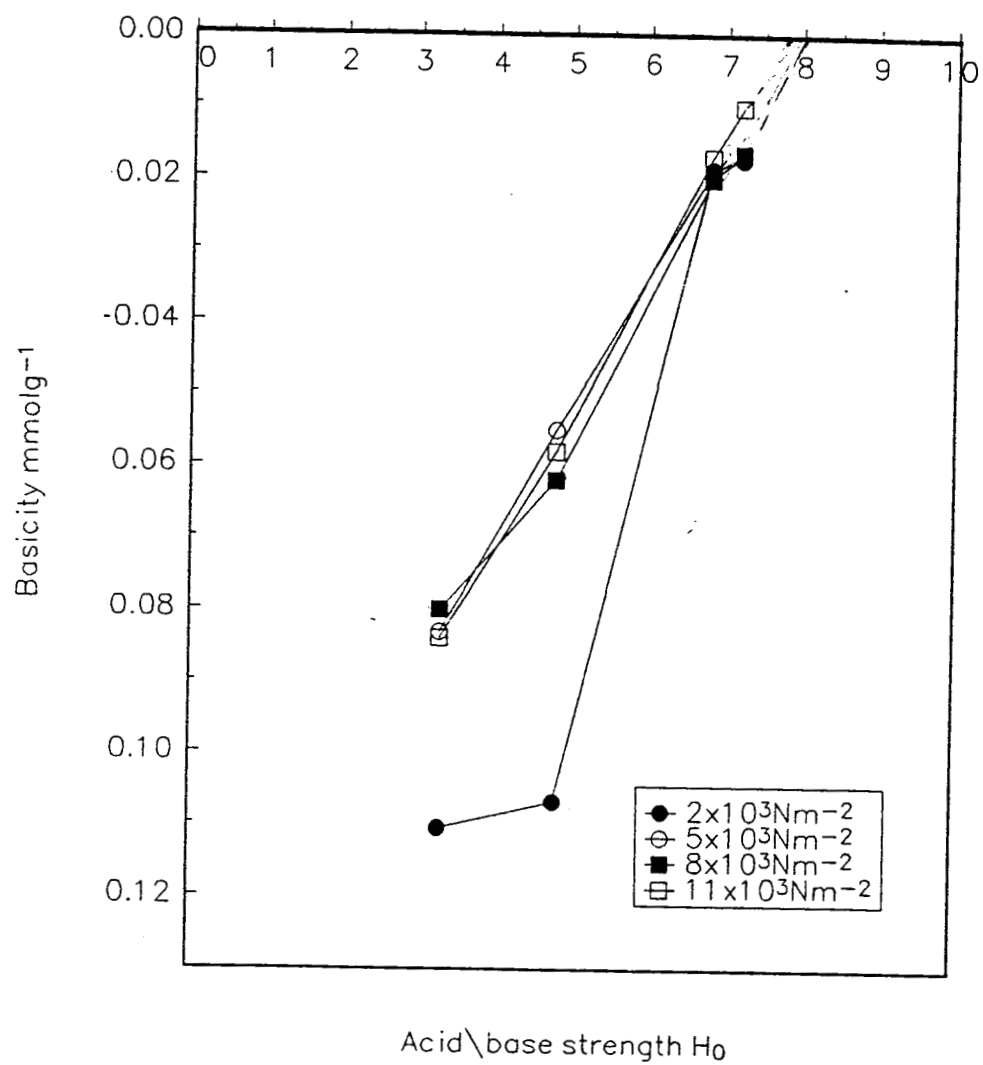


Fig. 3.11. Surface acidity/basicity of Al₂O₃

It is well known that compression produced defects on the surface [152]. In a powdered material compression produced an increase in dislocation density and densification, causing a reduction in intergranular porosity. Intergranular pores are inter communicative with one another and with the surface of the material by diffusion of the ions. Such movement of ions are obstructed in a densified solid. The variation in the surface acidic/basic properties of the above metal oxide catalysts were brought by the changes produced on the surface by compression.

Precompressed alumina had weak basic sites, where as lanthana, gadolina and dysprosia showed acidic sites. The H_{0max} was between 4 and 4.5 for the rare earth metal oxides. The various compression pressures applied were 2×10^3 , 5×10^3 , 8×10^3 and $11 \times 10^3 \text{ Nm}^{-2}$. Pre compression caused surface changes that enhanced acidic properties of the metal oxides. The co-ordinatively unsaturated M^{3+} ions were responsible for the above observation. Fig 3.12 represents the XRD of gadolinium oxide precompressed to a pressure of $8 \times 10^3 \text{ Nm}^{-2}$.

3.3. Mixed oxide systems

For mixed oxides, the characteristic surface properties can not be predicted quantitatively by comparing the independent properties of the parent-oxides. New acidic and basic sites are created on the catalyst surface by coprecipitation. The generation of new and strong acid sites on mixed oxides is attributed to a

Z01609.RAW

2

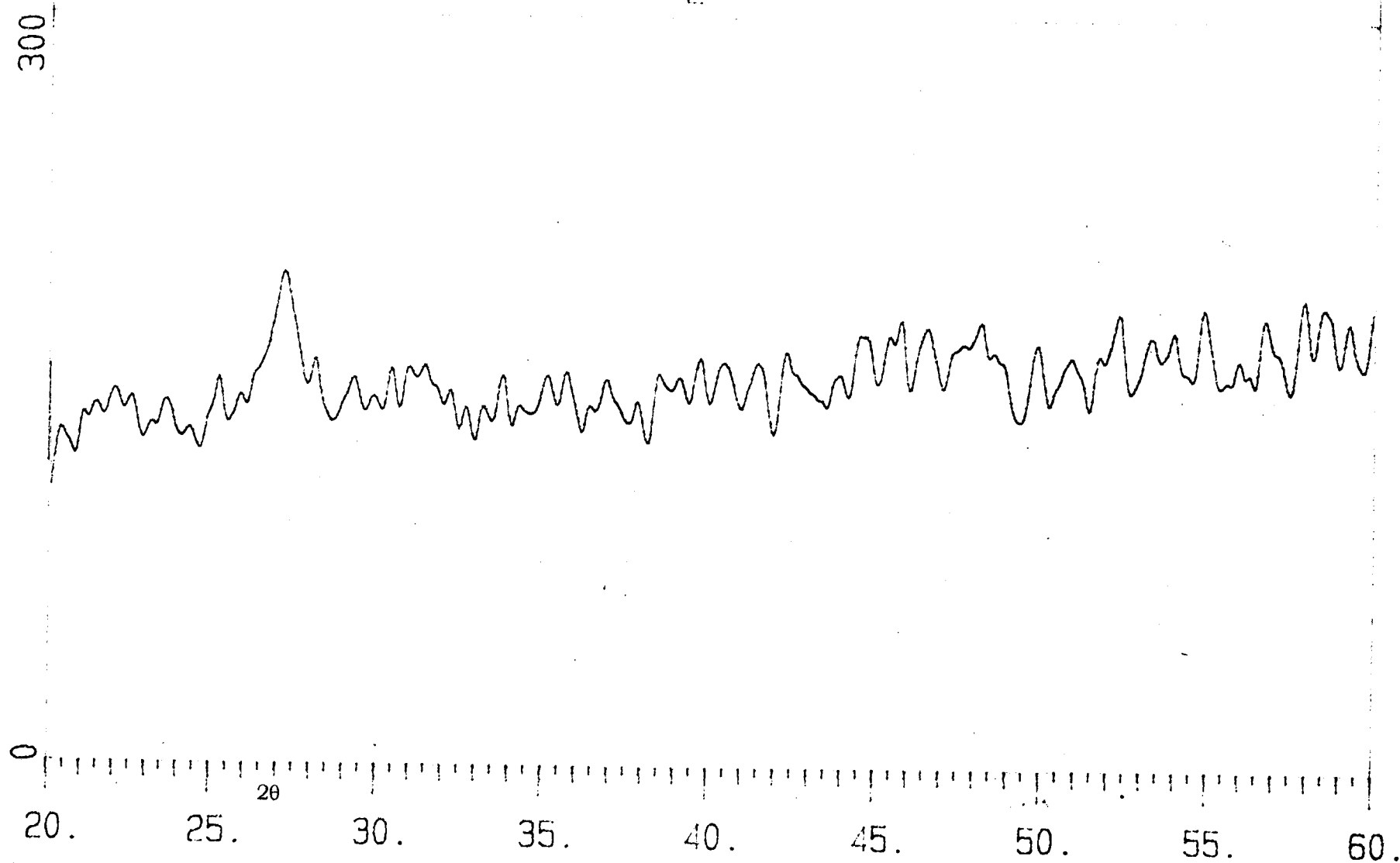


Fig. 3.12. XRD of pre compressed Gadolinium oxide
(pre comp. pr. $8 \times 10^3 \text{ Nm}^{-2}$; p.s. 106-125 microns)

charge imbalance localised on $M_1 - O - M_2$ bonds found in them, where M_1 and M_2 are the mixed metal ions. The binary oxides are found to be amorphous in nature [182]. $\gamma\text{-Al}_2\text{O}_3$, when mixed with rare earth elements, acquire thermal stability and can be used as a catalyst at high temp. without phase transformation [18,22]. Each rare earth element was easily spread on Al_2O_3 to form amorphous $\text{Ln} - \text{O} - \text{Al}$ or $\text{Ln} - \text{O} - \text{Ln}$ linkages. The $\text{Ln} - \text{O} - \text{Al}$ linkage acts as Lewis acid sites. The maximum acid strength and the structure of active sites are independent of the rare earth elements. It is mainly due to the ion-radii of Ln^{3+} which relates to the number of $\text{Ln} - \text{O} - \text{Al}$ units on the surface of catalysts [187, 188].

3.3.1. Lanthana - Alumina mixed oxide system

The binary oxide systems comprising of lanthana and alumina in different compositions were prepared by coprecipitation method. The mixed oxides will have an electronegativity in between that of lanthanum oxide and aluminium oxide. Mixed oxides of different composition containing 20, 40, 60 and 80 percent by weight of lanthanum oxide were prepared and activated to different temperatures 500, 600 and 700°C. The results were tabulated in Table 3.3. The various binary oxides were amorphous in nature (Fig. 3.13 to 3.18) and the surface area was determined by BET method. The XRD pattern showed crystalline nature only for single oxides. The surface area of single oxides were less than that of alumina. The oxides when added to the support oxide Al_2O_3 , the surface area

was increased [189]. At lower concentrations of rare earth oxides the binary oxide systems showed an increase in surface area.

The strength of the acid sites of alumina were weakened by the incorporation of lanthana. Pure lanthanum oxide was basic and the mixed oxide systems showed sites of intermediate basic strength or new acid sites were created on the mixed oxide surface [12, 190, 191]. The acidity of mixed oxides were attributed to the charge imbalance created on La - O - Al bonds [90-95]. In this binary oxide sytem, Al - O - Al, La - O - La bonds were also formed in addition to Al - O - La bonds, depending on their composition. The acid - base amount of the system was determined by the number of La - O - Al bonds per unit surface area. The acid-base properties of the mixed metal oxide system depend on the averaged electronegativity value of the component metal ions [192]. Oxides with lower electro-negativity values are stronger solid bases and weaker acids.

The charge imbalance might be expected even on single component metal oxides consisting of small particles, since the electronic properties of small sized metal oxide particles are somewhat different from those of the bulk [193, 194]. These differences are due to the surface imperfections. Typical imperfections are metal or oxygen vacancies causing the local charge imbalance. The existence of co-ordinatively unsaturated cation is responsible for the lewis acidity. For the

mixed oxides the charge imbalance arises due to the difference in electronic environment of the La - O - Al bonds. The acid base strength distribution and the acidity - basicity were given in Table 3.3. The corresponding H_{0max} values were obtained from Fig. 3.19 to 3.22. XRD studies revealed that the mixed oxide is purely amorphous, so that the metal ions were well dispersed on the surface.

Alumina showed weak acidic sites with an H_{0max} value of 5.7 at 500°C. The basic strength increased as the amount of lanthana is increased in the binary oxide system. It is clear from the Fig. 3.23 that the binary oxide containing about 60% by weight of lanthana showed maximum basic strength of H_{0max} 8.4 at 600°C (Table 3.3).

3.3.2. Gadolina - Alumina mixed oxide system

The acidity/basicity values corresponding to different acid/base strength at different activation temperatures were given in Table 3.4. The basic strength H_{0max} was increased when gadolina was incorporated into alumina by coprecipitation method. The mixed oxide system containing 60% by weight of gadolina exhibited a basic strength of 8.5 at 600°C. This is clear from Table 3.4 and Fig. 3.24 to 3.27. The sanderson electronegativity of Gd_2O_3 is less than that of Al_2O_3 and the basicity of Gd_2O_3/Al_2O_3 system increased with an increase in concentration of Gd_2O_3 . XRD measurements showed no evidence for large Gd_2O_3 crystallites suggesting that the gadolinium ions were well dispersed on the

Z01789.RAW

A 3

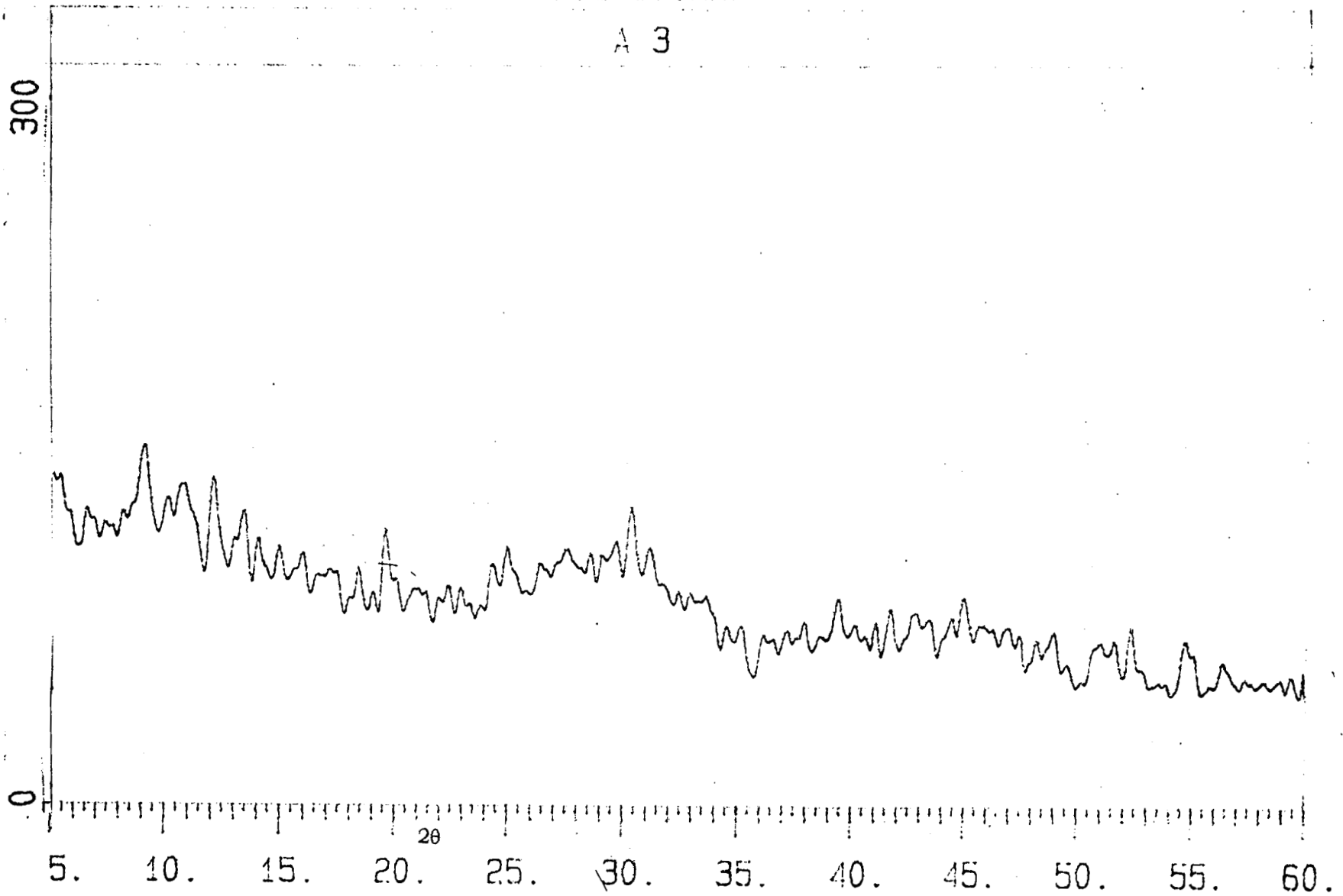


Fig. 3.13. XRD of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide
(wt. % of La_2O_3 = 40; temp. of activ. = 500°C ; p.s. .106-125 microns)

Z01642.RAW

3

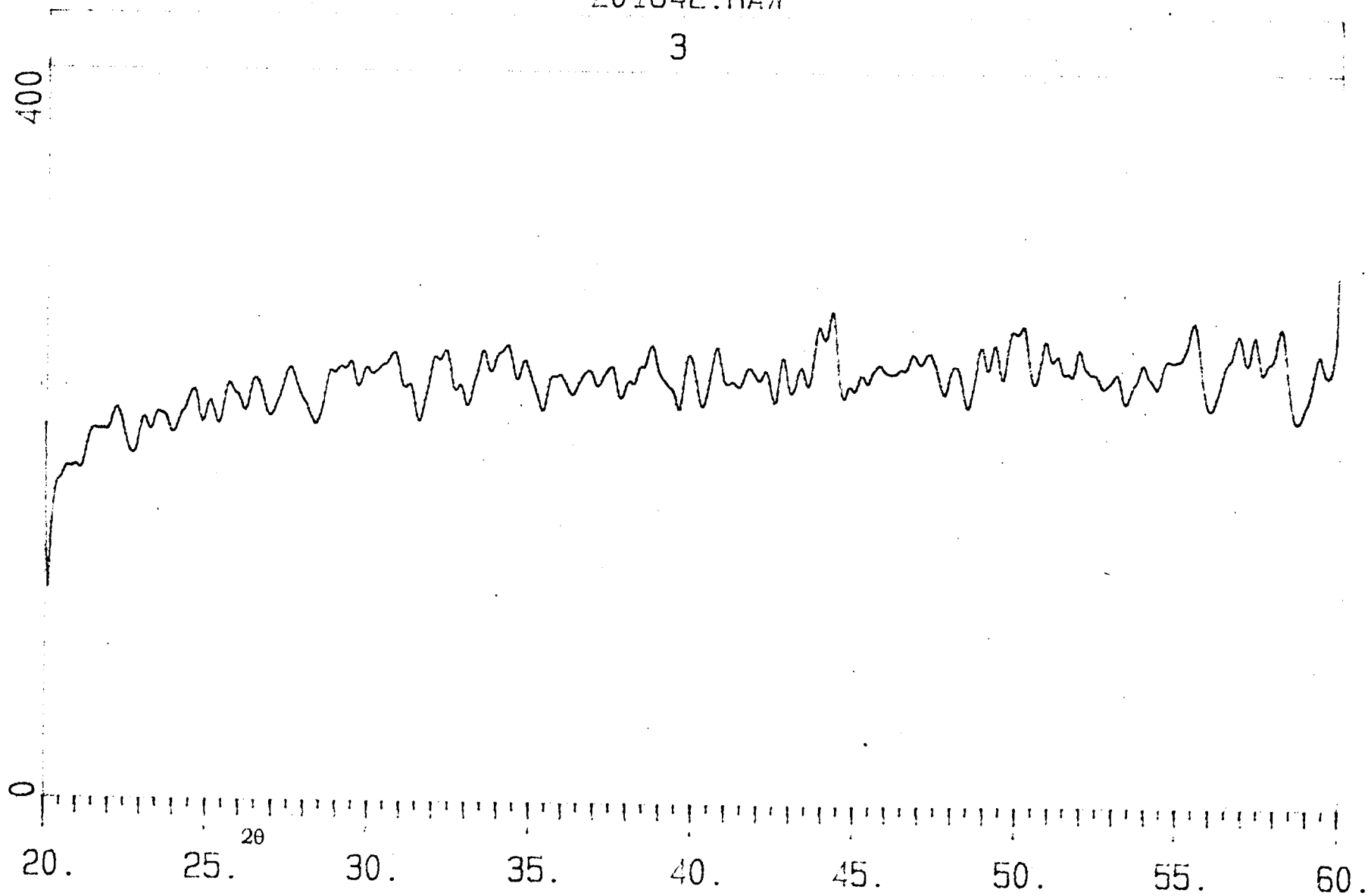


Fig. 3.14. XRD of $Gd_2O_3-Al_2O_3$ mixed oxide
(wt. % of Gd_2O_3 = 40; temp. of activ. = $500^\circ C$; p.s. 106-125 microns)

Z01643.RAW

4

400

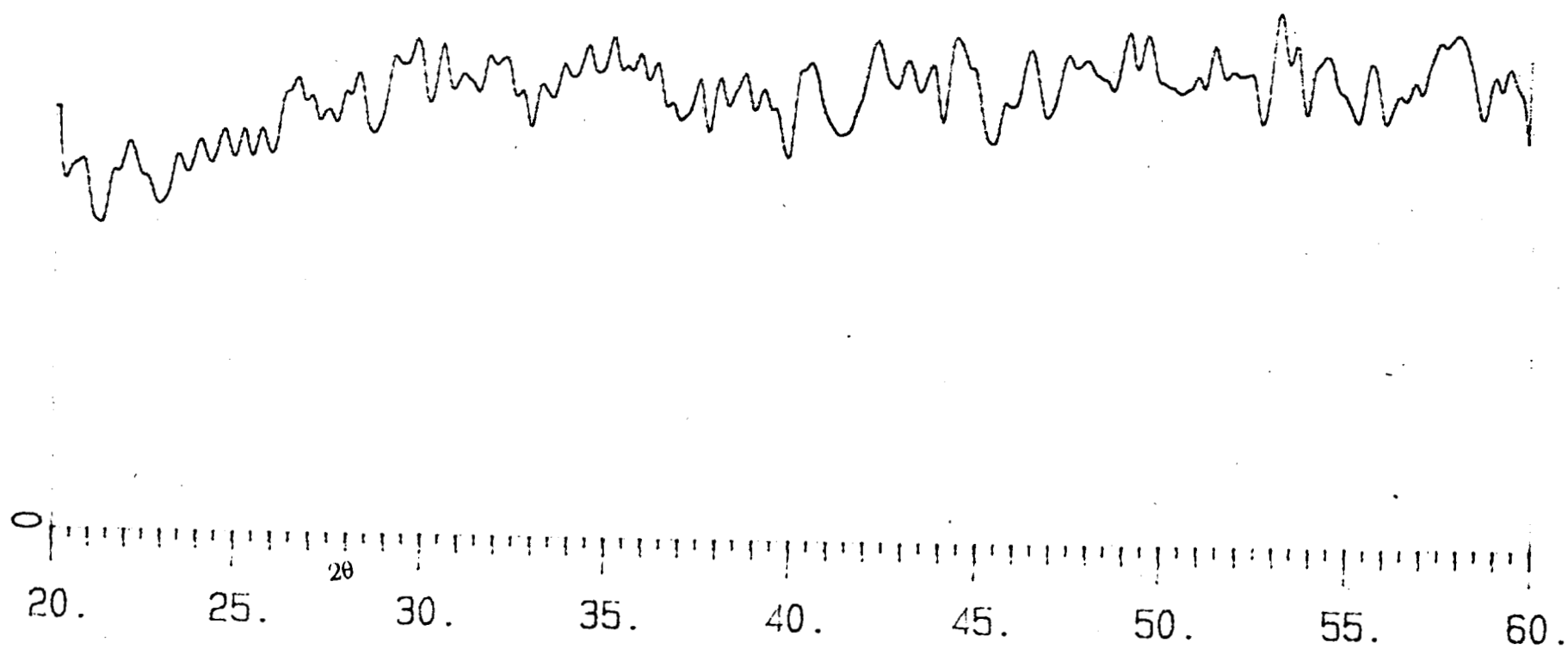


Fig. 3.15. XRD of $Gd_2O_3-Al_2O_3$ mixed oxide
(wt. % Gd_2O_3 = 60; temp. of activ. = 500°C; p.s. 106-125 microns)

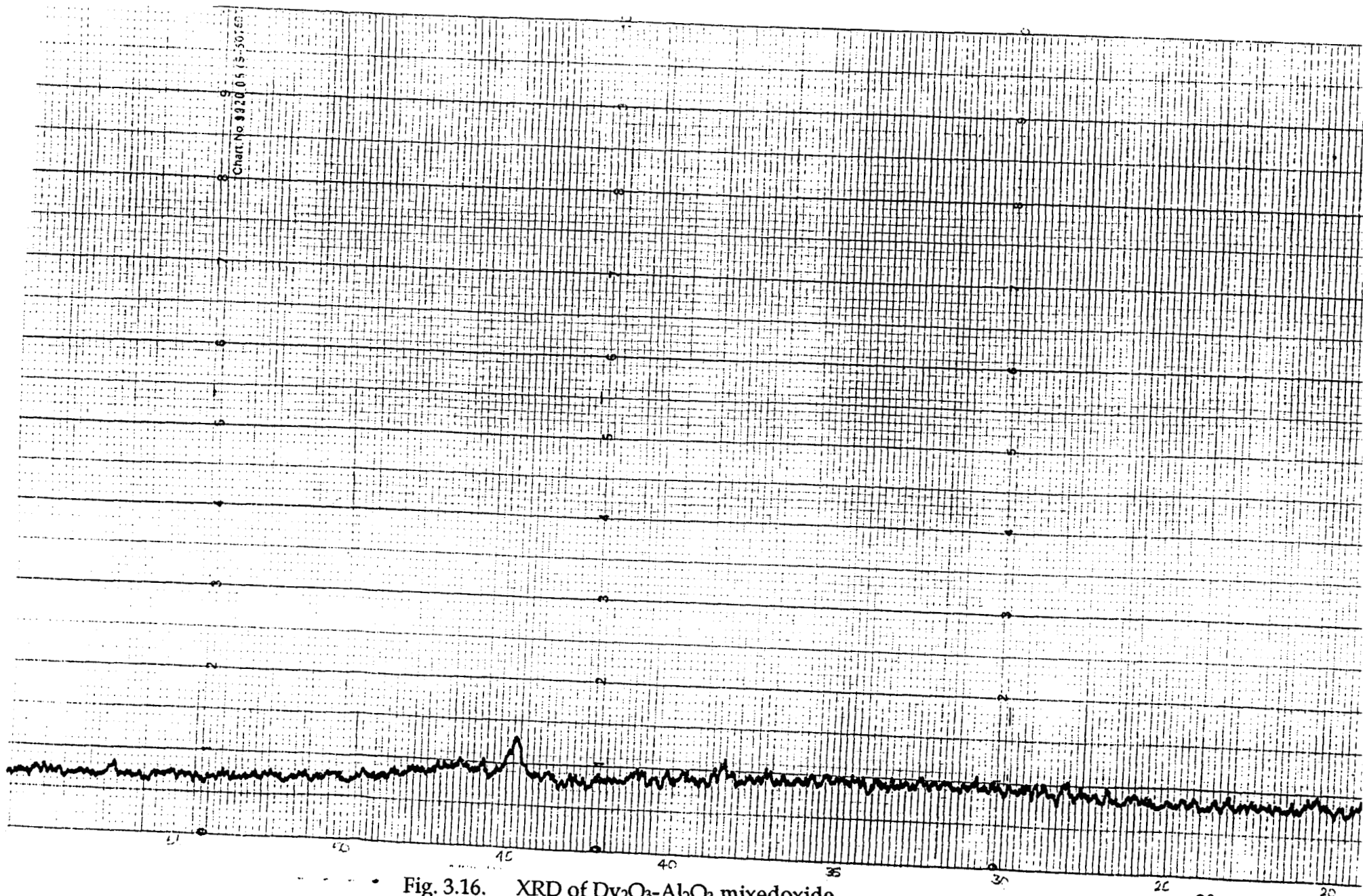


Fig. 3.16. XRD of $Dy_2O_3-Al_2O_3$ mixedoxide
(wt. % of $Dy_2O_3 = 20$; Temp. of activ. = $500^\circ C$; p.s. 106-125 microns)

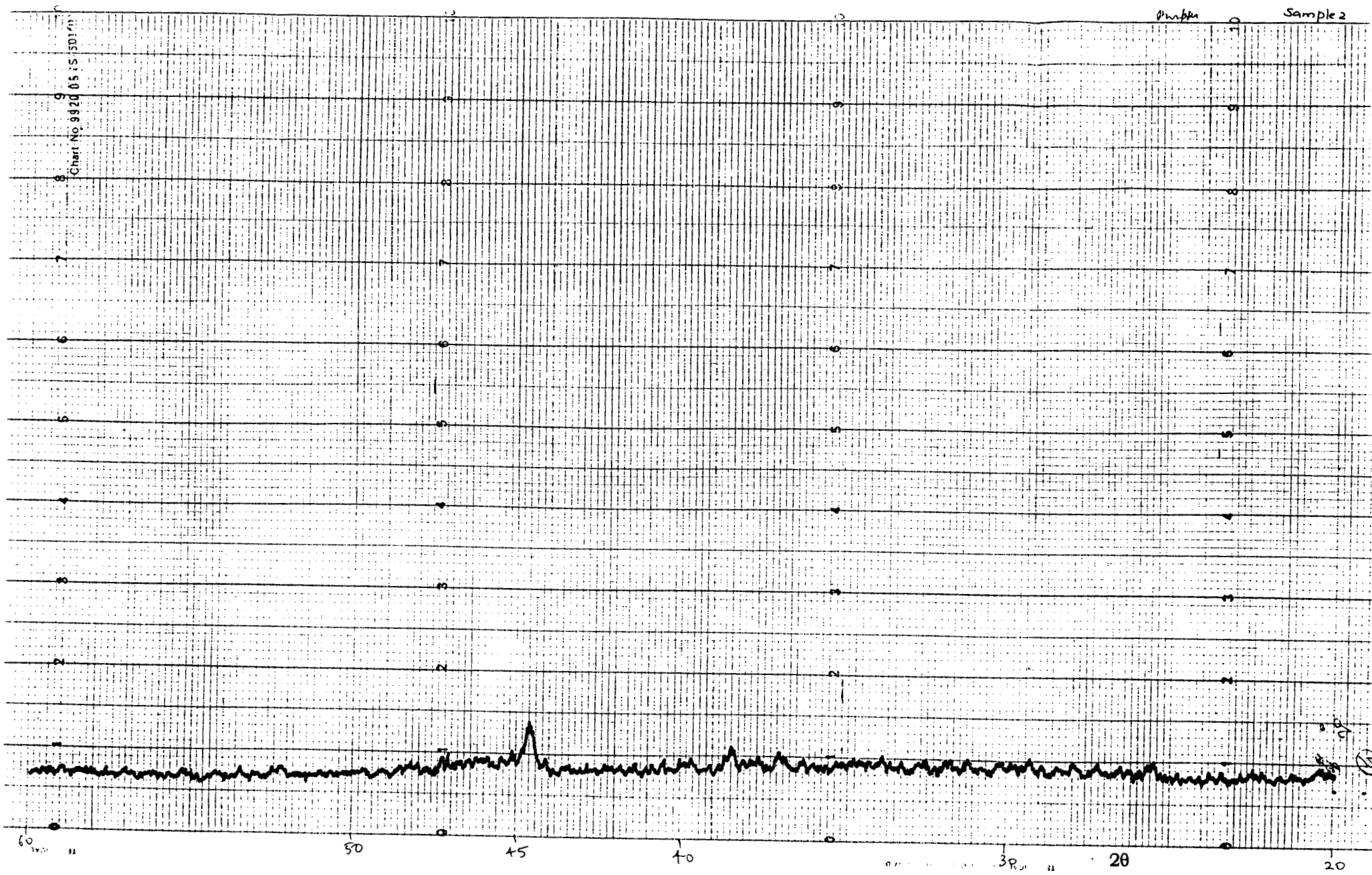


Fig. 3.17. XRD of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide
(wt. % of Dy_2O_3 = 20; temp. of activ. = 600°C; p.s. 106-125 microns)

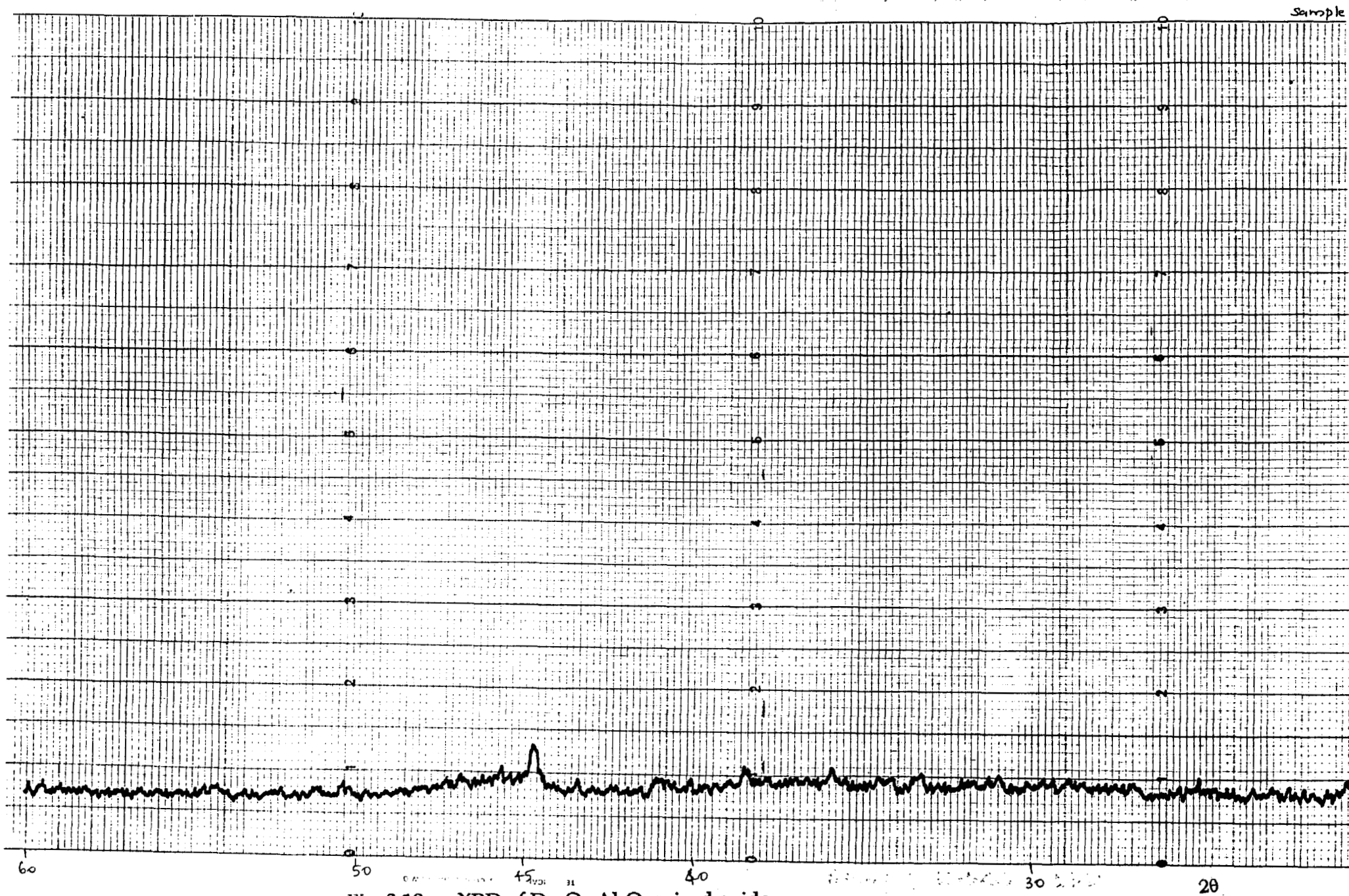


Fig. 3.18. XRD of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide.
(wt. % of $\text{Dy}_2\text{O}_3 = 20$; temp. of activ. = 700°C ; p.s. 106-125 microns)

TABLE 3.3

Surface Acidity/basicity of mixed oxides of Lanthanum and Aluminum activated at different temperatures

Particle size 106 - 125 microns

| Sl. No. | Percentage by weight La_2O_3 | Temp. of Activation $^\circ\text{C}$ | Surface area m^2g^{-1} | Basicity mmol g^{-1} | | | | $\text{H}_{0\text{max}}$ |
|---------|--|--------------------------------------|--|-------------------------------|---------------------|---------------------|---------------------|--------------------------|
| | | | | H_0
3.3 | H_0
4.8 | H_0
6.8 | H_0
7.2 | |
| 1. | 20 | 500 | 268.1384 | 0.1763 | 0.0729 | 0.0258 | 0.0145 | 7.8 |
| | | 600 | | 0.1527 | 0.0608 | 0.0243 | 0.0109 | 8.0 |
| | | 700 | | 0.1254 | 0.0487 | 0.0245 | 0.0164 | 8.0 |
| 2. | 40 | 500 | 77.5745 | 0.1624 | 0.0658 | 0.0539 | 0.0196 | 7.9 |
| | | 600 | | 0.1474 | 0.0525 | 0.0285 | 0.0163 | 7.8 |
| | | 700 | | 0.1363 | 0.0479 | 0.0262 | 0.0127 | 7.6 |
| 3. | 60 | 500 | 58.5467 | 0.1481 | 0.0729 | 0.0324 | 0.0187 | 8.1 |
| | | 600 | | 0.1668 | 0.0819 | 0.0387 | 0.0289 | 8.4 |
| | | 700 | | 0.1316 | 0.0616 | 0.0281 | 0.0185 | 8.3 |
| 4. | 80 | 500 | 39.7149 | 0.1328 | 0.0614 | 0.0240 | 0.0204 | 7.8 |
| | | 600 | | 0.1109 | 0.0239 | 0.0168 | 0.0094 | 7.7 |
| | | 700 | | 0.0977 | 0.0465 | 0.0248 | 0.0106 | 7.2 |

546.41
 NB 2998
 MAR/5
 TH

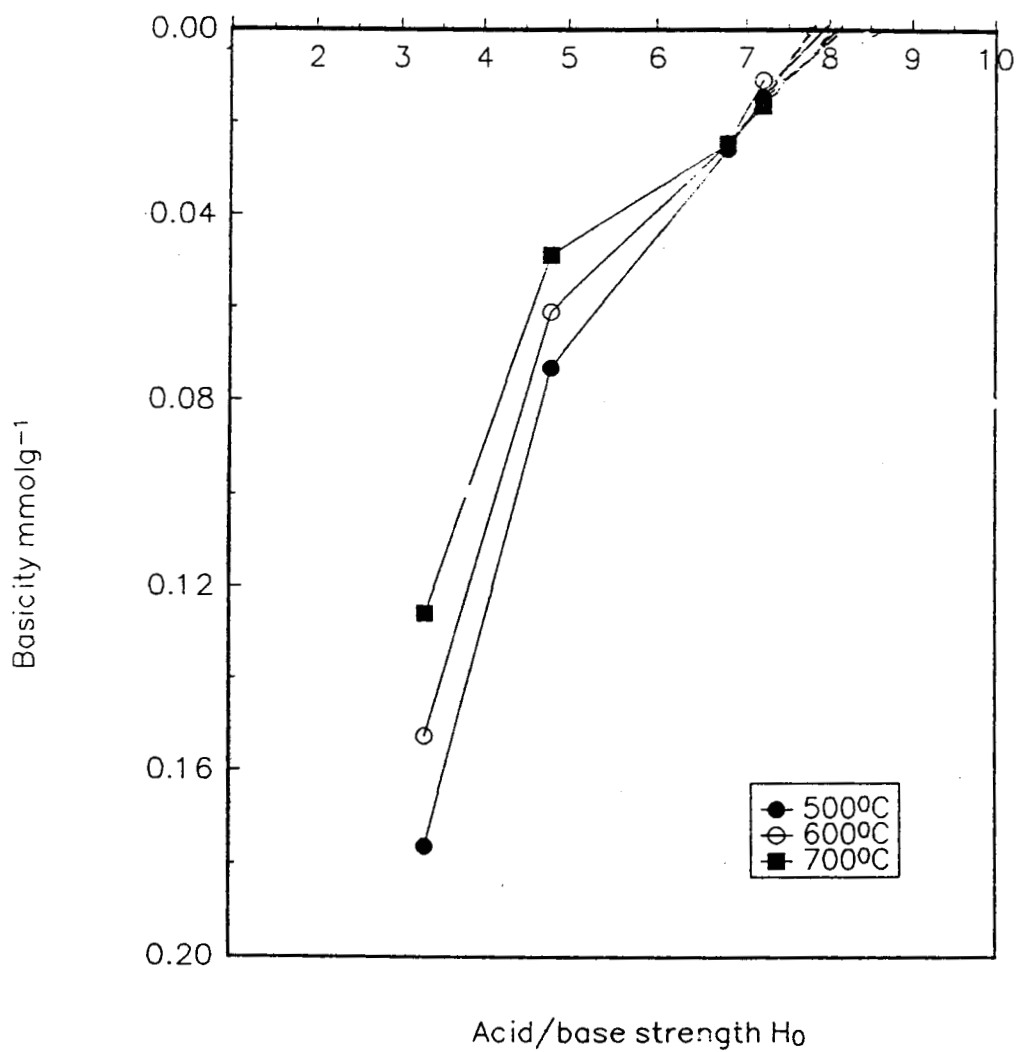


Fig. 3.19. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 20$; p.s. 106-125 microns)

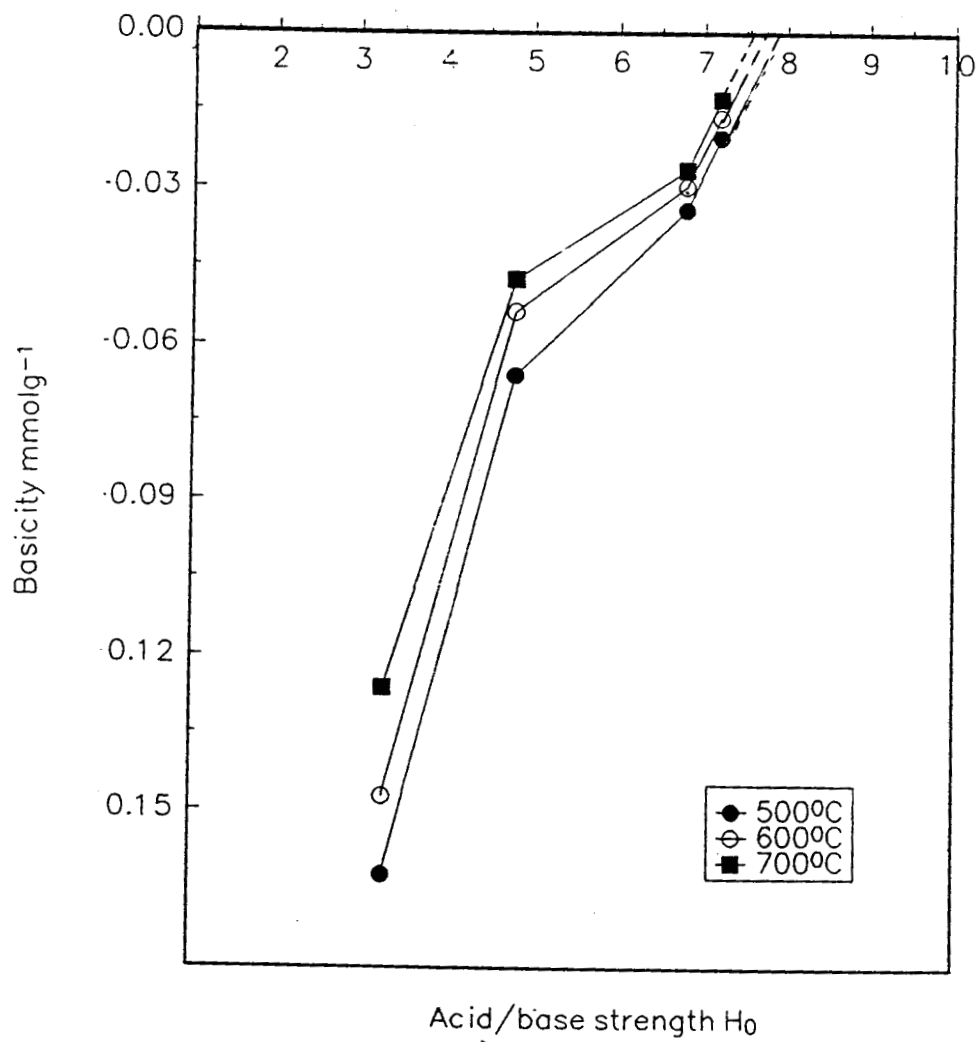


Fig. 3.20. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 40$; p.s. 106-125 microns)

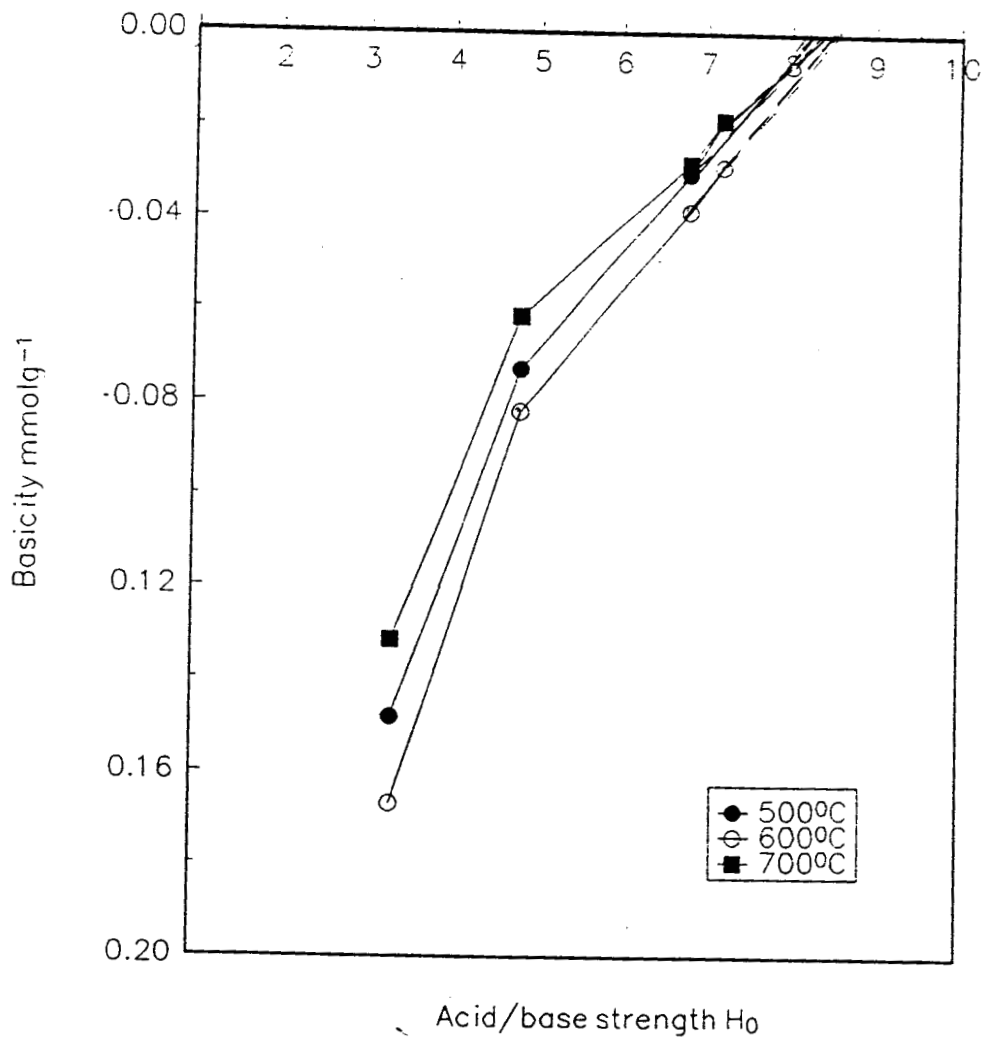


Fig. 3.21. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 60$; p.s. 106-125 microns)

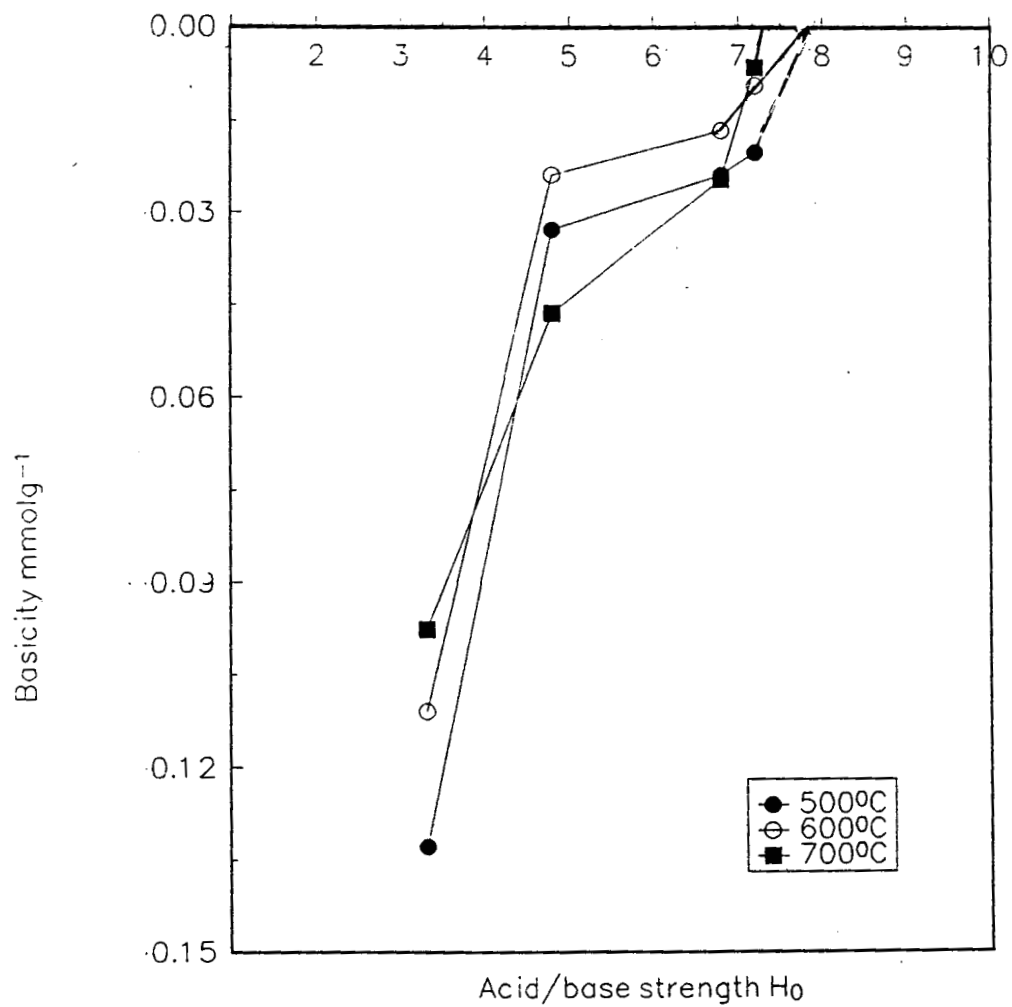


Fig. 3.22. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 80$; p.s. 106-125 microns),

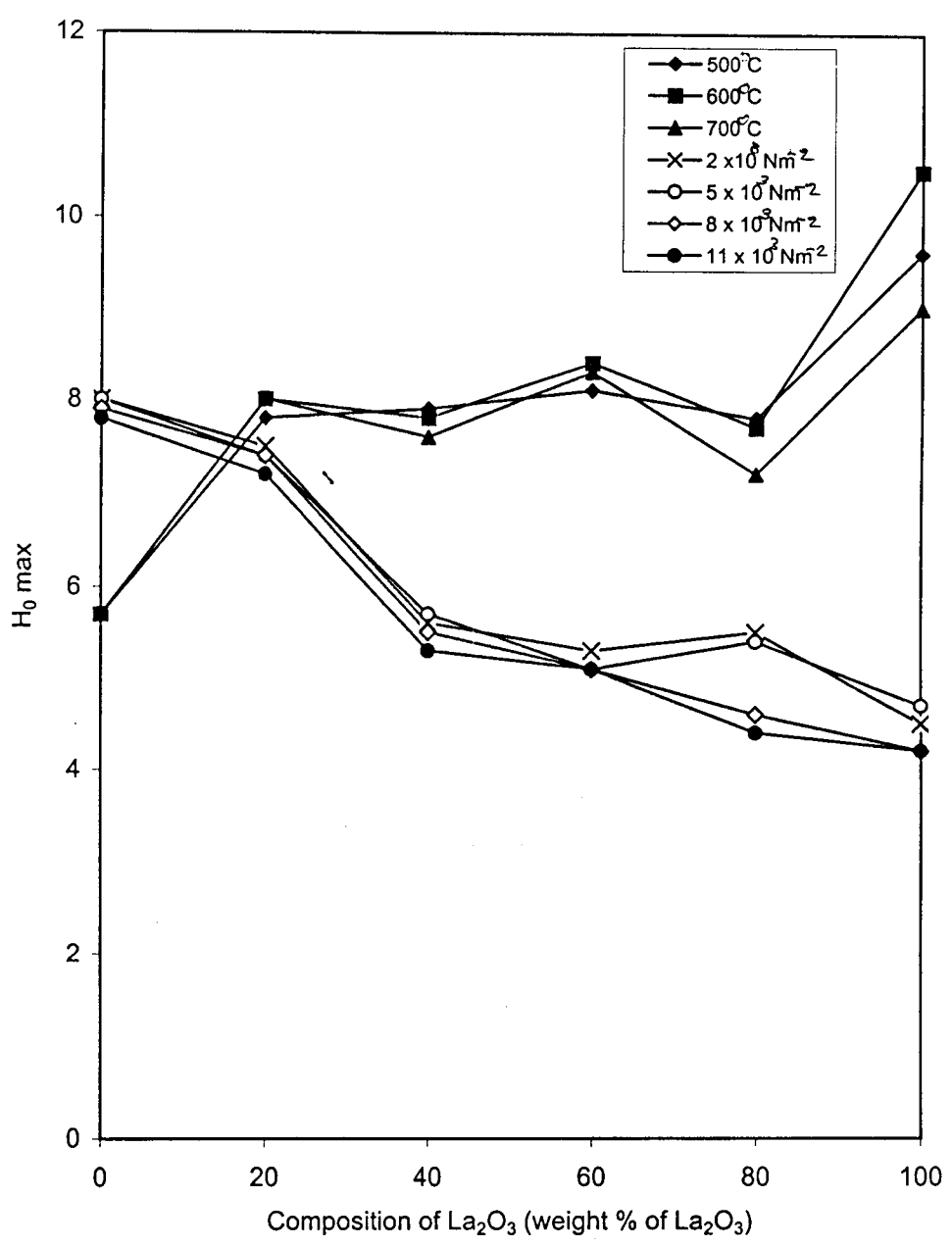


Fig 3.23 $H_0 \text{ max}$ Vs composition of $\text{La}_2\text{O}_3 - \text{Al}_2\text{O}_3$

TABLE 3.4

Surface Acidity/basicity of mixed oxides of Gadolinium-Aluminium activated at different temperatures

Particle size 106-125 microns

| Sl. No. | Percentage by weight of Gd ₂ O ₃ | Temp. of Activation °C | Surface area m ² g ⁻¹ | Basicity mmol g ⁻¹ | | | | H _{0max} |
|---------|--|------------------------|---|-------------------------------|--------------------|--------------------|--------------------|-------------------|
| | | | | H ₀ 3.3 | H ₀ 4.8 | H ₀ 6.8 | H ₀ 7.2 | |
| 1. | 20 | 500 | 175.9 | 0.0741 | 0.0512 | 0.0172 | 0.0162 | 8.1 |
| | | 600 | | 0.1084 | 0.0645 | 0.0188 | 0.0145 | 8.2 |
| | | 700 | | 0.1049 | 0.069 | 0.0209 | 0.0073 | 7.4 |
| 2. | 40 | 500 | 129.5 | 0.1298 | 0.0840 | 0.0328 | 0.0120 | 7.3 |
| | | 600 | | 0.1364 | 0.0872 | 0.2635 | 0.0109 | 7.3 |
| | | 700 | | 0.1260 | 0.0650 | 0.0247 | 0.0025 | 7.2 |
| 3. | 60 | 500 | 82.9 | 0.1071 | 0.0670 | 0.0321 | 0.0120 | 7.3 |
| | | 600 | | 0.1338 | 0.0821 | 0.0344 | 0.0289 | 8.5 |
| | | 700 | | 0.1211 | 0.0558 | 0.0314 | 0.0117 | 7.3 |
| 4. | 80 | 500 | 72.1 | 0.0854 | 0.0307 | 0.0175 | 0.0145 | 8.4 |
| | | 600 | | 0.0773 | 0.0385 | 0.0037 | 0.0134 | 7.7 |
| | | 700 | | 0.0703 | 0.0381 | 0.0213 | 0.0154 | 7.7 |

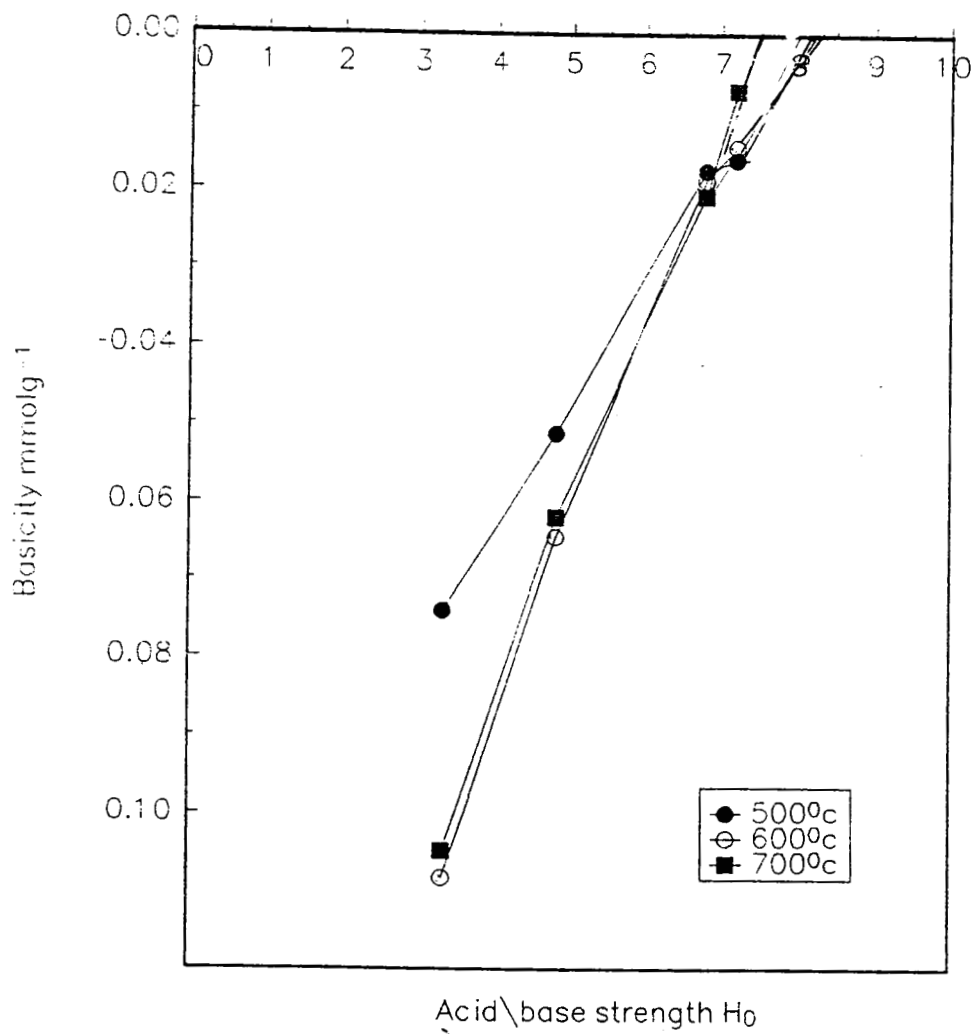


Fig. 3.24. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 20$; p.s. 106-125 microns)

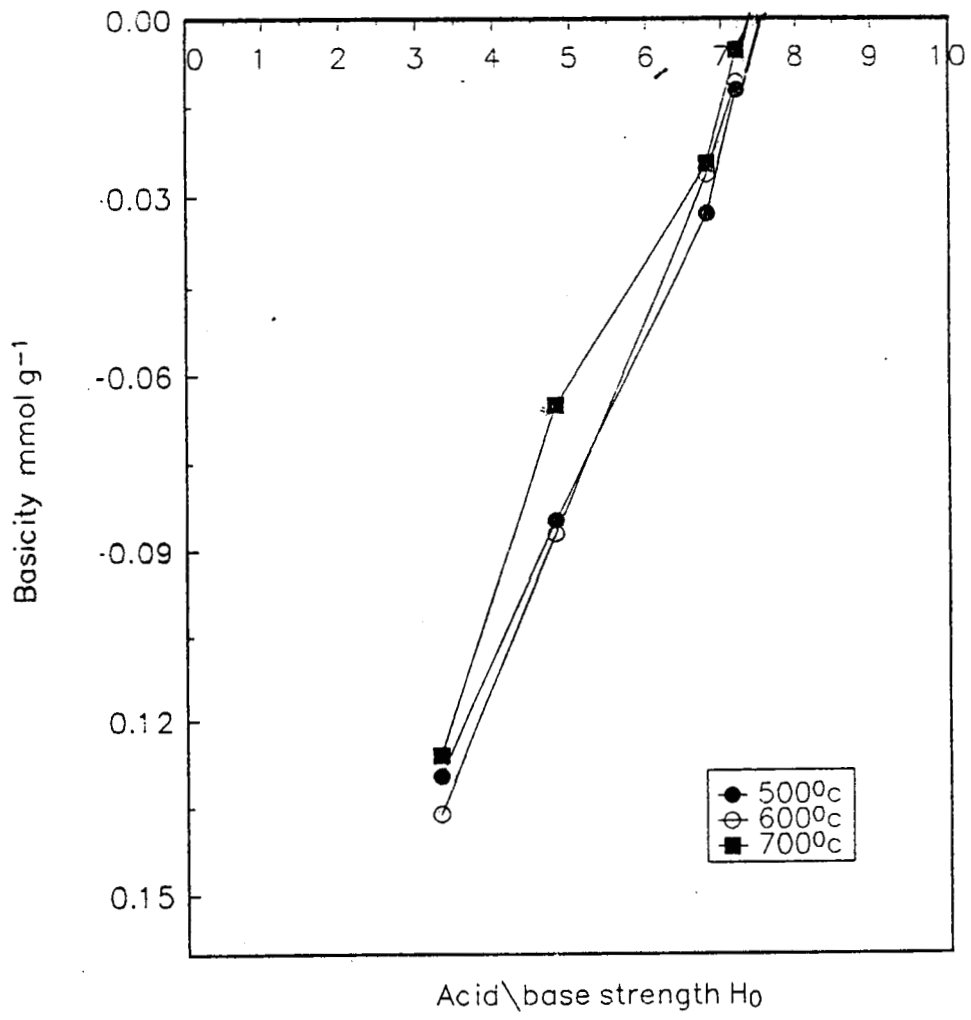


Fig. 3.25. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 40$; p.s. 106-125 microns)

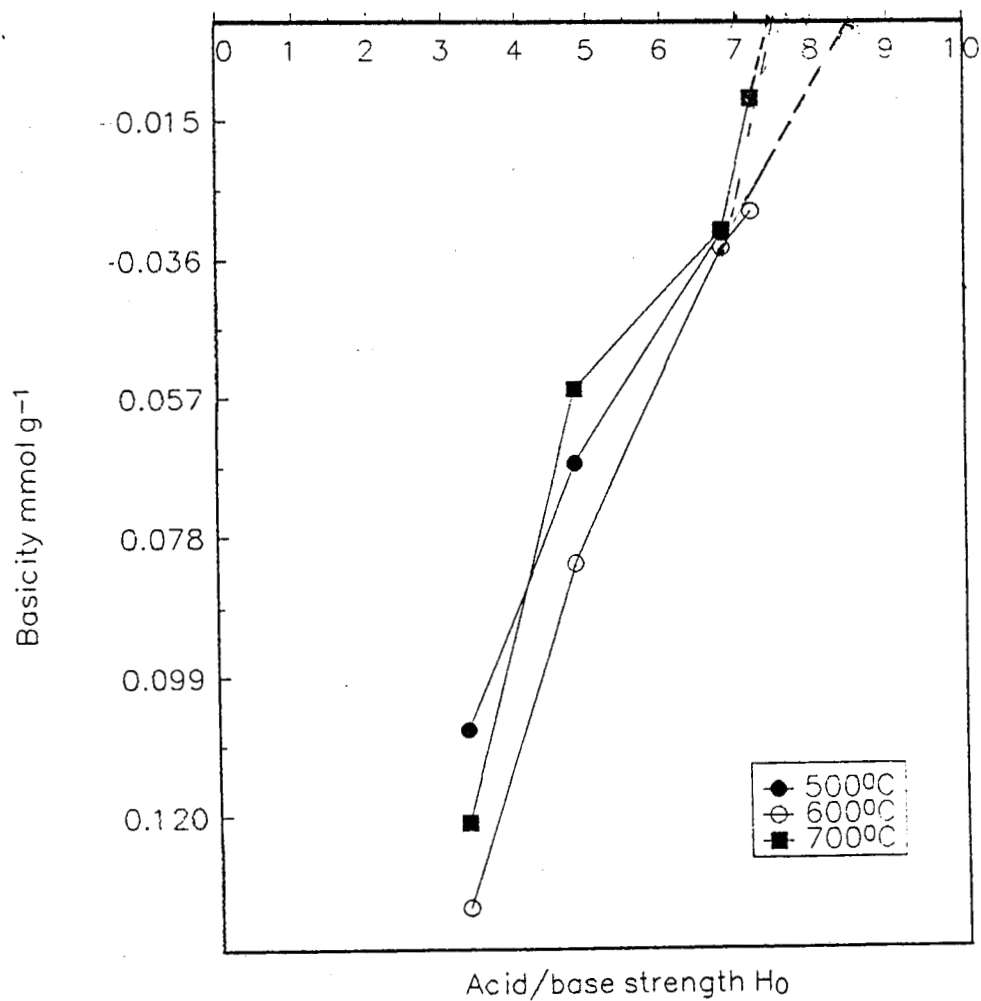


Fig. 3.26. Surface acidity/basicity of Gd₂O₃-Al₂O₃ mixed oxide (wt. % of Gd₂O₃ = 60; p.s. 106-125 microns)

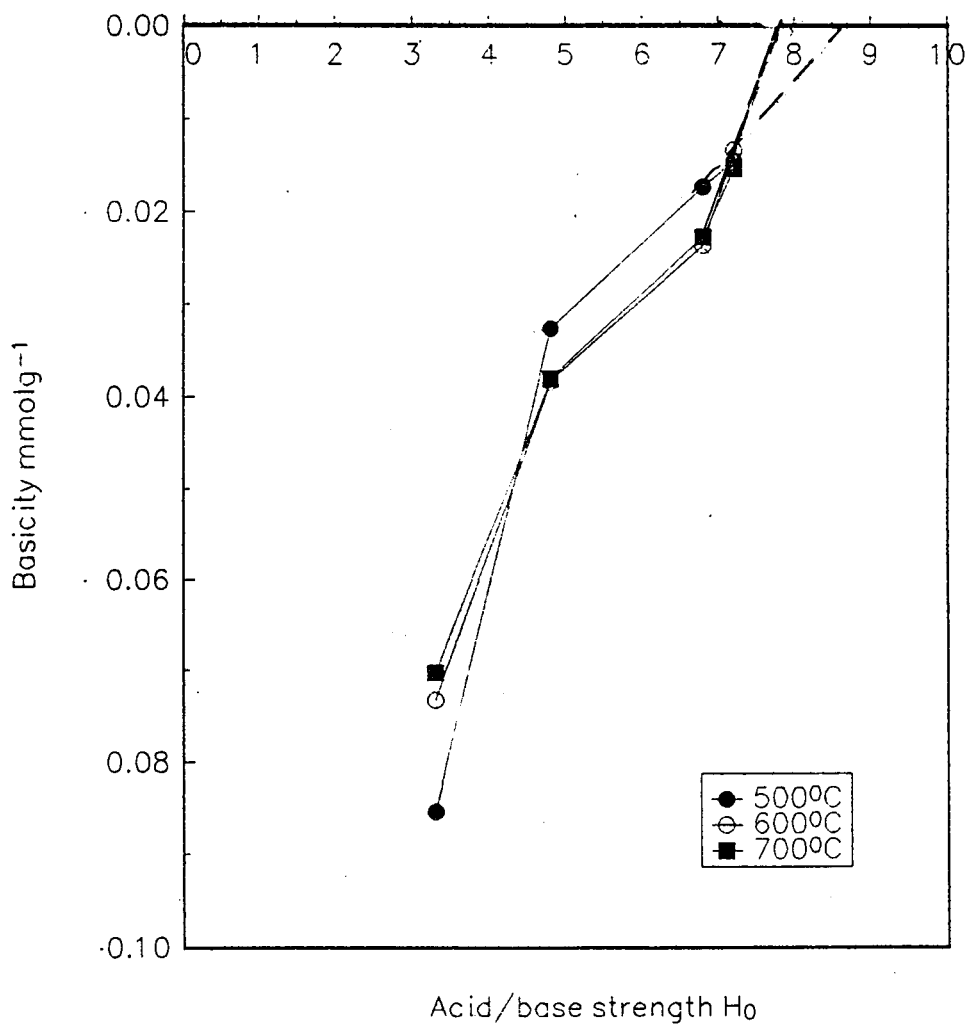


Fig. 3.27. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 80$; p.s. 106-125 microns)

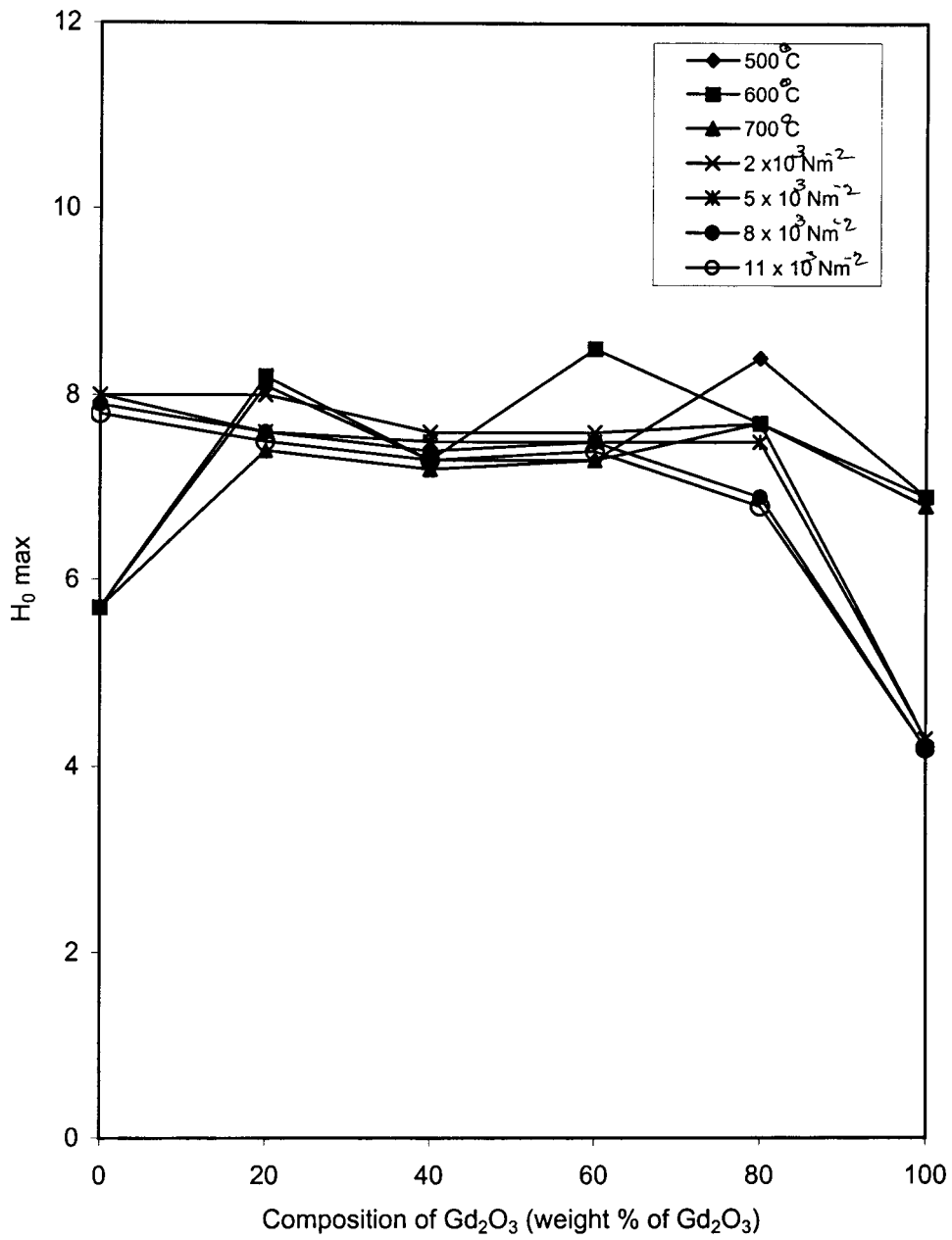


Fig. 3.28 $H_0 \text{ max}$ Vs composition of $\text{Gd}_2\text{O}_3 - \text{Al}_2\text{O}_3$

surface of alumina. The basicity of mixed oxides were higher than that of Gd_2O_3 . The mixed oxide system with 60% Gd_2O_3 by weight showed maximum basic strength of 8.5 at 600°C (Fig. 3.28).

The charge imbalance produced in Gd-O-Al bond was responsible for this observation. The low co-ordinated O^{2-} ions determined the amount of basic sites. The basic sites were due to weakly basic surface OH - groups and strongly basic O^{2-} centres. The characteristic basic sites estimated by titration method were contributed by Lewis and Bronsted sites. The surface hydroxyls on metal oxides were shown to differ in chemical properties and the difference in acidity/basicity of the hydroxyl groups of oxide surfaces were due to different electron donor properties of these groups on metal oxide surface [195]. The generation of new acid-base sites on metal oxides differ from those of component single oxides.

3.3.3. Dysprosia - Alumina mixed oxide system

The amount of acid/base sites were determined corresponding to different H_0 values at various activation temperatures and the values were represented in Table 3.5 and Fig 3.29 to 3,33. The effect of incorporation of dysprosia with alumina is as predicted in the case of lanthnum oxide and gadolinium oxide. The maximum basic strength was shown by the system containing 60% by weight of Dy_2O_3 (Fig. 3.33). The electronegativity of dysprosium oxide is less than that of alumina and the binary oxide system including dysprosium were more basic than

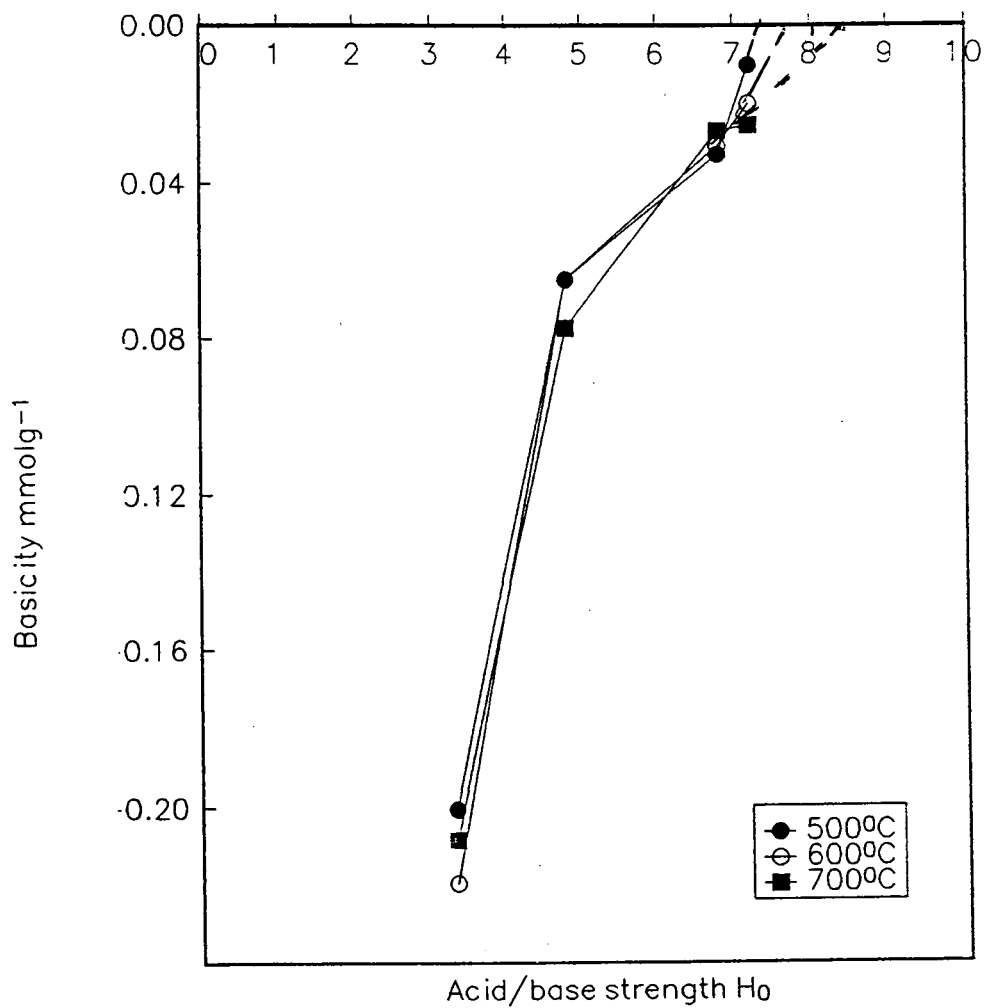


Fig. 3.29. Surface acidity/basicity of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Dy}_2\text{O}_3 = 20$; p.s. 106-125 microns)

TABLE 3.5

Surface Acidity/basicity of mixed oxides of Dysprosium and Aluminium activated at different temperatures

Particle size : 106-125 microns

| Sl. No. | Percentage of weight of Dy ₂ O ₃ | Temp. of Activation °C | Surface area m ² g ⁻¹ | Basicity mmol g ⁻¹ | | | | H _{0max} |
|---------|--|------------------------|---|-------------------------------|--------------------|--------------------|--------------------|-------------------|
| | | | | H ₀ 3.3 | H ₀ 4.8 | H ₀ 6.8 | H ₀ 7.2 | |
| 1. | 20 | 500 | 230.0 | 0.2006 | 0.0652 | 0.0329 | 0.0101 | 7.2 |
| | | 600 | | 0.2196 | 0.0651 | 0.0307 | 0.0198 | 7.6 |
| | | 700 | | 0.2084 | 0.0777 | 0.0269 | 0.0254 | 8.2 |
| 2. | 40 | 500 | 144.9 | 0.1416 | 0.0272 | 0.0230 | 0.0124 | 7.9 |
| | | 600 | | 0.1637 | 0.0718 | 0.0252 | 0.0179 | 8.0 |
| | | 700 | | 0.1451 | 0.0401 | 0.0171 | 0.0102 | 8.0 |
| 3. | 60 | 500 | 100 | 0.1259 | 0.0292 | 0.0207 | 0.0175 | 8.8 |
| | | 600 | | 0.1400 | 0.0530 | 0.0266 | 0.0952 | 8.6 |
| | | 700 | | 0.1339 | 0.0471 | 0.0146 | 0.0096 | 7.7 |
| 4. | 80 | 500 | 59.5 | 0.2048 | 0.0377 | 0.0177 | 0.0155 | 8.5 |
| | | 600 | | 0.2153 | 0.0441 | 0.0155 | 0.0088 | 7.8 |
| | | 700 | | 0.1744 | 0.0307 | 0.0162 | 0.0105 | 8.0 |

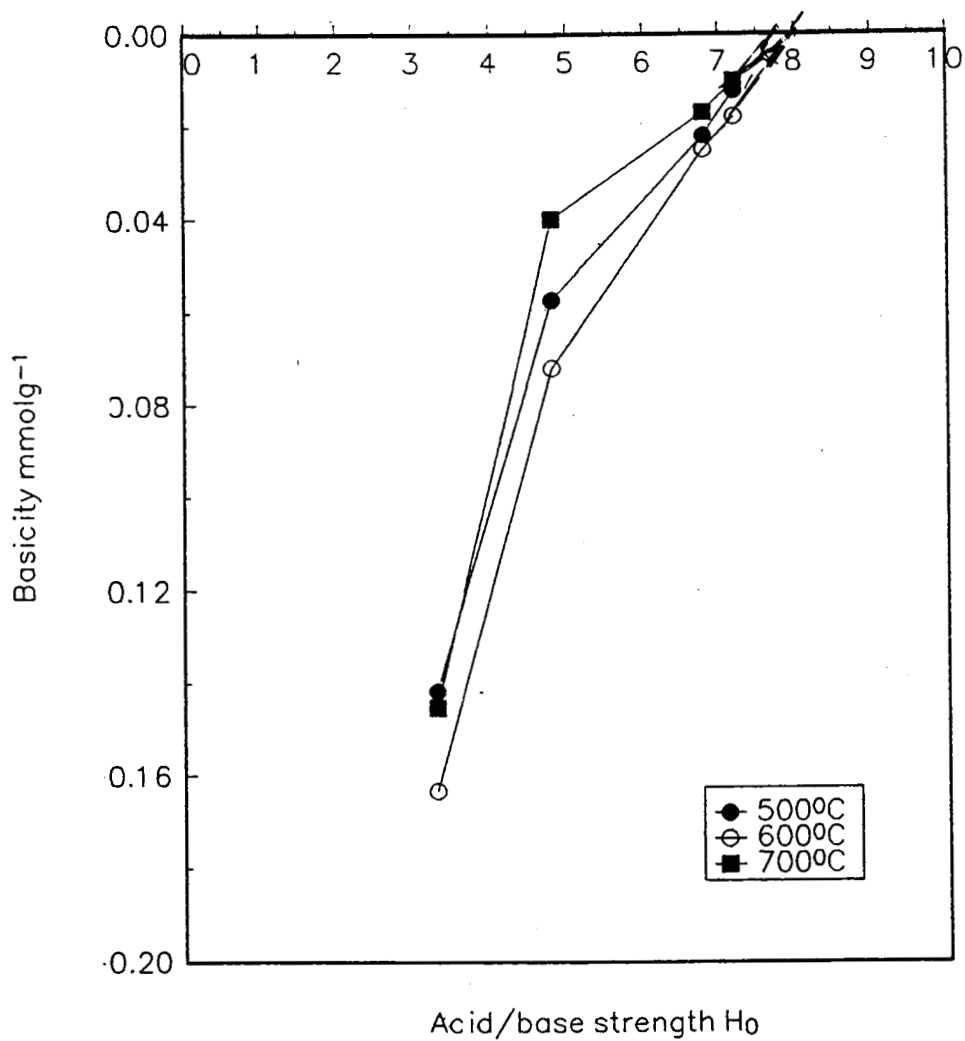


Fig. 3.30. Surface acidity/basicity of Dy₂O₃-Al₂O₃ mixed oxide (wt. % of Dy₂O₃ = 40; p.s. 106-125 microns)

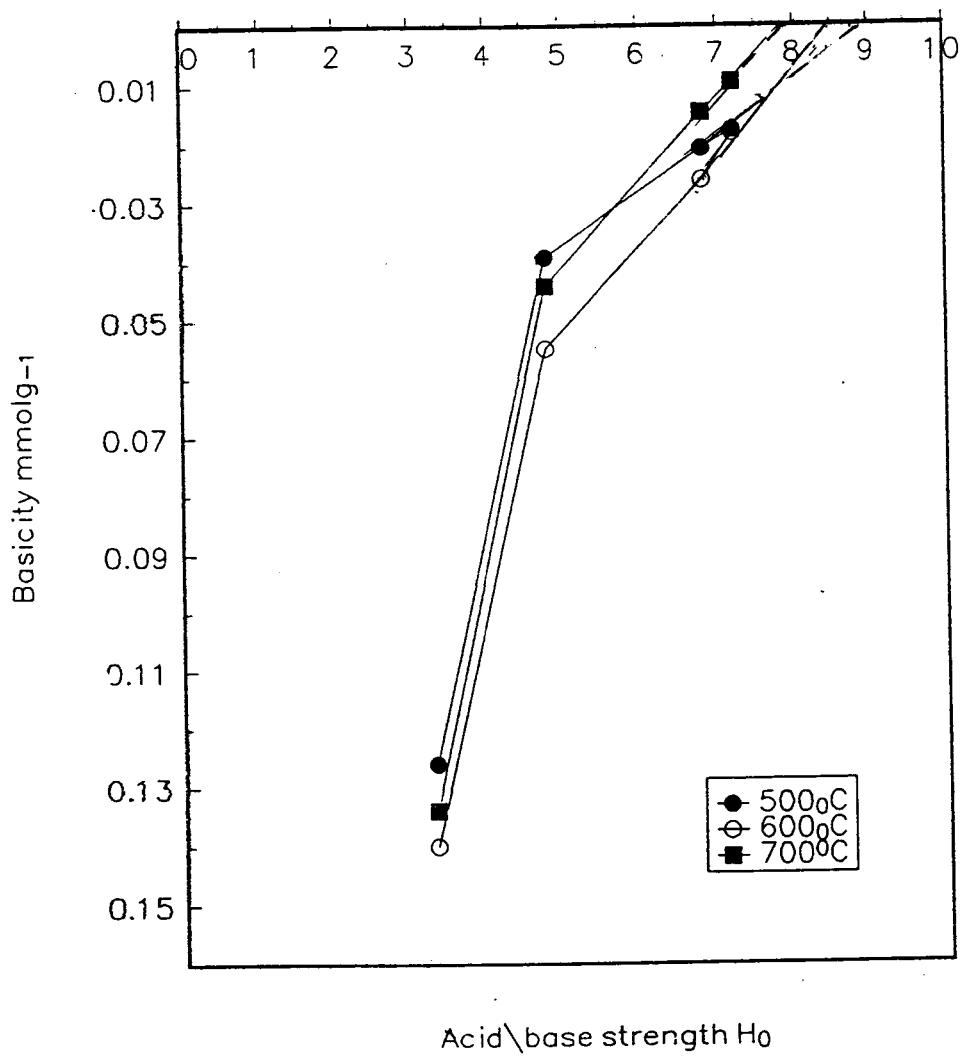


Fig. 3.31. Surface acidity/basicity of Dy₂O₃-Al₂O₃ mixed oxide (wt. % of Dy₂O₃ = 60; p.s. 106-125 microns)

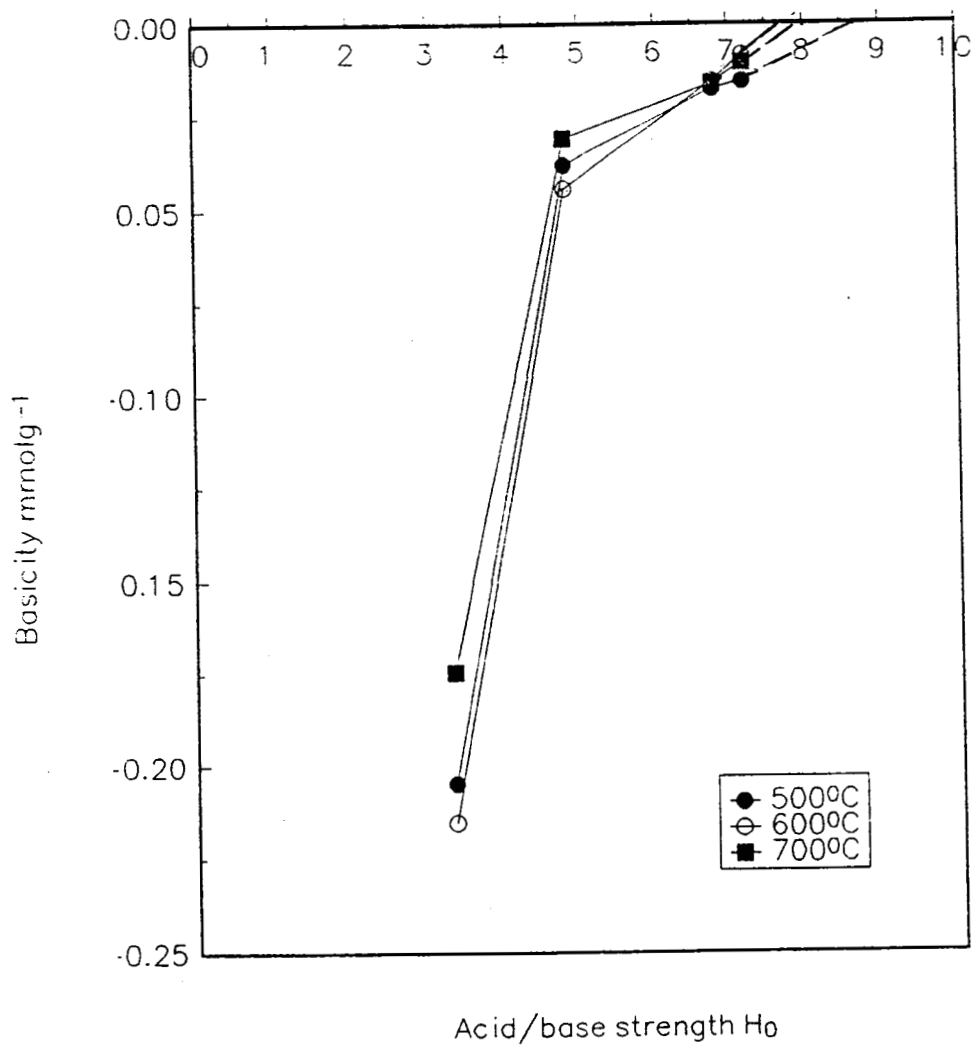


Fig. 3.32. Surface acidity/basicity of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Dy}_2\text{O}_3 = 80$; p.s. 106-125 microns)

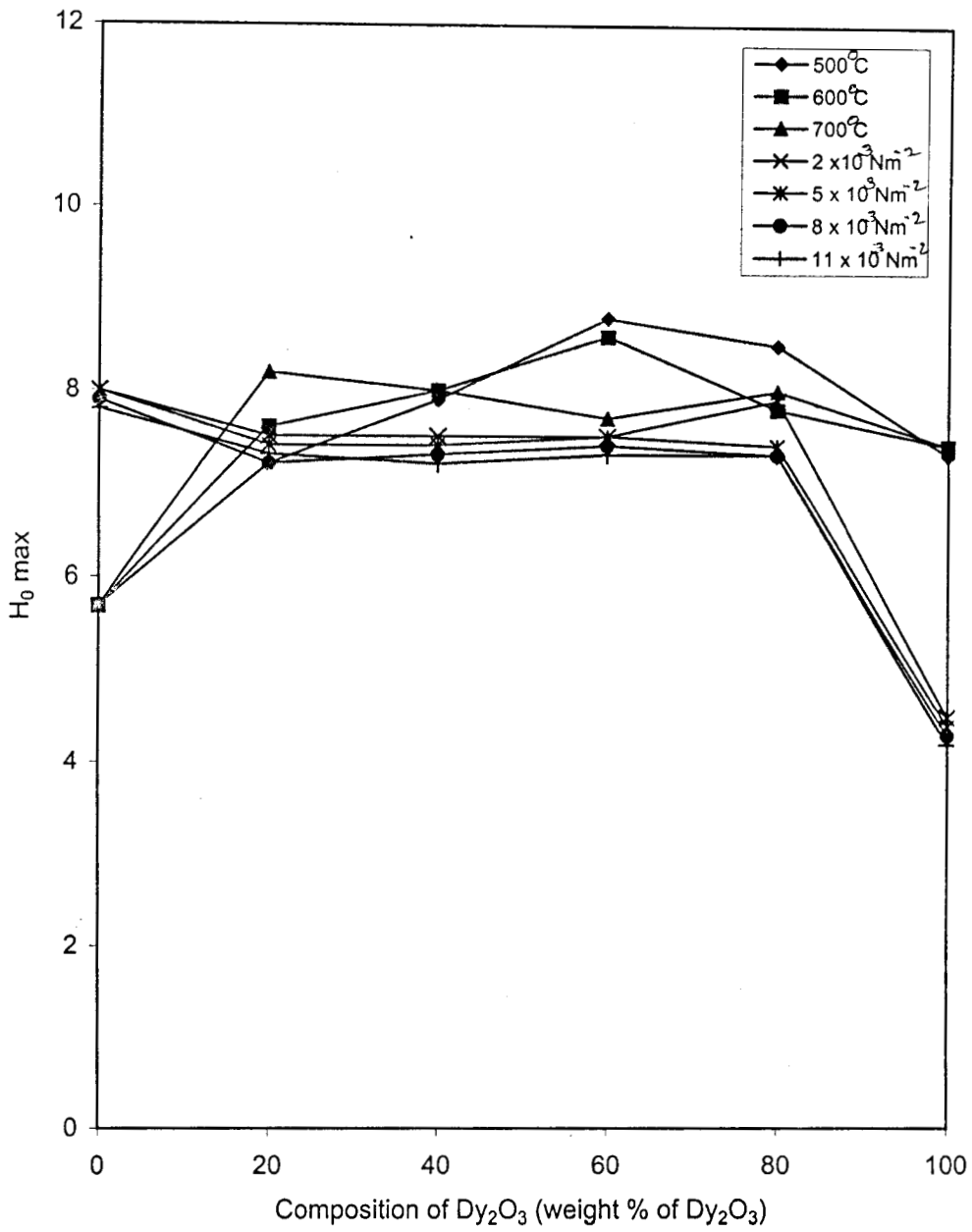


Fig. 3.33 $H_0 \text{ max}$ Vs Composition of $\text{Dy}_2\text{O}_3 - \text{Al}_2\text{O}_3$

alumina. XRD studies (Fig. 3.16 - 3.18) established the amorphous nature of binary oxide systems indicating the well dispersed state of ions on the mixed oxide surface systems. The charge imbalance localised on Dy-O-Al bonds were responsible for the surface basicity. This was due to the surface hydroxyl groups or trapped electron centres. At higher temperatures the trapped electron on the surface acts as basic sites. The surface area decreased as the weight percentage of dysprosia was increased (Table 3.5).

3.3.4. Effect of precompression on binary oxides

The effect of pre-compression on binary oxides was not as obvious as in single oxides. The basicity was reduced and the H_{0max} was less than that of alumina and higher than that of lanthana. The values were given in Table 3.6, 3.7 and 3.8. The corresponding H_{0max} values were represented in Fig. 3.34 to 3.45. Precompression had almost the same effect on gadolina alumina and dysprosia - alumina mixed oxide systems. The H_{0max} was in between that of alumina and the rare earth metal oxides. Compression produced acidic sites in the three mixed oxide systems (Table 3.6, 3.7 and 3.8). This is clear from Fig. 3.23, 3.28 and 3.33; where a comparative study of H_{0max} values against composition of the rare earth oxides at various temperatures and precompression pressures were represented. The effect was more evident in the $La_2O_3 - Al_2O_3$ systems where acid sites with H_{0max} values 4.4 were present. This implies that the surface La-O-Al bonds were

TABLE 3.6

Surface Acidity/basicity of mixed oxides of Lanthanum and Aluminium precompressed to different pressures

Particle size : 106-125 microns

| Sl. No. | Composition of mixed oxides wt. % of La ₂ O ₃ | Precompression pressure Nm ⁻² | Basicity mmol g ⁻¹ | | | | Acidity mmol g ⁻¹ | | | H ₀ max |
|---------|---|--|-------------------------------|--------------------|--------------------|--------------------|------------------------------|--------------------|--------------------|--------------------|
| | | | H ₀ 3.3 | H ₀ 4.8 | H ₀ 6.8 | H ₀ 7.2 | H ₀ 4.8 | H ₀ 6.8 | H ₀ 7.2 | |
| 1. | 20 | 2x10 ³ | 0.1629 | 0.0745 | 0.0187 | 0.0122 | | | | 7.5 |
| | | 5x10 ³ | 0.1631 | 0.0734 | 0.0280 | 0.0121 | | | | 7.4 |
| | | 8x10 ³ | 0.1409 | 0.0440 | 0.0128 | 0.0090 | | | | 7.4 |
| | | 11x10 ³ | 0.1307 | 0.0382 | 0.0112 | 0.0072 | | | | 7.2 |
| 2. | 40 | 2x10 ³ | 0.1452 | 0.0290 | | | | 0.0452 | 0.0679 | 5.6 |
| | | 5x10 ³ | 0.1306 | 0.0245 | | | | 0.0341 | 0.0458 | 5.7 |
| | | 8x10 ³ | 0.0955 | 0.0204 | | | | 0.0399 | 0.0505 | 5.5 |
| | | 11x10 ³ | 0.0944 | 0.0165 | | | | 0.0456 | 0.0609 | 5.3 |
| 3. | 60 | 2x10 ³ | 0.1235 | 0.0272 | | | | 0.0894 | 0.0930 | 5.3 |
| | | 5x10 ³ | 0.1076 | 0.0164 | | | | 0.0838 | 0.0968 | 5.1 |
| | | 8x10 ³ | 0.0872 | 0.0125 | | | | 0.0868 | 0.0928 | 5.1 |
| | | 11x10 ³ | 0.0824 | 0.0101 | | | | 0.0784 | 0.0832 | 5.1 |
| 4. | 80 | 2x10 ³ | 0.1235 | 0.0272 | | | | 0.02740 | 0.0340 | 5.5 |
| | | 5x10 ³ | 0.1076 | 0.0164 | | | | 0.0271 | 0.0320 | 5.4 |
| | | 8x10 ³ | 0.0872 | | | | 0.0275 | 0.0281 | 0.0308 | 4.6 |
| | | 11x10 ³ | 0.0824 | | | | 0.0205 | 0.0401 | 0.0430 | 4.4 |

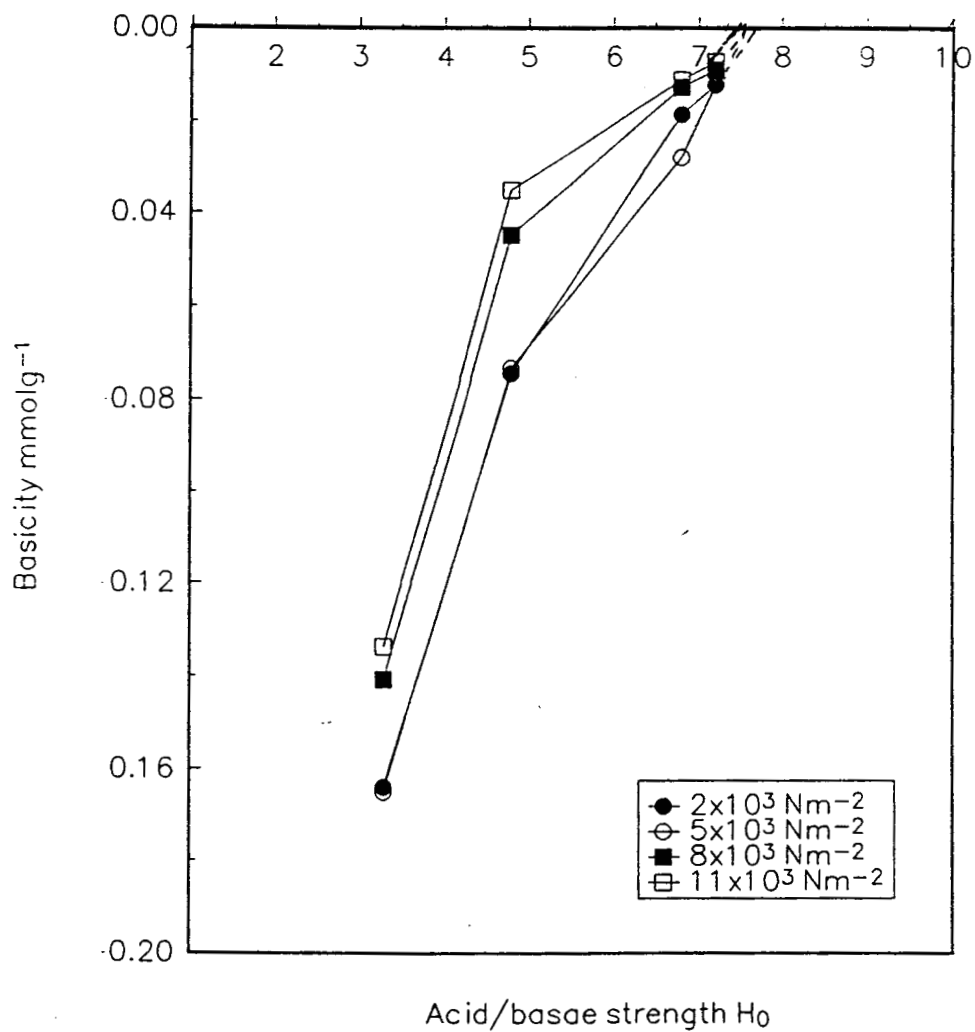


Fig. 3.34. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 20$; p.s. 106-125 microns)

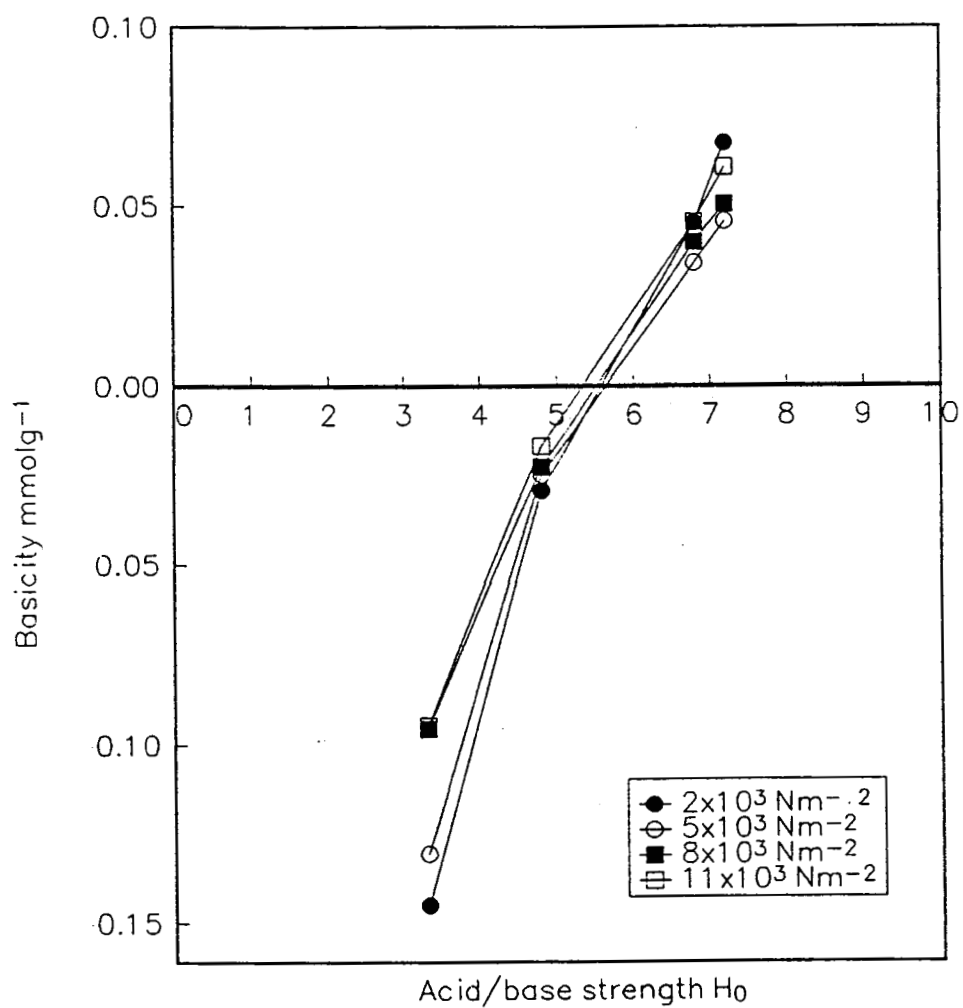


Fig. 3.35. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 40$; p.s. 106-125 microns)

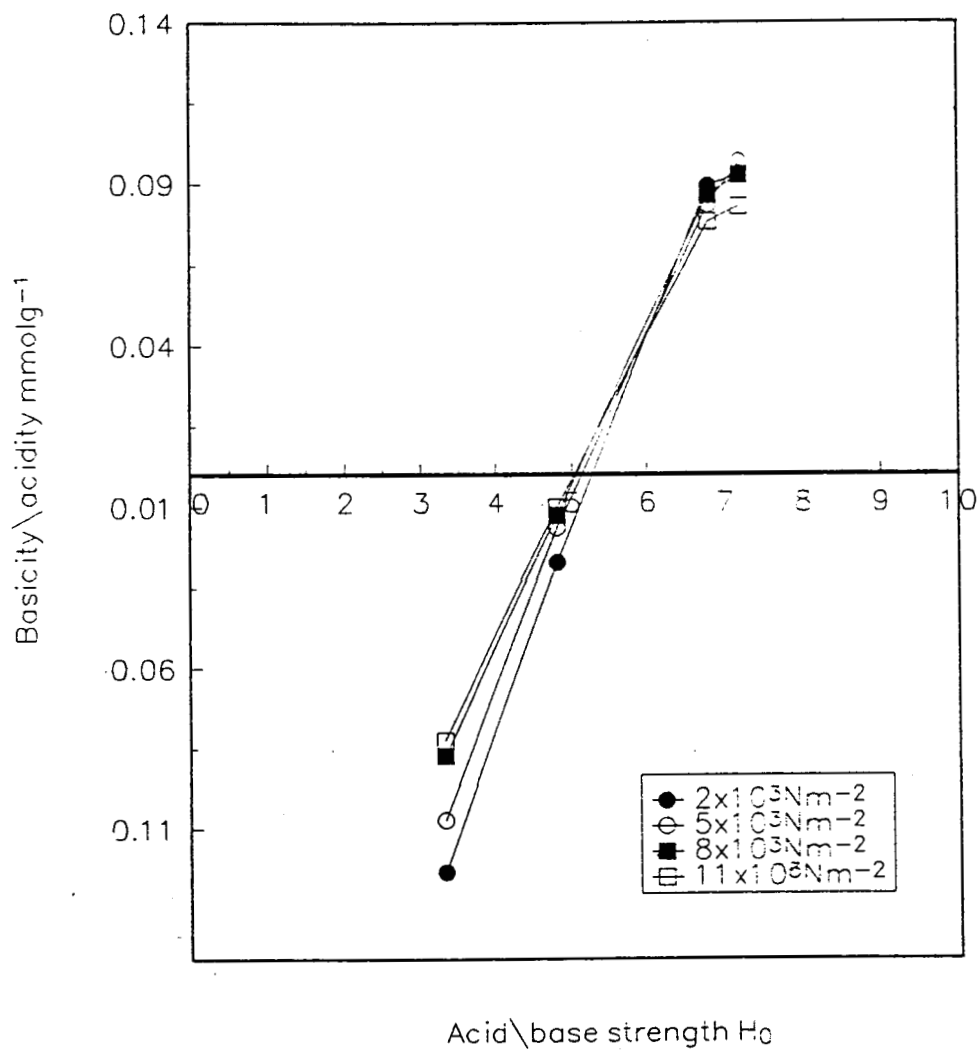


Fig. 3.36. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 60$; p.s. 106-125 microns)

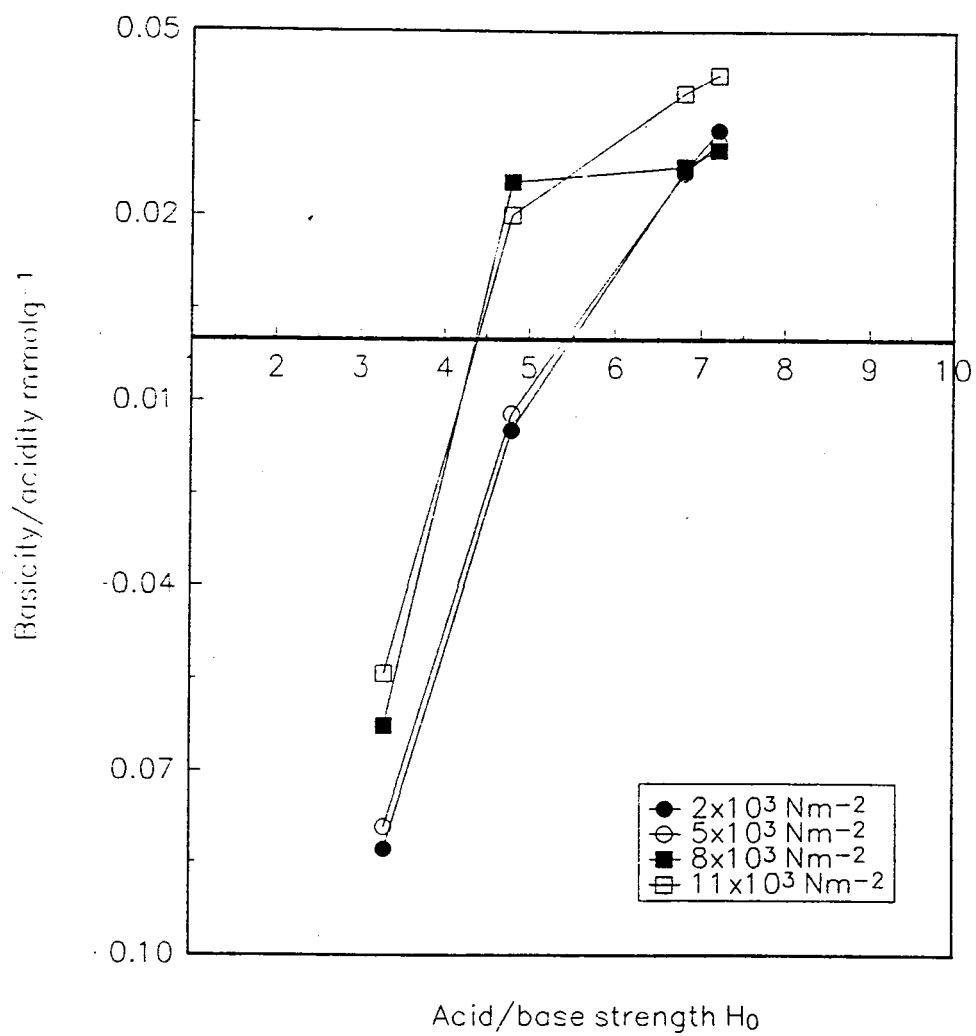


Fig. 3.37. Surface acidity/basicity of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{La}_2\text{O}_3 = 80$; p.s. 106-125 microns)

TABLE 3.7

Surface Acidity/basicity of Gadolinium - Aluminium mixed oxides Pre compressed to various pressures
Particle size 106 - 125 microns

| Composition of mixed oxides
Wt. % of Gd ₂ O ₃ | Precompression pressure Nm ⁻² | Basicity mmol g ⁻¹ | | | | Acidity mmol g ⁻¹ | H _o max |
|--|--|-------------------------------|-----------------------|-----------------------|-----------------------|------------------------------|--------------------|
| | | H _o
3.3 | H _o
4.8 | H _o
6.8 | H _o
7.2 | H _o
7.2 | |
| 20 | 2 x 10 ³ | 0.0781 | 0.0451 | 0.0186 | 0.0128 | | 8.0 |
| | 5 x 10 ³ | 0.0702 | 0.0430 | 0.0153 | 0.0117 | | 7.8 |
| | 8 x 10 ³ | 0.0640 | 0.0402 | 0.0135 | 0.0090 | | 7.6 |
| | 11 x 10 ³ | 0.0570 | 0.0307 | 0.0114 | 0.0082 | | 7.5 |
| 40 | 2 x 10 ³ | 0.1064 | 0.0848 | 0.0106 | 0.0091 | | 7.6 |
| | 5 x 10 ³ | 0.0943 | 0.0789 | 0.0161 | 0.0077 | | 7.5 |
| | 8 x 10 ³ | 0.0891 | 0.0542 | 0.0154 | 0.0068 | | 7.4 |
| | 11 x 10 ³ | 0.0538 | 0.0464 | 0.0105 | 0.0045 | | 7.3 |
| 60 | 2 x 10 ³ | 0.1011 | 0.0448 | 0.0169 | 0.0093 | | 7.6 |
| | 5 x 10 ³ | 0.0870 | 0.0317 | 0.0094 | 0.0089 | | 7.5 |
| | 8 x 10 ³ | 0.0704 | 0.0309 | 0.01535 | 0.0090 | | 7.5 |
| | 11 x 10 ³ | 0.0643 | 0.0203 | 0.0120 | 0.0069 | | 7.4 |
| 80 | 2 x 10 ³ | 0.0653 | 0.0274 | 0.0167 | | | 7.7 |
| | 5 x 10 ³ | 0.0630 | 0.0248 | 0.0237 | 0.0091 | | 7.5 |
| | 8 x 10 ³ | 0.0622 | 0.0222 | 0.0063 | 0.0134 | 0.0239 | 6.9 |
| | 11 x 10 ³ | 0.0597 | 0.0220 | 0.0051 | | 0.0299 | |

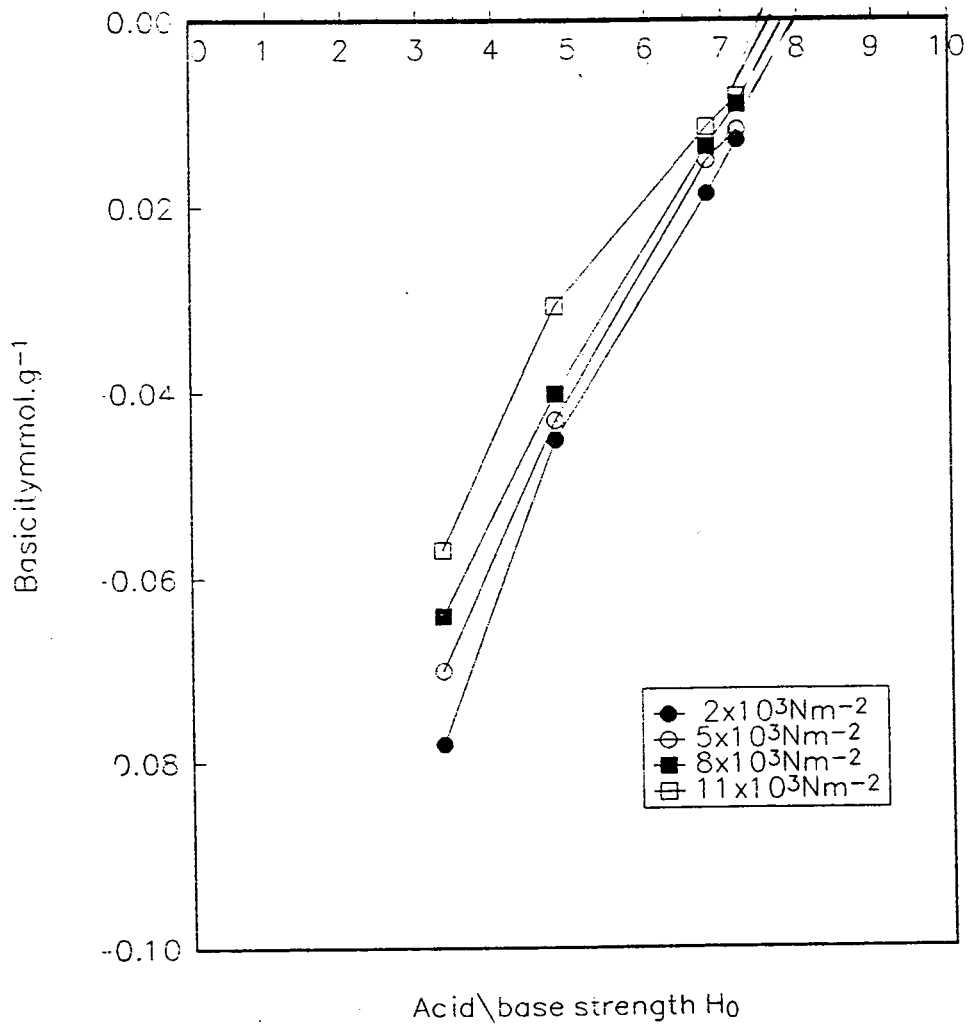


Fig. 3.38. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 20$; p.s. 106-125 microns)

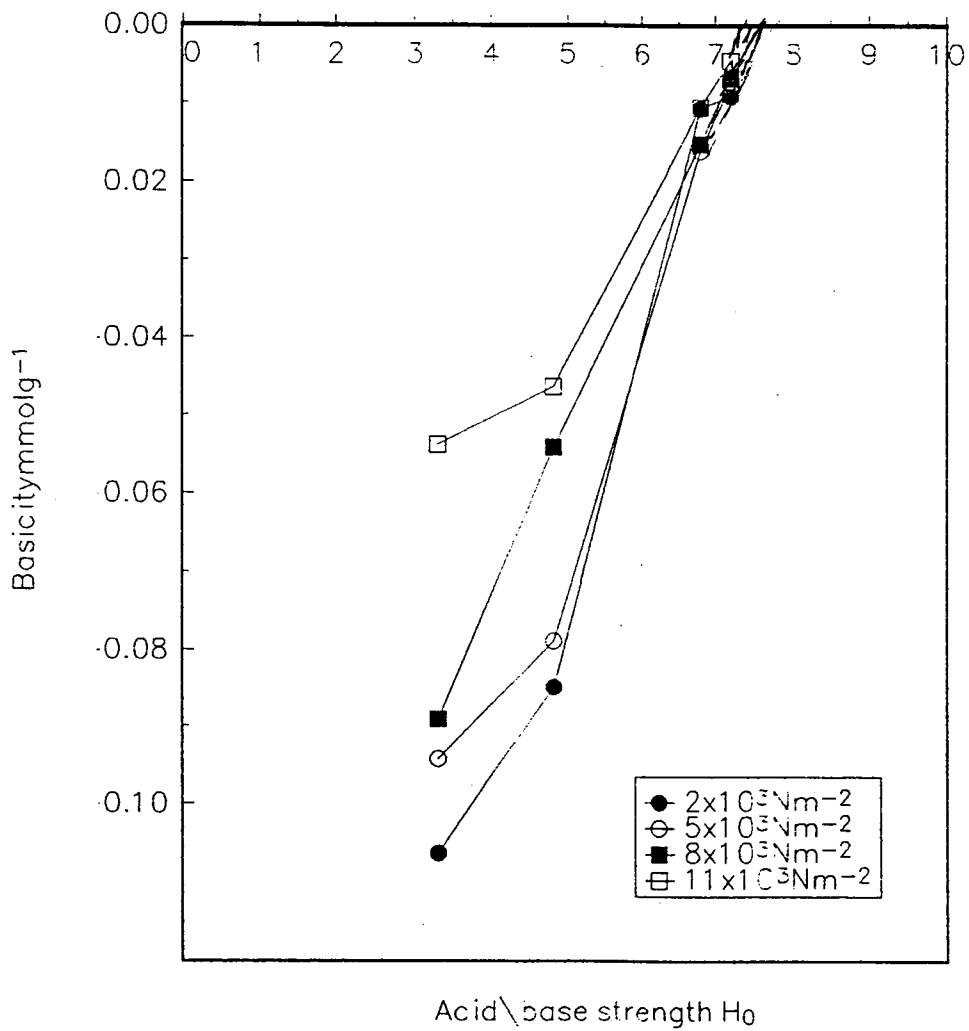


Fig. 3.39. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 40$; p.s. 106-125 microns)

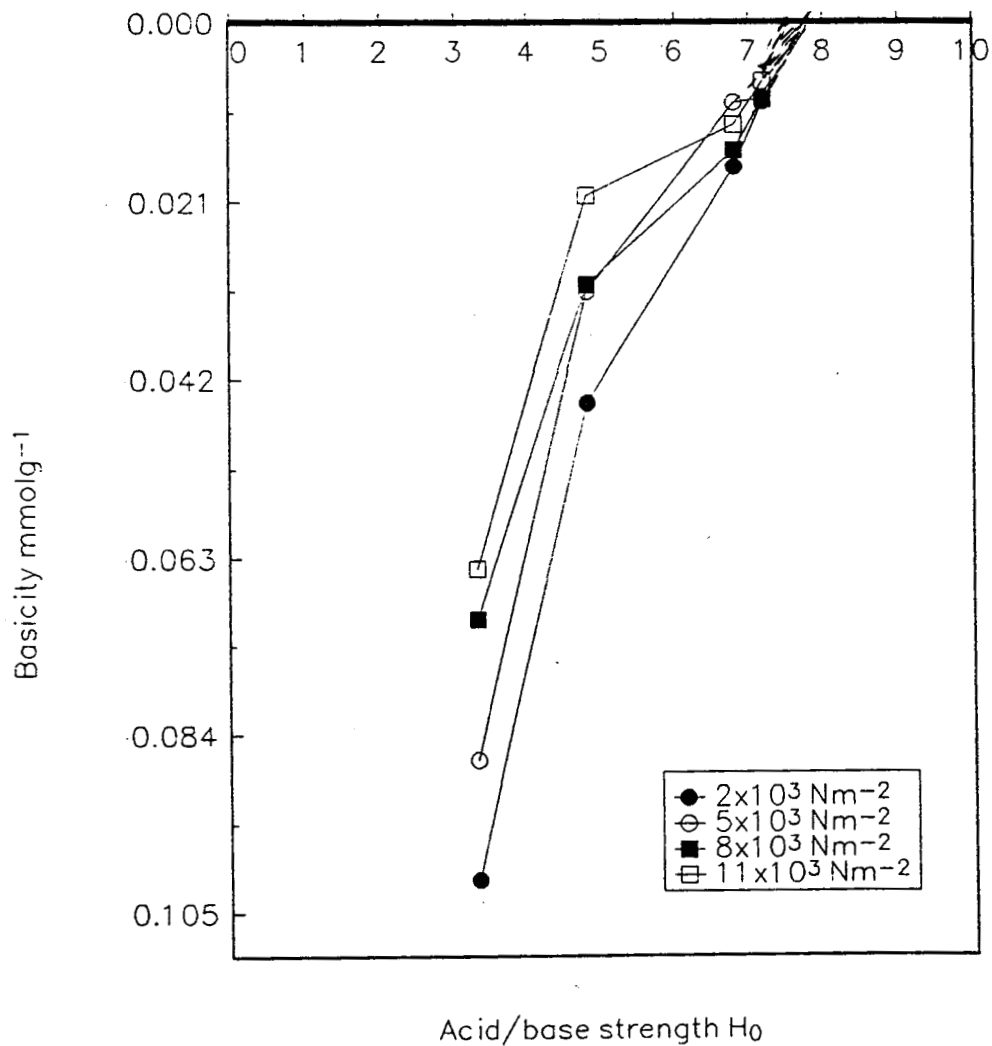


Fig. 3.40. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 60$; p.s. 106-125 microns)

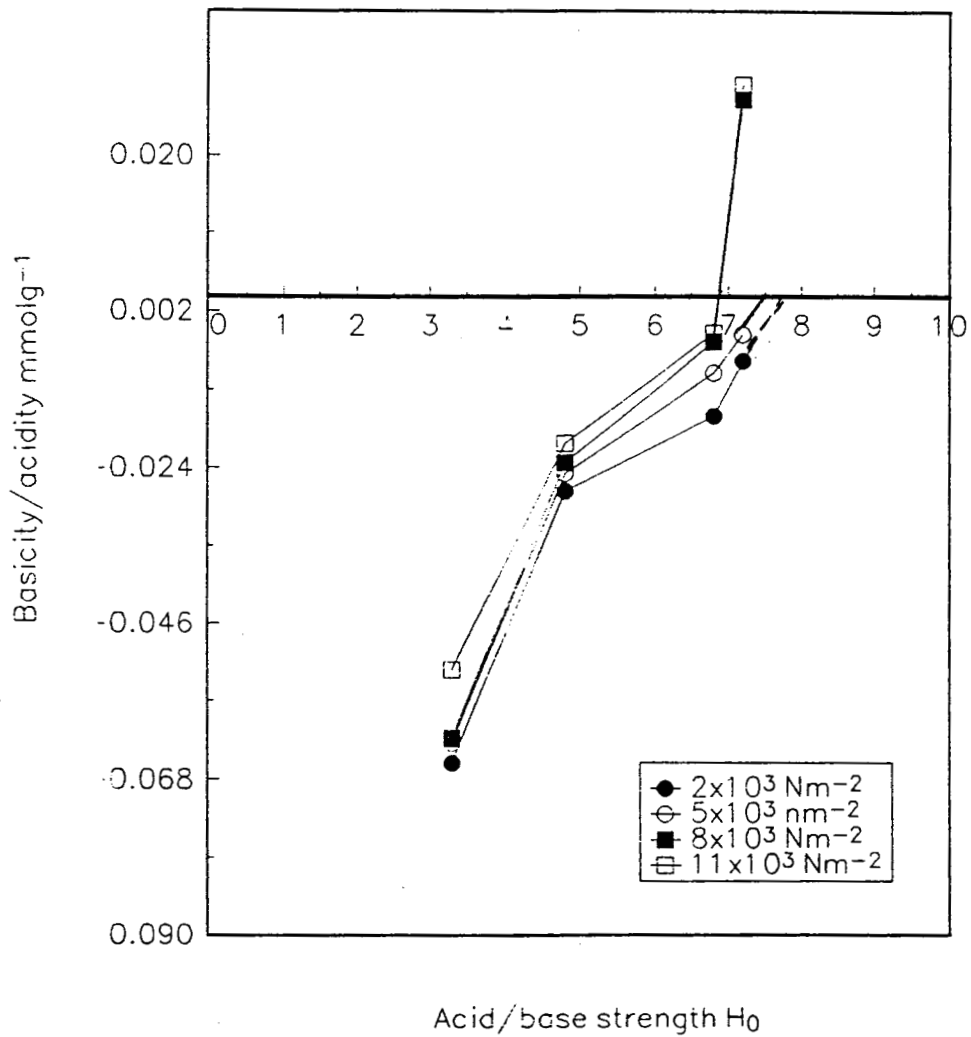


Fig. 3.41. Surface acidity/basicity of $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Gd}_2\text{O}_3 = 80$; p.s. 106-125 microns)

TABLE 3.8

Surface acidity/basicity of Dysprosium-Aluminium mixed oxide Pre compressed to various pressures

Particle size 106-125 microns

| Composition mixed oxides
Wt. % of Dy ₂ O ₃ | Precompression pressure
Nm ⁻² | Basicity mmol g ⁻¹ | | | | H ₀ max |
|---|---|-------------------------------|-----------------------|-----------------------|-----------------------|--------------------|
| | | H ₀
3:3 | H ₀
4.8 | H ₀
6.8 | H ₀
7.2 | |
| 20 | 2 x 10 ³ | 0.1554 | 0.0566 | 0.0184 | 0.0124 | 7.5 |
| | 5 x 10 ³ | 0.1425 | 0.02185 | 0.0105 | 0.0082 | 7.4 |
| | 8 x 10 ³ | 0.1005 | 0.0202 | 0.0127 | 0.0067 | 7.2 |
| | 11 x 10 ³ | 0.0676 | 0.0186 | 0.0120 | 0.0043 | 7.3 |
| 40 | 2 x 10 ³ | 0.1047 | 0.0387 | 0.0130 | 0.0063 | 7.5 |
| | 5 x 10 ³ | 0.0818 | 0.0305 | 0.0334 | 0.0052 | 7.4 |
| | 8 x 10 ³ | 0.0718 | 0.0248 | 0.0193 | 0.0050 | 7.3 |
| | 11 x 10 ³ | 0.0644 | 0.0274 | 0.0079 | 0.0030 | 7.2 |
| 60 | 2 x 10 ³ | 0.1250 | 0.0442 | 0.0103 | 0.0085 | 7.5 |
| | 5 x 10 ³ | 0.1273 | 0.0454 | 0.0108 | 0.0064 | 7.5 |
| | 8 x 10 ³ | 0.0932 | 0.0380 | 0.0092 | 0.0040 | 7.4 |
| | 11 x 10 ³ | 0.0802 | 0.0183 | 0.0060 | 0.0020 | 7.3 |
| 80 | 2 x 10 ³ | 0.1555 | 0.0263 | 0.0116 | 0.0071 | 7.9 |
| | 5 x 10 ³ | 0.1628 | 0.0214 | 0.0050 | -- | 7.4 |
| | 8 x 10 ³ | 0.1450 | 0.0350 | 0.0050 | -- | 7.3 |
| | 11 x 10 ³ | 0.1152 | 0.0158 | 0.0040 | -- | 7.3 |

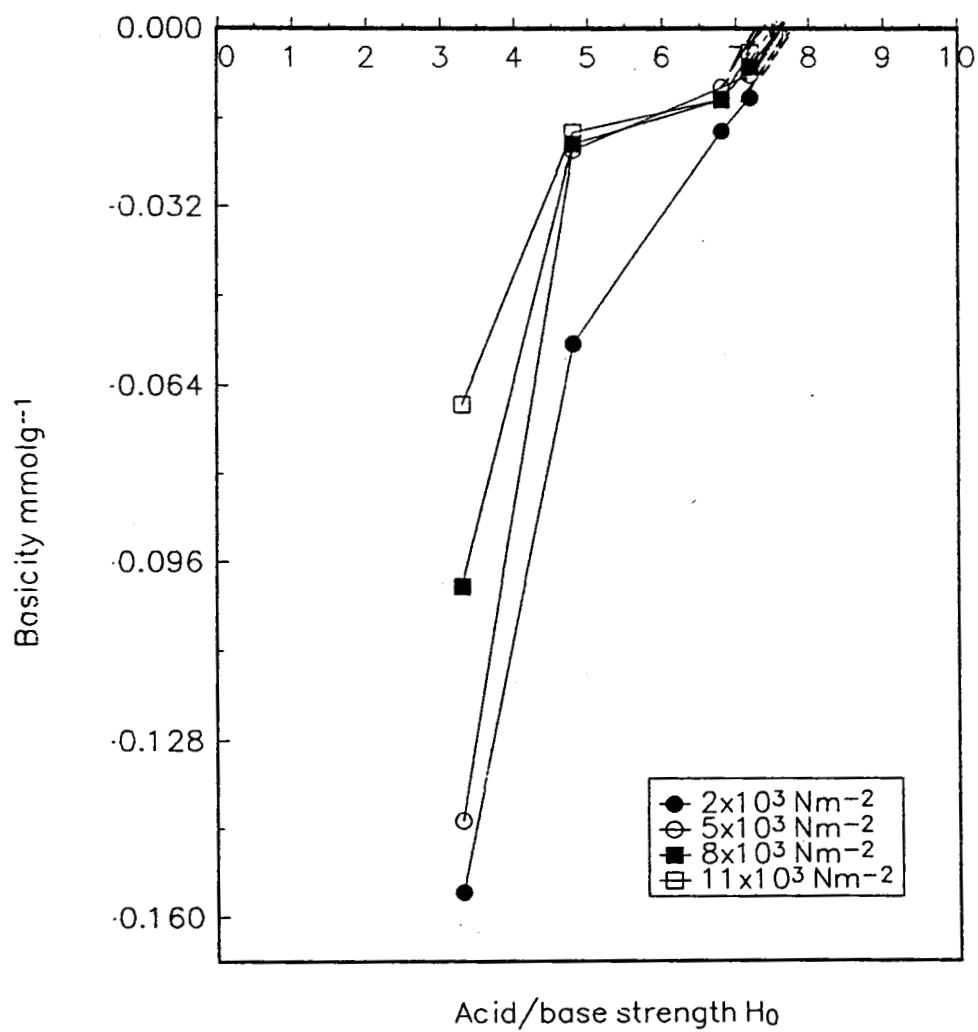


Fig. 3.42. Surface acidity/basicity of Dy₂O₃-Al₂O₃ mixed oxide (wt. % of Dy₂O₃ = 20; p.s. 106-125 microns)

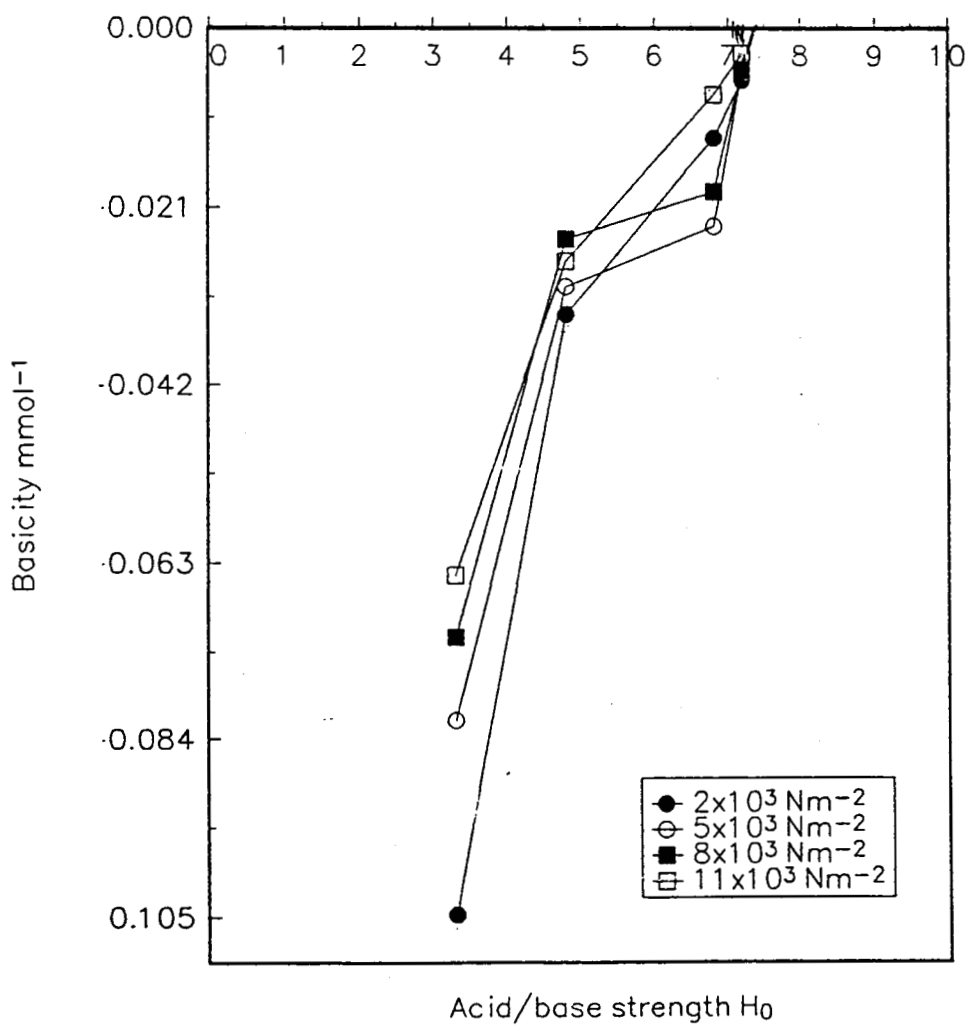


Fig. 3.43. Surface acidity/basicity of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Dy}_2\text{O}_3 = 40$; p.s. 106-125 microns)

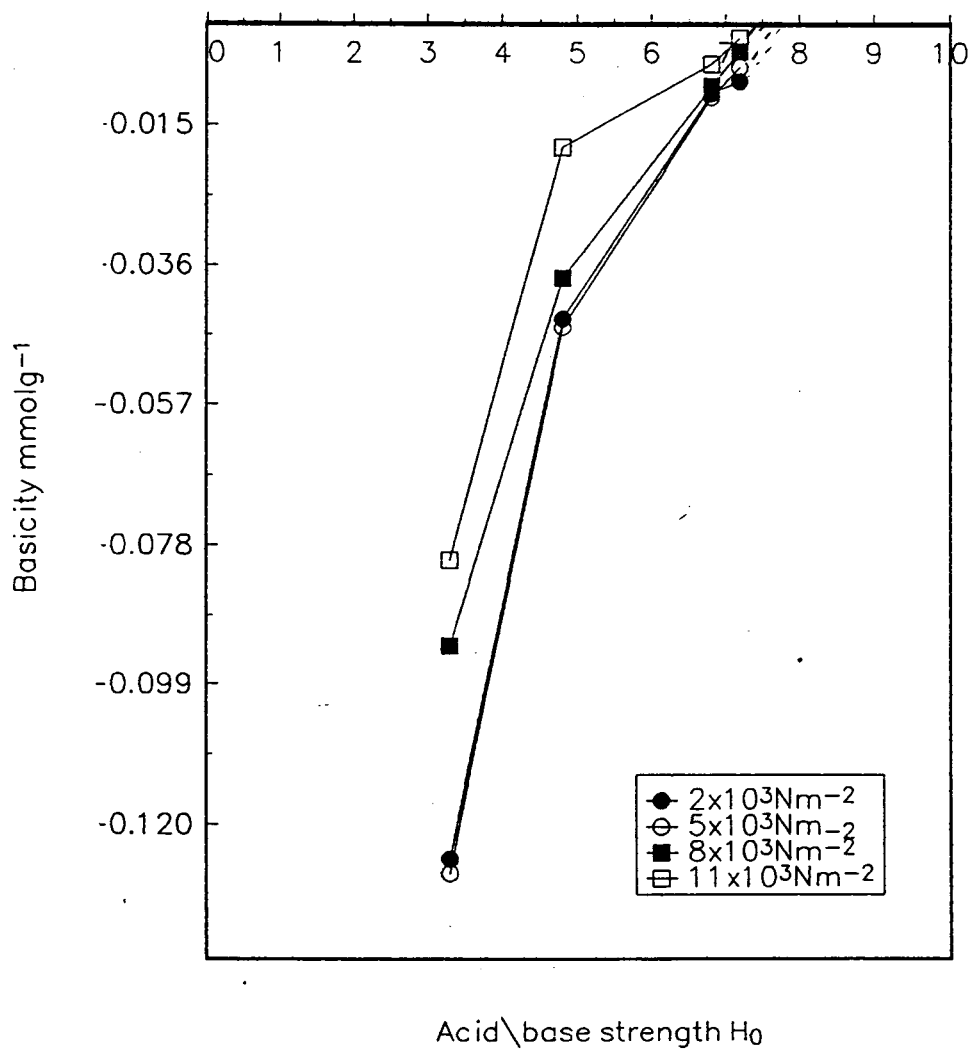


Fig. 3.44. Surface acidity/basicity of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxide (wt. % of $\text{Dy}_2\text{O}_3 = 60$; p.s. 106-125 microns)

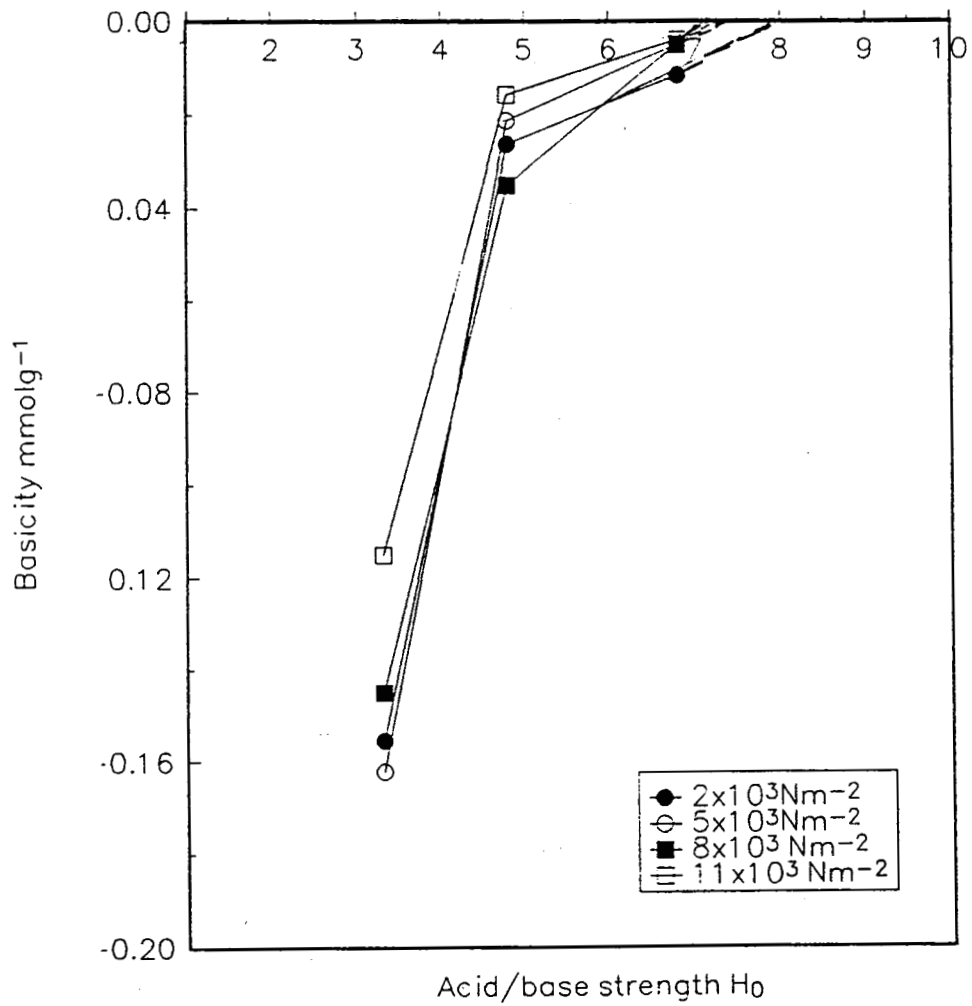


Fig. 3.45. Surface acidity/basicity of Dy₂O₃-Al₂O₃ mixed oxide (wt. % of Dy₂O₃ = 80; p.s. 106-125 micron)

Z01633.RAW

5

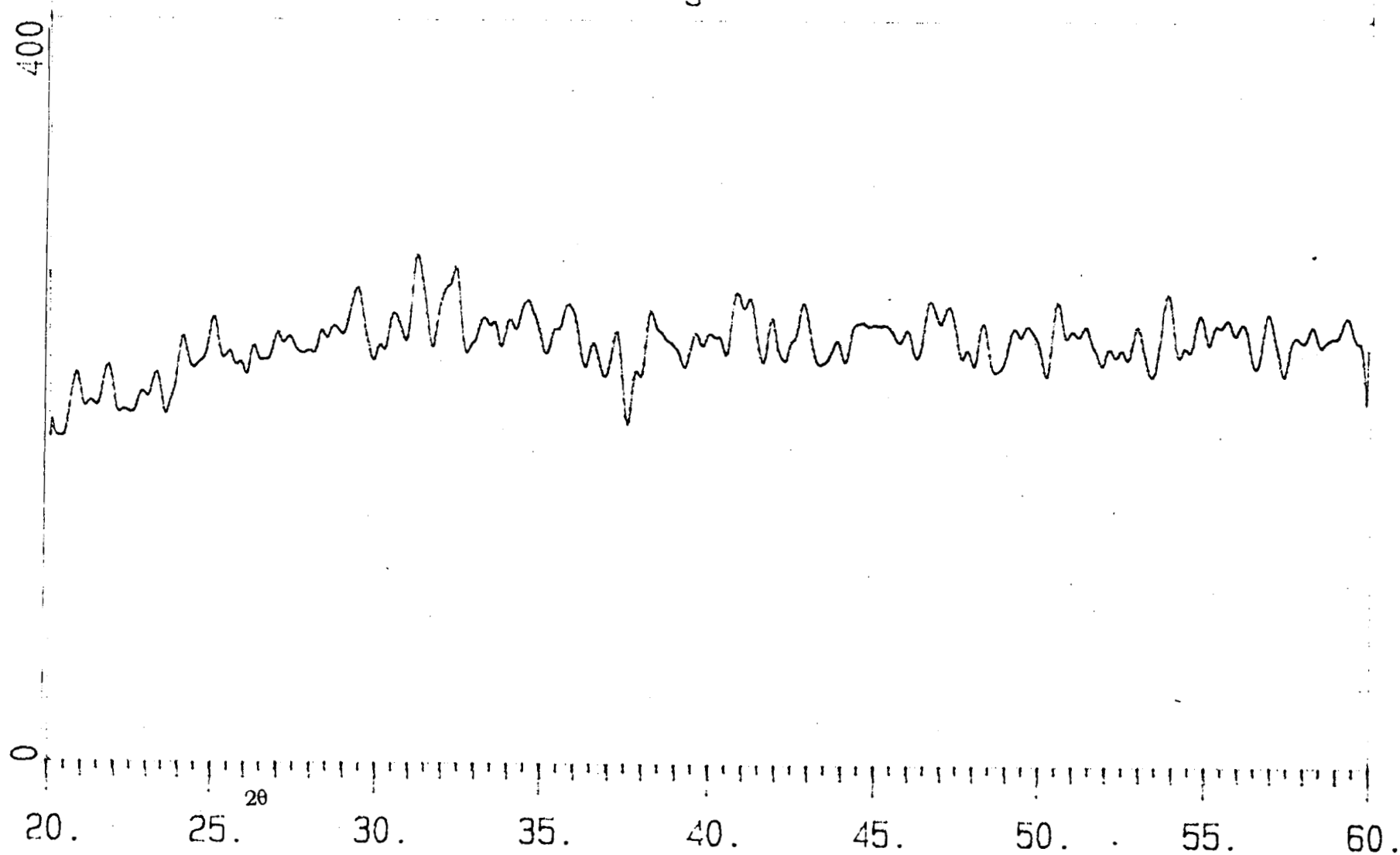


Fig. 3.46. XRD of $Gd_2O_2-Al_2O_3$ mixed oxide precompressed
(wt. % of $Gd_2O_3 = 60$; pre comp. pr. = $8 \times 10^3 Nm^{-2}$; p.s. = 106-125 microns)

more susceptible to compression than Gd-O-Al or Dy-O-Al bonds. These observations were explained by accepting the view that during precompression, imperfections in the surface produce cations with low co-ordination number. These samples were also found to be of amorphous nature by XRD studies (Fig. 3.12 and 3.46).

3.4. Gravimetric Estimation of Adsorbed Carbon dioxide

The basic nature of oxides was further established by the gravimetric adsorption of carbondioxide gas. It is an index of the basic sites available for chemisorption. The values were presented in Tables 3.9-3.12. The amount of chemisorbed carbondioxide gas was a measure of the total basicity of the oxide systems. The strength, with which it was adsorbed, was obtained by the measurement of heat of adsorption; which unfortunately could not be carried out. The thermally activated samples both single and mixed oxides agreed with the above observation. The amount of CO₂ gravimetrically adsorbed was negligible for alumina as expected [196]. The discrepancy in the values obtained was attributed to the amount of carbondioxide physisorbed. This is clear from Figs. 3.23, 3.28 and 3.33 where a comparative study of the H_{0max} values against the composition of the rare earth oxides at various temperatures and pre compression pressures were represented.

TABLE 3.9

Amount of CO₂ Chemisorbed and the catalytic activity of single oxides activated at different temperatures

| Name of the oxide | Temp. of activation °C | XRD Observation | H ₀ max | Amount of CO ₂ chemisorbed mmol g ⁻¹ | Rate constant kx10 ⁵ s ⁻¹ g ⁻¹ |
|--------------------------------|------------------------|-----------------|--------------------|--|---|
| La ₂ O ₃ | 500 | Crystalline | 9.6 | 0.4675 | 0.5964 |
| | 600 | | 10.5 | 0.4251 | 3.8300 |
| | 700 | | 9.0 | 0.4682 | 0.7878 |
| Gd ₂ O ₃ | 500 | Crystalline | 6.9 | 0.0956 | 2.280 |
| | 600 | | 6.9 | - | 7.327 |
| | 700 | | 6.8 | 0.0921 | 2.782 |
| Dy ₂ O ₃ | 500 | Crystalline | 7.3 | 0.3043 | 7.324 |
| | 600 | | 7.4 | 0.3309 | 10.03 |
| | 700 | | 7.5 | 0.4184 | 9.060 |
| Al ₂ O ₃ | 500 | Amorphous | 5.7 | - | 0.523 |
| | 600 | | 5.7 | - | - |
| | 700 | | 5.7 | - | - |

TABLE 3.10

Amount of CO₂ Chemisorbed and the catalytic activity of La₂O₃-Al₂O₃ mixed oxides at various temperatures

| Composit
ion of the
mixed
oxide
wt% of
La ₂ O ₃ | Temp. of
activation
°C | XRD
Observation | H ₀ max | Amount of
CO ₂
chemisorbed
mmolg ⁻¹ | Rate
constant
kx10 ⁵ s ⁻¹ g ⁻¹ |
|--|------------------------------|--------------------|--------------------|--|---|
| 20 | 500 | Amorphous | 7.8 | 0.3101 | 2.925 |
| | 600 | | 8.0 | 0.2203 | 0.4200 |
| | 700 | | 8.0 | 0.2213 | 0.1467 |
| 40 | 500 | | 7.9 | 0.4964 | 1.9190 |
| | 600 | | 7.8 | 0.2976 | 3.3770 |
| | 700 | | 7.6 | 0.4407 | 1.3700 |
| 40 | 500 | | 8.1 | 0.5045 | 4.9000 |
| | 600 | | 8.4 | 0.3629 | 5.8600 |
| | 700 | | 8.3 | 0.3028 | 4.8500 |
| 80 | 500 | | 7.8 | 0.4678 | 0.6804 |
| | 600 | | 7.7 | 0.4425 | 0.5935 |
| | 700 | | 7.2 | 0.2226 | 0.9839 |

TABLE 3.11

Amount of CO₂ Chemisorbed and the catalytic activity of Gd₂O₃ - Al₂O₃ mixed oxides at various temperatures

| Composit
ion of
oxide
wt% of
Gd ₂ O ₃ | Temp. of
activation
°C | XRD
Observation | H _{0 max} | Amount of
CO ₂
chemisorbed
mmolg ⁻¹ | Rate
constant
kx10 ⁵ s ⁻¹ g ⁻¹ |
|---|------------------------------|--------------------|--------------------|--|---|
| 20 | 500 | Amorphous | 8.1 | 0.1673 | 3.4200 |
| | 600 | | 8.2 | 0.1373 | 2.1560 |
| | 700 | | 7.4 | 0.1921 | 3.8830 |
| 40 | 500 | Amorphous | 7.3 | 0.1371 | 1.8360 |
| | 600 | | 7.3 | 0.1660 | 4.2800 |
| | 700 | | 7.2 | 0.1786 | 5.2200 |
| 60 | 500 | | 7.3 | 0.2680 | 2.6868 |
| | 600 | | 8.5 | 0.3485 | 8.3230 |
| | 700 | | 7.3 | 0.4397 | 4.6380 |
| 80 | 500 | | 8.4 | 0.4594 | 1.2760 |
| | 600 | | 7.7 | 0.3263 | 3.2300 |
| | 700 | | 7.7 | 0.3956 | 4.7850 |

TABLE 3.12

Amount of CO₂ Chemisorbed and the catalytic activity of Dy₂O₃-Al₂O₃ mixed oxides at various temperatures

| Compositi
on of
mixed
oxide
wt.% of
Dy ₂ O ₃ | Temp. of
activation
°C | XRD
Observation | H _{0 max} | Amount of
CO ₂
chemisorbed
mmolg ⁻¹ | Rate
constant
kx10 ⁵ s ⁻¹ g ⁻¹ |
|---|------------------------------|--------------------|--------------------|--|---|
| 20 | 500 | Amorphous | 7.2 | 0.2734 | 4.1530 |
| | 600 | | 7.6 | 0.3728 | 7.6200 |
| | 700 | | 8.2 | 0.5679 | 7.7560 |
| 40 | 500 | | 7.9 | 0.3761 | 7.6560 |
| | 600 | | 8.0 | 0.3245 | 12.990 |
| | 700 | | 8.0 | 0.4237 | 10.2300 |
| 60 | 500 | | 8.8 | 0.3761 | 6.4550 |
| | 600 | | 8.6 | 0.3765 | 8.0300 |
| | 700 | | 7.7 | 0.2245 | 9.4550 |
| 80 | 500 | | 8.5 | 0.4237 | 2.4820 |
| | 600 | | 7.8 | 0.24 | 5.6120 |
| | 700 | | 8.0 | 0.3577 | 4.4140 |

The behaviour of the precompressed samples were different from those of the thermally activated oxides. They showed very little affinity towards chemisorption of carbondioxide. It was suggested that precompression caused reduction in the number of basic sites capable of chemisorption of carbondioxide.

3.5. Catalytic Reduction of Benzophenone

The reduction of benzophenone in the presence of propanol-2 was carried out as a test reaction to study the catalytic efficiency of these systems of both single and mixed metal oxides. It is known that the reduction of benzophenone was difficult to carry out because the carbonyl group is conjugated to the ring system [197]. The rate constant 'k' was calculated in each case as a first order reaction. The values are given in Tables 3.9 to 3.12. The products formed were confirmed by TLC and IR spectral studies. The main product benzhydrol was isolated and purified and its IR spectrum was compared with standard values. Both were found to be identical (Figs. 3.47 and 3.48).

The data showed that the catalytic activity depended on both surface acidity and basicity, however the relationship is not straight forward. Basic sites had an important role in the reaction as evident from the data. But the lack of linear correlation between catalytic activity and basicity implies that basic sites were not the only controlling factor of the reaction. The variation of rate

PERKIN ELMER

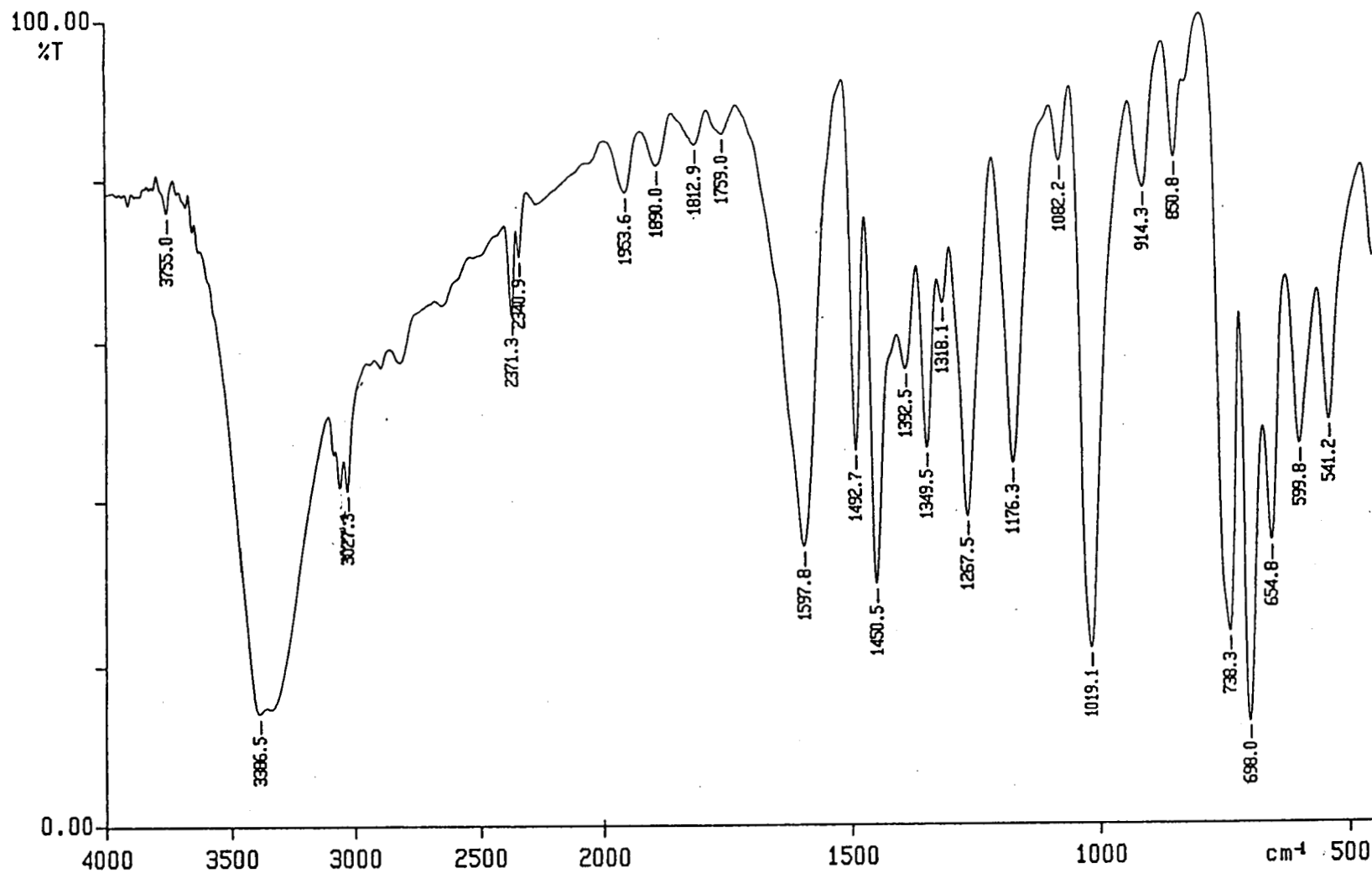


Fig. 3.47. IR spectrum of benzhydrol obtained by catalytic reduction of benzophenone.

01/03/22 10:48 smg
X: 4 scans, 4.0cm⁻¹, flat, smooth, abex

PERKIN ELMER

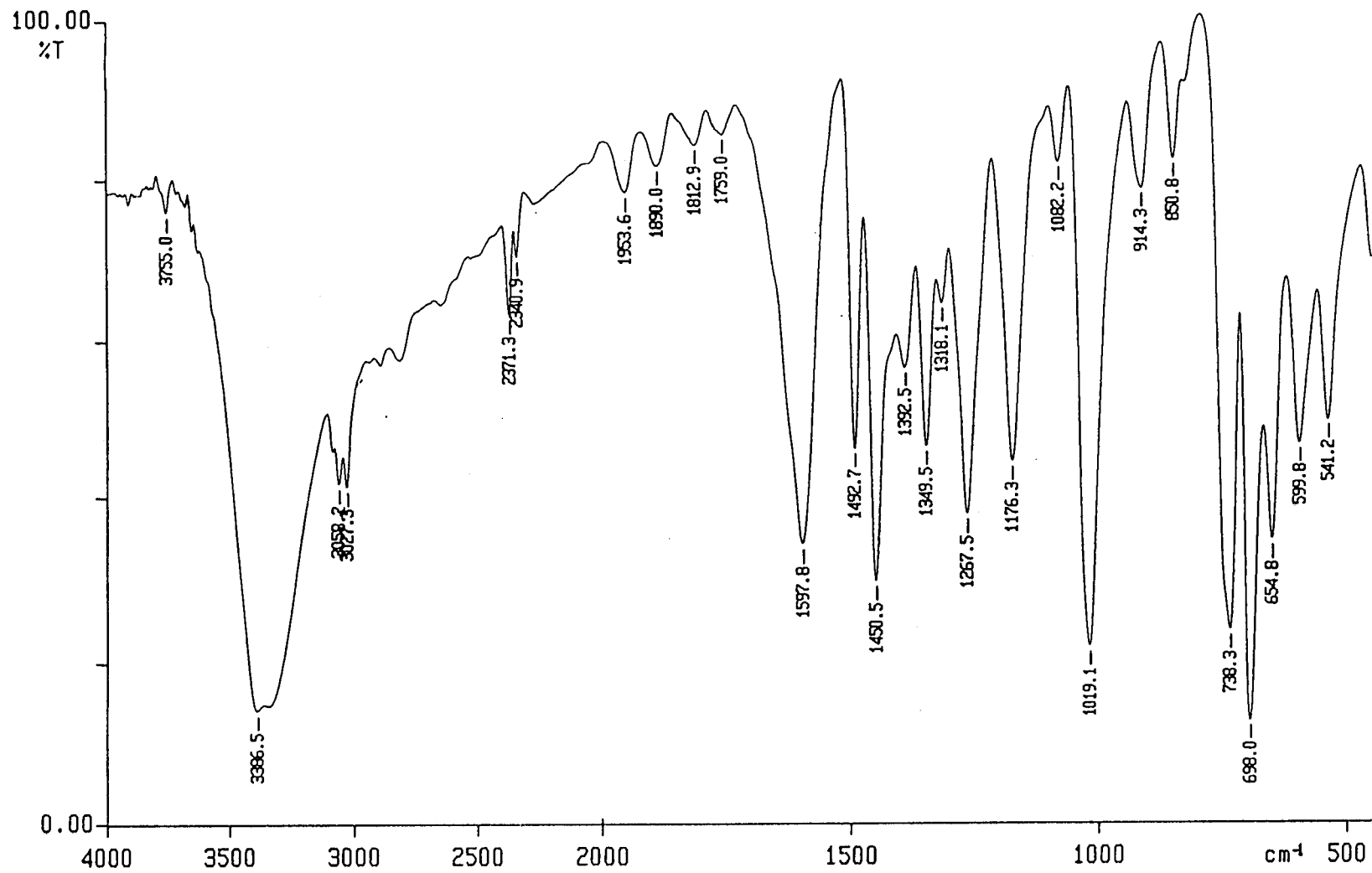


Fig. 3.48. IR spectrum of benzhydrol

01/03/22 10:43 smg

X: 4 scans, 4.0cm-1, flat, smooth, abex

constants with the concentration of rare earth oxides are shown in the Figs. 3.49 to 3.51.

Compressed samples were found to be less effective for the reduction where as thermally activated samples were powerful catalysts to cause the reduction of benzophenone to benzhydrol. The reaction is supposed to have taken place through the hydride transfer from propanol-2 to the reacting species through the catalyst. The proposed mechanism for the reaction is given in Fig 3.52. The rate determining step is the one subsequent to the adsorption of isopropanol and carbonyl compound to the catalyst.

The thermally activated single oxides and mixed oxides were found to be effective catalysts for the reduction (Table 3.9-3.12). Of the single oxides, lanthana (La_2O_3) at 600°C is the most effective. Gadolina and dysporosia were also good, but to a lesser extent. Alumina showed least activity. Binary oxides of $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$, $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ and $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ were also effective in the catalytic reduction. The $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ binary oxides showed maximum activity when they were activated to 600°C and with a composition of 60% by weight of lanthanum oxide. The $\text{Gd}_2\text{O}_3\text{-Al}_2\text{O}_3$ binary oxides also showed the same behaviour. They were effective at an activation temperature of 600°C and the composition with 60% by weight of Gd_2O_3 was much more effective in this system. $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ mixed oxides also acted as a good catalyst for the conversion. The catalytic

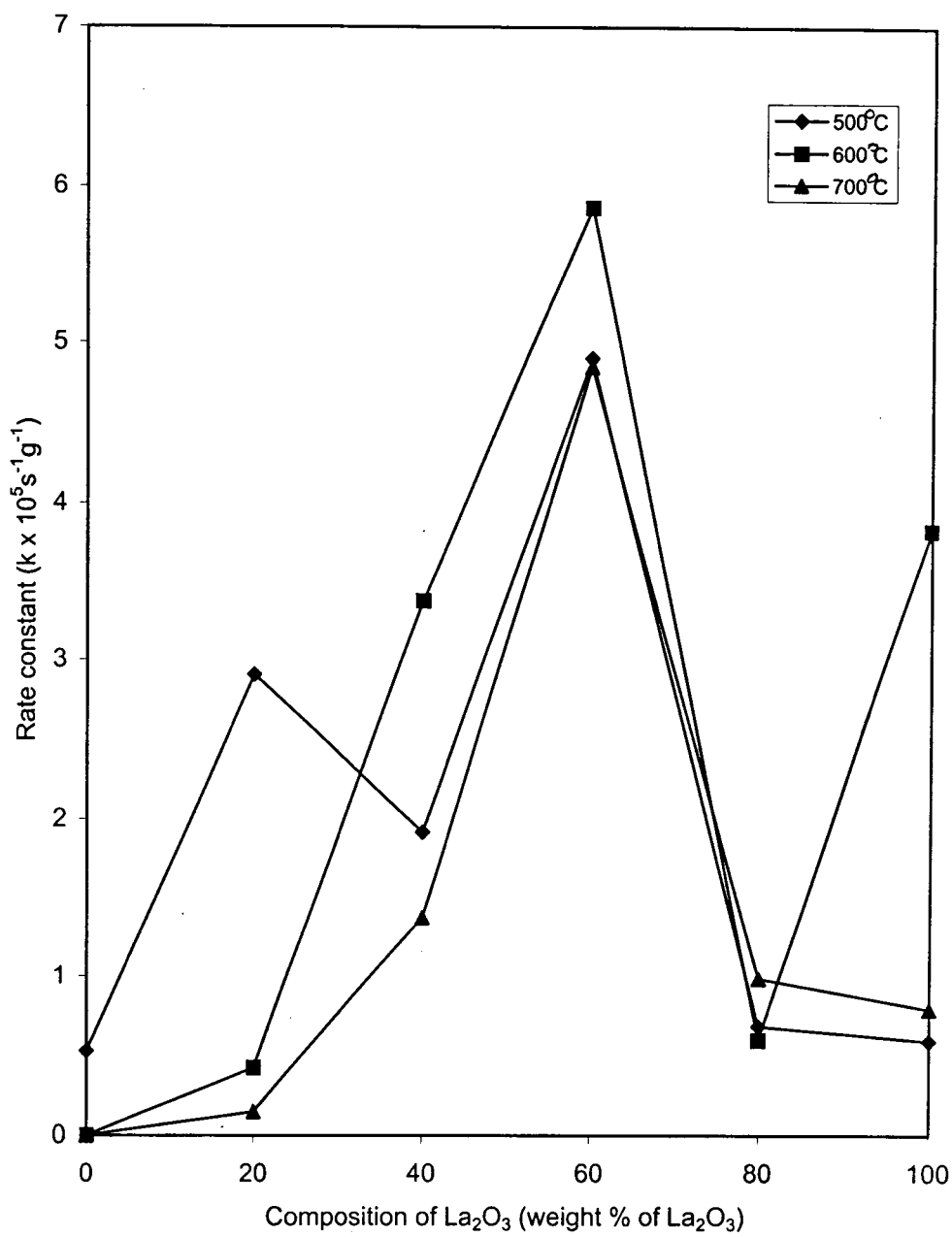


Fig 3.49 Rate constant Vs composition of La₂O₃

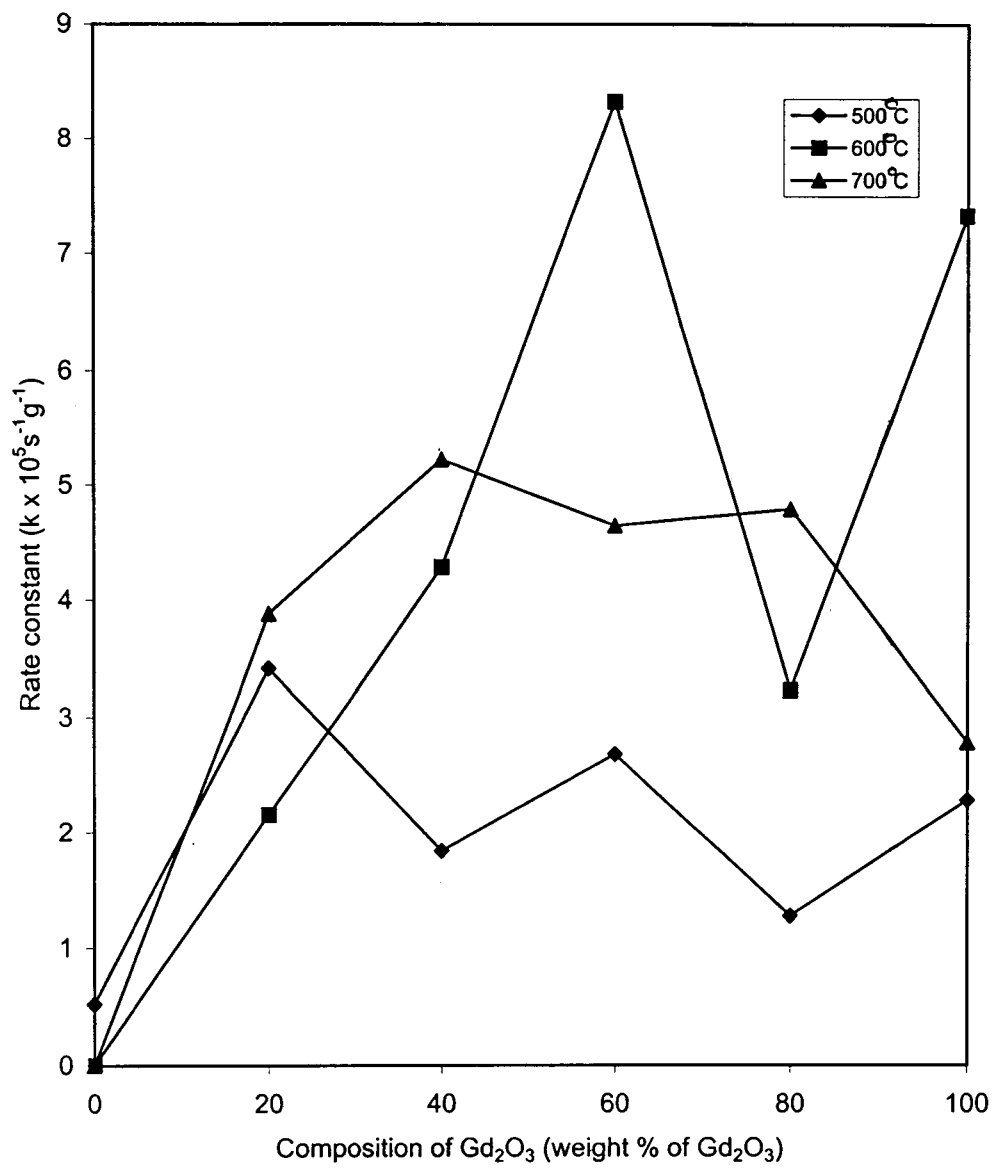


Fig 3.50 Rate constant Vs composition of Gd₂O₃

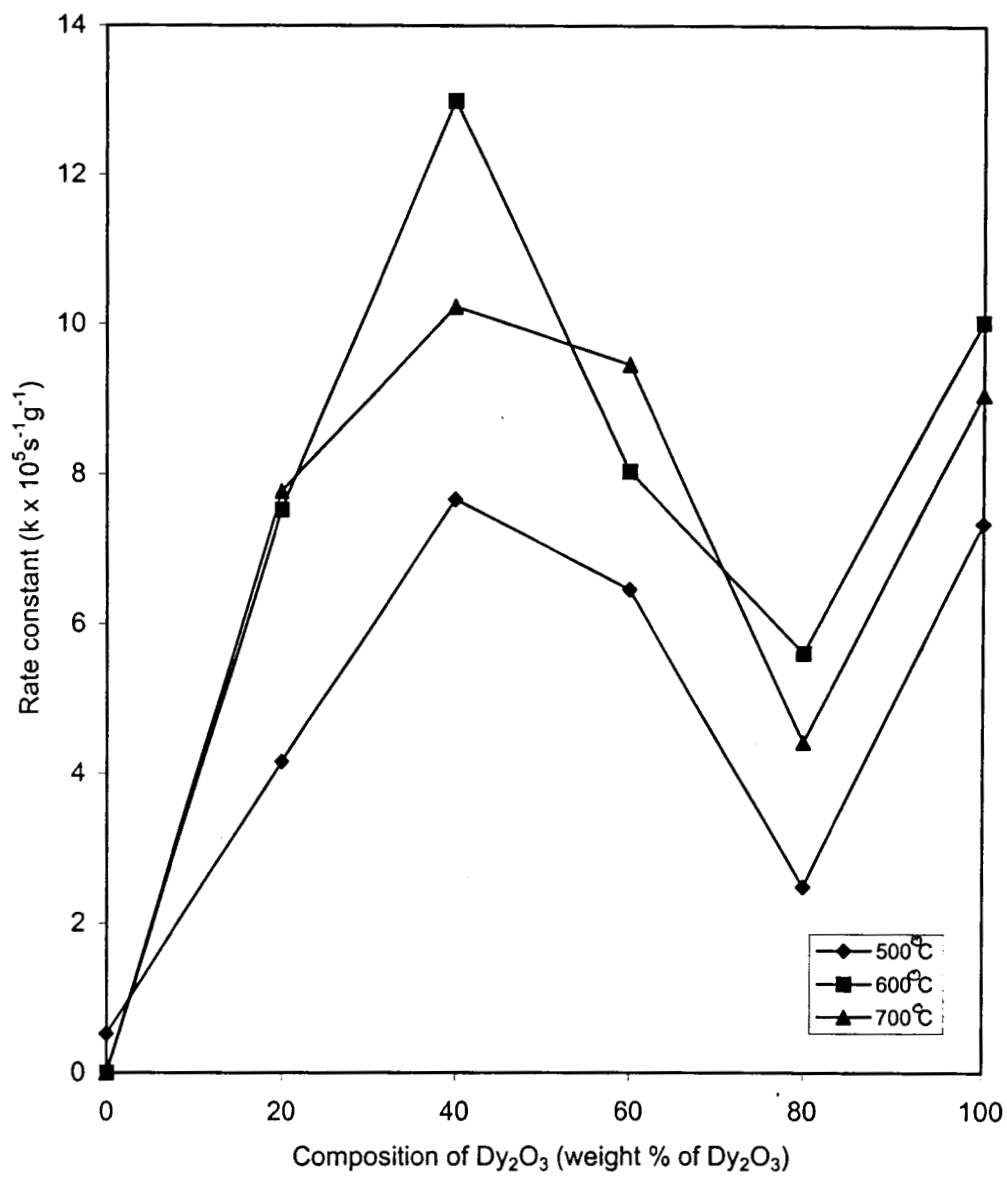


Fig. 3.51 Rate constant Vs. composition of Dy₂O₃

efficiency was maximum for the composition containing 40% percent by wt of Dy_2O_3 and when activated to a temperature of 600°C . The reaction is initiated by abstraction of an H^+ from 2-propanol by the basic sites of the catalysts and the slow step is hydride transfer from the adsorbed 2-propanol to the adsorbed carbonyl compound [185, 186] as shown in the figure 3.52.

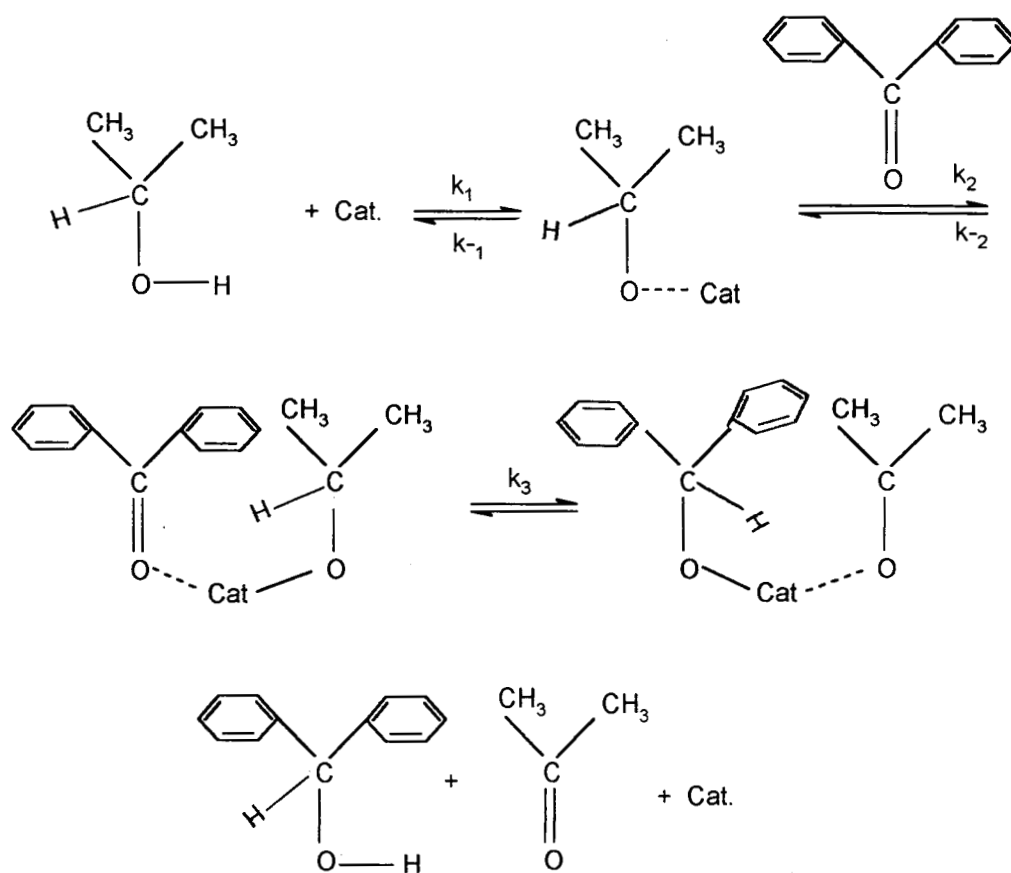


Fig. 3.52. MPV reduction of Benzophenone

3.6. Conclusion

Rare earth metal oxides have wide application in industry as catalytic supporter and promoter especially as automotive exhaust treatment, where the oxygen storage capacity and the reducibility of the rare earth oxide (CeO_2) is made use of. Another important application in industry is the syn gas conversion which is based on the basic property and reducibility of the rare earth oxide (eg. La_2O_3). Rare earth oxides supported on alumina can prevent the phase transformation of γ -alumina to α -alumina at higher temperatures. The phase transformation of alumina is a very serious hazard in industry.

Rare earth metal oxides have surface acidic or basic properties and it vary with their electronegativity and other intrinsic defects. The basicity was in the order $\text{La}_2\text{O}_3 > \text{Dy}_2\text{O}_3 > \text{Gd}_2\text{O}_3 > \text{Al}_2\text{O}_3$. Their surface property vary with temperature of activation, method of preparation and other pretreatment techniques. The single oxides and mixed oxides have different surface characteristics. They vary in surface acidic/basic properties, surface area, crystalline nature etc, according to the method of preparation composition and pretreatment methods. The catalytic activity and selectivity are determined by these characteristic properties.

In the present study it is observed that the single oxides were crystalline and have low surface area. They showed surface basic properties. The mixed

oxides were prepared by incorporating with alumina and the basic properties, BET surface area and XRD are measured. They showed an increase in surface area and were amorphous in nature on thermal activation. They are used as catalyst in the MPV reduction of benzophenone. Benzophenone is reluctant to undergo reduction due to the presence of conjugated carbonyl group and steric hindrance. But the catalysts were good enough to reduce benzophenone to benzhydrol, where the product is isolated in almost pure form.

Thermal activation enhances the catalytic properties but pre compression did not produce such notable changes. They exhibit catalytic activity to a very lesser extent. It may be due to the sintering caused by pre-compression or because of the absence of sites of suitable energy to bring about the reaction in the metal oxides. The pre compressed oxides showed a decrease in basic properties and an increase in acidic properties.

Surface acidity/basicity investigations have received considerable attention in recent years because they can provide significant information in determining the behaviour of solid surfaces. Determination of the strength of acid/base sites and their distribution on the surface are important requirements to understand the catalytic properties. Titration methods were employed using solutions of n-butylamine and trichloro acetic acid (TCA) in benzene. Different Hammett

indicators were used to characterise the acid/base strengths of the solid surfaces of the various metal oxide catalysts.

These solid acids and bases have a prime position in heterogeneous catalytic reactions. They are good substitute for the highly corrosive or toxic acids and bases. Even though they are costly, they are valuable addition to the field of clean technology.

**SURFACE ACIDITY/BASICITY OF
RARE EARTH METAL-ALUMINIUM MIXED
OXIDE CATALYSTS**

**THESIS SUBMITTED
TO THE UNIVERSITY OF CALICUT
IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY
IN THE FACULTY OF SCIENCE**

By

MARIAMMA CHERIAN

**DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALICUT
KERALA – 673 636
INDIA**

AUGUST 2002

REFERENCES

1. Mross W.D., Catal. Rev. Sci. Eng. 1983, 25, 581.
2. Rosynek, M.P., Catal. Rev. Sci. Eng. 1977, 16, 111.
3. Wada, K., Watanabe Y., Saitoh, F., Susuki, T., Appl. Cat. A. 1992, 88, 23.
4. J.N. Bronsted, Z. Phys. Chem . A, 169, 52, 1934.
5. G.N Lewis Valency and structure of Atoms and molecules. Chemical Catalog Co. (1923).
6. G.C. Bond, Heterogenous Catalysis, Principles and Applications, Oxford, 1986.
7. Weilberbe H. and Weiss J., J. Chem. Soc. 2164 (1948).
8. Walling C., J. Am. Chem. Soc., 72, 1164, 1950.
9. Tamele M.W., Faraday Soc. Discussion 8, 270, 1950.
10. Pines H. Veseley, J.A ., I Patieff Y.N, J. Am. Chem. Soc 1955, 77, 6314.
11. Kokes, R.J., Dent A.L., Advan. Catal. 1972, 22, 1.
12. Hattori, H., Yoshi, M., Tanabe, K., Proceedings of the 5th International Congress on Catalysts. Miani Beach F, 1972, p.223.
13. J. Haber, Preparatives in Catalysis. Blackweal Scientific Publications 37, 1992.

14. R.Kohes, J. Intra. Soc. Chem. Rep., 6, 77, 1972.
15. R.L Buswell ; Jr. G.L Haller, K.C Taylor and J.F Read. *Adr. Catal.*, 29(1), 1969.
16. Tanabe K., *Solid acids and bases*. Academic Press, New York, 1970.
17. H. Pines and C.N. Pillai, J.A. in *Chem. Soc.*, 83, 3270, 1961.
18. Arai, Machida, M., *Appl. Catal. A.*, 1996, 138 (161-176).
19. S.G. Hindin and S.W. Weller, *J. Phy. Chem.* 60, 1501, 1956.
20. J.E Mapes and R.R Eishems. *J. Phy. Chem.* 58, 809, 1954.
21. E.P Parry. *J. Catal.*, 2, 371, 1963.
22. Burtin P., Brunelle, J.P., Pijolat M. et al. *Appl. Catal.* 34, 239, 1987.
23. Tanabe K. Misono M; Ono, Y; Hattori H., *New solid Acids and bases*, Kodansh (Tokyo Elseveir) 1989, p.39.
24. Coluccia S., Tench A.J., *Proceedings of the 7th international congress on catalysis*. Tokyo. Japan, 1980, p.1160.
25. Moeller T., *Chemistry of Lanthanides Pergamon*, New York (1973).
26. N.E. Topp. Elsevier, *The Chemistry of Rare Earth Elements* Amsterdam, 1965.
27. Liu Shang-Lin, Miao, Qing; Xiang, Guo-Xing; Sheng, Shi-shani; Chen, Men-Rong; *J. Nat .Gas. Chem.* 7(3) 189-197, 1998.

28. Wu-Joseph Hui-Zhao; Wan, Chung-Zong; PCT. Int. Appl. W.O. 9842437. Al. Oct 1998.
29. Kata A; Yamashita H and Matsucha S., *Studies in Surface Science Catalysis*, Vol. 46.
30. Bernand B., Garbouskie and Print M. *Appl. Catal.* 75, 119, 1991.
31. Imamura H., Yoshimochi H., Harada Y., *J. Mol. Catal.* 66, 33, 1991.
32. K.M. Minachev, *Proc. Int. Cong. Catal.* 5th 219 (1973).
33. Fukuda Y., Hattori H., Tanabe K., *Bull. Chem. Soc., Jpn*, 1978, 51, 3151.
34. Imizu Y., Sato K., Hattori H., *J. Catal.* 1981, 71, 64.
35. Utiyama M., Hattori H., Tanabe K., *J. Catal.* 1978, 4, 237.
36. L.P. Hammett, *Physical Organic Chemistry Chapter 9*. Mc Graw Hills. 1940
37. Hammett, L.P., Dyerup A.J., *J. Am. Chem. Soc.* 1932, 54, 2721.
38. Bensi H.A; *J. Am. Chem. Soc.*, 1956, 78, 5490.
39. Jerry March. *Advanced Organic Chemistry, Fourth edition*, John Wiley and Sons, 1992, p.913.
40. S. Malinowski and S. Szczeparska, *J. Catal.* 2, 310, 1963.
41. T. Yamanaka and K. Tanabe. *J. Phy. Chem.* 79, 2409, 1975.
42. T. Yamanaka and Tanabe K. *J. Phy. Chem.* 80, 1723 (1976).
43. Forni L. *Catal. Rev.* 1973, 8, 65.

44. Bensi H.A., Winguirt B.H.C., *Adv. Catal.* 1978, 27, 97.
45. M. Balikova. *React Kinet. Catal. Lett.* 2, 323, 1975.
46. Kikuchi N., J.I. Take and Y. Yoneda, *J. Catal.* 1971, 21, 164.
47. O. Johnson, *J. Phy. Chem.*, 59, 327, 1955.
48. K. Tanabe and T. Yamaguchi, *J. Res. Inst. Catalysis Hokkinido Univ.* 14, 93, 1966.
49. H.P. Lettin and M.C Hobson. Jr. *Advances in catalysis Vol. 14*, p.115, Academic Press, 1963.
50. A.N.Terenin Jr. *Advances in Catalysis, Vol.15*, p.227, 1964.
51. Delgass W.N., Haller G.L; Kellerman R., Lunsford J.H., *Spectroscopy in Hetrogenous Catalysis.* Academic Press, New York, 1979.
52. Haller G.T., *Catal. Rev. Sc. Eng.*, 1981, 477.
53. Anderson M.W., Klinowski, *J. Zeolites*, 1986, 6, 455.
54. Parry E.P., *J. Catal.* 1963, 2, 371.
55. Basila M.R. Kantner T.R., Rhee K.H., *J. Phy. Chem.*, 1964, 68, 3197.
56. Hughes T.R., White H.M. *J. Phy. Chem.*, 1967, 71, 2192.
57. Dalha J., Turek A.M., Jehng J.M., Wacha I.E., *J. Catal.* 1992, 135, 186.
58. Emeis C.A., *J. Catal.* 1993, 141, 347.
59. Fsuji H., Yagi F., Hattori H., *Chem. Lett.* 1991, 1881.

60. Fukuda Y; Tanabe K; Bull Chem. Soc. Jpn. 1973, 46, 1616.
61. Evans J.V., Whateley T.L., Trans. Faraday Soc. 1967, 63, 2769.
62. Auroux A., Yin Y.S., Vedrinc J.C., Appl. Catal. 1988, 36, 323.
63. Kapustin G.L., Brueva T.R., Klyachiko A.L., Beran B., Wichler Iova B; Appl. Catal. 1988, 42, 239.
64. Themm H., J. Phy. Chem., 1987, 91, 8.
65. Spiewak B.C., Handy B.E., Sharma S.B., Dumesic J.A., Catal. Lett., 1994, 23, 207.
66. Cardona-Martinez, N., Dumesic J.A., J. Catal. 1991, 128, 23.
67. Parillo D.J., Gorte R.J., Catal Lett., 1992, 16, 17.
68. Parillo D.J., Lee C., Gorte R.J. Appl. Catal A., 1994, 110, 67.
69. Zhang G., Hattori H., Tanabe K., Appl. Catal. 1988, 36, 189.
70. Okamoto Y., Ogawa M., Maczawa A., Imanaka T., J. Catal. 1988, 112, 427.
71. Thomas J.M., Klinowski J. Adv. Catal., 1985, 33, 256.
72. Mustikhin Y.M., Mudrakovosky J.L., Nosov A.V., Prog. NMR spectroscopy 1991, 23, 259.
73. Brummer E., Ernst H., Freude D., Frohlich T., Hunger M., Pfeifer H. J. Catal. 1991, 127, 34.

74. Haw J.F., Richardson B.R., Oshino I.S., Lazo N.D., Speed J.D., J. Am. Chem. Soc. 1989, 111, 2052.
75. Freude D., Ochme W., Schniedel H., Staudte B., J. Catal. 1977, 49, 123.
76. Freude D., Pfeifer H., Plass W., Staudite B., J. Mol. Catal. 1981, 12, 1.
77. Pfeifer H., J. Chem. Soc. Faraday trans I, 1998, 84, 3477.
78. Ernst H., Freude D., Wolf I., Chem. Phy. Lett. 1993, 212, 583.
79. Haw J.F., Chuang I.S., Hawkins B.L., Maciel G.E., J. Am. Chem. Soc. 1983, 105, 7206.
80. Rothwell W.P., Shen W., Lunsford J.H., J. Am. Chem. Soc. 1984, 106, 3452.
81. Lunsford J.H., Rothwell W.P., Shen W., J. Am. Chem. Soc. 1985, 107, 1540.
82. Battusis L., Frye J.S., Maciel G.E., J. Am. Chem. Soc., 1986, 108, 7119.
83. F.C. Tomkins, Pure Appl. Chem. 9 (1964) 387.
84. J.A. Hedvall, Solid State, Chemistry Elseveir Amsteden, 1966.
85. C.J. Diene and A.C. Damask in J.H. de. Boer (Ed.) Reactivity of solids. Elseveir, Amsterdam, 1965.
86. I. Tamm. Phy . Z.S.S.S.R. 1, 1932, 733.
87. W.E. Garner and M.G. Tanner, J. Chem. Soc., 1930, 47.
88. Robert M., Hazen and Larry W. Finger Comparative Crystal Chemistry 1984, page 149, Wiley Interscience Publication.

89. Robert M. Hazen and Larry W. Finger, *Comparative Crystal Chemistry* 1984. page 166, Wiley Interscience Publication.
90. C.L. Thomas, *Ind. Eng. Chem.* 41, 2564, 1949.
91. K. Tanabe, T. Takeshita, *Advances in catalysis* Academic Press. New York, 17, 315, 1967.
92. K. Nishiwaki, N. Kakkuta, A., Uno and H. Nakadayashi, *J. Catal.* 118, 498, 1989.
93. J.R. Anderson, *Structure of Metallic Catalysts*, Academic Press, New York, 1975.
94. G. Connell and J.A. Dumesic, *J. Catal.*, 105, 285, 1987.
95. K. Tanabe, *Catalysis, Science and Technology*, ed. by J.R. Anderson and M. Boudart, *Spinger-Verlag*, New York, 1981, Vol.2, p.231.
96. Connell, G. and J.A. Dumesic, *J. Catal.* 102, 216, 1986.
97. H. Nakayashi., M. Kokuta and A. Uno, *Bull Chem Soc. Jpn* (1991) 64, 2428.
98. Newton, R.C. and B.J. Wood; *Volume behaviour of Silicates, Solid Solutions A.M Minerals* 1980, 65, (733-745).
99. M.J. Fuller and M.E. Warwick, *J. Catal.* 39 (1975).
100. A.L. Wilds, *Org. React.* 2, 178, 1944.
101. M. Onishi, M. Matsuda and K. Hiraki *Chem. Lett.*, 1984, 1157.

102. F. Martinelli, G. Mestroni; A. Camus and G. Zassinowich, *J. Organomet. Chem.* 229 (383) 1981.
103. G. Fragale, Gargano, M. and M. Rossi, *J. Mol. Catal.*, 5, 65, 1979.
104. J. Bium, S. Shrelzer., D. Albin and Y. Sasson, *J. Mol. Catal.* 16, 167, 1982.
105. T. Tatsumi., M. Shibagaki and H. Tominaga *J. Mol Catal.*, 13, 331, 1981.
106. Y. Ishit, T. Nakumo., A Inada., Y. Kishigami, K. Sakurai and Ogawa *J. Org. Chem.*, 51, 240, 1986.
107. L.H. Klemm and D.R. Taylor, *J. Org. Chem.* 35, 3216, 1976, p.30.
108. H. Niiyama and E. Echigoya, *Bull Chem Soc. Jpn*, 45, 938, 1972.
109. K.M Minachev, O.K Atalyam and M.A Markov; *Jzu. Akad Nauk. SSSR Scr. Khim.* 1978, 270, 87.
110. Shibagaki M., K. Takahashi and H. Matushita, *Bull. Chem. Soc. Jpn.* 61 (3283-3288) 1988.
111. Y. Ishii, T. Nakano, A., Inada; Y. Kishi; J. Gami; K. Sakurai; I.M. Ogawa; *Org. chem.* 1986, 51 (240-242).
112. Yang Xiang Bi Yingh; Lisenz; Zhenkaiji; Wuyue Cuihuaxuebao. 143 (174-179) 1993. (Chinese) Am. Chemical Society, 1997 (copy rights reserved).
113. N. Hideo, T. Shizuka, K. Masahiro, M. Koichi, W. Katushiko *Appl. Surf. Sci* 121/122, 404-407 (1997).

114. W. Israel, E., J. Jih-Mirn, D., Goutam, W. Bert. M., Guloants V.V., Benziger, J.B., Sunderasan, S., *J. Catal.* 170 (75-88), 1997.
115. Uphade, B.S., Mulla, S.A.R., Choudhary, V.R., *Stud. Surf. Sci. Catal.* 113 (1015-1021), 1998.
116. Loginov, Ayu., Chapayeva A. Yu, Chokoyer. H.K., Ikonnikov I.A., *Catal. Today* 17 (85-94) 1993.
117. Wilde, P.M., Fritsch, E., Reller A. Gauche, V., Brunner P. *J Anal. Chem.* 346(1-3), 383-388, 1993.
118. Li, Shi-Yao; Beil-Lu; *React. Kinetic. Catal. Lett* 57 (1) (183-190) 1996.
119. Imamura H., Sakata Y., Tsuchiya S., *J Alloys. Compd.*, 193 (1-2) 62-64. 1993.
120. Cakamolo E., Onnishi T., Arakawa T., *Stud. Surf. Sci. Catal.* 84(1537-40), 1994 .
121. W. Guang, W. Li Huai, LIO Yiji Yijun; *Chin Chem. Lett.* 10(5) 433-434. 1999.
122. Sohier M.P Wrobel G; Bonnelle J.P; Mareeq J.P *Appl. Catal A* 1992 84(2) 169-86
123. Liao, Qiaoli; Q in Yongming; Zhao; Jiushengi Zhang Liu; *Proc. Int. Conf. Pet-refin petn chem. Process* 1991, 2 (682-688). A review edited by Hou.zianglio.
124. Jiang Zhichang; Yuzhengiang; Shenskikong; Li shuben; wang hougli *chem. Ind.* 1992, 46 (75-83)

125. Waquif .M . Bachelier; Jean, saur, odette, Lavalley, Jean Claude, J. Mol. Catal. 72(1) 127-38, 1992.
126. Lavalley. J.C., Catal Today 27(3-4) 377-401. 1996.
127. Datka, J., Turek A.M; Jehng J.M ; Wachs I.E ; J Catal 135(1) (186-99) 1992.
128. Sugunan S; Jalaja J. Chem. Commu. 59(12)(2604-10)1994.
129. Gervasini A; Bellussi G; Fenyvessi J; Aurox A. J.Phy.Chem. 99(14)517-525 1995.
130. Gervasini A; Fencyvesi J; Aurox A; Langmuir. 12(22)5 356-5364(1996)
131. Sugunan S;Rani G.Devika; Unnikrishnan P.A Mater sei.1995 2 (5) 245-246
132. Busca guido, Catal. Today. 41(1-3). P(191-206) 1998 .
133. Y.Yamamoto; T.Tanaka; T. Matsuyama, T. Funahiki, S. Yoshid, Solid state communications. 111 (1999) 137-142.
134. G. Connell and J.A. Dumesic, Journal of Catalysis, 101 (103-113), 1986.
135. J. Shen, M.J. Lochhead, K.L. Bray Yichen J.A. Dumesic. J. Phy. Chem. 1995, 99, 2384-2392.
136. T. Arai, K. Mayura, K. Domen and T. Onishi Bull. Chem. Soc-Jpn. 62,349-353 (1989).
137. Bamwenda, Gratian R., Dbuchi; Akirai Ogata; Atswsni D. J. Mol. Catalysis, A., Chem. 126 (2-3), 151-159, 1997.

138. Z.Leithang; Z. Xiaaming, Zu Vinyong, 10(5), 539-542, Chinese 1998.
139. Yamamoto T, T.Tanaka, T.Matsuyama Takuzo Funahiki and S.Yoshida. J. Phy. Chem. B. 2001. 105 (1908-1916).
140. V.R.Choudhary and V.H. Rane J. Catal. 1991 130, 411.
141. J. Jayasree and C.S.Narayanan. Bull. Chem. Soc. Jpn. 1995 68(84-88).
142. M. Miki, K. Naonobi., M. Yuchi., J. Catal. 134(1) 340-348, 1992.
143. Nakabayshi H. Bull. Chem. Soc. Jpn. 65(3) (914-916) 1992.
144. Hess A. Kemnitz E., Appl. Catal. A. 149(2) (373-389) 1997.
145. Liu Shang-Lini Mian; Qing; Xiang, Guo-Xing Sheng, Shi-shan; Chen, Men-Rong, J. Nat. Gas Chem. 7(3) 189-197(1998).
146. Bing Hu and Ian D Gay. J. Phy. Chem. B. 2001. 105, 217-219.
147. R.L. Richardson and S.W. Benson, J. Phy. Chem.,, Vol. 61, 1957 (405).
148. Harrison Philip G. Catal. Today, 17(3), 483, 1993.
149. Chiu-Hsun Lin, Kenneth, D. Camphell, Jixiang Wang and J.H. Lunsford, J. Phy. Chem. 1986, 90, 534.
150. Francots, Oudet, P., Courtine and Alain Veju, J. Catalysis 114 (112-120), 1988.
151. R. Sumathi, K. Johnson, B. Viswanathan and T.K. Varadarajan, Indian Journal of Chemistry, Vol. 36A, Jan. 1999, 40.

152. L.C. Normand, J. Barrault, R. Breault, I. Illilaire and A. Klennemann, *J. Phy. Chem.*, 1991, 95 (257-269).
153. Suciu George Dan Palent CA Section, 51 (fossil fuels, Derivatives and Related products), Cross references, 45, 47.
154. Aline Auroux and A. Gervasini, *J. Phy. Chem.*, 1990, 94 (6371-6379).
155. R.J. Gorte, M.T. Aronson, W.E. Francth and David White, *J. Am. Chem. Soc.*, 1989, 111 (840-846).
156. K.M. Minachev, Khodakov, Y.S. and Naksalunov, V.S. *J. Catal.* 1977, 49 (207-215).
157. Connell G. and Dumesie J.A., *J. Catal.* 102, 216, 1986.
158. Katada, N., Toyama T., Niwa, M., Tsubouchi, T., Murakami Y., *Res. Chem. Intermed.* 1996, 9, 137.
159. Cheung T.K., Gates B.C., *Top. Catal.* 1998, 6 (41-47).
160. Iglesia, E., Barton D.G., Soled S.L., Miseo, S. *et al.* *Stud. Surf. Sci. Catal.* 1996, 10, 533.
161. Shabtai, J., Lazer R., Biron E., *J. Mol. Catal.* 1984, 27, 35.
162. Creighton E.J. Huskens. J, Vanderwaal J.C; Van Bekkum H; *Stud. Surf. Sci. Catal.* 108 (531-537) 1997.

163. Braun Eric; Leze Antoine; Touet Joc; Tetrahedron; Asymmetry 3(7) (841-4) 1992.
164. S. Wenchung; Cantrell William R; Carison John A; Tetrahedron Lett. 36(22) (3797-800), 1995.
165. Epple. M; Ebbinghaus. S; J.Therm. Anal. Calorium.; 52(1). 165-176, 1998
166. A.V. Salker, D.K. Chakrabarty and H.V. Kheer, Indian Journal of Chemistry, Vol. 28A, June 1989, p.458-462.
167. Koithoff I.M and Elving P.J. Treatise on analytical chemistry Part-II Analytical Chemistry of elements. Inter science NewY ork, 1966.
168. A systematic Analytical chemistry of Elements Rare earth, page 17.
169. Encyclopedia of Industrial Chemical Analysis Volume 17 page 473.Ed.by Foster Dee and Leslie. S.Ettre. Interscience New York.
170. Rodnas E, Hattoria and Tayoshima . T, React Kinct catal Lett. 16 (1981) 23.
171. Vogels textbook of practical organic chemistry fifth edition first ISE Reprint. 1998.page 392.
172. Vogels text book of practical organic chemistry fifth edition first Reprint 1998, page 402.
173. M.P. Kannan, T. Ganga Devi, Thermochemica Acta, 292 (1997), 105-109.
174. H.A Bensi, J. Phy. Chem. 61, 970 (1957).

175. K.R.P. Sabu, K.V.C Rao and C.G.R. Nair . Bull Chem., Soc. Jpn. 64(1920-1925) 1991.
176. S. Malinowskii, S. Szezepanska and J. Sloczynski, J Catal., 7, 67 (1964).
177. Yamanaka, T., Tanabe K., J. Phy. Chem., 74, 1975, 91.
178. Kortum, G., Angrew. Chem., 70, 651, 1958.
179. Sanderson, R.T., Chemical Periodicity, Chapt. 6, Reinhold, New York, 1960.
180. Nakamoy, S., Jizuka, T., Tanabe K., J. Catal. 1978, 51.
181. Zeltlin H., Kondo, N. and Jordan, W., J. Phy. Chem. Solids, 25, 641 (1964),
Zelt in H., Frei, R., and He Carter M., J. Catal. 4, 77, 1965.
182. K. Magavo and K. Fsumi, J. Adhes. Sci. Tech., 4 (1978) 59.
183. Che-M. and Tech, A., J., Advances in Catalysis (D.D. Eley, H. Pines and P. Eweksz, Eds.) Vol. 31, p.77. Academic Press, SanDiago, 1982.
184. Sanderson, R.T., Inorganic Chemistry, page 81, Reinhold, New York, East West Student Edn., 1971.
- 184a. The Rare Earths by F.H. Spedding and A.H. Daane, Wiley, New York. A Treatise on Inorganic Chemistry, Vol. I by H. Remy Elsevier, Amsterdam.
185. Shabtai, J., Lazer, R., Biron, E., J. Mol. Catal., 1984, 27, 35.
186. Hideshi Hattori, Chemical Review, 1995,95, 537-558.

187. Yamamoto T., Matsuyama T., Tanaka T., Funabiki, T. and Yoshida, S. Phys. Chem. Phys. 1991, 1, 2841.
188. Yamamoto T., Matsuyama T., Tanaka T., Funabiki T. and Yoshida S., J. Mol. Catal. A. Chem. 2000, 155 (43-58).
189. G. Wang, H. Hattori and K. Tanabe, Bull. Chem. Soc., Jpn. 56, 2407, 1983.
190. G. Connell and T.A. Takeshita, Advances in Catalysis, Vol. 17, p.315, Academic Press, NewYork, 1967.
191. G. Connell and J.A. Dumesic, J. Catal. 105, 285, 1987.
192. Bennesi, H.A. and Winquest, B.H.C. Adv. Catal., 27, 1978, 123.
193. Zeppelin H., Kondo N. and Jordan, W., J. Phy. Chem. Solids, 25, 64, 1964.
194. Zeppelin H., Frei, R. and McCarter M., J. Catal. 477 (1965).
195. K. Tanabe, Bull. Chem. Soc. Jpn. 26, 1973, 2985.
196. C.L. Kibby and W. Keithal, J. Catal., 31, 65 (1978).
197. Modern Methods of Organic Synthesis, Third Edn. W. Corruthers, p.458.

N/B 2998