ACID-BASE, SURFACE ELECTRON DONATING AND CATALYTIC PROPERTIES OF BINARY OXIDES OF Zr WITH RARE EARTH ELEMENTS

THESIS SUBMITTED TO THE
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
IN PARTIAL FULFILMENT OF THE
REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN

CHEMISTRY

BY

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NOVEMBER 1997

to my

Beloved Parents....

CERTIFICATE

This is to certify that the thesis herewith is an authentic record of research work carried out by the author under my supervision, in partial fulfilment of the requirements for the degree of doctor of philosophy of Cochin University of Science and Technology, and further that no part thereof has been presented before for any other degree.

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DECLARATION

I hereby declare that the work presented in this thesis entitled, "Acid-Base, Surface electron donating and catalytic properties of binary oxides of Zr with rare earth elements" is entirely original and was carried out by me independently under the supervision of Dr.S.Sugunan, Professor in Physical Chemistry, Department of Applied Chemistry, Cochin University of Science and Technology, Kochin-22, India. I further declare that this thesis has not formed the basis for the award of any other degree or diploma, fellowship or associateship of any university or Institution.

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Acknowledgements

It is with all sincerity and regards that I express my deep sense of gratitude to my research supervisor, Dr. S. Sugunan, Professor in Physical chemistry, Department of Applied Chemistry, Cochin University of science and Technology, Kochi-22, for his meticulous guidance, pertinent encouragement, inspiring discussions and valuable suggestions throughout this investigation. During my research period, he has given me the much needed boost and showed a very good direction to my career. His subtle teachings have broadened my knowledge in the area of heterogeneous catalysis and has given me more confidence to explore new frontiers. I will ever remain to him for his inspiring guidance, wise counsel, unfailing attention and suggestions which led to the accomplishment of my research with very successful.

It is my pleasant duty to express my greatefulness and sincere thanks to Prof. P. Madhavan Pillai, Head of Applied Chemistry for providing the necessary facilities for my work and for his affectionate encouragement. I am equally indebted to all other teachers of my department for their inspirations and timely help for my work.

I earnestly thank Dr. J Thomas, Associate professor and Head, and Dr. Samuel Joseph, Professor, Aromatic and Medicinal Plants Research Station, Odakkaly, Govt. of Kerala, for providing facilities for GC analysis in the phytochemical Laboratory.

I wish to thank Prof. C.S. Swamy, Coordinator, Catalysis Division, Indian Institute of Technology, Madras for providing me with the BET data for surface area determination and authorities of the regional Sophisticated Instrumentation Centre, IIT.

Madras for providing the ESR spectral data. I am also previleged to acknowledge my thanks to Dr. Lalithambika for their help in providing me BET surface area data in timely.

It gives me immense pleasure to express my heartfelt thanks to my fellow research scholars, Binsy Varghese, Bindhu Jacob, T.M.Jyothi, K. Sreekumar, C.R. Seena, N.K.Renuka and C.G.Ramankutty for their warmth encouragement and cooperation and timely help.

I feel extremely happy to thank my friends, office staffs and well wishers of the Dept. of Applied Chemistry for their help. I owe a special regards to Dr. P.A. Unnikrishnan for his sincere help in finishing my thesis work. I pay my respect to my seniors for their willing help, friendly encouragement and unstinted support during my research period.

I must greatfully Acknowledge Mr.Binoy Jose, Mr.K.Sreekumar and Ms. N.K.Renuka, for their valuable help in typing my thesis. I have been fortunate in having their willing help and continuos encouragements at all stages of my work.

Financial assistance from CSIR New Delhi during my junior research fellowship is greatfully acknowledged.

I Would like to record my deep felt affection, thanks and love to my beloved parents, brothers and sisters for their unmitigated encouragement, unflinching support, love and prayers which really have been the catalyst for what I am today.

It is with all sincerity and special regrds that I express my deep sense of gratitude to my colleagues in the chemistry department of Bharata Mata College, Thrikkakara, Kochi-21 for their cooperation and timely help.

Last, but not the least, I remember my cordial friends, Jinny, Sajan, Murali, Indulekha, Sabu, Shaji and Nelson for their words of encouragement during my travails. Special regards to my beloved parents, sisters and brothers for their constant and affectionate encouragements, love and care which proved to be very essential.

Finally, it gives me pleasure to express my heart-felt gratitude to all those who have been there all the while during my research period, lending their help in every possible way to come out of the course with flying colours.

ANTO PAUL

PREFACE

The subject of catalysis has undergone rapid advancement in the last three decades. The developments of a host of analytical tools have helped in the understanding of the fundamental aspects of catalysis at the molecular level. On the other hand, the technological advancements achieved in this area have revolutionised chemical industry, in particular the petroleum, petrochemical, fine chemical and allied industries. Catalysis holds the key to clean technology. With more and more stringent demand for clean environment the catalysis science is going to play the most important role not only in chemical industry, but also in areas such as pollution control, power generation and transportation.

Because of the great importance of acid-catalysis in the petrochemical industry extensive research work has been carried out concerning the fundamental and applied aspects of catalysis by acids. The initial discovery that several hydrocarbon reactions can be catalysed by acids stimulated great interest in academic as well as industrial laboratories. In contrast, base catalysed reactions have receive little attention in heterogeneous catalysis, although it has been recognisd for a long time that hydrocarbons may undergo various reactions in solution in the presence of bases.

An interesting and important feature of solid acid-base catalysis is that in many cases, both acidic and basic sites exists simultaneously on the surface. It was argued that these dual acid-base sites could provide new routes for reactions involving a dual site mechanisms. In addition, considerable interest has been directed to the possible correlation between catalytic activity and acidic/or basic properties the catalyst. The search for correlations has been implemented through appropriate measurements of number, nature, strength, location and environment of the acid or base active sites. A number of chemical and physical methods have been developed and have provided valuable information on the interpretation of the catalytic effects.

The important objectives of the thesis are:

(i) Determination of electron donor strength of the oxides.

(ii) Determination of acidity/basicity at different strengths

(iii) Catalytic activity the oxides for certain reactions

As to the content of this thesis, we shall start with an introduction in chapter.1 where the importance and catalytic reactions of zirconia and rare earth oxides were revealed. It is followed by a thorough review in chapter 2. Discussion of the experimental methods then follow in chapter.3. Chapter.4 onwards begins the results and discussion of work, where chapter 4 deals with the surface electron donor properties of the oxides, chapter 5 discusses the acid-base properties of the oxides and chapter 6 consider the various acid-base sites and their importance as active sites in certain organic reactions as a measure of catalytic activity of oxides. Finally the chapter 7 focuses with the important leading conclusions arising out of the thesis work.

The results described in this thesis work which have been published/ communicated and are under preparation are given below.

1. Acid-base characteristics of binary oxides of Zr with Ce and La

   S.Sugunan, G.V.Chemparathy and **Anto Paul**, J.Mat. Sci. and Eng., 3, 45 (1996).

2. Surface acidity/basicity and Catalytic activity of mixed oxides of Zr, La and Al.

   S.Sugunan and **Anto Paul**, Indian J. of Chem., 36A, 300 (1997).

3. Strength and distribution of electron donor sites on ZrO_2-Dy_2O_3 mixed oxide systems

   S.Sugunan and **Anto Paul**, J. Collect. Czech. Chem. Commun. (in press).

4. Acid-base properties and catalytic activity of ZrO_2-Y_2O_3 systems.

   S.Sugunan and **Anto Paul**, Indian J. of Chem. (in press)

5. Adsorption of electron acceptors adsorbed on mixed oxides of ZrO_2 -Y_2O_3 mixed oxide systems

   Sugunan and **Anto Paul** (communicated to J. of Mat Science)

6. Cyclohexanol conversion as a measure of strength of basicity of ZrO_2-Y_2O_3 mixed oxides.

   S.Sugunan and **Anto Paul** (Communicated to React. Kinet. Catal. Lett.)

7. Basicity and catalytic activity of ZrO_2-Dy_2O_3 mixed oxide systems.

   S.Sugunan and **Anto Paul** (Communicated to Indian J. of Chem.)

The papers under preparation are

8. Surface electron donor and acid/base properties of binary oxides of zirconia with gadolinium oxide.

   S.Sugunan and **Anto Paul**

9. Comparative study of acid-base properties of mixed oxides of ZrO_2 with rare earth oxides by esterification of butanol.

   S.Sugunan and **Anto Paul**

10. Catalytic oxidation of cyclohexanol on ZrO_2-Dy_2O_3 systems as an Oppenauer oxidation.

    S.Sugunan and **Anto Paul**

11. Catalytic activity of ZrO_2-Gd_2O_3 mixed oxides for the Reduction of cyclohexanone and oxidation of cyclohexanol.

    S.Sugunan and **Anto Paul**

12. Acidity and comparative surface properties of ZrO_2, Y_2O_3, Dy_2O_3 and Gd_2O_3 and their binary oxides.

    S.Sugunan and **Anto Paul**

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CHAPTER 1

INTRODUCTION

Solid acids and bases are useful catalysts for many important catalytic reactions, including the cracking of hydrocarbons, the isomerisation, polymerisation and hydration of olefines, the alkylation of aromatics and the dehydration of alcohols etc [1,2]. Extensive investigations on solid acid and base catalysis in past several years led to the discovery of a number of new types of solid acids and bases including single oxides, binary oxides and ternary oxides having a wide variety of applications. Extensively investigated research and study of solid catalysts over the last few years have resulted in major contribution to both fundamental research and industrial development particularly in the field of petroleum chemistry. The relevance of solid catalysts in the field of heterogeneous catalysis is under extensive study.

As industry is turning increasingly toward the use of solid catalysts instead of liquid ones, metal oxides are being studied. Systematic study of the correlation between catalytic activity and selectivity and surface properties of oxides provided the identification of an optimum catalyst. Solid acids and bases have been characterised by the amount, strength and nature of acid - base centers on the surface, and by studying catalytic activities towards particular reactions. The characterisation not only depend upon the purity of the materials and the method of preparation, but also upon heat treatment, composition and irradiation. The nature and catalytic activities of solid acid materials were elucidated through the investigation of the structure of acid-base centres by comparison with the kinetics of homogeneous acid-base catalysis [2]. Comparatively little work that has been performed on solid bases gives promise that these also find applications as effective catalysts for important reactions.

Transition metal oxides are technologically important materials that have found many applications. For example, in the chemical industry these oxides are functional components in the catalysts used in a large number of processes to convert hydrocarbons to other chemicals. They are also used as electrode materials in electrochemical processes. In the electronic industry, they are used to make conductors in films. The recently discovered high temperature super conductors are multi-component transitional metal oxides.

Among these applications, perhaps the use of transition metal oxides as catalysts is the most technologically advanced and economically important application. It is also an area in which much progress has been made in recent years in terms of understanding of the fundamental process that occur, primarily because advances in instrumentation and experimental techniques have made it possible to study of the interface between the metal oxide and fluid phase in greater detail than ever before. In particular, developments in surface science techniques have provided very detailed picture about the structure, chemical composition and electronic properties of the surfaces.

In addition to being used as catalyst, transition metal oxides are also precursors for other important catalysts. It is quite conceivable that the detailed structures, morphologies or other properties of the transition metal oxide precursors could affect the properties of the final catalysts. Understanding catalysis requires an understanding of the surface chemistry, which deals with the bonding and reaction of an adsorbate with the surface and the influence of the surface on the bonding and the reaction between adsorbates. It is apparent that an important part of any effort toward obtaining such an understanding is the ability to characterize the physical and chemical properties of a surface. In recent years much progress has been made in the understanding of the metallic surfaces [3-6]. Table 1.1 provides a list of properties that are important in the surface chemistry of transition metal oxides. Many of them either do not apply or apply only to a limited extent to the metals.

Common to many of the properties listed above, is the fact that the metal oxides are made up of metal cations and oxygen anions. The ionicity of lattice which is often less than that predicted by formal oxidation states, results in the presence of charged adsorbate species and the common heterolytic dissociative adsorption of molecules. Surface exposed cations and anions form acidic and basic sites as well as acid base pair sites. The fact that the cations often have a number of commonly obtainable oxidation states resulted in the ability of the oxides to undergo oxidation and reduction and the possibility of the presence of rather higher density of cationic and anionic vacancies.

Table. 1: Properties that are important in the surface chemistry of transition metal oxides.

1. Presence of cations and anions in stoichiometric ratios.
2. Possibility of covalent and ionic bonding between cations and anions.
3. Presence of strong electric field normal to the surface.
4. Presence of charged adsorbed species.
5. Presence of surface acidity and basicity.
6. Presence of cationic and anionic vacancies.
7. Ability of cations to undergo oxidation and reduction.
8. High mobility of lattice oxygen as an active site in a reaction.
9. Interaction of solid with incident photons that leads to the photo assisted surface chemical process

ZrO_2 is finding immense use as a catalyst support material, in a variety of catalysed reactions [7-9]. The interest is ascribed to the following two properties of ZrO_2 1). as a carrier it gives rise to a unique kind of interaction between the active phase and the support. 2). it is chemically more inert than the classical supports [Al_2O_3 and SiO_2). The advent of partially and fully stabilised ZrO_2 during the last two decades has led to the significant studies in diverse fields such as high temperature refractories, chemical gas sensors, thermal coatings and catalysis [10-13]. More specifically this material has attracted a great deal of attention in the field of catalysis as it possess a combination of uniqueness in its chemical properties viz. acidity, basicity and redoxibility in several applications [7]. ZrO_2 can also be converted into super acid by impregnation with sulfates [14].

Zirconia is an important material that finds application in several fields. It exhibits catalytic activities for a number of reactions, where the characteristic behaviour of ZrO_2 was considered to be due to the acid-base bifunctional catalysis [15]. However, the drawbacks with this material lies in its low surface area at high calcination temperature (corresponding to the reaction temperature of many chemical industrial process). A number of attempts have been made to prepare high surface area catalysts using various precipitation methods and stabilising agents. It has been established that the homogeneous precipitation increases the textural properties of mixed oxides and oxyhydroxides. Furthermore the anion present during the precipitation influences the nature of the precipitate and so also the surface properties of the solids. The effect of anions on the acid-base properties of ZrO_2 prepared by homogeneous precipitation method has been reported by Parida et.al [16].

Zirconia supported catalysts were received considerable attraction in catalytic functionalities [17-20]. Zirconia supported catalysts were found to have better catalytic properties than the catalysts prepared on other oxide supports [21-22]. Catalysis by superacids has emerged as a field of an advanced study. Both liquid and solid super acids are used as catalysts for a large number of acid catalysed reactions. Among the various solid super acids used, sulfate promoted ZrO_2, TiO_2, Fe_2O_3 etc. are the major important class of catalysts from the point of view of high catalytic activity, better selectivity, thermal stability and reusability [23]. It was found that sulfated ZrO_2 catalyses various acid catalysed reactions very efficiently. It has also been observed that it has advantage over other solid super acids, such as cation exchanged resins due to low cost and high thermal stability [24].

It is well known that ZrO_2 at low temperature shows a monoclinic distortion with an effective sevenfold coordination [11]. However by substitution of small amount of Zr^{4+} by ions such as Y^{3+}, Ca^{2+} and Mg^{2+} etc., oxygen vacancies can easily be created to stabilise the cubic phase at room temperature. In addition, solid solution of ZrO_2 by various transition metal ions such as La(III), Co(III), Cr(III), Cu(II) etc. have also been widely investigated [26-29]. The formation of cubic ZrO_2 by introduction of Mn^{2+} ion to the lattice at the calcination temperature as low as 773 K was reported by Kesavaraj et.al [30] and they have reported the stabilisation mechanism as well as its role in controlling their catalytic activity due to redox behaviour of manganese in complete oxidation of carbon monoxide.

The lanthanide oxides are making the history of the catalyst very important. Although the fundamental and surface properties of alkali, alkaline earth metal and other basic oxides have been studied in detail [1], equivalent information about rare earth oxides are much less. The catalytic activity of rare earth oxides has been reviewed in a book by Tanabe et.al [2]. Rare earth oxides were classified as basic oxides by using O_{18} binding energy studies [30]. The dependence between surface basicity and catalytic properties among rare earth oxides have been explored to only a limited extent. Systematic studies of the correlation between catalytic activity and selectivity and acid-base properties of the catalyst surface has enabled the determination of the optimum catalyst in terms of acidity and basicity.

Rare earth oxides constitute a family of refractories which resemble the alkaline earth oxides in many respects, but offers a unique opportunity to study the effect of smoothly varying periodic trends on catalytic behaviour. In particular, the gradual increase in tetravalent ionic radius and consequent increase in ionic charge density, in going from La^{3+} (1.06A°) to Lu^{3+} (0.85A°) results in a corresponding decrease in basicity of the sesqui oxides (M_2O_3) across the series [31]. Furthermore with only a few irregularities the effect of this basicity trend on catalytic properties can be assessed independently of other electronic and solid parameters such as d electron configuration, crystal structure and preferred stoichiometry, which are largely invariant through out the oxide series. All La^{3+} ions for example lack 5d electrons and differ from each other electronically only in respective configuration of highly shielded 4f electrons.

Catalytic behaviour of rare earth oxides have been explored for many reactions and a wide variety of catalytic properties have been known [32]. The use of rare earth oxides as promotors or supports in catalytic reactions has grown extensively in past few years, due to its interesting properties encounterd in automotive pollution control by catalysis or syngas conversion. In catalysis by automotive pollution control, the reducibility of some of the rare earth oxides (eg.CeO_2) have been put forward to explain the increase in performance of rare earth modified catalysts [33]. Rare earth oxides are thought to participate in the catalytic reaction, acting as an oxygen storage component to stabilize the dispersion of the catalytic noble metals and to improve thermal stability of ammonia. In syngas conversion both reducibility and basicity of rare earth oxides are involved.

It was suggested that the catalytic activity of lanthanide oxides depend on the electronic configuration of the inner 4f subshell [34-35]. The rare earth oxides are interesting that they exhibit activity as oxidation catalysts and have low work functions (2.7 eV) [36]. Thus they have both of the required attributes of negative surface ionisers (NSI). They can function as catalytic oxidisers to produce oxide species that have relatively high electron affinities and they can provide a low work function surface which helps to ionise the subliming molecule or perhaps to allow the preformed ions to escape more easily from the surface as ions.

The rare earth oxides are refractory materials, hence they are stable at high temperatures and in the atmospheric conditions. This combination of properties provide an oppertunity to study the oxidation of metallic rhenium using rare earth oxides as catalysts by observations of the rhenium oxide negative ions. Because of their high melting points, rare earth oxides are superior in thermal stability to catalysts containing low melting metal oxides/salts for the catalytic reactions. The rare earth oxides are hardly reducible, which character is studied for the catalyst support which is applied under reducing atmosphere.

In general, the transition elements exhibit several valance states and their oxides are semiconductors that have a pronounced paramagnetism caused by the holes in the d band. In this respect, the rare earth oxides provide a contrast, since valance states other than trivalent are relatively uncommon and their paramagnetism arises from incomplete 4f orbitals which are screened from external influence by 5s and 5p electrons. Furthermore three different crystal forms have been found in the rare earth oxides. The most common being cubic form (C form) and hexagonal form (A form) in which the coordination number of metal ion is 6 and 7 respectively, and the B structure, about which little is known [37]. To evaluate the effect of paramagnetism crystal structure and crystal field on catalytic activity, the activity of the lanthanide series of oxides in their various crystal forms for dehydrogenation of cyclohexanone have been reported. The fact that there is little correlation between paramagnetism and catalytic activity of the lanthanide oxide suggested that unpaired 4f electrons are not participating in the mechanism. The effect of crystal structure is not significant on the activity of the rare earth oxides.

According to Tanabe [38], the acid-base properties of mixed metal oxides can be varied by choosing different metal oxide constituents at different concentrations and by choosing the pretreatment of the sample. We have done an investigation on the properties of mixed oxides of ZrO_2 with rare earth oxides such as Dy_2O_3, Y_2O_3 and Gd_2O_3. Surface acidity and basicity investigation have received considerable attention recently, because these properties can provide significant information in determining the behavior of solid surface. Determination of the strength of acid-base strength and distribution of acid base sites exposed on the solid surfaces as well as their distribution are necessary requirement to understand the catalytic properties of the solids. The conversion and selectivity of a reaction depend not only on the nature of the active sites but also on their number and strength. Therefore we have been determined acidity/basicity at different acid-base strengths by titration method using a series of Hammett indicators on a common H_o scale. The acid-base properties have been correlated with the catalytic activity of the oxides for certain organic reactions. The strength and distribution of electron donor sites on the surface oxides were also determined by the adsorption of different electron acceptors from acetonitrile solution. Since all the surface properties vary with pretreatment temperature, variation of acid-base, electron donating and catalytic activity of the oxides were also studied at different temperatures.

REFERENCES

1. K.Tanabe "*Solid acids and bases*", academic press, New York, (1970).
2. K.Tanabe, M.Misono, Y.Ono and H.Hattori, "*New solid acids and bases*", Kodansha, New York (1989).
3. G.A.Somarjai, "*Chemistry in two dimensions: surfcaes,* " Cornell university press, New York, (1981).
4. T.N.rhodin and G.Erh, "*the nature of surface chemical bonds*", Ed. ,North Holland Pub. Co.,New York (1979).
5. S.R.Morison, "*The chemical physics of surfaces*" Plenum press, New York, 1977.
6. G.Erh and J.Kuppenss, "*Low energy electrons and surface chemistry,*" Weinheim , Germany, (1985).
7. K.Tanabe, *Mater. Chem. Phy*, **13**, 347, (1985).
8. P.D.L.Mercerra, J.C. Van Ommen, E.D.W. Doesburg, A.J. Burggrat and J.R.H.Ross, *Appl. Cat.*, **57**, 127 (1994).
9. T.Iizuka, Y.Tanaka and K.Tanabe, *J. Cat.*, **76**, 1 (1982).
10. A.M.Chirino, andR.J.S proute, *Ame.Chem. Ceram. Soc. Bull.*, **59**, 604, (1980).
11. B.H.Davis, *Appl. Cat. Surf. Sci.*, **19**, 200 (1984).
12. G.Fischer, *Ceram. Bull*, **65**, 1355 (1980).
13. R.G. Silver, C.J. Hous, and J.G. Ekerdt , *J. Cat.*, **118**, 400 (1989).
14. X.Song and A.H.Sayari, *Cat. Rev. Sci. Eng.*, **83 (3)**, 329 (1996).

15. A.C.Q.M.Meijers, A.M.De jong, L.M.P. Van Gruijthsuen and J.W.Neimantsverdriet, *Appl. Cat.*,**70**, 53 (1991).

16. A.K.M.Parida et. al, "*Catalysis in modern trends*", Ed. N.M.Gupta and D.K. Chakrabarthy, Narosa Publication, New Delhi, 315, (1995).

17. K.C.Pratt, J.V.Sanders and V.Chrstov, *J. Cat.*, **124**, 416 (1990).

18. B.M.Reddy, K.V.R.Chary, B.R.Rao, N.S.Subramanyam and C.S.Sunandana, *Polyhedron,* **5**, 191 (1986).

19. J.Sedlack and Z.Vits, *Colloid Czech. Chem. Comm.*, **54**, 2064 (1989).

20. T.Khono, T.Yokono, Y.Sanadu, K.Yamashita, H.Hattori and K.Makino, *Appl. Cat.* **29** 201 (1986).

21. T.Ono, H.miyata, Y.kobokawa, *J. Chem. Soc. Faraday Trans.*, 1(**83**), 1761, (1983).

22. N.Nakano, T.Iizuka, H. Hattori, and K.Tanabe, *J. Cat.*, **59**, 1, (1979).

23. L.T.S.Throat, N.M.Yadav, *Appl. Cat A(general)*, **90**, 73 (1992).

24. H.Hono and K.Arata, *J. Chem. Soc. Comm.*, **24**, 1148, (1979).

25. P.Duwez, F.Odell and F.H.Brown, *J. Ame. Ceram. Soc.*, **35**,107, (1952).

26. Y.C.Zhang, K.Dwight and A.Wold, *J. Mat. Res. Bull.*, **21**, 853 (1986).

27. P.Wu, R.Korshaw, Kdwight and A.Wold, *J Mater. Res. Bull.*, **23**, 475, (1988).

28. A.M.George, N.C.Mishra and N.C.Jadadevan, *J. Mat. Sci. Lett.*, **11**, 404, (1992).

29. A.Kesavaraja and A.V. Ramasamy, *J. Mat. Sci*, **9**, 837 (1994).

30. H.Vinek, H.Noller, M.Ebel and K.Schwarz, *J. Chem. Soc. Far. Trans.*, 1(**73**), 734 (1977)

31. T.Moller, "*Chemistry of the Lanthanides*", Pergamon, New York, 1973.

32. M.P.Rosynek, *Cat. Rev.*, **16**, 111, 1977.

33. K.C.Taylors, "*Catalysis Science and Technology*", Springer Verlag, Berlin, 5, p119, ((1984).

34. A.Wepttss and G.Kim, "*Industrial application of rare earth elements*", ACS symposium series, No 164, A.C.S.7, p 117, (1964).

35 J.C.Summers and A.J.Ausen., *J. Cat.*, **58**, 131, (1979).

36. L.A.Sazanov, E.V.Artamonov and G.N.Mitrofanova, *Kinet. Cat.*, **12**, 378 (1971).

37. K.M.Minachev, *Proc. Int. Congr. Catal.*, **5**, 219 (1973)

38. V.S.Fomenko, "*Handbook of thermionic properties*", Plenum, NewYork, (1966).

39. M.C.B.Mc Gough and G.Houghton, *J. Phy. Chem.*, **65**, 1887, (1961).

40. K.Tanabe, "*In Catalytic Science and Technology*", Springer Verlag, New York, p.231 (1981).

CHAPTER 2

REVIEW

2.1. ELECTRON DONOR-ACCEPTOR PROPERTIES

The formation of radical ions on the surface by elctron transfer process is well established. The presence of electron donor sites on metal oxide surfaces are already reported [1-6]. The adsorption of electron acceptors/donors on the metal oxide will form corresponding radical ions, due to the electron transfer form adsorbent to the adsorbate. By measuring the radical forming activity of metal oxides, their electron donor or acceptor strength have been investigated [7-9] and this method has also been used for characterization of oxides [10-13].

The electron donor strength of metal oxide can be defined as the conversion power of an electron acceptor to its anion radical. If a strong electron acceptor is adsorbed on a metal oxide surface, the anion formation will take place at all donor sites. If a weak electron acceptor is adsorbed on the surface, the anion radical formation is expected only at the strong donor sites. If a very weak electron acceptor is adsorbed on the surface, the anion formation is not expected even at the strong donor sites. Thus the electron donocity of an oxide surface can be expressed as the limiting electron affinity value of electron acceptor at which the anion radical formation is not observed on the metal oxide surface.

The formation of anion radicals on metal oxide surface by the adsorption of electron acceptors have been established by many workers [14-17]. Flockhart et. al obtained experimental evidence for the presence of electron donor sites on the surface of alumina by electron spin resonance spectroscopy technique [7,12,17]. They attempted the adsorption of TCNQ and chloranil for the estimation of electron donor properties of alumina surface of gibbsite, γ alumina and η alumina. In this respect they associated the electron donor sites with unsolvated hydroxyl ions and defect centers involving oxide ions [14]. The formation of anion radicals by the adsorption of nitrocompounds on the surface of MgO powder have been studied by ESR and reflectance spectrophotometry [9]. They found that negative radicals are formed on clean MgO surfaces in vacuum where as this no longer occurs if surface is contaminated with water and CO_2..

K. Kirota et. al were reported the formation of anion species when TCNE and benzophenone were adsorbed on ZnO and Al_2O_3 in vacuum[18]. Chemisorption of O_2 on MgO was observed under condition which involve different types of electron transfer process, either from electron donor centers formed by irradiation or by the addition of intrinsic impurity ions [19-20]. Carbon dioxide was adsorbed as CO_2^- ions by electron transfer from S center on irradiated MgO [21]. The electron donor properties of metal oxides (MgO, $AlCl_3$, SiO_2, TiO_2, ZnO & NiO) were investigated by means of TCNQ adsorption by Hosaka et.al [12]. The order of radical forming activity determined by esr spectroscopy is as follows: MgO > ZnO > Al_2O_3 > TiO_2 > SiO_2 > NiO. The electron donor properties of metal oxide surfaces might be dependent on the nature of the semiconducting oxide and the surface hydroxyl ions. The reduction of I_2 to iodide ion occurs readily on the surface of partially dehydrated catalytic aluminas and silica aluminas [22]. An increase in alumina content results in an increase in reducing activity. These studies concur with those obtained with the study of reduction of TCNE on alumina surfaces.

The radical ion of nitrogen heterocycles and sulfur heterocycles have been generated and studied on a verity of oxide surfaces including SiO_2-Al_2O_3 and Mo_2O_3-Al_2O_3 by K.S. Seshdri and L. B. Petrakis [23-24]. The adsorption of a series of aromatic hydrocarbons from solution on hydroxylated and dehydroxylated surfaces have been investigated [25]. The dehydration of silica surfaces sharply diminishes the adsorption of aromatic hydrocarbons. Che et. al [26] carried out systematic studies of adsorption of TCNE on the surface of TiO_2 and MgO. They found that electron donor centres are associated with OH groups present on the surfaces of the solid activated at low temperatures and coordinated O_2^- ions at higher temperatures. The electron donor properties of the several oxide powders activated in vacuum at temperatures up to 1200 K have been investigated using the esr spectroscopy of adsorbed azobenzene radical as a probe molecule [27]. The results show the correlation between electron donor activity and the Lewis base strength indicating a direct connection between basic centers and electron donor sites.

Pigmentary samples of TiO_2 react with electron acceptors such as quinones, TCNE and TCNQ to give paramagnetic species [28] and it has been confirmed by visible absorption spectral measurements. A comparative study of variation of surface properties and catalytic activity of TiO_2 preheated in vacuum for the dehydration of formic acid has shown that the active sites in the reaction are the electron donor sites, the number of which have been determined by the adsorption of TCNE or trinitrobenzene and esr analysis of the paramagnetic anions formed [29].

The electron donor strength on a metal oxide is the conversion ratio of an electron acceptor adsorbed into its anion radical. The strength and distribution of electron donor sites of titania surface was evaluated by adsorption of four electron acceptors with electron affinities ranging from 1.26 to 2.84 eV from acetonitrile solution [30]. The concentration of anion radicals formed on the surface, as a result of electron transfer decreased with decreasing electron affinity of the acceptors. The decrease was very steeply between 1.26 and 1.77 eV. These results suggest that the limit of electron transfer from the titania surface to the electron acceptor ranged between 1.77 and 1.26 eV in terms of the electron affinity of the acceptor. The electron donor strength of alumina surface has also been studied by measuring the adsorption isotherms, ESR and electronic spectra [10].

The electron donor property of ZrO_2-TiO_2 systems were investigated by means of the adsorption of TCNQ [31] which has a much lower donocity than TiO_2.

The electron donor properties of metal oxides depend upon the pretreatment temperatures. The adsorptive characteristics of ZrO_2 have also been investigated by studying the adsorption of TCNQ [32], N_2, Ar and H_2O [33]. The radical concentrations decreased with increase in temperature, reached a minimum value at 700°C and then increased with rise in temperature. This behaviour has been explained by a change in the number of electron donor sites and their strength [32]. Surface properties were found to depend primarily upon the amount of irreversibly adsorbed water retained by the sample. Water was irreversibly adsorbed on ZrO_2 in amounts far in excess of that required for a classical chemisorbed monolayer [33].

Fowkes et.al had studied the adsorption of acidic and basic molecules from neutral solvents on Fe_2O_3, SiO_2 and TiO_2 [34-36]. They found that the calorimetric heats of adsorption were actually the heats of acid-base interaction governed by the Drago equation [37] and that the Drago constants can be accurately determined for the surface sites of these inorganic solids. Adsorption of tetrachloro-p- benzoquinone (chloranil) from basic solvents on metal oxides, such as alumina and titania were carried out to understand the acid-base interaction at the interface [38] The amount of chloranil adsorbed decreased with an increase of acid-base interaction between the basic solvents and chloranil and also decreased with an increase in acid-base interaction between the acidic solvent and electron donor sites of the surface for both the metal oxides. The change in concentration of chloranil radicals formed was correlated with the acid-base interaction at the interfaces.

The electron donor properties of γ-alumina, silica and their supported palladium oxide have been studied [39]. It was observed that while γ alumina had both electron donor and acceptor sites, γ alumina supported palladium oxide showed better electron acceptor properties than donor properties. Silica supported palladium oxide showed only electron acceptor properties. For binary oxides the electron donor property of the surface depend upon the composition of the mixed oxides.

The electronic state of the adsorbed species was studied by UV-vis spectroscopoy in addition to ESR spectroscopy to confirm the electron transfer process [10-12]. The bands appeared at 400 nm corresponds to the physically adsorbed neutral TCNQ molecule. The band extending to region of 600 nm was related to the dimeric TCNQ anion radical which absorbs light at 643 nm [40]. This tentative attribution was supported by the characteristic features that neutral TCNQ absorbs only at 395 nm, that TCNQ has a high electron affinity and TCNQ anion radical are stable even at room temperature. Chloranil adsorbed samples gave absorption band at 745 nm [38]. ESR and electronic spectra provided evidence that TCNQ anion radicals are formed as a measure of electron transfer from metal oxide surface to adsorbed TCNQ.

Adsorption studies have also been studied for the characterisation and for the determination of the role of adsorbed species on the catalytic activity of perovskite type oxides [19,41-42]. These include mainly equilibrium and kinetics of adsorption successive or simultaneous adsorption of two gases, infra red spectroscopy and temperature programmed desorption.

It is also possible that cationic species will be formed on adsorbent of an electron acceptor if a strong electron donor is used as the adsorbate. Several examples of the observation of positive ions on electron acceptor sites in SiO_2-Al_2O_3 and zeolite systems have been reported [2,19-21, 45-46]. The presence of electron deficient centres on strongly dehydrated alumina surfaces sufficiently powerful to promote the formation of positive radical ions from aromatic hydrocarbons have also been demonstrated [5, 45, 47-48]. The formation of cationic species adsorbed on surfaces has been established by studies of the adsorption of hydrocarbons on SiO_2-Al_2O_3 catalysts [1-5].

Edlund et. al observed the ESR absorption spectra of singly charged monomeric and dimeric cation radicals at 77 K in a γ-irradiated C_6H_5 - silica gel systems [49]. The formation of cation radical of triphenylamine on the surface of synthetic zeolite and anion radicals of naphthalene and biphenyl on silica gel have also been reported. Kinell et.al detected the cation radicals of naphthalene, anthracene, phenanthrane and biphenyl on SiO_2 gel by esr spectra [50].

Esumi etc. al studied the solvent effect on the acid-base interaction of electron acceptors with metal oxides like Al_2O_3 and TiO_2 [51-52]. The saturated amounts of TCNQ adsorbed decreased considerably with increasing basicity of solvent or acidity of solvent for both metal oxides. The results were interpreted in terms of acid-base theory by Drago equation [38]. TCNQ radical concentration for both metal oxides decreased with increasing basicity of solvent. The adsorption on metal oxide was found to be strongly influenced by interaction between basic solvents and TCNQ or between basic solvent and donor sites of the metal oxides. Solvent effect of several aromatic solvents in charge transfer adsorption of TCNQ into metal oxide was also studied and it was found that TCNQ radical concentration depends on ionisation potential of the solvent [53].

Applying the relation between solubility and chemical potential expressed by Miller [54] it was found that adsorption of TCNE anion radical salts on alumina is not affected by solubility, but depend on the nature of cation. K.Esumi et. al measured the zeta potential of Al_2O_3 and TiO_2 by adsorption of TCNQ from organic solvents [55]. They found that the zeta potential of oxide decreased with increasing concentration of TCNQ in acetonitrile and ethyl acetate indicating that TCNQ anion radical formed on oxide surface contribute to the decrease in zeta potential. Fomin et. al have shown that electron transfer does occur in certain solvent systems provided a suitable acceptor is present [56].

Plasma treatment has become attractive [57] as a method for surface treatment, probably because it is a dry process at low temperature with a relatively low pressure gas.

Esumi et. al [58] have studied surface modification of mesocarbon microbeads by various plasma treatment and found that it renders the surface more acidic owing to the formation of carbonyl group, whereas nitrogen or ammonia plasma treatment renders the surface more basic owing to the formation of amino group. Taking into consideration of these plasma treatments for carbon, there is a probability of modifying the electron donor properties of metal oxides by plasma treatment. The interaction of plasma treated metal oxides with TCNQ in acetonitrile solution was studied by measuring their adsorption intensity of TCNQ in acetonitrile solution [59]. The electron donocity is increased by the ammonia and nitrogen plasma treatments.

The electron donor properties of two component metal oxide systems like SiO_2-Al_2O_3, SiO_2-TiO_2, Al_2O_3-TiO_2 and ZrO_2-TiO_2 were studied by the adsorption of TCNQ [53,60]. Two component metal oxides showed lower radical forming activity than parent oxides and change in activity with composition was characteristic of metal oxide systems. These systems exhibited electron donor properties which would not be qualitatively predicted from consideration of the independent properties of the parent oxides [61-62]. The electron donor properties of some of the rare earth oxides and alumina supported rare earth oxides have also been studied [63-66] and the correlation with catalytic activity for certain organic reaction was also reported.

2.2. ACID-BASE PROPERTIES

It has been seen that surprisingly a large number of solids have surface acidity and basicity. The metal oxides and sulfides whose acid-base properties have already been reported are Al_2O_3, SiO_2, MgO, CaO, ZnO, SrO, BaO, TiO_2, V_2O_3, Sb_2O_3, Cr_2O_3, As_2O_3, CeO_2, ZnS and CdS. These solid acids and bases have found use as catalysts for many important reactions which find immense applications in heterogeneous catalysis [67,68]. Extensive investigations on solid acids and base catalysis in past few years discovered a number of new types of catalysts including single oxides, binary oxides and ternary systems having a wide variety of applications in different fields. Systematic studies on the correlation between catalytic activity and selectivity and acid-base properties of the catalyst surface has led to the determination of the optimum catalyst in terms of their surface properties.

The acid and basic properties of oxide catalysts are very important for the development of scientific criteria in the catalyst applications. The determination of the strength of acidic and basic sites exposed on the solid surface as well as their distribution is a necessary requirement to understand the catalytic properties of solid acids and bases. A complete description of acidic and basic properties of solid surface requires the determination of acidic and base strength, acid or base amount and nature of the such sites.

The acid strength of a solid surface is defined as its proton donating ability. Walling [69] defined acid strength of a solid as the ability of a surface to convert an adsorbed base into its conjugate acid. The strength of an acid can be characterised by its disassociation constant Ka

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

which is usually reported in terms of the parameter pKa. pKa values of the solid surfaces cannot be measured directly. Hammett and Deyrup [70] proposed an ordering of the acid strengths based on the Hammett acidity function H_o. H_o scale permits the comparison of the strength of acids taking into account their capability to transfer a proton to neutral molecule of a basic indicator. Deyrup defined an indicator as a non-ionised or a neutral substance capable of adding a single hydrogen ion per molecule in such a way that a colour change indicates the extent of the reaction.

If the reaction proceeded by the proton transfer from surface to adsorbate, the acidity function Ho can be expressed as

$$H_0 = pKa + \log \frac{[B]}{[BH^+]}$$

where [B] and [BH+] are the concentrations of neutral base and its conjugate acid.

If the reaction takes place by means of electron pair transfer from the adsorbate to the surface, then H_o is expressed by

$$H_o = pKa + \log\frac{[B]}{[AB]}$$

where [AB] is the concentration of the neutral base which reacted with the Lewis acid or electron pair acceptor A. Decreasing value of H_o indicates an increase in acid strength. Basic strength of a solid surface is defined as the ability of the surface to convert an adsorbed neutral acid to its conjugate base. That is the ability of the surface to convert an electron pair to an adsorbed acid. When an acid indicator is adsorbed on a solid from a non polar solvent the colour of the acid indicator is changed to that of its conjugate base, provided that the surface has necessary base strength to impart electron pair to the acid. Base strength is quantitatively expressed by the Hammett and Deyrup H- functions, after the analogy of acid strength Ho function.

For the reaction of an acid indicator BH with a solid base B,

$$BH + B = B^- + BH^+$$

the basic strength H. is given by

$$H_- = pKa + \log\frac{[B^-]}{[BH]}$$

where [BH] is the concentration of the acidic form of the indicator and [B.] is the concentration of the basic form.

For studies of solid acid-base catalysis, quantitative information on the acid base strength distribution of solid acid or base is essential. Quantitative determinations of acid base strength are known as acidity and basicity respectively. The acid or base amount usually expressed as the number or mmol of sites per unit weight or per unit surface area of the solid surface. A variety of methods have been suggested, which differ from each other in their chemical and physical principles and none of them can be regarded as universal in its use. Several reviews dealing with surface acidity and basicity of solid catalysts have been published [67-68,72-73]. The main methods for the quantitative acid base determination are the non aqueous titration method using Hammett indicators and gaseous acid or base adsorption.

The indicator method was originally reported by Walling [69] and is in extensive use. The colour of the suitable indicator adsorbed on a surface will give a measure of its acid strength. If colour is that of the acid form of the indicator, then the value of the H_o function of the surface is equal to or lower than the pKa value of the conjugate acid of the indicator. That is the measure of the acid strength of the surface is the pK_{BH^+} value of the weakest basic indicator which after adsorption exhibits the colour of the conjugate acid. Lower values of the H_o corresponds to the greater acid strength.

The titration method for the acidity determination was reported by Benesi [71] which is based on Johnsons experiment [74] and has been subsequently modified [75-76]. The amine titration method gives sum of the amounts of the both Bronsted and Lewis acid, since the surface will react with either electron pair (-N=) of the indicator or that of the amine (=N) to form a co-ordination bond [67]. Hirschler proposed the use of acidity function Hr for the determination of protonic surface acidity by using any carbinol and phenyl methyl indicators [77]

Even though the titration method is limited to white coloured surface this method is rarely applied to coloured or dark samples where the usual colour change is difficult to observe. In such cases the titration method is carried out by mixing a white substance of known acidity with the sample or by employing spectroscopic method [67,68.85-86]. The end point is taken when the color change is observed on white solid and a correction is made for the amount of n-butylamine used for the added white material. Volts et. al [87] determined Hammett acidities of chromia catalysts using F10 Al_2O_3 and S-34 silica alumina as white solid (indicator catalyst). Trambouze and co workers found that the acid amount of coloured samples can be determined by calorimetric titration method using n-butylamine, ethyl acetate or dioxane as the titrating base [88].

The amount of gaseous bases which a solid acid can adsorb chemically from gaseous phase is a measure of the amount of acid on its surface. When gaseous bases are adsorbed on acid sites, a base adsorbed on a strong acid site is more stable than one adsorbed on a weak acid site which, is more difficult to desorbe. As elevated temperature stimulates the evacuation of the adsorbed bases from acid sites those at weaker sites will be preferentially evacuated. Thus the proportion of adsorbed base evacuated at various temperatures can give a measure of acid strength. When prolonged subsequent evacuation does not produce no further decrease in sample weight, then the base which is retained up on the sample is understood to be chemically adsorbed [67-68].

The bases used as adsorbate so far include quinoline, pyridine, piperidine trimethylamine, n-butylamine, pyrol and ammonia [67]. The various bases are adsorbed to different extent even by the same catalyst. Temperature programmed desorption of basic molecules was also used for the estimation of acid amount together with the acid strength of the solid [79].

The transformation of an indicator into its conjugate acid form can be detected spectrophotometrically and spectroscopic method was introduced by Leftin and Hobson and Terenin. [80-81]. Drussell and Sommers presented the use of a series of fluoresent indicators for use in spectrofluorometric titration [82]. UV spectrophotometry has been applied for measurement of acid strength of SiO_2-Al_2O_3 catalysts using 4-benzoazodiphenylamine, 4-nitroaniline and 2,4-dinitroquinoxaline[83]. The adsorption of pyridine on V-Ti mixed oxide prepared by the gas phase method has been studied by IR spectroscopy [84]. V_2O_5-TiO_2 oxides exhibited both Bronsted and Lewis acid sites.

J.Take et.al studied surface acidity by the titration of solid acid with indicator itself in a non polar solvent and it determines the number of acid sites from the amount of indicator adsorbed at saturation [89]. Yoshizumi et. al determined acid strength distribution on SiO_2-Al_2O_3 catalyst calorimetrically by measuring the heat of adsorption of n-butylamine from benzene solution [90]

Previously reported methods for the determination of the acid amount measures either Lewis acid or Bronsted acid. It is necessary to distinguish between Bronsted acid and Lewis acid sites for the catalytic action of solid catalysts. Malinowski and Szczepanska measured the amount of Bronsted acid by potentiometric titration of a solid acid in anhydrous picoline with 0.1 N NaOH [91]. Leftin and Hall [92] reported that amount of Lewis acid can be determined from the amount of triphenyl carbonium ion formed when the solid acid abstracts a hydride ion from triphenyl methane as shown below.

In an IR study of pyridine chemisorbed on SiO_2-Al_2O_3 catalysts of varying Si content, Schwarz discovered a new method for the measurement of Lewis and Bronsted acid sites

[93]. The spectrum of pyridine which is coordinatively bonded to the surface is very different from that of the pyridinium ion also permit differentiation between acid types on the surface of a solid acid [94].

The acid properties of single oxides TiO_2, SiO_2, Mo_2O_3 Al_2O_3 and binary oxides have also been studied [73]. Many combination of transition metal oxides have also found to show remarkable acidic properties [95-100]. C.G.R. Nair and coworkers reported the acid base properties of single oxides, binary oxides and ternary oxides prepared from SiO_2 , Al_2O_3 and Mo_2O_3 by precipitation method at different pH [101]. They employed titration method of Benesi [71].

The amount of basic sites can be determined by titrating a suspension in benzene of a solid on which an indicator has been adsorbed in its conjugate basic form with benzoic acid dissolved in benzene. The benzoic acid titres are a measure of the amount of basic sites having basic strength corresponding to the pKa value of the indicator used [67]. Gaseous acid adsorption method can also be used for basicity determination. Acidic molecules like CO_2, NO and phenol are used as adsorbates [67,102]. Adsorption of phenol is not preferred because it is easily dissociated to adsorb on both acidic and basic sites. NO is used for the measurement of unusually strong basic sites [103].

A method of determining the basicity at various basic strength by titrating a solid suspended in benzene with trichloroacetic acid using a series of Hammett indicators was proposed by K.Tanabe and T.Yamanaka [104]. J.Take developed a method for the determination of basic strength of solid suspended in cyclohexane with benzoic acid using a series of Hammett indicators [105]. They found that base strength of alkaline earth oxides increased remarkably upon heat treatment in vacuum. TPD measurements of desorbed CO_2 were also used for the measurement of basicity of alkaline earth oxides [106]. Ai have also reported the correlation between basicity measurements and oxidation activity [107].

Y.Namanaka and K.Tanabe determined the basicity of a series of oxides and found the order of basicity as follows, $ZnO > \gamma\ Al_2O_3 > BaO >$ Act. $Al_2O_3 > B_2O_3 > ZrO_2 > MgSO_4 > MoO_3$ [104]. Basicity of Al_2O_3-MgO catalysts have also been studied. Fedorynska et.al studied the acidic and basic properties of alumina-silica catalysts. They found that the basicity of aluminosilicates is closely associated with decrease in amount of Al_2O_3 [108]. J.L.Zotin et. al prepared alumina from $Al(OH)_3$ prepared by different routes and characterised then in terms of their acidic and basic properties [109].

G.W. Wang et al. measured the acid base properties of ZrO_2-SnO_2 with different composition by indicator method [79]. A series of UV spectroscopic studies have been made for indicators adsorbed on alkaline earth oxides and adsorption maxima of the spectra was correlated with the basic strength of the solid [83,110]. Basicity of Al_2O_3 -MgO catalysts have been studied. In the series of Al_2O_3-MgO catalysts those containing about 75 % Al_2O_3 showed highest basicity [111]. Microcalorimetric measurements of the differential heat of adsorption were used to probe the distribution of acid strength on a series of silica supported catalysts [112]. .

The acid base nature and catalytic activity of rare earth oxides have been reviewed by Tanabe et al [73]. The rare earth oxides have been classified as the basic metal oxides on the basis of O_{18} binding energy study [113]. Nakashima et al measured the basicity of Sm_2O_3 by benzoic acid titration method [114]. The basicity of rare earth oxides are responsible for the catalytic activity for many reactions [115]. V.R.Choudhary and V.H.Rane determined acid and base properties of metal oxides by stepwise thermal desorption of CO_2 from 323 to 1173 K and TPD of ammonia [116]. Acid base properties of some rare earth oxides and binary oxides with Al_2O_3, ZrO_2 have also been measured by titration method using Hammett indicators following Tanabe method [117-119]. Activity of the oxides were correlated with acid-base proprties on a common Ho scale.

According to Tanabe [120] the acid base properties of mixed metal oxides can be varied by choosing different metal oxide compositions at different concentrations and changing the heat treatment of sample. Depositing oxides of following cations Ga^{2+}, Zn^{2+}, Al3+, Fe^{2+}, Mg^{2+}, Si^{2+} on to SiO_2 increased the acid strength of the catalyst. Gallium oxide is the most electronegative oxide and when it is added to SiO_2 strong acid sites are generated. Both Lewis and Bronsted acid sites are present on the surface [121]. IR spectroscopic studies of benzene adsorbed on several K.H.β zeolites where the extent of proton exchange (K/Al %) varied from 0 to 88.32 % have been undertaken at different conditions [122].

It was reported that acid/base property of metal oxides depend upon the pretreatment temperature. The acidity of alkaline earth oxide increased remarkably up on heat treatment in vacuum [93]. It has already been reported that the generation of strong acid sites depend on both pretreatment temperature and surface composition [123]. J.B Peri has demonstrated that site quality depends upon the evacuation temperature and at least five kinds of hydroxyl species were identified on the surface of the alumina [124].

The generation of acid sites on mixed oxides was first proposed by Thomas [125] and further modified by Tanabe and coworkers [126]. Connel and Dumesic have studied the generation of new and strong acid sites on SiO_2 surface by the addition of several kinds of dopant cations [127]. It has been widely accepted that the generation of acid sites on the mixed oxides was ascribed to charge imbalance localized on M_1-O-M_2 bondings formed on the mixed oxides, where M_1 is the host metal ion and M_2 is the dopant metal ion [126]. The charge imbalance might be expected even on the single component metal oxides consisting of small particles, since the electronic properties of small size metal or oxide particles are some what different from those of the bulk materials [127]. These differences are partially attributed to the surface imperfections of crystallographic structures in small sized particles. The relation between particle size and surface acidity of metal oxides have also been reported [128].

H.Nakabayashi [129] studied the mixed oxides of TiO_2-SiO_2 and TiO_2-Al_2O_3 by IR spectroscopy after pyridine adsorption. Both Lewis and Brosted acid site were found on the surface of SiO_2-TiO_2 mixed oxides though no Bronsted sites were found on the surface of pure SiO_2 and TiO_2, while on the surface of TiO_2-Al_2O_3 mixed oxide no Bronsted sites were generated. Recently he has developed an idea that new and strong acid sites will be generated on finely divided pure metal oxides and has demonstrated an increase in acid strength with decrease in particle size.

The existence of coordinately unsaturated cations were proposed to be responsible for Lewis acidity [130]. A coordinatively unsaturated center can chemisorb molecule of water resulting in the production of Bronsted acid sites [67]. At low activation temperature Bronsted acid sites are responsible for the acidity and at higher temperatures because of desorption of chemisorbed water molecules Lewis sites are probable. Two types of electron sources are reported for the basicity of the metal oxides. One of them surface hydroxyl ion and the latter is trapped electron at intrinsic defect sites on the lattice. Since the concentration of the former decreases with increase in temperature, the trapped electron centers must be responsible for the increase in basicity of the oxide with increasing in temperature. Surface lattice oxygen ions also considered to be involved in many basic sites.

2.3. CATALYTIC ACTIVITY

In heterogeneous catalysis by metal oxides many correlations between the catalytic activity, including its selectivity and acidity/basicity of the oxides have been indicated. Several studies have been reported to have systematic comparison of the acidic and catalytic properties of metal oxides and mixed metal oxides [67,73]. Solid acid catalysts are backbone of major process of petroleum chemistry such as cracking, hydrocracking reforming, isomerisation and disproportionation of aromatics [67]. There are many industrially important reactions catalysed by homogeneous bases such as oligomerisation, alkylation, addition, cyclisation, oxidation,dehydrogenation etc. [131].

Hydrogen transfer reactions have been studied and found its importance in organic chemistry by many workers. In these Meerwin Pondorf Verly reduction (MPV) is a well known reaction, the mechanism of which involves a hydride transfer from aluminium isopropoxide to the carbonyl carbon of the ketone. MPV reduction was discovered in 1925 and has been used successfully in a number of instances [132]. It is prominent in terms of its compatibility with many different types of functional groups, selectivity for reduction and low cost of isopropanol [133]. But this method calls for not only the addition of excess of catalyst (100-200 % amount) but also the neutralisation of alkoxide salt with strong acids. Therefore it has disadvantages such as need for tedious work ups in purification process and the unreusability of the catalyst as the disadvantage.

Many heterogeneous catalysts for the reduction are known. The use of heterogeneous catalysts such as MgO [133], MgO-SiO_2 [134], CaO [135] and Al_2O_3 [136] have also been reported to be successful. Kibby and Keithhall [137] have reported a hydrogen transfer reaction between alcohols and aldehydes over hydroxy apatite catalysts and proposed a mechanism similar to that of original MPV reduction. The advantage of the heterogeneous catalysts over conventional catalysts are easy product separation, the lack of a need for maintaining water free conditions, reusability of the catalyst and durability of the activity.

Reduction of aldehydes and ketones and the amidation and esterification of carboxylic acids proceeded efficiently over hydrous Zr(IV) oxides [138-140]. The reduction of carboxylic acids and esters with 2-propanol over hydrous Zr(IV) oxide and several other heterogeneous catalysts in vapour phase have also been reported [141]. These methods have advantage in purification of process, but they need to be carried out in vapour phase and require a high reaction temperature. Shibagaki et. al [138] studied the liquid phase reduction of aldehydes and ketones with 2-propanol over hydrous Zr(IV) oxides. Studies on the kinetic isotope effect have indicated that the reaction rate is of first order dependence in each of the concentrations of carbonyl compounds, 2- propanol and the catalyst. An observation of the primary isotope effect has suggested that a step of hydride transfer from adsorbed 2-propanol to adsorbed carbonyl compound constitute the rate determining step for the reduction.

The reduction with 2-propanol as a hydrogen source over hydrous tin (IV) oxide has been proved to be successful. The reduction of aliphatic carboxylic acids gives the corresponding alcohols. Aromatic carboxylic acids and their derivatives were further reduced and corresponding hydrocarbons were obtained. The reduction of aromatic ketones and derivatives of benzoyl alcohols also give hydrocarbons [142]. The reduction of methyl benzoate and benzoic acid on Y_2O_3 catalysts under H_2 gas has been examined by IR spectroscopic flow reaction at 250-450° C [143]. Some rare earth oxides and their mixed oxides with alumina and perovskite compound were also found to be effective catalyst for the reduction of ketones with 2-propanol as a hydrogen source [42-43, 65-66,115-117].

The reverse reaction of MPV reduction is known as Oppenauer oxidation. In 1937 Oppenauer showed that unsolvated steroid alcohols could be oxidised to the corresponding ketones in excellent yields through the use of aluminium t-butoxide in the presence of a large amount of acetone, which can act as hydrogen acceptor, the large excess serving to shift the equilibrium in the desired direction [144]. In view of reversible nature of the reaction many statements as to the mechanism of MPV reduction are equally applicable to Oppenauer oxidation. Activation of the alcoholic hydrogen atom by the aluminium resulting in the hydrogen bonding has also been proposed by Woodward et.al [145].

Generally oxidation has been carried out by the use of metal alkoxide catalysts [140]. The most common catalysts used are aluminium t- butoxide, isopropoxides and phenoxides. Aluminium isopropoxides has been found to be best reagent for the oxidation [140,146]. In the modified reactions benzophenone was used as the oxidising agent since it cannot undergo condensation in the presence of a strongly basic catalysts. According to Oppenauer a solvent is necessary for oxidation of alcohols. Toluene is used occasionally [147]. Time and temperature can be varied over a wide range depending up on the alcohol to be oxidised, although the maximum temperature that can be attained was controlled by the choice of the solvent and hydrogen acceptor.

Heterogeneous catalysts for oxidation reaction have also been reported, which find advantages over the conventional reactions. SiO_2, MgO, and Al_2O_3 have been proved to be successful [148]. Kuno et.al have shown that liquid phase reduction of primary and secondary alcohols proceeded very efficiently using benzophenone as the hydrogen acceptor [149]. The influence of hydrogen acceptor on the oxidation rate has been investigated by the use of several ketones and the oxidation rate was influenced by the electron density and sterric hindrance around the carbonyl group. The dependence of the reaction temperature was also investigated. The reaction of acids with alcohols was also developed to produce esters by catalysis with oxides.

2.3.1. Acid-base property and catalytic activity

Good correlation has been found in many cases between the total amount of acids and the catalytic activities of the solids. K.Tanabe has reported the correlation of activity of several reactions with acidity/basicity of oxide surface [67]. The nature and catalytic activity of the metal oxides, sulfates etc. were elucidated through the investigation of the structure of acid base centres and by the comparison with the kinetics of homogeneous acid base catalysis. The conversion and selectivity of a reaction depend upon the acid-base behaviour of the surface. The selectivity of solid catalysts is influenced by the acid-base properties and many other factors such as geometric structure (particularly pore structure) the distribution of sites and the polarity of the surface sites.

Catalytic activities of alumina in a range of reactions such as the isomerisation of hydrocarbons, the polymerisation of olefines etc. have been attributed to the acidic properties of surface [72,124], where the acidity remarkably changes with the degree of hydration. The influence of the acid strength of solid catalyst on their catalytic activity per unit surface amount of acid in the dimerisation of propylene, isobutylene and the dehydration of isopropyl alcohol have been studied by Dzisko [151]. The metal oxides show difference in the value of acidity depending upon the method of preparation. H.Pines and C.N. Pillai [152] reported that alumina catalysts prepared from sodium aluminate were only weakly acidic while alumina prepared from aluminium isopropoxide was slightly acidic, the former one did not cause extensive isomerisation of olefines during dehydration of alcohol. H.Pines and H.Haag [153] proposed that Al_2O_3 had intrinsic acidity which was responsible for the typically acid catalysed reaction such as dehydration of alcohols and skeletal isomerisatoin of 3,3-dimethylbutene and cyclohexene.

Minachev et.al studied the hydrogenation of ethylene at low temperature as part of a study of the catalytic activity of rare earth oxides. La_2O_3 activated at high temperature was found to be highly active and activity has been correlated with basicity [154]. In the case SiO_2-Al_2O_3 and NiO-SiO_2 oxides, Ozaki and Kimura suggested that the Lewis acid sites could be effective for isomerisation, a proton being donated by the olefine molecule chemisorbed on the Lewis acid sites [155].

H.Hattori et.al studied the double bond migration of 2-propenyl ethers to 1-propenyl ether over solid base catalysts to develope a heterogeneous catalyst for reaction and to elucidate the reaction mechanism [156]. Among the catalysts, CaO exhibited the highest activity and La_2O_3, SrO and MgO also showed higher activities. ThO_2. ZrO_2, and Y_2O_3 were slightly active, but ZnO, Al_2O_3 and SiO_2-Al_2O_3 were completely inactive. The inactivity of oxides is probably because of the capacity of acidic sites on the surface to adsorb strongly the reactant by the lone pairs on the oxygen atoms. Double bond migration of alkylamines to enamine over basic oxide catalysts was also reported [157}. The double bond migration of n-butene over alumina was considered to be catalysed by Lewis acid sites [158].

The hydrogenation and isomerisation of n-butenes over basic La_2O_3 and ZnO were also reported [154,159-161]. Rosynek et.al [160] studied the catalytic activity of La_2O_3 and showed that basic sites were essential for the isomerisation of butenes. The isomerisation of butenes over several ThO_2 catalysts were also reported while investigating the nature of the active sites on the basis of observed surface properties and mechanistic study of reactions [162]. The number of basic sites of La_2O_3, Y_2O_3 and CeO_2 were determined and correlated with the catalytic activity for the decomposition of 4-hydroxy 4-methyl 2-pentanone and isomerisation of butene. The catalytic activity of these catalysts were attributed to basicity and good correlation of basicity with activity was found [163].

E.Rodenas et.al studied in detail the surface and catalytic properties of TiO_2-Al_2O_3 of various composition which were prepared from co-precipitation of $Ti(SO_4)_2$ and $Al_2(SO_4)_3$ with urea as well as with aqueous ammonia [164]. The effect of preparation method on the difference in composition between the surface layer and the bulk and on the acid-base and oxidising/reducing properties and catalytic activities for 1-butene isomerisation and 2-butanol dehydration have been examined. A good correlation was found between the acidity and activity for the dehydration. It has been reported that the results concerning the characterisation of acidity and basicity of a large series of metal oxides including supports, active phase and promoters have been reported by A.Gervasini et. al [165,166]. They studied the decomposition of isopropanol as test reaction for the determination of acid base character of catalyst .

The first order rate constant for the formation of benzyl benzoate from benzaldehyde over CaO calcined at various temperatures was found to change in parallel with the change in catalyst activity. There was good correlation between the activity and the amount of base per unit surface area [167]. The catalytic activity for oxidation and olefine isomerisation of the ternary system MoO_3-$B_{12}O_3$-P_2O_5 catalysts have been correlated with acid/base properties between the catalyst and the reactant [95]. The acidity and the basicity of a series of TiO_2-P_2O_5 and V_2O_5 system was measured by using static and pulse method and the catalytic behavior of the reactant was correlated with the acid base properties. Oxygen mobilities and acidity-basicity behaviour are responsible for their catalytic action [168]. Vapour phase conversion of cyclohexanol to cyclohexanon in the presence of different basic catalyst showed that some of them are able to activate dehydration and dehydrogenation simultaneously. The dehydrogenation activity was related to the existence of basic sites originating from the oxygen in the oxide lattice [169].

M. Waqif et. al studied acid properties of pure and sulfate promoted metal oxides and they used dehydration of methanol to dimethyl ether as the test reaction. It was found that this reaction is sensitive to sample acidity. J.L.Sotin [109] studied acid base properties and textural properties of aluminas prepared from aluminium hydroxides containing controlled amount of impurities. It was established that besides basicity the pore size distribution of alumina strongly influence the catalytic activity in H_2S -SO_2 reaction due to the capillary condensation of sulfur in small pores.

Involvement of surface acid/base properties was tested by studying the benzonitrile formation from benzaldehyde and ammonia [171]. Investigations were carried out to have a systematic comparison of the acidic and catalytic properties of single oxides like SiO_2, TiO_2, Al_2O_3, MoO_3 and their binary oxides and ternary oxides. The acid base strength distributions were determined by titration methods and correlated with the catalytic activity for the alkylation of toluene and the dehydration of 2-propanol. Mosial catalysts (oxides of molybdenum) showed high activity towards the alkylation of toluene [101]. The acidic properties of a series of TiO_2- SiO_2 systems and their relations to the catalytic activities have been reported for the amination of phenol with ammonia to produce aniline eventhough both of single oxides SiO_2 and TiO_2 showed little acidity [171].

It was found that activity of the oxides depend upon the pretreatment temperature. For TiO_2-SiO_2 mixed oxides obtained by co-precipitation methods highest activity was found at 500°C [171]. The variation in catalytic activity of rare earth oxides and their analogous scandia and yttria in ethylene hydrogenation was studied as a function of pretreatment temperature between -12°C and 20°C [154]. Correlation between the surface properties and the catalytic activity of anhydrous ZrO_2 calcined at several temperatures was investigated, the best activity was obtained for the oxide calcined at 300°C [172].

Surface acidic priorities of Nb_2O_5 in H_2O and its catalytic activity for the isomerisation of 1-butene, polymerisation of propylene and the dehydration of 2-butanol were examined by Iizuka. et al. The active sites on the catalyst preheated at moderate temperatures were ascribed mainly to Bronsted acid sites on the basis of IR study of adsorbed pyridine [173]. The catalytic activity for the decomposition of iso-butyl propionate in a homogeneous system was correlated with acid strength of Keggin type heteropoly acids [174]. The cis trans isomerisation of crotononitrile has been investigated using various catalyst including Al_2O_3-MgO, CaO, Na_2CO_3 and NaOH supported on SiO_2 gel and some organic compounds. It was found that the isomerisation is a base-acid bifunctional catalysis. The catalytic activity of butene over Sm_2O_3 has also been investigated in view of acid-base catalysis.

Concentration of Bronsted and Lewis acid sites on sulfated zirconia catalyst was determined by using 31_P mass NMR spectroscopy [176]. The treatment at lower temperatures resulted in the generation of Bronsted acid sites and at higher temperatures three types of Lewis sites were generated. In a related study the catalytic activity of these oxides for alkylation of isobutene with 2-butanol was determined at different temperatures and the activity was found to depend upon the acidity.

2.4. ZIRCONIA AND RARE EARTH OXIDES AS CATALYSTS

ZrO_2 exhibit catalytic activity for a number of reactions. The interest in ZrO_2 as a catalytic material could be ascribed to its uniqueness in being the only single metal oxide which possess four chemical properties viz. acidity, basicity, oxidising and reducing properties [177]. It has been reported that zirconia shows specific catalytic activities for the cleavage of C–H bonds [178], the hydrogenation of 1-3-butadiene by molecular hydrogen and hydrogen donor molecules such as cyclohexadiene [179-181] and high selectivities for the formation of 1-olefine from secondary alcohols [182] and isobutane in the reaction of $CO + H_2$ [183]. All these characteristic behaviour of ZrO_2 were considered to be due to the acid base functional catalysis. Fugi et al found that ZrO_2 is an excellent support to $La_{0.8}$ Sr_2 CoO_3 catalysts used for complete oxidation of propane [184].

Several ZrO_2 supported catalysts were prepared by metals like Pd, Cu and metal oxides like MgO SiO_2 and CrO_3 [185-187]. In an earlier report on Cu supported catalysts, it was found that Cu supported on ZrO_2 is superior to Cu supported on other oxides [188]. Cu supported ZrO_2 was found to be ideal catalyst for dehydrogenation of cyclohexanol, the selectivity to cyclohexanol was found to be 100 %, which is a typical property of the copper assisted by the predominant basic character of ZrO_2 [189]. The role of ZrO_2 as a support to the chromia catalyst in the aromatisation of isophoron to 3,5-xylenol which has importance as an industrially potential intermediate has also been studied [190].

Hydrodesulphurisation of sulfur containing aromatics has been major operation in the petroleum chemistry [191-192]. ZrO_2 as a support is receiving attention in recent years. It has been reported that Mo supported on ZrO_2 exhibit higher catalytic activity than Al_2O_3 supported systems [193]. Reddy et. al [194] reported hydrosulphurisation and hydrogenation activities of MoS_2/ZrO_2. Combining these values with that of Mo supported on Al_2O_3 it was found that MoS_2/Al_2O_3 is marginally more active than MoS_2/Al_2O_3. The activity for thiophene hydrodesulphurisation was also evaluated by Sedlack et. al [195]. It has been reported that activity per gram of metal is higher in the case of MoS_2/Al_2O_3. However Pratt et al [196] reported higher activity for MoS_2/ZrO_2 compared to Al_2O_3 supported on ZrO_2 for the same investigation. They have found that the morphology of the catalyst is different from that on Al_2O_3 supported ones.

Zirconium-Molybdate catalyst has been also found to be good catalyst for esterification reaction [197]. The presence of acid sites on the catalyst indicate good potential for application in Bronsted catalysis. It has also been observed that amorphous ZrO_2 possess greater number of acid sites as compared to crystalline material and the amorphous materials are more active [198]. The ion exchange property of α- zirconium phosphate has been examined in detail [199] and the hydrogen form has shown to be an acid catalyst.

Phenyl ethers and substituted phenyl ethers are important intermediates for the manufacture of different agrochemical and pharmaceutical based products. Heterogeneous esterification process using TiO_2, ZrO_2, ThO_2 etc., overcome the drawbacks over the conventional routs and provided a unique way for the large production of salt free ethers with high selectivity [200-201]. Depolymerisation of paraldehyde in non aqueous solvents catalysed by heterogeneous acids like ZrO_2, SnO_2-ZrO_2 have been studied and the activity was correlated with acid strength distribution of oxides calcined at various temperatures [202].

The conventional route for the synthesis of anthraquinone by Friedel Crafts reaction containing two steps involves the use of $AlCl_3$ and oleum leading to corrosion and environmental pollution. Continuos search was on for a suitable catalyst that can substitute for $AlCl_3$ and H_2SO_4 and also to make the process continuos in a single step. Several papers are reported describing the posibility of employing super acids such as SO_4^- /ZrO_2 and rare earth exchanged Y zeolites for promoting the Fried Crafts acylation [203-206]. Acidic sites as well as basic sites are involved in the activity for the isomerization of 1-butene. Acid - base pair sites are probably exposed Zr ions with adjacent O^2- ions which are generated by the removal of H_2O molecules from neighboring OH groups.

ZrO_2 aerogels are attracting much attention because of their promising potential as catalysts of use in combustion and hydrogenation, piezoelectric ceramics and thermal barriers [207]. However zirconia aerogels have been less investigated and used than those of silica and alumina. It therefore appeared essential to obtain a deep and systematic insight into the synthetic chemistry of ZrO_2 based materials with optimum properties for selected areas of use. CeO_2-ZrO_2 aerogels have been characterized in order to elucidate the effect of the structural homogeneity as the stability of their total surface area at high temperature [208]. Fe_2O_3/ZrO_2 catalysts prepared by impregnation and co-precipitation methods were used for catalytic hydrogenation of CO and the role of zirconia in the catalyst was discussed by Chen et.al [209].

The stabilised cubic zirconia is widely studied and used as solid electrolytes for fuel cells, oxygen sensors and so on, because of its high ionic conductivity due to oxygen ion migration, its stability in wide temperature range and its negligible electronic conductivity. A systematic study of the structural and dynamical properties of oxygen conductor yttria stabilised zirconia for different dopant concentrations using a method of molecular dynamic simulation has been reported [210]. The reactivity of V_2O_5 with TiO_2-ZrO_2 mixed oxide support was investigated by the X-ray powder diffraction technique [211]. Catalytic activity of copper oxide catalyst for CO oxidation can be significantly enhanced by the oxygen ion conducting support, yttria stabilised zirconia [YSZ] which leads to supported copper oxide exhibiting a precious metal like catalytic behavior [212]. The activity enhancement of yttria stabilised supported copper oxide was attributed to the surface oxygen vacancy of YSZ support providing a second reaction pathway by means of the formation of interfacial active center, although the redox cycle mechanism is still operative on the CuO/YSZ catalyst. Catalytic property of ZrO_2-SiO_2 for cyclohexanone conversion has been studied. Textural and morphological properties were correlated to explain catalytic behavior [213].

Although the investigations of the catalytic properties of rare earth sesquioxides have been multiplied, the primary modes of surface interaction on these materials remains largely undefined. Rare earth oxides are important in the fact that they find application in many catalytic reactions. It has been suggested that addition of CeO_2 and other earth oxides to alumina can stabilise the surface area and the spinel transition phases of the alumina support used in automotive catalysis [214].

Recent studies have demonstrated that several of the lanthanide sesquioxides (M_2O_3) are effective catalysts for the oxidative coupling of methane to ethane and ethylene [215]. The catalytic activity of rare earth oxides could be attributed to their basic property. Campbell et. al have indicated that the addition of rare earth oxides for the abstraction of H from the methane molecule to form methyl radicals can best be related to the basicity of the oxides [115,216]. Good correlation was found between the basicity and catalytic activity for the decomposition of 4-hydroxy 4-methyl -2-propanone on La_2O_3, similar to that of alkaline earth oxides [217]. The comparison of the catalytic activity and selectivity with the basicity of the catalyst shows that the higher conversion activity, C_2 -selectivity and C_2 yield observed for La_2O_3 are consistent with higher basicity [116]. Otzuka [215,218] have shown that among the rare earth oxides Sm_2O_3 shows highest activity and C_2 selectivity for C_2-hydrocarbons in oxidative coupling of methane.

Empirical studies have demonstrated that, following appropriate pretreatment, rare earth sesquioxides are active catalysts for a variety of reactions including o/p hydrogen conversion [219], deuterium exchange reactions of hydrocarbons [220], H_2-D_2 equilibration [221], alcohol dehydration [222], olefine isomerisation [223], decomposition of N_2O and NO [224], and oxidation reaction of H_2 [225] and CO [224] and hydrocarbons [224]. In the last several years, it has been found in a series of the catalytic oxidations that the catalytic activity of the lanthanide oxides significantly differ from each other. Saznov and coworkers [226] measured the active cation energies of the isotopic exchange of oxygen and of the desorption of CO in the oxidation of CO and found that the dependence of activation energies on the atomic number was similar to that of the magnetic moment. Minachev et.al [225] compared the catalytic activity in the oxidation of H_2 and propylene and found that catalytic activity depends on the binding energy of oxygen with the surface and on the valance of the lanthanide ions.

Bakumento and Chashenikov [227] found in the oxidation of hydrogen that activity of Er and Nd oxides were lower than Ce, Pr and Tb oxides with the tetravalent ions, which was explained on the basis of the heat formation of oxides. Lazukin and coworkers [228] found a good correlation between the activation energy of the oxidation of propylene and that of the electrical conductivity and concluded that the electron transfer from the reactant or intermediate to the catalyst surface is involved in the rate determining step. Some of the authors [225-226] suggested from these that the catalytic activity of the lanthanide oxides depend up on the electronic configuration of the inner 4f subshell.

The catalytic oxidation of butane was studied over a series of lanthanide oxides inorder to investigate the effect of electronic configuration on the catalytic activity [229]. La_2O_3 was one of the least active catalyst. CeO_2 was the most active one and the activity decreased with an increase in the atomic number from Ce to Gd. The activity of Tb was the second highest and again the dependence of the activity on the atomic number was in good agreement with the heat of formation of oxide. The dependence of the electrical conductivity and the heat of formation could be related to the stability of M_4^+ ion, to which the catalytic activity could be related by assuming that the rate determining step is the oxidation of M^{3+} ion to the M^{4+} ion. A good correlation was obtained between catalytic activity and fourth ionisation potential as a measure of the stability of M^{4+} ion relative to the trivalent ion. The correlation of catalytic activity with the atomic number was interpretted in terms of two factors based on the electronic configuration of the 4f subshell and the exchange energy between the 4f electrons.

Rare earth oxides are stable to high temperatures with respect to its valance and crystallographic structures. They are also hardly reducible. The addition of some rare earth oxides to Rh -Al_2 O_3 catalysts enhanced the activity of hydrogenation of CO to methane. There was linear correlation between the CO skeleton propagation of the hydrocarbons formed and the basicity of the rare earth oxides [230]. Surface parameters and thermal dehydration/rehydration behaviour of $La(OH)_3/La_2O_3$ system have been examined with a view towards establishing suitable methods for preparing different catalytic forms of the rare earth oxides [222].

Temperature programmed desorption (TPD) and O_{18}- tracer technique have been adopted to examine the contribution of the lattice oxygen (oxide ion) in rare earth oxide like Pr_6O_{11} to the oxidation of CO [231]. The TPD measurements revealed that some of the lattice oxygen atom could be reduced by CO forming CO_2. However the oxygen vacancies formed by the reduction were completely filled with oxide ions, if oxygen existed in the gaseous phase. The multipath way (dehydration/dehydrogenation) conversion of ethanol has been used to investigate the nature of behaviour of catalytically active sites on La_2O_3 and Nd_2O_3 [232].

Minachev [225] has summarised many of the catalytic properties of Dy_2O_3 with particular reference to organic reactions. The activity of Dy_2O_3 is very similar to that of erbium oxide and it is especially active towards n-butane cracking and double bond migration of 1-butene. Many studies have been made in the case of reactions involving hydrogen or oxygen adsorption on Dy_2O_3 [233]. The hydrogen-deuterium exchange reactions occur with Dy_2O_3 above 250 K and shows a temperature dependence similar to the p-hydrogen conversion, leading to the conclusion that both these reaction involve equivalent dossociative mechanisms at these temperatures [234]. Selwood [235] studied the non dissociative mechanism in a magnetic field and observed an increase in activity towards p-hydrogen conversion in a strong field but no change in activity in a weak field. Oxygen exchange reactions indicate that activity increases with a rise in mobility of surface oxygen with Dy_2O_3 becoming active above 600°C.

The reduction of methyl benzoate and benzoic acid on Y_2O_3 under hydrogen has been examined by using an IR spectroscopic flow reactor at 250-450°C [236]. CO hydrogenation over mixed oxides of 3A and 5A groups (Y_2O_3, La_2O_3, CeO2 and ZrO_2) with 3B group (Al_2O_3, Ga_2O_3 and In_2O_3) was carried out and found good variation with rare earth concentrations [143]. Taylor and Diamond have reported that paramagnetic substances like Gd_2O_3, Dy_2O_3 are more active than non-paramagnetic substance. Selectivities of rare earth oxides for dehydration of butanols have also been reviewed and established the good correlation between product distribution and catalytic properties [228].

REFERENCES

1. B.M.Bronwer, *Chem.Indu.*, 177 (1961).
2. J.J.Rooney and R.C.Pink, *Proc. Chem. Soc.*, 70 (1961).
3. W.K.Hall, *J. Cat.*, **1** 53, (1962).
4. H.P.Leftin and M.C.Hobson, *Advan. Cat.*, **14**, 372 (1963).
5. A.Terenin, *J.Cat.*, **15**, 256 (1964).
6. R.P.Porter and W.K.Hall, *J.Cat.*, **5**, 366, (1966).
7. B.D.Flockhart, J.A.N.Scott and R.C.Pink, *Trans Faraday Soc.*, **62**,730 (1966).
8. B.D.Flockhart, I.R.Leith and R.C.Pink, *Trans Faraday Soc.*, **66**, 469 (1970).
9. A.J.Tench and R.L. Nerlson, *Trans. Far., Trans. Far.*, **63**, 2254 (1967).
10. K.Meguro and K.Esumi, *J. Colloid Inter. Sci.*, **59**, 93 (1977).
11. K.Esumi and K.Meguro, *J. Colloid Inter.Sci.*, **66**, 192 (1978).
12. H.Hosaka, T.Fujiwara and K.Meguro, *Bull. Chem. Soc. Jpn.*, **44**, 2616, (1971).
13. B.D.Flockhart, K.Y. Lieth and R.C.Pink, *J.Chem. Soc. Faraday*, 1(**76**), 2026, (1980).
14. B.D.Flockhart, K.Y.Leith and R.C.Pink, *J.Chem. Soc. Faraday*, **65**, 542, (1969).
15. G.Cordishi, V.Indovinio and A.Limino, *J.Chem. Soc. Faraday*, **70**, 2189, (1974).
16. V.V.Subha Rao, R.D.Iyengar and A.C.Zettlemoyer, *J. Cat.*, **12**, 278 (1968).
17. B.D.Flockhart, C.Naccache, J.A.N.Scott and R.C.Pink, *Chem. Comm.*, **11**, 238 (1965).
18. H.Kirota, K.Kuwata and Y.Agaki, *Bull. Chem. Soc. Jpn.*, 38(**12**), 2209 (1965).

19. A.J.Tench and R.L.Nelson, *J. Chem. Phy.*, **44**, 1714, (1966).

20. J.H.Lunsford and J.P.Jayne, *J.Chem. Phy.*, **44**, 1487 (1966).

21. J.H.Lunsford and J.P.Jayne, *J. Chem. Phy.*, **69**, 2182 (1965).

22. B.D.Flockhart, K.Y.Leith and R.C.Pink, *J. Cat.*, **32**, 20 (1974).

23. L.Petrakis and K.S.Seshadri, *Bull. Chem. Soc. Jpn.*, **43**, 1317 (1970).

24. L.Petrakis and K.S.Seshadri, *J. Phy. Chem.*, **76**, 1443 (1972).

25. Y.A.Eltekov, V.V. Khopiena and A.V.Kiselve, *Faraday. Trans.*, **68**, 889 (1972).

26. M.Che, C. Naccache, and B.Imelik, *J.Cat.*, **24**, 238 (1972).

27. D.Cordche and V. Indovina, *Bull. Chem. Soc. Jpn.*, **49**, 2341 (1976).

28. R.S.Davison and R.M. Slater, *Bull. Chem. Soc. Jpn.*, **48**, 2416 (19750.

29. M.A.Enriquiz and J.P.Fraissard, *J. Cat.*, **74**, 77 (1982).

30. K.Esumi and K.Meguro, *Bull. Chem. Soc. Jpn.*, **55**, 1647 (1982).

31. K.Esumi, H.Shimada and K.Meguro, *Bull. Chem. Soc. Jpn.*, **50**, 2795 (1977).

32. K.Esumi and K.Meguro, *Bull. Chem. Soc. Jpn.*, **55**, 315 (1982).

33. H.F.Holmes, E.L.Fuller and R.A.Beh, *J. Colloid Int. Sci.*, **47**, 365 (1985).

34. S.T.Joslin and F.M.Fowkes, *Ind. Eng. Chem. Prod. Res. Dev.*, **24**, 369 (1985).

35. F.M.Fowkes, D.C.McCarthy and J.A.Wolfe, *J. Poly. Sci.*, **22**, 547 (1984).

36. F.M.Fowkes, Y.C. Huang, B.A.Shab, M.J.Kulp and T.B.Llyod, *Coll. Surf.*, **29**, 243 (1988).

37. K.Esumi, K.Miyata, F.Waki and K.Meguro, *Bull. Chem. Soc.Jpn.*, **59**, 3363 (1986).

38. R.S.Drago, L.B.Parry and C.S. Chamerlain, *J. Ame. Chem. Soc.*, *J. Ame.Chem. Soc.*, **99**, 3203 (1977).

39. I.Bodrikov, K.Khulbe and R.S.Mann, *J. Cat.*, **43**, 339 (1976).

40. B.H.Boyd and W.D.Philips, *J. Chem. Phy.*, **43**, 2927 (1965).

41. J.M.D.Tascon, A.M.O.Olivan, L.G.Tejuca and A.T.Bell, *J. Phy. Chem.*, **90**, 791 (1986).

42. M.A.Ulla, E.F.Miro and E.A.Lombardo, *Proc. Iberoam, Symp. Catal.*, 8th, La Rabida, Spain, 475 (1982).

43. S.Sugunan and V. Meera, *J. Mat. Sci. Tech.*, **11**, 229 (1995).

44. S.Sugunan and V.Meera, *Collect. Czech. Chem. Comm.*, **60**, 977 (1995).

45. J.A.N.Scott, B.D.Flockhart and R.C.Pink, *Proc. Chem. Soc.*, 139 (1964).

46. D.N.Stamires and J.Tekevich, *J. Ame. Chem. Soc.*, **86**, 749 (1964).

47. A.J.De Rossert, C.G.Finstorm and C.J.Adams, *J. Cat.*, **1**, 235 (1962).

48. E.P.Parry, *J.Cat*, **2**, 371 (1963).

49. O.Edlund, P.O.Kinell, A.Lund and A. Shimizu, *J. Chem. Phy.*, **46**, 3678 (1967).

50. P.O.Kinell, A.Lund and A.Shiniezu, *J.Phy.Chem.*, **73**, 4175 (1969).

51. K.Esumi, K.Miyata and K.Meguro, *Bull. Chem. Soc. Jpn.* ,58, 3524 (1985).

52. K.Esumi, K.Miyata, F.Waki and K.Meguro, *Colloid Surf. Sci.* 20, 8 (1986).

53. H.Hosaka and K.Megura, *Colloid Poly. Sci.* 252, 322 (1974).

54. L.Miller, *J. Phy. Chem.*, 1, 653 (1987).

55. K.Esumi, K.Meguro and K.Megara, *J.Colloid. Int. Sci.*, 141, 578 (1991).

56. G.V.Fomin, L.A.Blyumenfeld and V.I.Sukhorukov, *Proc. Acad. Sci.*, (USSR), **157**, 819 (1964).

57. J.R.Hollaban and A.T. Bell, *Techniques and Application of Plasma Chemistry*, Wiley, New York (1974).

58. K.Esumi, M.Sugira, T.Mori, K.Megura and H.Honda, *Colloid Surf.*, **19**, 331 (1986).

59. K.Esumi, N.Nishina and K.Meguro, *J. Surf. Sci. Tech.*, **4**, 207 (1988).

60. H.Hosaka, N.Kawashima and K.Meguro, *Bull. Chem. Soc. Jpn.*, **50**, 2795 (1977).

61. H.Murayama, K.Kobayashi, M.Koistu and K.Meguro, *J. Colloid Int. Sci.*, **32**, 470 (1970).

62. H.Murayama andK.Meguro, *Bull. Chem. Soc. Jpn.*, **43**, 2386 (1970).

63. S.Sugunan and G.D.Rani, *Indian J. Chem.*, 32 A, 993 (1993).

64. S.Sugunan and K.B Sherly and G.D.Rani, *React. Kinet. Catal.* Lett., 51, 525 (1993)., 43, 375 (1991).

65. S.Sugunan and J.J.Malayan, *React. Kinet. Catal. Lett.*, 55, 399 (1995)., *Collect., Czech. Chem. Commun.*, 59, 2604 (1994).

66. S.Sugunan and B.varghese, *React. Kinet. Catal. Lett.*, 57, 87 (1996).

67. K.Tanabe, *Solid acids and bases*, Academic Press, NewYork, 1970.

68. L.Forni, *Cat. Rev.*, **8**, 65 (1974).

69. C.Walling, *J.Ame. Chem. Soc.*, **54**, 2721 (1932).

70. Hammett and Deyrup, *J. Ame. Chem. Soc.*, **54**, 2721, 1932, L.P.Hammett , *Chem. Rev.*, 16, 67, (1935), L.P.Hammett, *Phy.Org.Chem.*,Chap. 9 McGraw Hill, 1940.

71. H.A.Benesi, *J. Ame .Chem. Soc.*, **78**, 5490 (1956).

72. H.Pines and J.Ravoire, *J. Phy. Chem.*, **65**, 1851 (1961).

73. K.Tanabe, M.Misono, Y.Ono and H.Hattori, *New Solids and Bases,* Kodansha, New York, 1989.

74. O.Johnson, *J. Phy. Chem. Soc.*, **59**, 287 (1955).

75. H.A.Benesi, *J. Ame. Chem. Soc.*, **61**, 970 (1957).

76. A.E.Hirshler and A.Schieder, *J. Chem. Eng. Data,* **6**, 313 (1961).

77. A.E.Hirshler, *J. Cat.*, **2**, 428 (1963).

78. R.L.Richardson and S.W. Benson, *J. Phy. Chem.*, **61**, 405 (1955).

79. W.G.Wang, H.hattori and K.Tanabe , *Bull. Chem. Soc. Jpn.*, **26**, 2407 (1983).

80. H.P.Leftin and M.C.Hobson, *Adv. Cat.*, **14**, 115 (1968).

81. A.N.Terenin, *Adv. Cat.*, **15**, 227, (1964).

82. H.V.Drussel and A.L.Sommers, *J. Anal. Chem.*, **38**, 172 (1966).

83. H.Zeitlin, R.Frei and M.Mecaster, *J. Cat.*, 77, (1965).

84. H.Miyata, K.Fujii and T.Ono, *J. Chem. Soc. Faraday Trans.*, **84(9)**, 3121 (1988).

85. K.Tanabe and Wattanabe, *J. Res. Inst. Cat.*, Hokkaido, **64**, 1954 (1960).

86. K.Sugiyama, Y.Kakanu, K.Miura and T.Matsushita, *Bull. Chem. Soc. Jpn.*, **58**, 1826 (1985).

87. S.E.Volts, A.E.Hirschler and A.Smith, *J. Phy. Chem.*, **64**, 1954 (1960).

88. Y.Trambouze, L.DeMourgous and M.Perrin, *J. Phy. Chem.*, **5**, 213, (1954).

89. J.Take, H.Kaway and Y.yoneda, *Bull. Chem. Soc. Jpn.*, **59**, 9 (1977).

90. H.Yoshisumi, Y.Shimadu and T. Shirosaki, *Chem. Lett.*, 107 (1973).

91. S.Malinowski and S.szczepanska, *J. Cat.*, **46**, 310 (1963).

92. H.P.Leftin and W.K.Hall, *Actes. Cong. Int. Cat.*, **65** ,58 (1962).

93. J.A. Shwartz, *J. Vac. Sci. Tech.*, **12**, 32 (1975).

94. E.P.Parry, *J. Cat.*, **2**, 371 (1963).

95. K.Shibata, T.Kiyoura, K.Kitagawa, K.Sumiyoshi and K.Tanabe, *Bull. Chem.Soc. Jpn.*, **46**, 2985 (1973).

96. H.A.Benesi and B.H.C.Winquest, *Adv. Cat.*, **27**, 123 (1978).

97. M.Ai, *Bull. Chem.Soc. Jpn.*, **49**, 1328 (1976).

98. H.Miyata, K.Fuji and T.Ono, *J. Chem. Soc. Faraday Tran.*, 1(**84**), 3121 (1988).

99. T.Kotaigawa, *Bull. Chem. Soc. Jpn.*, **47**, 950 (1974).

100. T.Morimoto, J.Imai and N.Nagao, *J. Phy. Chem.*, **78**, 704 (1974).

101. K.R.P.Sabu, K.V.C.Rao and C.G.R.Nair, *Bull. Chem. Soc . Jpn.*, **64**, 1920 (1991)., **64**, 1926 (1991).

102. B.Xu, T.Yamaguchi and K.Tanabe, *Mat. Chem. Phy.*, **19**, 291 (1988).

103. I.Iizuka, Y.endo, H.hattori and K.Tanabe, *Chem. Lett.*, 803, 1976.

104. Y.Yamanaka and K.Tanabe, *J. Phy. Chem.*, **79**, 2409 (1975).

105. J.Take, N.Nikuchi and Y.Yoneda, *J.Cat.*, **21**, 164 (1971).

106. G.Zhang, H.Hattori and K.Tanabe, *Appl. Cat.*, **36**, 1616 (1973).

107. M.Ai, *J.Cat.*, **54**, 223 (1978).

108. E.Fedorynska, T.W.Woznikwski, S.Malinowski, E.Ahmed and A.Madura, *J. Colloid Inter sci.*, **69**, 469 (1979).

109. J.L.Zotin and A.C.Faro Jr, *Appl. Cat.*, **75**, 55 (1991).

110. J.Take, T.Isuruya, T.Sato and Y.Yoneda, *Bull. Chem. Soc. Jpn.*, **45**, 3409 (1972).

111. L.Nodlek and J.Malik, *React. Kinet. Cat. Lett.*, 14(**3**), 381 (1980).

112. N.C.Martinez and J.A.Domesic, *J. Cat.*, **127**, 106 (1991).

113. H.Vinek, H.Noller, M.Ebel and K.Schwarz, *J. Chem. Soc.Far.Tran.*, 1 (**73**), 734 1977).

114. Y.Nakashima, Y.Sakata, S.H.Imamunesa and S.Tsuchiya, *Bull. Chem. Soc. Jpn.*, **63**, 3373 (190).

115. K.D.Campbell, H.Zhang and J.H.Lunsford, *J. Phy. Chem.*, **92**, 750 (1988).

116. V.R.Choudhary and V.H.Rane, *J. Cat.*, 141, 1991.

117. S.Sugunan, S.Kurur and A.Paul, *Indian J. Chem.*, **33A**, 1096 (1994).

118. S.Sugunan, G.V.Chemparathy and A.Paul, *Indian J. Eng. and Mat Sci.*, **3**, 45 (1996).

119. S.Sugunan and A.Paul, *Indian J. Chem.*, **36A**, 300 (1997).

120. K.Tanabe, "*In Catalytic Science and Tech.*", Vol.2, p 231, Springer Verley, New York, 1981.

121. H.Miyata, K.Fuji and T.Ono, J. *Chem. Soc. Far. Tran.*, 84 (**9**), 3121 (1988).

122. J.P.Shen, J.Ma, T.Sun and D.Jiang, *J. Chem. Soc. Far. Trans.*, **90**, 1351 (1994).

123. J.B.Peri, J. *Phy. Chem.*, **69**, 231 (1965).

124. C.L.Thomas, *Ind. Eng. Chem.*, **4**, 2564 (1949).

125. K.Tanabe and T.Takeshita, "*Advances in Catalysis*", Vol.17, p 315, Academic Press, New York, 1967.

126. G.Connel and J.A.Domesic, *J. Cat.*, 165, 285 (1987).

127. K.Nishiwaki, N.Kakuta, A.Ueno and H.Nakabayashi, *J. Cat.*, 118, 498 (1989).

128. H.Nakabayashi, N.Kakuta and A.Ueno, *Bull. Chem. Soc.Jpn.*, 64, 2428 (1991).

129. H.Nakabayashi, *Bull. Chem. Soc. Jpn*, 65(3), 914 (1992).

130. G.Connel and J.A.Domesic, *J. Cat.*, 101, 103 (1986).

131. H.Pines and W.M. Stalick, "*Base Catalysed Reactions of Hydrocarbons and Related Compounds*", Academic Press, New York, London, 1977.

132. A.L.Wiles, *Org. React.*, **2**, 178 (1944).

133. Y.Okamato, T.Imanaka, S.Teranesh, *Bull.Chem. Soc. Jpn.*, **45**, 3207 (1972).

134. H.Nijiyama and E.Echigoya, *Bull. Chem. Soc. Jpn.*, **45**, 9328 (1972).

135. Y.Schachter and H.Pines, *J.cat.*, **11**, 104 (1968).

136. W.R.Patterson and R.L.Burwell Jr., *J. Ame. Chem. Soc.*, **93**, 833 (1971).

137. C.L.Kibby and W.Keithhall, *J. Cat.*, **31**, 65 (1973).

138. M.Shibagaki, K.Takahashi, H.Kuno and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **61**, 3283 (1988).

139. M.Shibagaki, K.Takahashi, H.Kuno and H,matsushita, *Chem. Lett.* 1633, (1989).

140. C.Djerasi, *Org. React.*, **6**, 207 (1951).

141. K.Takahasi, M.Shibagaki, H.Kuno, H.Kawakashi and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **62**, 1337 (1969).

142. K.Takahashi, M.Shibagaki, H.Kuno and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **67**, 107 (1994).

143. S.T.King and E.J.Stronjy, *J. Cat.*, **24**, (1983).

144. Oppenauer, *React.Trans. Chem.*, **56**, 137 (1937).

145. Woodward, Wenler and Brutechy, *J. Ame. Chem. Soc.*,**17**, 1423 (1945).

146. Yamashita and Honjo, *J. Ame. Chem. Soc. Jpn.*, **63**, 135 (1942).

147. Macker, Wittla, Jones and Crooke, *J. Ame. Chem. Soc.*, **64**, 1283 (1942).

148. R.Schwarts and A.Juhasz, *Rev. Roum. Chem. Soc.*, **31**, 131 (1980).

149. H.Kuno, K.Takehashi, M.Shibagaki and H.Matsushita, *Bull.Chem. Soc. Jpn.*, **63**, 1943, (1990), **64**, 312 (1991).

150. K.Takahashi, M.Shibagaki, H.Kuno, H.Kawakami and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **62**, 1141, (1989).

151. V.A.Dzisko, *Proce. Intern. Congr. Catalysis*, 3rd Amsterdam. (1964).

152. H.Pines and C.N.Pillai, *J.Ame. Chem. Soc.*, **83**, 1961.

153. H.Pines and O.Waag, *J.Ame. Chem. Soc.*, **82**, 247 (1960).

154. K.M.Minachev, Yu.S.Khodakov and V.S.Nakshriov, *J. Cat.*, **49**, 207 (1977).

155. A.Ozaki and K.Kimura, *J.Cat.*, **3**, 395 (1964).

156. H.MAtsushita and H.Hattori, *J. Cat.*, **85**, 45 (1984).

157. A.Hattori, H.Hattori and K.Tanabe, *J.Cat.*, **65**, 245 (1980).

158. J.B.Peri, *J. Cat.*, **31**, 65 (1962).

159. J.Goldwasser and W.K.Wall, *J. Cat.*, **71**, 53 (1987).

160. M.P.Rosynek and M.T.Magnuson, *J. Cat.*, **48**, 417, 1977.

161. M.P.Rosynek and M.T.Magnuson, *J. Cat.* **1**, 285 (1977).

162. Y.Nakano, T.Iizuka , H.Hattori and K.Tanabe, *J. Cat.*, **69**, 434 (1981).

163. Y.Fukuda, H.hattori and K.Tanabe, *Bull. Chem. Soc. Jpn.*, **51**, 3150 (1978).

164. E.Rodenas, T.Yamaguchi, H.Hattori and K.Tanabe, *J. Cat.*, **69**, 434, (1981).

165. A.Gervasini and A.Aurox, *J. Phy. Chem.*, **94**, 6317, (1990).

166. A.Gervasini and A. Aurox, *J. Cat.*, **131**, 190 (1991).

167. K.Saito and K.Tanabe, *J. Poly. Sci.*, **11**, 206 (1969).

168. M.Ai and T.Ikawa, *J. Cat.*, **40**, 203 (1974).

169. C.P.Bezouchanov and A.Alzihen, *Cat. Lett.*, **11**, 245 (1991).

170. M.Waquif, J.Bachelier. O.Sair and J.C.Lavelly, *J. Mol. Cat.*, **72**, 127 (1992).

171. M.Itoh, H.Hattori and K.Tanabe, *J. Cat.*, **35**, 225 (1974).

172. M.Shibagaki, K.Takahashi, H.Kuno and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **63**, 258 (1990).

173. T.Iizuka, K.Ogasawara and K.Tanabe, *Bull. Chem. Soc. Jpn.*, **56**, 2927, 1983.

174. T.Okuhara, C.Hu, M.Hashimoto and M.Misono, *Bull. Chem. Soc. Jpn.*, **67**, 1186 1994).

175. M.Ichikawa, M.Somai, T.Ohnishu and K.Tamaru, *Trans. Faraday. Soc.*, **63**, 2012 (1967).

176. J.H.Lunsford, H.Sang, S.M. Campbell, C.H.Liang and R.G.Anthony, *Cat. Lett.*, **27**, 305 (1994).

177. P.D.L.Mercera, J.C.Van Ommen, E,D.W.Doesburg, A.J.Burggaraaf and J.R.H.Ross, *Appl. Cat.*, **57**, 127 (1990).

178. T.Yamaguchi, Y. Nakano and K.Tanabe, *Chem. Lett.* 1053 (1976).

179. T.Yamaguchi and J.W.Hightower, *J. Ame. Chem. Soc.*, **99**, 4201, (1977).

180. Y.Nakano, T.Yamaguchi and K.Tanabe, *J. Cat.*, **80**, 307 (1983).

181. H.Shimatzu and T.Yamaguchi, *J. Cat.*, **90**, 160 (1984).

182. T.Yamaguchi, H.Sasaka and K.Tanabe, *Chem. Lett.*, 1017 (1975).

183 K.Maruya, A.Inaba, T.Machashi, T.Domen and T.Onoishi, *J. Chem.Soc. Farad. Trans.*, **177**, 2815 (1981).

184. H.Fuji, N.Mizono and M.Mizono, *Chem. Lett.*, 2147 (1987).

185. M.A.Vaurman, I.E.Wachs, D.J.Stufktens and A.Osakam, *J. Mol. Cat.*, **80**, 209 (1993).

186. H.Suzaka and H.Hattori, *Appl. Catal.*, **47**, L7 (1989).

187. Ch.Schild, A.Wokaun, R.A.Koppel and A.Baiken, *J. Cat.*, **130**, 657, (1991).

188. G.C.Chinchen, K.C.Waugh and D.A.Whan, *Appl. Cat.*, **25**, 101 (1986).

189. A.Rachil, V.D.Kumari.and P.K.Rao, *Catalysi in Modern Trends.*, Narosa Publication, New Delhi, 1995, 346.

190. P.S.S.Prasad, D.D.Raju, K.S.R.Rao, N.Lingaih, G.S.Selvapathy and P.K.Rao, in B.Viswanathan and K.Chakrabarthy *"Catalysis Today, Modern Trends.*, Narosa Pubn, New Delhi, 351 (1995).

191. F.E.Massoth, *Adv.Cat.*, **27**, 265 (1978).

192. V.H.J.DeBeer, C.Bevelander, T.H.M. VanSintFiet, P.G.A.J. Wertler and C.H.Amberg, *J. Cat.*, **43**, 68 (1976).

193. T.Ono, H.Miyata Y.Kubokawa, *J. Chem. Soc. Far. Tran.*, **83**, 1761 (1983).

194. B.M. Reddy, K.V.R.Chary, B.R.Rao, V.S.Subramanyam and C.S.Sunandana, *Polyhedron*, 5, 191 (1980).

195. J.Sedlack and Z.Vits, *Collect. Czech. Chem. Comm.*, **54**, 2064 (1989).

196. K.C.Pratt, J.V.Sanders and V.Christov, *J. Cat.*, **124**, 416, (1990).

197. A.Shivasankar and U.Chadasamma,in B.Viswanathan and C.N.Pillai, (Eds) "*Recent Developement in Catalysis*", *Theory and Practicals,* Narosa Pubn, New delhi, 489, (1990).

198. A.Clearfield and D.S.Thakkur, *J. Cat.*, **65**, 185 (1980).

199. T.Hattori, A.Ishigura and Y.Muragkami, *J. Inorg. Nucl, Chem.*, **40**, 1107 (178).

200. B.H.Davis and W.S.Thakkur, *J.Cat.*, **65**, 185 (1980).

201. S.Karuppannasamy, K.Narayanan and C.N.Pillai, *Bull. Chem. Soc.*,**66**, 28 (1980).

202. Nawale, in B.Viswanathan and K.Chakrabarthy "*Modern Trends in Catalysis, Theory and Practicals*", Naroasa Pubn, New Delhi, 1995.

203. M.Hino and K.Arata, J.Chem.Soc. Comm., 112, (1985).

204. C.Gauthier, B.Chichi, A.Finich and P.Genestic, *J. Mol. Cat.*, **50**, 219 (1989), Appl. Cat., **30**, 365 (1981).

205. K.Arata, *Trends in Phy.Chem.*, **2**, 1 (1991).

206. S.Goto, M.Goto and Y.Kumaro, *React. Kinet. Cat. Lett.*, **41**, 27 (1990).

207. R.Stevens, "*Zirconia and Zirconia Ceramics, Magnesium Electron Ltd.*, London, 1986, Cat.Today 20 (1994).

208. Y.Sun and P.Sermon, *J. Mat. Chem.*, 6(**6**), 1025 (1996).

209. K.Chen, Y.Fan, Z.Hu and Q.Yan, *Cat.Lett.*, **36**, 139 (1991).

210. F.Shimojo, T.Okabi, F.Tanchibana, M.Kobayashi and H.Okazaki , *J. Phy. Soc. Jpn.*, **61,** 2348 (1992).

211. B.M.Reddy, B.Manohar and S.Mehdi, *J. Solid state Chem.*, **97**, 233 (1992).

212. W.P.Dow and T.J.Huang, *J. Cat.*, **160**, 171 (1996).

213. J.A.Navio, G.Colon, M.Macias, J.M.Campelo, A.A.Romero and J.M.Marinas, *J. Cat.*, **161**, 605 (1996).

214. C.Morterra, V.Bolis and G.Magnacca, *J. Chem. Soc. Far. Trans.*, **22**, 1996 (1991).

215. K.Otsuka, K.Jinno and A.Morikawa, *Chem. Lett.* 499 (1985).

216. C.H.Lin, K.D.Campbell, J.X.Wang and J.H.Lunsford, *J. Phy. Chem.*, **90**, 534 (1986).

217. Y.Fukudo, H.Hattori and K.Tanabe, *Bull. Chem. Soc . Jpn.*, **51**, 3150 (1978).

218. K.Otsuka, K.Jinno andM.Morikawa, *Chem. Lett.* 483 (1987).

219. P.W.Selwood, *Cat. Rev.*, **16**, 111 (1977).

220. K.M.Minachev, E.G.Vakk, R.V.Dmitrier and E.A.Nasedkin, *IZV, Akad, Nauk, SSSR, Ser, Khim*, **3**, 421, (1964).

221. K.M.Minachev, , J.W.Hightower, *Catalysis* North Holland, 219 (1973).

222. M.P.Rosynek and D.T.Magnuson, *J. Cat.*, **46**, 402 (1977).

223. M.P.Rosynek, J.S.Fox and J.L.Jensen, *J. Cat.*, **71**, 64 (1981).

224. J.F.Read, J. Cat., **28**, 428 (1973)., E.R.S.Winter, *J.Cat.*, **22**, 158 (1971).

225. K.M.Minachev, *Proc. Int. Cong. Cat.*, **5**, 219 (1973).

226. L.A.Sazanov, E.V.Aratamonov and G.N.Metrofanova, *Kinet. Cat.*, **12**, 378 (1971).

227. T.T.Bakumenko and I.T.Chachenokava, *Kinet. Cat.*, **10**, 796 (1969).

228. V.I.Lazukin, K.M.Kholyavenko, M.V.Rubanik and A.I. Khanik, *Catal.*, **29**, (1971).

229. T.Hattori, J.I.Inoko and Y.Murakami, *J. Cat.*, **42,** 60 (1976).

230. Y.Takita, T.Yoko, N.Egashisa and F.Hori, *Bull. Chem. Soc. Jpn.*, **55**, 2653 (1982).

231. Y.takasu, M.Matsui and Y.Matsuda, *J.Cat.*, **76**, 61 (1982).

232. M.P.Rosynek, R.J.Koprowski and G.N.Dellisante, *J. Cat.*, **122**, 80 (1990).

233. J.F.Read, *J. Cat.*, **50**, 490 (1972).

234. D.R.Ashmead, D.D.Eley and R.Ruthan, *J. Cat.*, **3**, 280 (1964).

235. P.W.Selwood, *J. Cat.*, **22**, 123 (1971).

236. T.Arai, K.Maruya, K.Domen and T.Onishi, *Bull. Chem. Soc. Jpn.*, **62**, 349 (1989).

237. H.S.Taylor and H.Diammond, *J. Ame. Chem. Soc.*, **57**, 1251 (1935).

238. S.Burnal and J.M.Trillo, *J. Cat.*, **66**, 184 (1980).

CHAPTER 3

EXPERIMENTAL

3.1. MATERIALS

3.1.1. Single oxides

The rare earth oxides (Y_2O_3, Dy_2O_3 and Gd_2O_3) were prepared from their nitrate salts obtained from Indian Rare Earths Ltd Udyogamandal, Kerala and ZrO_2 was prepared from zirconyl nitrate obtained from Romali Bombay. All the oxides were prepared by hydroxide method [1] using 1:1 ammonia .

Hydroxide method

Nitrate Solution of the sample (250 ml) containing definite weight of oxide was heated to boiling and 1:1 ammonia solution was added dropwise with stirring until the precipitation was complete. Concentrated ammonium hydroxide solution (an amount equal to one tenth volume of solution) was then added with stirring. Ammonia solution was added till the trecipitation was completed. It was then allowed to digest on a steam bath until the precipitate was flocculated and settled. The precipitate was then filtered on a Whatman No.41 filter paper and washed with small portions of an aqueous solution containing 1 g of ammonium nitrate and 10 ml of concentrated ammonium hydroxide in 100 ml, until the precipitate was free from NO_3^- ions. The precipitate was kept in an air oven at 110°C for overnight and was ignited in a china dish at 300°C for 2 h .

3.1.2. Mixed oxides

Mixed oxides of Zr with rare earth metals of the following compositions (20, 40, 60 and 80 % by weight of rare earth oxide) were prepared by co-precipitation method [2] from their nitrate salt solutions.

Aqueous ammonia (1:1) solution was added to the boiling solution containing calculated amount of nitrate salts, until the precipitation was complete. The precipitate after flocculation and digestion, was filtered by washing till free of nitrate ions. It was then dried by keeping in an air oven at 110°C for 2 h and then calcined in an electric furnace at 300°C in air for 2 h. Calcined samples were then sieved to get particles of 100-200 mesh size. The sieved samples activated at different temperatures of 300, 500 and 800°C were used for each experiment. The composition of mixed oxides obtained by precipitation method was determined by atomic absorption spectroscopic method(Perkin Elmer 23-80). The catalyst has been activated at a particular temperature for 2 h before each experiment.

3.1.3. Electron acceptors

Electron acceptors used for the adsorption study are 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-p-benzoquinone (chloranil), p-dinitrobenzene (PDNB) and m-dinitrobenzene (MDNB).

TCNQ was obtained from Merck Schuchandt and was purified by repeated recrystallisation from acetonitrile (3).

Chloranil was obtained from Sisco Research Laboratories Pvt. Ltd., and was purified by recrystallisation from benzene [4].

p-Dinitrobenzene was supplied by Koch-Light Laboratories Ltd. and was purified by recrystallisation from chloroform [5].

m-Dinitrobenzene was obtained from Loba -Chemie Industrial Company and was purified by recrystallisaion from CCl_4 [6].

3.1.4. Solvents

Acetonitrile

SQ grade Acetonitrile obtained from Qualigens Fine Chemicals was first dried by passing through a column filled with silica gel (60-120 mesh) activated at 110° C for 2 h.

It was then distilled with anhydrous phosphorus pentoxide and the fraction between 79-82°C was collected [7].

Benzene

Benzene used for the acidity/basicity measurements was purified by the following procedure [8].

SQ grade benzene obtained from Qualigens Fine Chemicals was shaken repeatedly with about 15 % of the volume of concentrated sulfuric acid in a stoppered separating funnel until the acid layer was colourless on standing. After shaking, the mixture was allowed to settle and lower layer was drawn off. It was then washed twice with water to remove most of the acid, then with 10 % sodium carbonate solution and finally with water. It was dried with anhydrous $CaCl_2$. It was filtered and distilled and the distillate was kept over sodium wire for one day. It was then distilled and fraction boiling at 80° C was collected.

3.1.5. Hammett Indicators

Hammett indicators used for the nonaqueous titration method for the determination of acid - base strength distribution are following:

Crystal violet (Romali)

Dimethyl yellow (Loba Chemie Industrial Company)

Methyl red (E.Merck India Pvt. Ltd)

Neutral red (Romali)

Bromothymol blue (Qualigens Fine Chemicals)

Thymol blue (Qualigens Fine Chemicals)

4-Nitroaniline (Indian Drug and Pharmaceuticals Ltd.)

Trichloro acetic acid (SQ grade) obtained from Qualigens Fine Chemicals and n-butylamine (S.d Fine Chemicals Pvt. Ltd) were used without further purification for titration .

3.1.6. Reagents used for activity measurements

Cyclohexanone

Commercial cyclohexanone obtained from BDH was purified through the bisulphite method [9]. A saturated solution of sodium bisulphite was prepared from 40 g of finely powdered sodium bisulphite. The volume of the resulting solution was measured and it was treated with 70 % of its volume of rectified spirit. Sufficient water was added to dissolve the precipitate which has been separated. 20 g of cyclohexanone was introduced into the aqueous alcoholic bisulphite solution with stirring and the mixture was allowed to stand for 30 minutes. The crystalline bisulphite compound was filtered off at the pump and washed it with a little rectified spirit.

The bisulphite compound was transferred to a separating funnel and decomposed with 80 ml of 10 % NaOH solution. The liberated cyclohexanone was removed. The aqueous solution layer was saturated with salt and extracted it with 30 ml of ether. The ether extract was combined with the ketone layer and dried with 5 g of anhydrous magnesium sulfate. The dried ethereal solution was filtered into a 50 ml distilling flask, attached with a condenser and distilled off the ether using a water bath. The resultant cyclohexanone was distilled and the fraction distilling at 153°C was collected.

Benzophenone

Benzophenone was supplied by Sisco Research Laboratories Pvt. Ltd. and was purified by recrystallization from ethanol [10].

2-Propanol

LR grade reagent obtained from Merck was further purified by adding about 200 g of quick lime to 1 litre of 2-propanol. It was kept for 3-4 days, then refluxed for 4 h and was distilled. The fraction distilling at 82°C was collected [11].

Xylene

Extra pure quality xylene obtained from Merck was used as such.

Cyclohexanol

Cyclohexanol obtained from Merck was refluxed with freshly ignited CaO till the CaO was absorbed complete water present in cyclohexanol and then fractionally distilled. The fraction distilling at 161.1°C was collected [12]

Toluene

SQ grade toluene obtained from Qualigens Fine Chemicals was shaken twice with cold concentrated H_2SO_4 (100 ml of acid for 1 litre of toluene), then with water, aqueous 5 % $NaHCO_3$ and again with water. The process was repeated for several times. Then it was dried successively with $CaSO_4$ and P_2O_5, finally distilled and the fraction distilling at 110°C was collected [13]. The distilled toluene was preserved under sodium wire.

n-Decane

LR grade reagent obtained from S.d. Fine Chemicals Pvt. Ltd. was further purified by shaking with conc H_2SO_4. It was washed with water and aqueous $NaHCO_3$. Finally it was washed with more water. Then it was dried with $MgSO_4$, refluxed with sodium and distilled. The fraction distilling at 174°C was collected [14].

1-Butanol

LR grade reagent obtained from Merck was further purified by drying with anhydrous potassium carbonate and was fractionally distilled. The fraction distilling at 116.5°C was collected [15].

Acetic acid

LR grade reagent obtained from Merck was purified by adding some acetic anhydride to react with the water present. It was then heated for 1 h just below boiling in the presence of 2 g CrO_3 per 100 ml and was then fractionally distilled. The fraction distilling at 116-118°C was collected [16]. The pure form of acetic acid was used for the esterification of butanol.

3.2. METHODS

3.2.1. Adsorption studies [17]

The oxides were activated at particular temperature for 2 hours prior to each experiment. The oxide (0.5 g) was placed in a 250 ml test tube and outgassed at 10^{-5} Torr for 1 h. Into the test tube which was fitted with a mercury sealed stirrer, 20 ml of a solution of an electron acceptor in organic solvent (acetonitrile) was then poured in. After the solution had subsequently been stirred for 4 h at 25°C in a thermostat bath, the oxide was collected by filtration. The reflectance spectra of the dried samples were recorded on a Shimadzu 160A UV-visible spectrophotometer with a 200-0531 reflectance attachment.

The ESR spectra of the adsorbed samples were measured at room temperature using varian E-112 X/Q band ESR spectrophotometer. Radical concentrations were determined by comparison of area obtained by double integration of the first derivative curve for the sample and standard solution of 1,1-diphenyl-2-picryl-hydrazyl in benzene. The amount of electron acceptor adsorbed was determined from the difference in concentration before and after adsorption. The absorbance of electron acceptors was measured by means of a UV-vis spectrophotometer (Shimadzu 160A) at the λ_{max} of the electron acceptor in the solvent. The λ_{max} values of the MDNB, PDNB, chloranil and TCNQ in acetonitrile was 237, 262, 288 and 393.5 nm respectively.

Infra red spectra of oxides were taken on a Perkin Elmer PE-983 infra red spectrophotometer.

The specific area of the oxides were determined by BET method (bY the adsorption of nitrogen) using Carlo -Erba Strumentazione Sorptomatic series 1800. The

Table 3.1. Surface area of the mixed oxides of ZrO_2 -Dy_2O_3 systems at different activation temperatures (m^2 g^{-1})

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	200.30	61.49	25.77
20	219.33	117.23	39.75
40	192.85	108.75	27.33
60	128.45	74.51	23.37
80	49.84	61.49	24.57
100	24.35	24.41	29.53

Table 3.2. Surface area of the mixed oxides of ZrO_2 -Y_2O_3 systems at different activation temperatures (m^2 g^{-1})

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	200.30	61.49	25.77
20	210.69	122.34	56.99
40	187.85	118.40	44.71
60	214.88	123.16	47.98
80	131.69	108.41	61.79
100	46.30	81.50	38.00

Table 3.3. Surface area of the mixed oxides of ZrO_2 -Gd_2O_3 systems at different activation temperatures (m^2 g^{-1})

Catalyst	Temperature (° C)	surface area (m^2/gm)
0	500	61.49
20	500	106.13
40	500	101.98
60	500	70.35
80	500	43.10
100	300	11.95
100	500	13.45
100	800	12.46

surface area of oxides in $m^2 g^{-1}$ activated at different temperatures are given in Tables 3.1 to 3.3.

3.2.2. Acidity/basicity measurements

The sieved oxides samples were activated at required particular temperature for 2 h prior to each experiment

The acidity/basicity of oxides were determined on a common Ho scale using the same Hammett indicators. Non aqueous titration method was employed.

The acidity at various acid strength of a solid was measured by titrating 0.1 g of the solid suspended in 5 ml of benzene with a 0.1 N solution of n-butyl amine in benzene. At the end point basic color of indicators appeared [18]. The colour of the benzene was also changed to that of acid colour of the indicator. The colour of the adsorbed indicator can give a measure of acid strength.

The basicity was measured by titrating the 0.I g of activated solid suspended in 5 ml benzene with a 0.1 N solution of trichloroacetic acid in benzene using the same Hammett indicators used for acidity measurements [19]. The colours of the indicators on the surface of the oxides at the end point of the titration were the same as the colors which appeared by adsorption of respective indicators on the acid sites. The colour of the benzene solution was the basic colour of the indicator at the end point but it turned to be the acidic colour by adding an excess of the acid. As the results for a titration lasting 1 h were the same as those for a titration lasting 20 h, 1 h was taken for titration.

3.2.3. Catalytic activity measurements

a) Oxidation of cyclohexanol

In a round bottomed flask (20 cm^3) equipped with a reflex condenser were placed catalyst (100-200 mesh size, o.5 g), 10 cm^3 of a toluene of cyclohexanol (0.25 m mol) benzophenone (14.6m mol) and n-decane (0.20 mmol) as an internal standard. The contents were heated under gentle reflux for 2 h at 110° C. After reaction catalyst was separatd by filtration. The amount of cyclohexanol formed was determined by means of CHEMITO-8510 gas chromatograph, by noting the product formation at various time intervals [21].

b) Reduction of cyclohexanone

In a 25 ml round bottomed flask equipped with a reflux condenser 5 mmol of cyclohexanone (in 20 ml isopropanol) and 0.5 g of the catalyst was heated under gentle reflux. The contents were kept under gentle reflux for 8 h. The reaction products were analysed periodically. The products was separated by simple filtration. The activity is reported as the first order rate constant for the conversion of cyclohexanone per minute per m^2 of the catalyst surface. The reaction was followed using a Shimadzu UV-visible spectrophotometer by noting the change in absorbance of cyclohexanones in the reaction mixture at 283 nm [22].

c) Esterification of acetic acid using 1-butanol

The esterification reaction was carried out in a 25 ml round bottomed flask equipped with a reflux condenser in which the catalyst (0.5 g), acetic acid (2m mol) and n-butanol (32 m mol) were placed, n-decane was added as the internal standard. The reaction temperature was maintained 98°C and stirred continuously on a magnetic stirrer for 5 h [23].

The reaction was followed by the product analysis by means of a Chemito-8510 gas chromatograph by comparison of its retention time with that of the standard samples. From the peak area of the product, the concentration of the product was calculated with reference to that of the internal standard

REFERENCESS

1. "Encyclopeadia of Industrial Chemical analysis", F.D.Snell and L.S.Ettre, Vol.17 Interscience, New York, p.475 (1973).
2. T.Arai, K.Maruya, K.Domen and T.Onishi, *Bull., Chem., Soc. Jpn.*, **62**, 349 (1989).
3. E.S.Acker and W.R.Hertler, *J. Ame. Chem. Soc.*, **84**, 3370 (1962).
4. L.F.Flesser and M.Flesser, "*Reagents for Organic synthesis*", John Wiley, New York, p.125 (1967).
5. B.S.Furness, A.J.Hannford, V.Rogers, P.W.G. Smith and A.R.Tatchell, "*Vogel's Text Book of Practical Organic Chemistry*", 4th ed., p.708 (ELBS London) 1978.
6. Ibid, p.60.
7. A.I.Vogel, "*A Text Book of Practical Organic Chemistry*", 3rd **ed.**, p.407, ELBS London (1973).
9. A.I.Vogel, "*A Text Book of Practical Organic Chemistry*", 3rd ed., p.172 ELBS London (1973).
10. Ibid, p.342.
11. D.D.Perrin, W.L.F.Armarego and D.R.Perrin, "*Purification of Laboratory Chemicals*", 2nd ed., p.123 (1983).

12. A.I.Vogel, "*A Text Book of Practaical Organic Chemistry*", 3rd ed., p.886 ELBS London (1973).

13. Ibid, p.185.

14. Ibid, p.487.

15. Ibid, P.170.

16. D.D.Ferrin, W.L.F.Armarego and D.R.Perrin: "*Purification of Laboratory Chemicals*", 2nd ed., Pergamon Press, p.123 (1993).

17. K.Esumi, K.Miyata and K.Meguro, *Bull.Chem. Soc. Jpn.*, 59, 3363 (1986).

18. T.Yamanaka and K.Tanabe, *J. Phy. Chem.*, 79, 2409 (1978).

19. B.N.Figgis and R.S.Nyholm, *J. Chem. Soc.*, 4190 (1958).

20. B.N.Figgis and J.Lewis, "Modern Co-ordinatio Chemistry", Interscience, New York (1960).

21. H.Kuno, K.Takahashi, M.Shibagaki and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **63**, 1943 (1990).

22. M.Shibagaki, K.Takahashi, H.Kuno and H.Matsushita, *Bull.Chem.Soc. Jpn.*, **61**, 328 (1988).

23. K.Takahashi, M.Shibagaki and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **62**, 2353 (1989).

CHAPTER 4

ELECTRON DONOR PROPERTIES OF MIXED OXIDES OF ZrO_2 WITH RARE EARTH OXIDES

4.1. INTRODUCTION

On the surface of the metal oxides and mixed metal oxides the electron donor sites are widely distributed from low electron affinity to high electron affinity values. When an electron acceptor is adsorbed on a metal oxides, it has been observed that electron transfer occurs from the surface to the electron acceptor, resulting in the formation of the corresponding anion radicals on the metal oxides [1-4]. Surface electron donor properties of some of the rare earth oxides have been reported [5-8]. The electron transfer mechanism is one of the charging origin for particles. However until now the study of electron transfer charge origin has been limited to the particles in organic liquid systems. When metal oxides are in contact with organic solvents, a charge on their surface is generated. As one of the charge mechanisms in organic liquids, the donor acceptor interaction between a solid surface and an organic liquid has been discussed [9]. That is, the surface charge depends on the donocity of the organic liquid. The donocity of the organic liquid depends on the basicity of the solvent. It is expected that surface charges of oxides would decrease as the basic character of organic liquid increases, due to the electron transfer from solvent to the surface of metal oxides [10]. Adsorption of electron acceptors on metal oxides have been investigated to estimate the electron donor properties of metal oxides and their characterisation [2, 5, 11-12]. This chapter deals with the results and discussion of electron donor properties of mixed oxides of ZrO_2 with rare earth elements (Dy, Y and Gd) by the adsorption of electron acceptors with various electron affinity values.

4.2. EXPERIMENTAL

The strength and distribution of electron donor sites on the surface of oxides were determined by the adsorption of different electron acceptors from acetonitrile solution, which is a very weak base. The list of electron acceptor employed are given in Table 4-1. The amount of electron acceptor adsorbed was determined by means of UV-vis spectrophotometry and adsorbed state of electron acceptor was studied by ESR and electronic spectra. The detailed experimental procedures are given in chapter 3.

4.3. RESULTS AND DISCUSSION

The surface electron properties of the metal oxides and mixed metal oxides have been determined by the adsorption of four electron acceptors with different electron affinity values varying from 1.26 to 2.84 eV on the surface, to form corresponding anion radicals. Since the electron donating properties vary with the activation temperatures, the oxides activated at different temperatures of 300, 500 and 800°C were used.

Table 4.1. Electron acceptor used for adsorption studies.

Electron acceptor	electron affinity values (eV)
m-dinitrobenzene(MDNB)	1.26
p-dinitrobenzene (PDNB)	1.77
2,3,5,6-tetrachloro1,4-benzoquinone (chloranil)	2.40.
7,7,8,8-tetracyano quino-dimethane (TCNQ)	2.84

In the case of PDNB and MDNB the adsorption was found to be so negligible at all activation temperatures irrespective of composition that the amount could hardly be determined. TCNQ and chloranil gave adsorption with characteristic results. The adsorption isotherms of TCNQ and chloranil from acetonitrile can be classified as Langmuir adsorption isotherms. It is obtained by plotting the amount of the electron acceptor adsorbed (C_{ads}) against equilibrium concentration (C_{eq}). From such plots the limiting amount of electron acceptor adsorbed can be calculated. The data are given in Tables 4.2 to 4.6. It was verified by the linear form of Langmuir isotherm, where the

Table 4.2. Limiting amount of chloranil adsorbed on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures (10^{-5} mol m^{-2})

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	6.92	10.6	7.88
20	6.50	6.43	2.06
40	7.58	7.47	6.71
60	4.83	8.92	7.19
80	7.41	12.82	7.35
100	1.78	2.46	4.12

Table 4.3 Limiting amount of TCNQ adosorbed on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures (10^{-5} mol m^{-2}).

Catalyst (% of Y_2O_3)	Activation temperature (° C)		
	300	500	800
0	9.64	20.8	10.7
20	9.11	9.04	2.64
40	11.94	11.56	6.94
60	6.96	13.7	8.22
80	13.16	15.9	7.90
100	5.72	7.22	9.41

Table 4.4. Limiting amount of chloranil adsorbed on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures. (10^{-5} mol m^{-2})

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	6.92	10.6	7.88
20	6.15	6.92	2.85
40	5.94	6.78	5.65
60	8.46	7.85	6.85
80	20.32	13. 7	6.37
100	-	1.93	4.96

Table 4.5. Limiting amount of TCNQ adsorbed on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures (10^{-5} mol m^{-2}).

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	9.64	20.80	10.67
20	6.41	12.71	6.96
40	8.62	13.49	6.22
60	14.90	17.74	9.44
80	22.14	29.66	8.75
100	1.51	4.075	6.03

Table 4.6. Limiting amount of chloranil and TCNQ adsorbed ZrO_2-Gd_2O_3 oxides at 500°C (10^{-5} mol m^{-2})

Catalyst (% of Gd_2O_3)	Activation Temperature (°C)	Electron acceptor	
		Chloranil	TCNQ
0	300	6.92	9.64
0	500	10.6	20.80
0	800	7.88	10.67
20	500	4.33	16.51
40	500	6.66	12.26
60	500	6.99	16.54
80	500	15.64	32.13
100	300	-	3.68
100	500	34.65	35.35
100	800	19.63	47.85

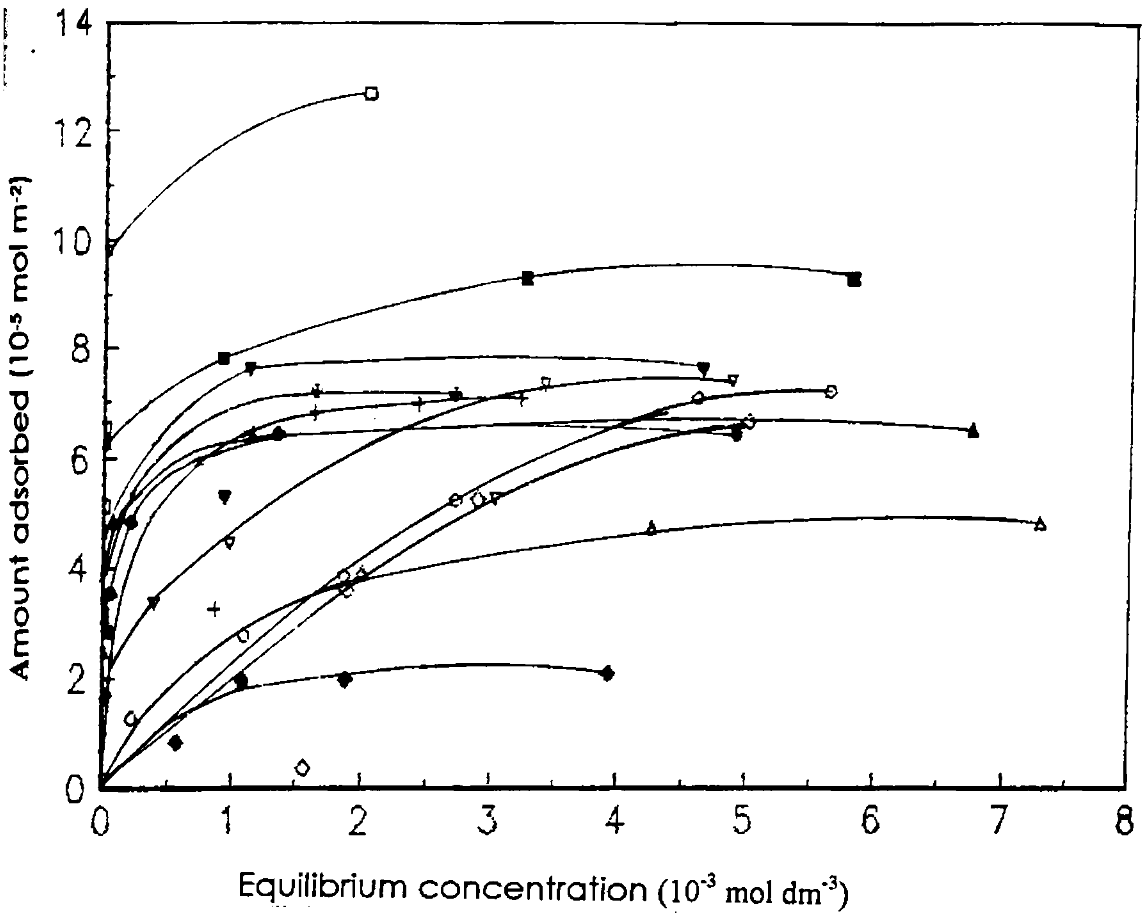


Fig. 4.1 Adsorption of chloranil adsorbed on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

[ZY$_1$- (80 %ZrO_2 & 20 % Y_2O_3) ZY$_2$ - (60 % ZrO_2 & 40 % Y_2O_3)

ZY$_3$ - (40 % ZrO_2 & 60 % Y_2O_3) ZY$_4$ - (20 % ZrO_2 & 80 % Y_2O_3)]

[▲]	ZY$_1$-300°C	[●]	ZY$_1$-500°C	[◆]	ZY$_1$-800°C
[▼]	ZY$_2$-300°C	[o]	ZY$_2$-500°C	[◇]	ZY$_2$-800°C
[△]	ZY$_3$-300°C	[■]	ZY$_3$-500oC	[+]	ZY$_3$-800°C
[▽]	ZY$_4$-300°C	[□]	ZY$_4$-500°C	[*]	ZY$_4$-800°C

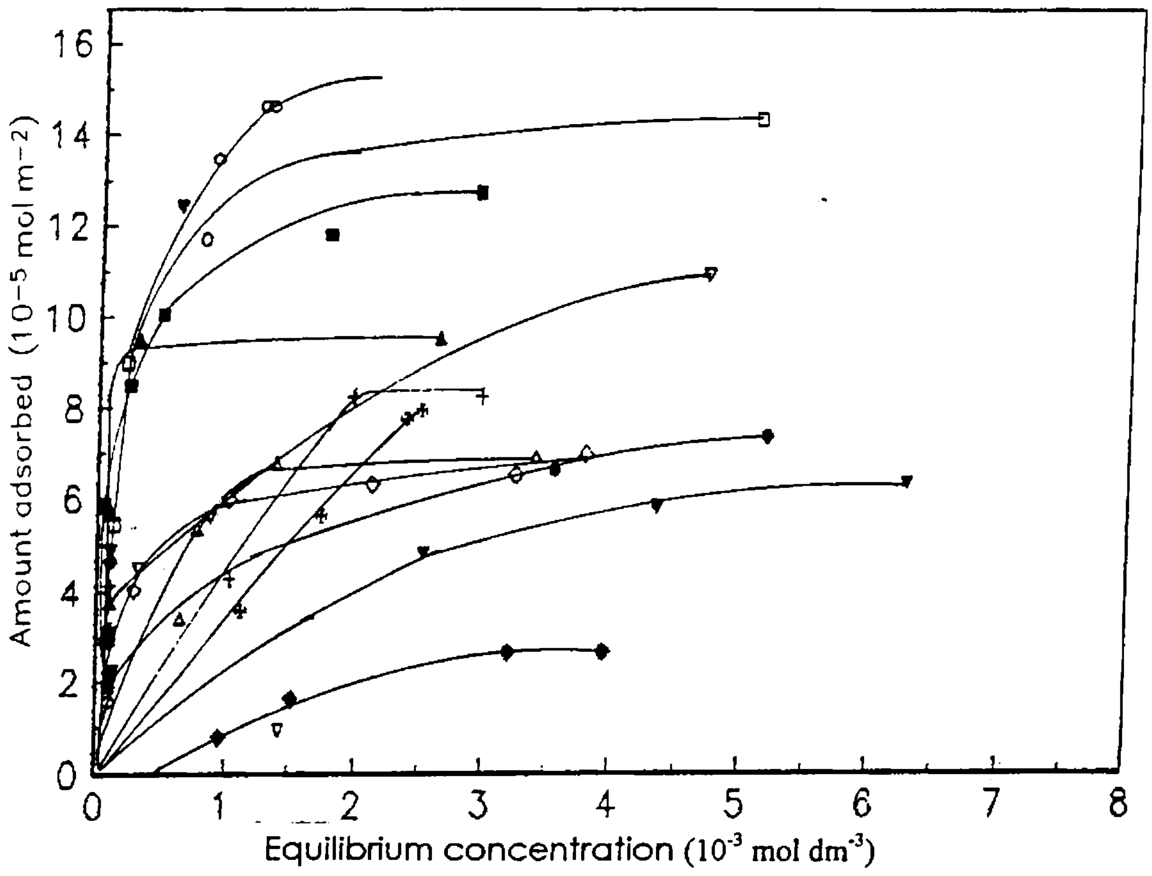


Fig. 4.2 Adsorption of TCNQ on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

[ZY_1- (80 % ZrO_2 & 20 % Y_2O_3) ZY_2 - (60 % ZrO_2 & 40 % Y_2O_3)

ZY_3 - (40 % ZrO_2 & 60 % Y_2O_3) ZY_4 - (20 % ZrO_2 & 80 % Y_2O_3)]

[▲]	ZY_1-300°C	[●]	ZY_1-500°C	[◆]	ZY_1-800°C
[▼]	ZY_2-300°C	[○]	ZY_2-500°C	[◇]	ZY_2-800°C
[△]	ZY_3-300°C	[■]	ZY_3-500oC	[+]	ZY_3-800°C
[▽]	ZY_4-300°C	[□]	ZY_4-500°C	[•]	ZY_4-800°C

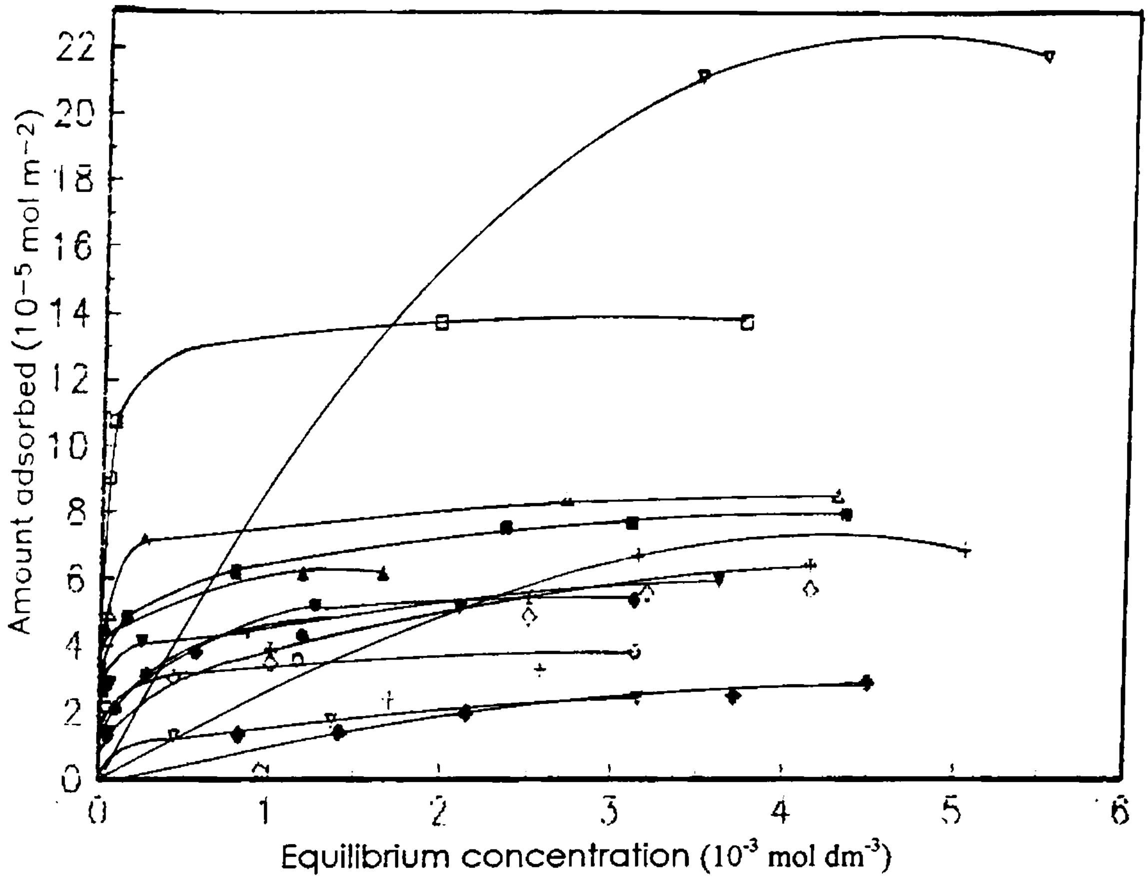


Fig. 4.3 Adsorption of chloranil on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

[ZD_1 - (80 % ZrO_2 & 20 % Dy_2O_3) ZD_2 - (60 % ZrO_2 & 40 % Dy_2O_3)
ZD_3 - (40 % ZrO_2 & 60 % Dy_2O_3) ZD_4 - (20 % ZrO_2 & 80 % Dy_2O_3)]

[▲]	ZD_1-300°C	[●]	ZD_1-500°C	[◆]	ZD_1-800°C
[▼]	ZD_2-300°C	[○]	ZD_2-500°C	[◇]	ZD_2-800°C
[△]	ZD_3-300°C	[■]	ZD_3-500°C	[+]	ZD_3-800°C
[▽]	ZD_4-300°C	[□]	ZD_4-500°C	[*]	ZD_4-800°C

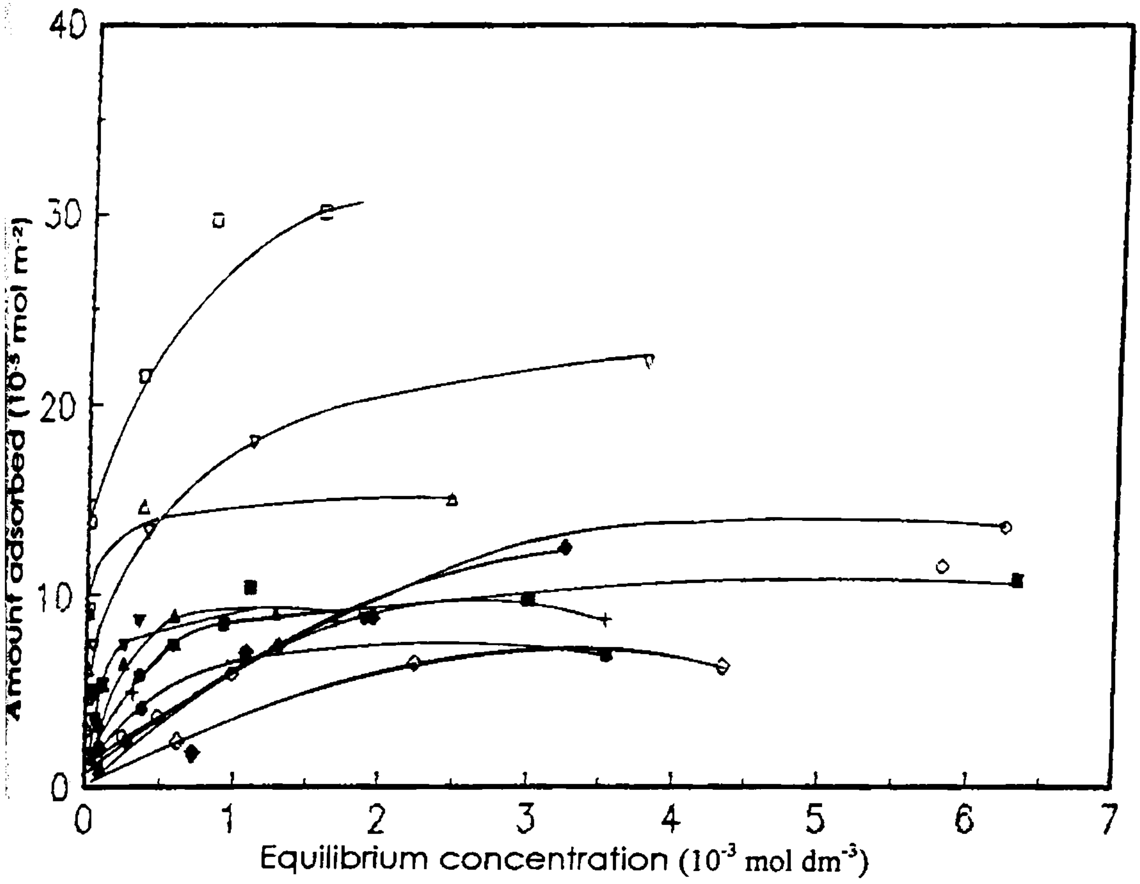


Fig. 4.4 Adsorption of TCNQ on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

[ZD$_1$- (80 % ZrO_2 & 20 % Dy_2O_3)

ZD$_2$ - (60 % ZrO_2 & 40 % Dy_2O_3)

ZD$_3$ - (40 % ZrO_2 & 60 % Dy_2O_3)

ZD$_4$ - (20 % ZrO_2 & 80 % Dy_2O_3)]

[▲]	ZD$_1$-300°C	[●]	ZD$_1$-500°C	[♦]	ZD$_1$-800°C
[▼]	ZD$_2$-300°C	[○]	ZD$_2$-500°C	[◇]	ZD$_2$-800°C
[△]	ZD$_3$-300°C	[■]	ZD$_3$-500°C	[+]	ZD$_3$-800°C
[▽]	ZD$_4$-300°C	[□]	ZD$_4$-500°C	[*]	ZD$_4$-800°C

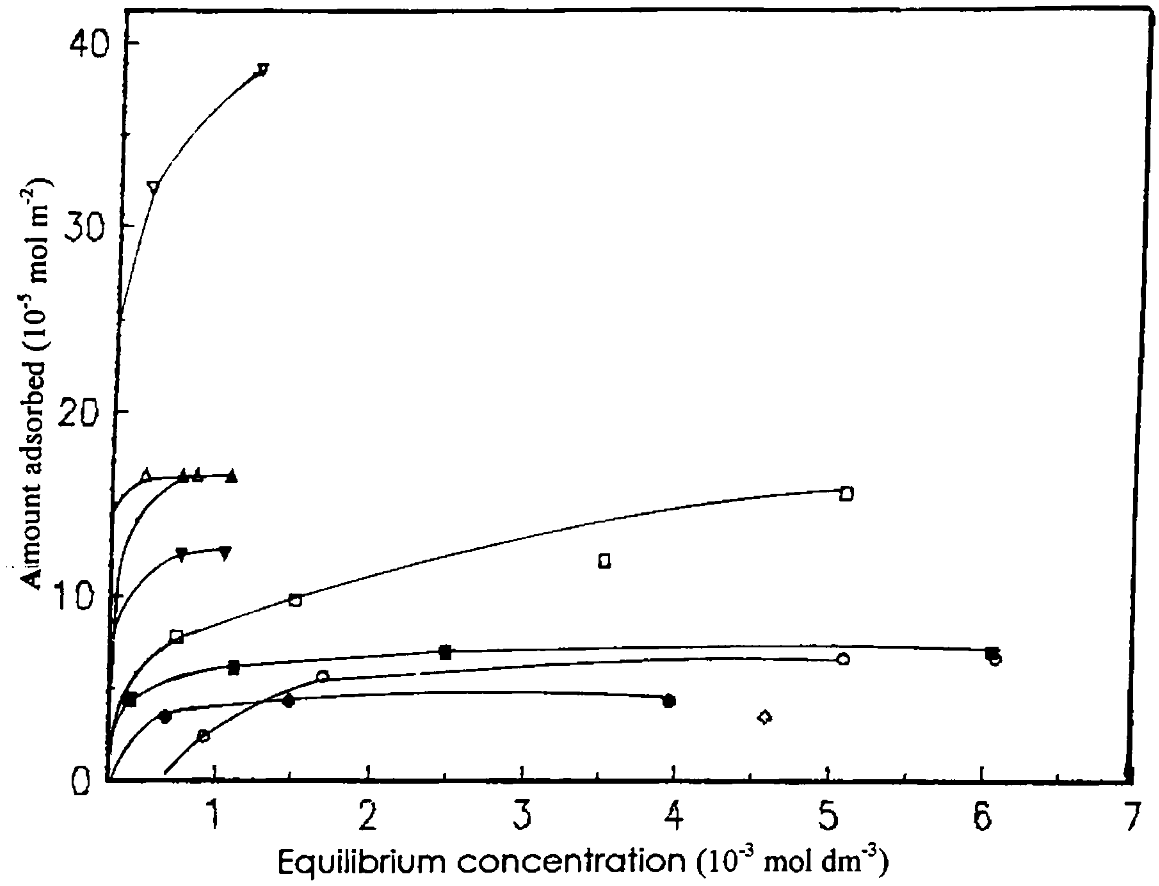


Fig. 4.5. Adsorption of chloranil and TCNQ on ZrO_2-Gd_2O_3 mixed oxides at 500°C

[ZG$_1$- (80 % ZrO_2 & 20 % Gd_2O_3)

ZG$_2$ - (60 % ZrO_2 & 40 % Gd_2O_3)

ZG$_3$ - (40 % ZrO_2 & 60 % Gd_2O_3) ,

ZG$_4$ - (20 % ZrO_2 & 80 % Gd_2O_3)]

CN-CHLORANIL

TN - TCNQ

ZG$_1$-CN
ZG$_2$-CN
ZG$_3$-CN
ZG$_4$-CN

ZG$_1$-TN
ZG$_2$-TN
ZG$_3$-TN
ZG$_4$-TN

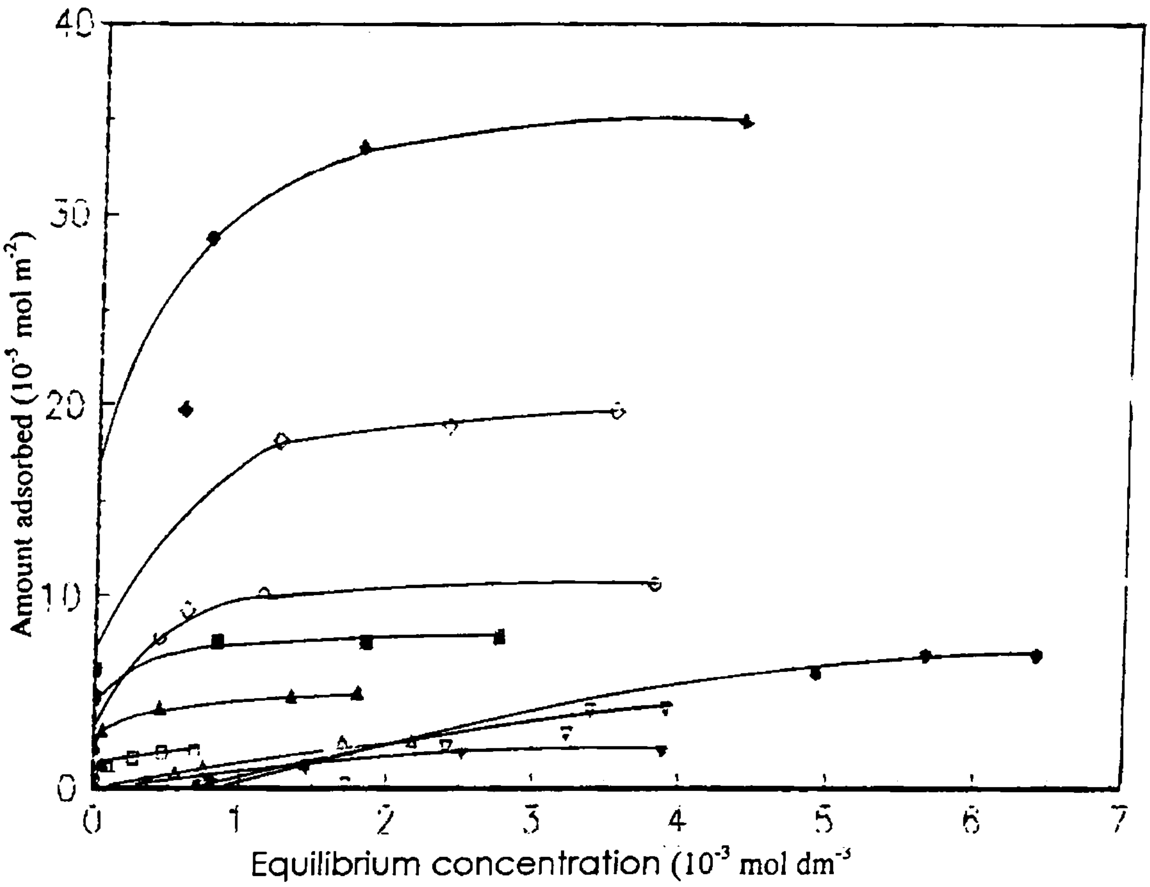
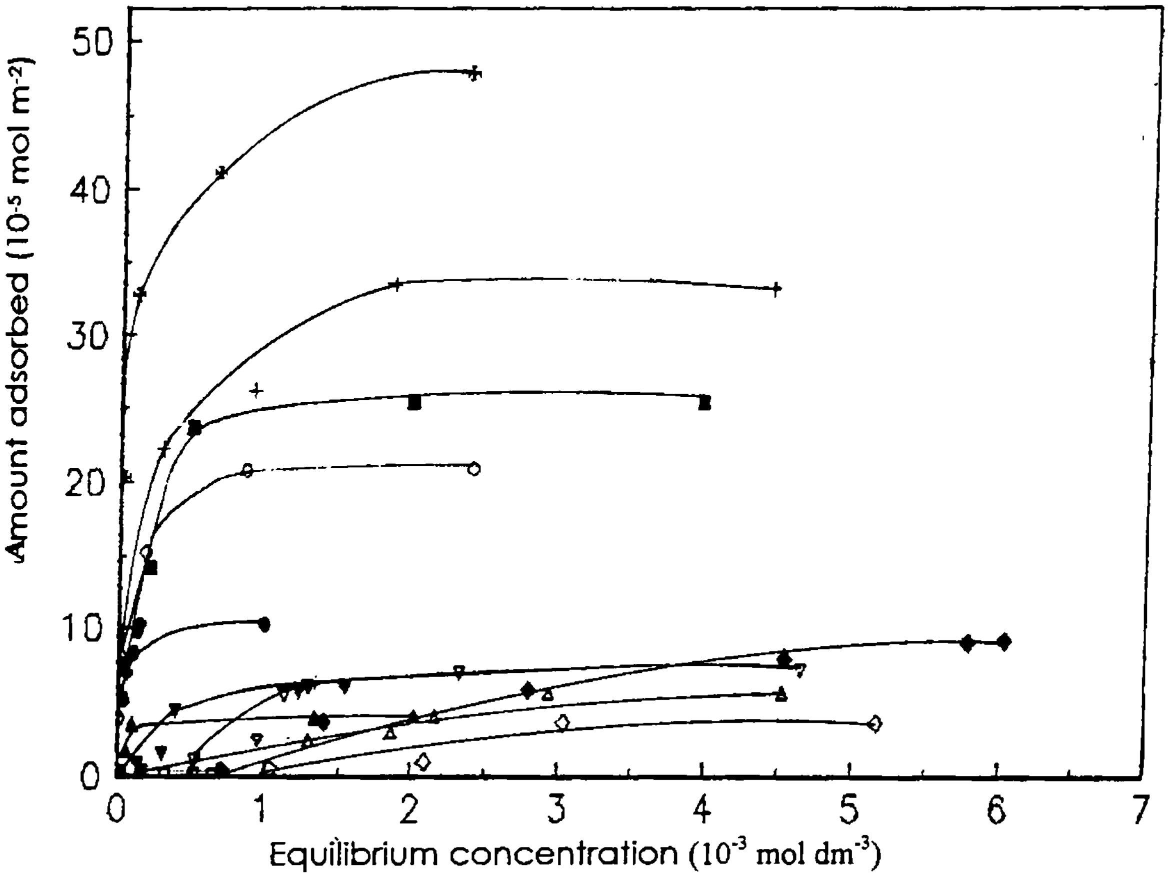


Fig. 4.6 Adsorption of chloranil on metal oxides at different activation temperatures

[▲]	ZrO_2.300°C	[●]	ZrO_2.500°C	[◆]	ZrO_2-800°C
[▼]	Dy_2O_3-300°C	[○]	Dy_2O_3-500°C	[◇]	Dy_2O_3-800°C
[△]	Y_2O_3-300°C	[■]	Y_2O_3-500°C	[+]	Y_2O_3-800°C
[▽]	Gd_2O_3-300°C	[□]	Gd_2O_3-500°C	[*]	Gd_2O_3-800°C



Equilibrium concentration (10^{-3} mol dm^{-3})

Fig. 4.7 Adsorption of TCNQ on metal oxides at different activation temperatures

[▲]	ZrO_2-300°C	[●]]	ZrO_2-500°C	[◆]	ZrO_2-800°C
[▼]	Dy_2O_3-300°C	[○]	Dy_2O_3-500°C	[◇]	Dy_2O_3-800°C
[△]	Y_2O_3-300°C	[■]	Y_2O_3-500°C	[+]	Y_2O_3-800°C
[▽]	Gd_2O_3-300°C	[□]	Gd_2O_3-500°C	[*]	Gd_2O_3-800°C

C_{eq}/C_{ads} was plotted against equilibrium concentration(C_{eq}). The Langmuir adsorption isotherm obtained by the adsorption of chloranil and TCNQ are given in figure 4.1 to 4.7. The linear form of the Langmuir isotherms are also given in figure 4.8 and 4.9.

When electron acceptors are adsorbed from the solution, the surface developed a remarkable colouration characteristics of each electron acceptors adsorbed, owing to the interaction between electron acceptor and the oxide surface [13]. Chloranil gave pink colour and TCNQ gave a bluish green colour. The colouration indicates the formation of new adsorbed species on the surface. It was confirmed by the evidence that the coloured metal oxides showed esr absorption indicating the formation of new free radical species. Figure 4.10 shows the esr of the sample adsorbed with TCNQ (C_{ads}=7.04 x 10^{-5} mol m^{-2}) on the surface. The radical concentrations were calculated by comparing the areas obtained by double integration of the first derivative curve for the sample and standard solution of 2,2-diphenyl 1-picrylhydrazil in benzene. The plot of radical concentration against equilibrium concentrations of electron acceptor in solution also corresponds to the Langmuir adsorption isotherms (figures 4.11 to 4.12). From such plots the limiting radical concentrations of electron acceptor adsorbed can also be estimated. The samples coloured by TCNQ adsorption gave an unresolved esr spectra with a g value of 2.003. These spectra have been identified as being those of TCNQ anion radicals [14]. The

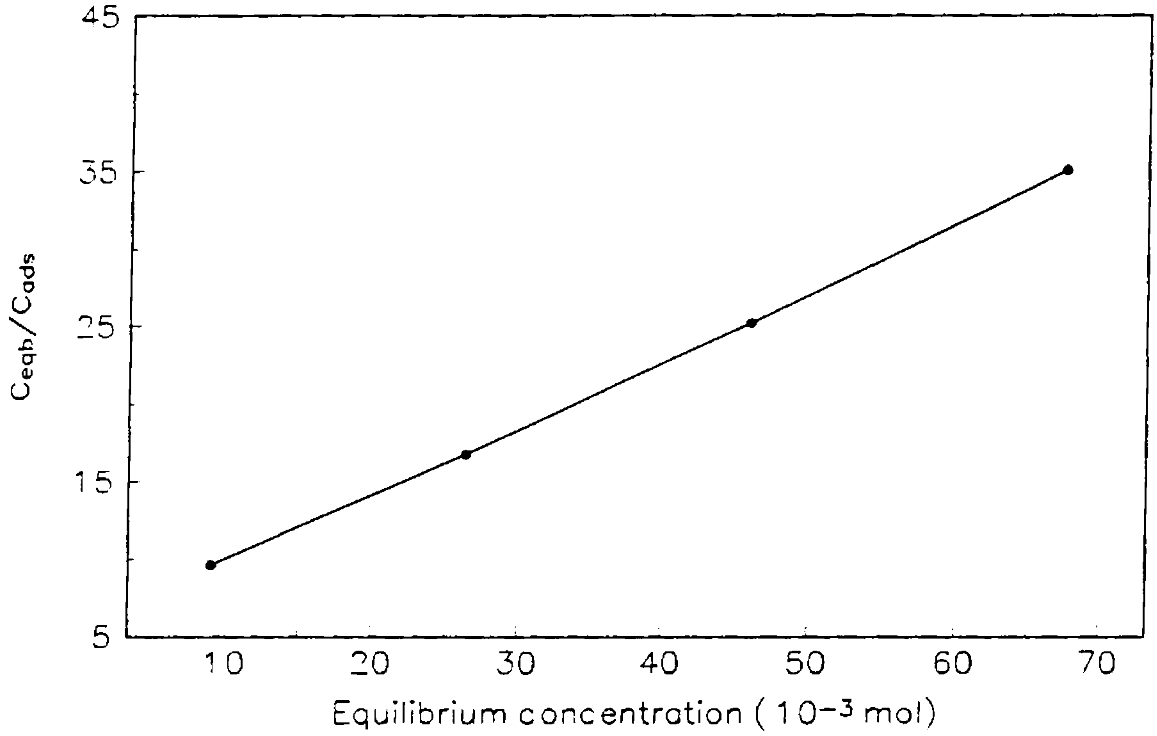


Fig. 4.8 Linear form of Langmuir isothermobtained for adsorption of Chloranil in acetonitrile on Dy_2O_3 at 500°C.

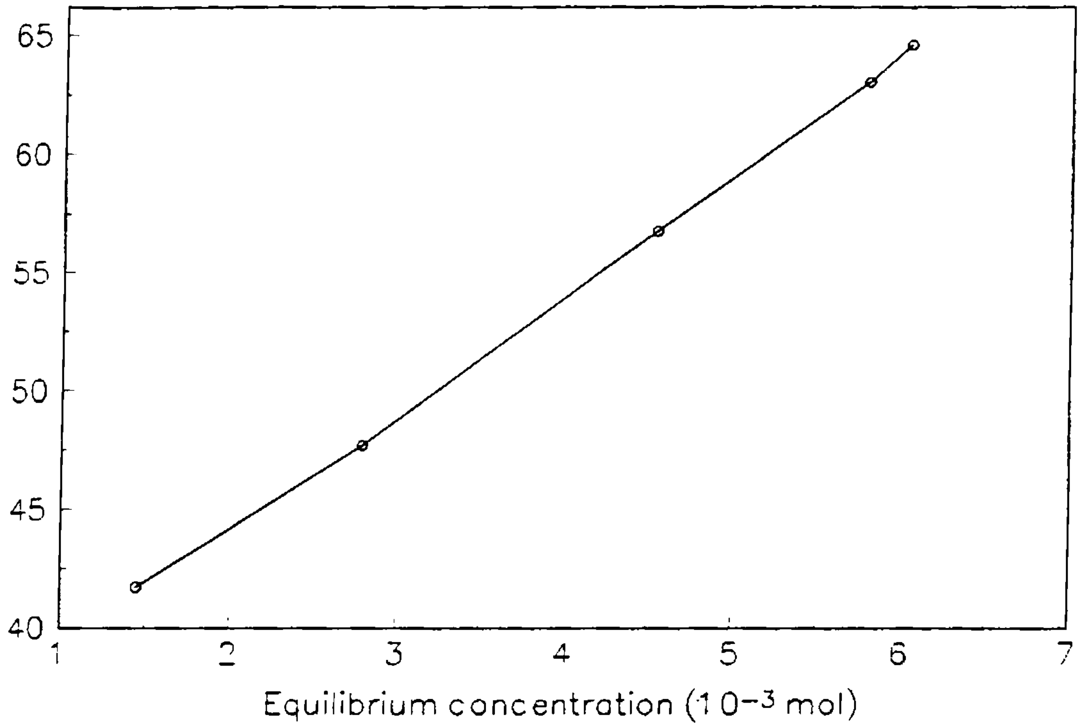
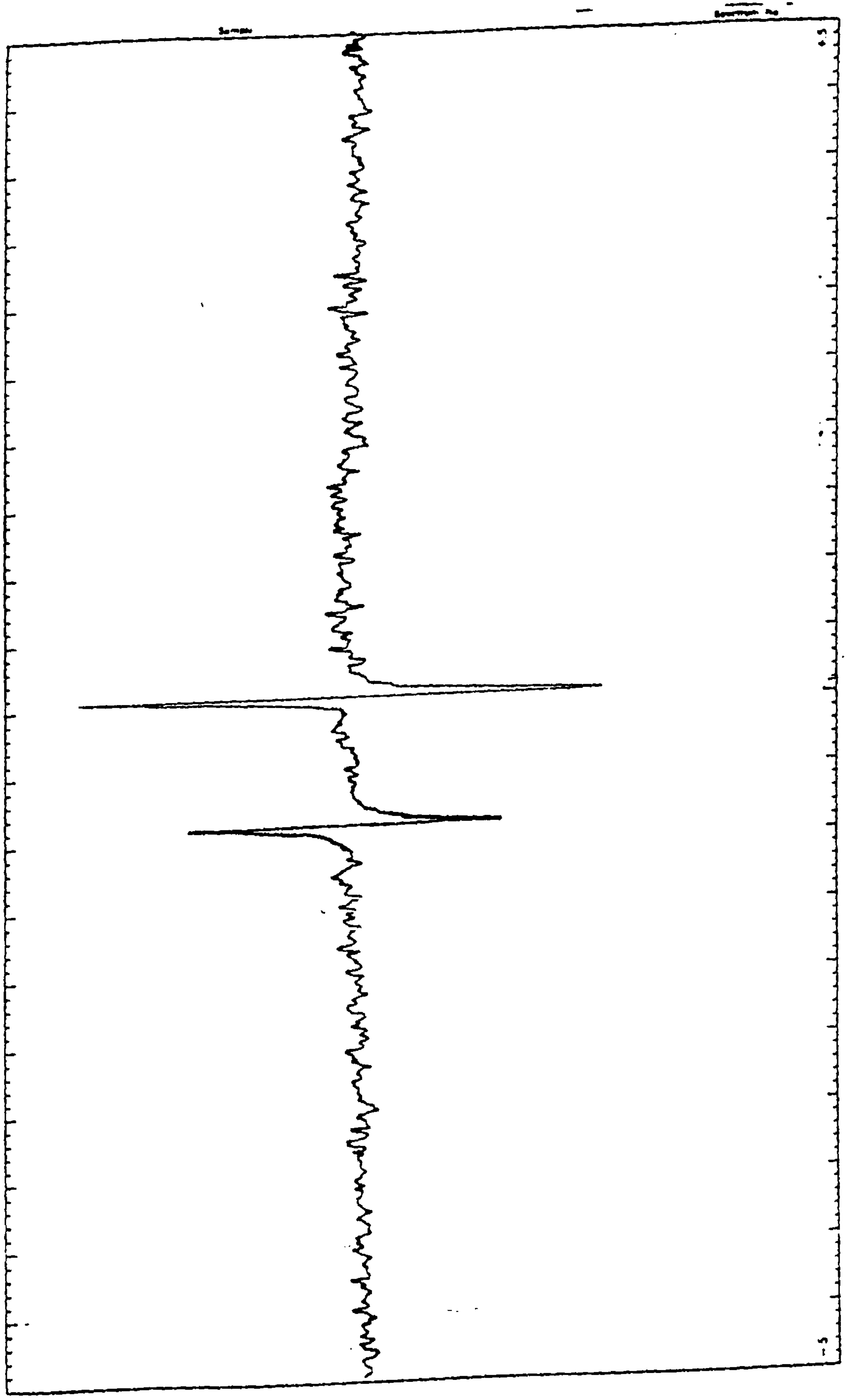


Fig. 4.9 Linear form of Langmuir isotherm obtained for adsorption of TCNQ in acetonitrile on Y_2O_3 at 800°C

Fig. 4.10 ESR spectra of TCNQ adsorbed sample.



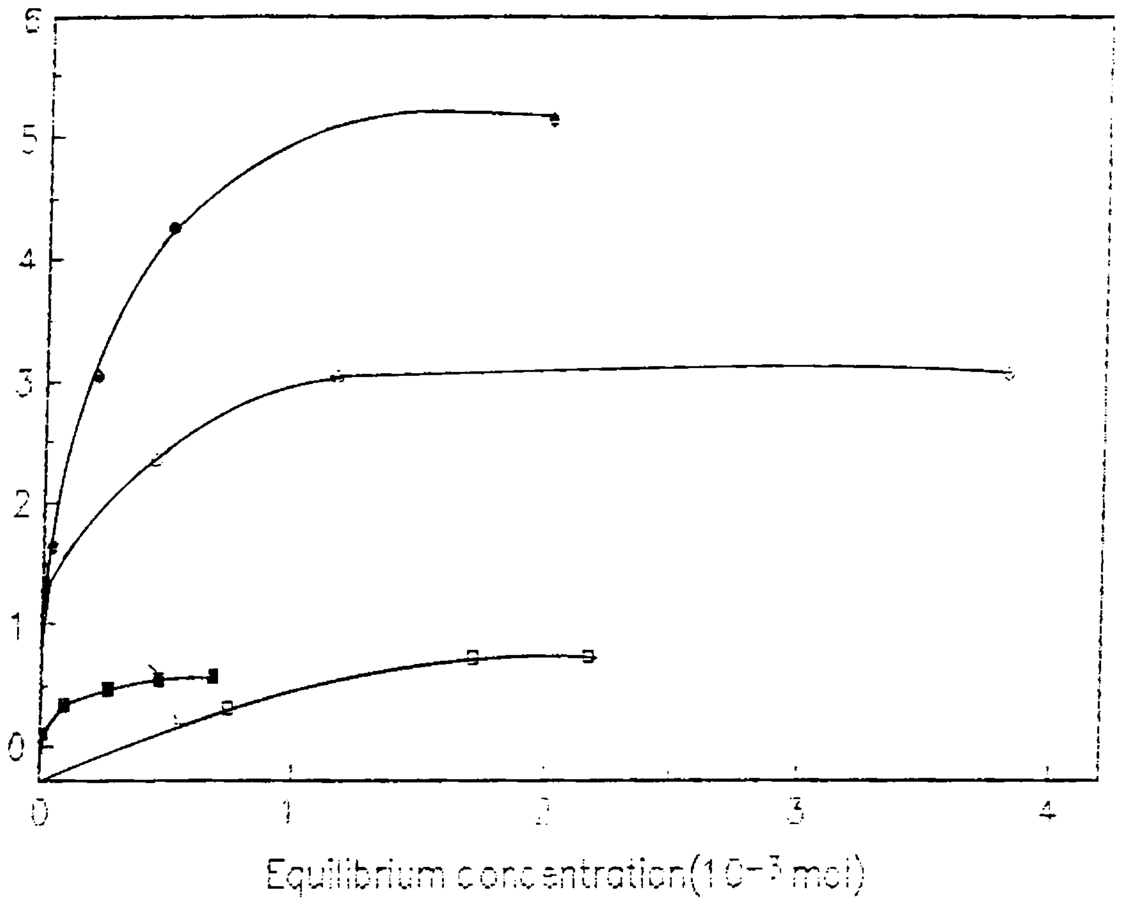


Fig. 4.11 Radical concentration against equilibrium concentration of chloranil on metal oxides at activation temperature of 500°C.

[●]]	ZrO_2-300°C	[■]	Y_2O_3-300°C
[○]	Dy_2O_3-300°C	[□]	Gd_2O_3-300°C

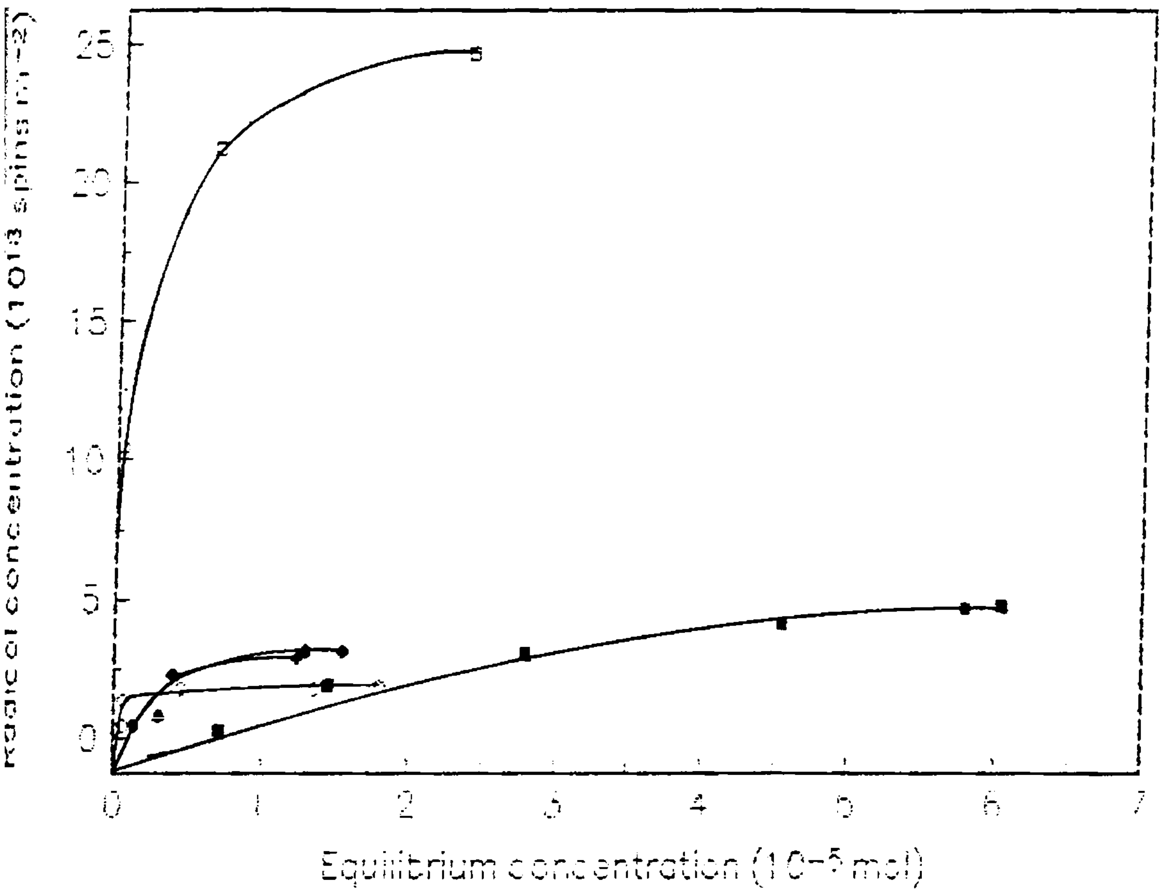


Fig. 4.12 Radical concentration against equilibrium concentration of TCNQ on metal oxides at activation temperature of 500°C.

[●] ZrO_2-300°C

[■] Y_2O_3-300°C

[○] Dy_2O_3-300°C

[□] Gd_2O_3-300°C

coloured samples obtained by the adsorption of chloranil gives an unresolved esr spectra with the g value of 2.011[15].

The nature of interaction during adsorption and the adsorbed state of the electron acceptors electronic reflectance spectra (figure 4.13). The bands appearing below 400 nm corresponds to physically adsorbed state of neutral TCNQ which has an absorption band at 395 nm [16]. The bands near 600 nm is attributed to the dimeric TCNQ anion radical which absorbs at 643 nm [17]. The broad band extending up to the 700 nm corresponds to chloranil anion radicals [18]. The esr and electronic spectra provides evidence that anion radical formation of electron acceptors on the surface is resulted from the electron transfer from oxides surface to the electron acceptors.

The limiting amount of radical concentrations of electron acceptors on the surface is a measure of the total number of electron donor sites on the surface. The data are given in Tables 4.7 to 4.11. The electron donor strength of a metal oxides surface can be defined as conversion ratio of an electron acceptor adsorbed on the surface into its anion radical. The electron donocity of the`oxides is found to depend upon electron affinity of the electron acceptors adsorbed. The amount of electron acceptors adsorbed or the radical concentrations on the surface increased with increasing electron affinity of the electron acceptor.

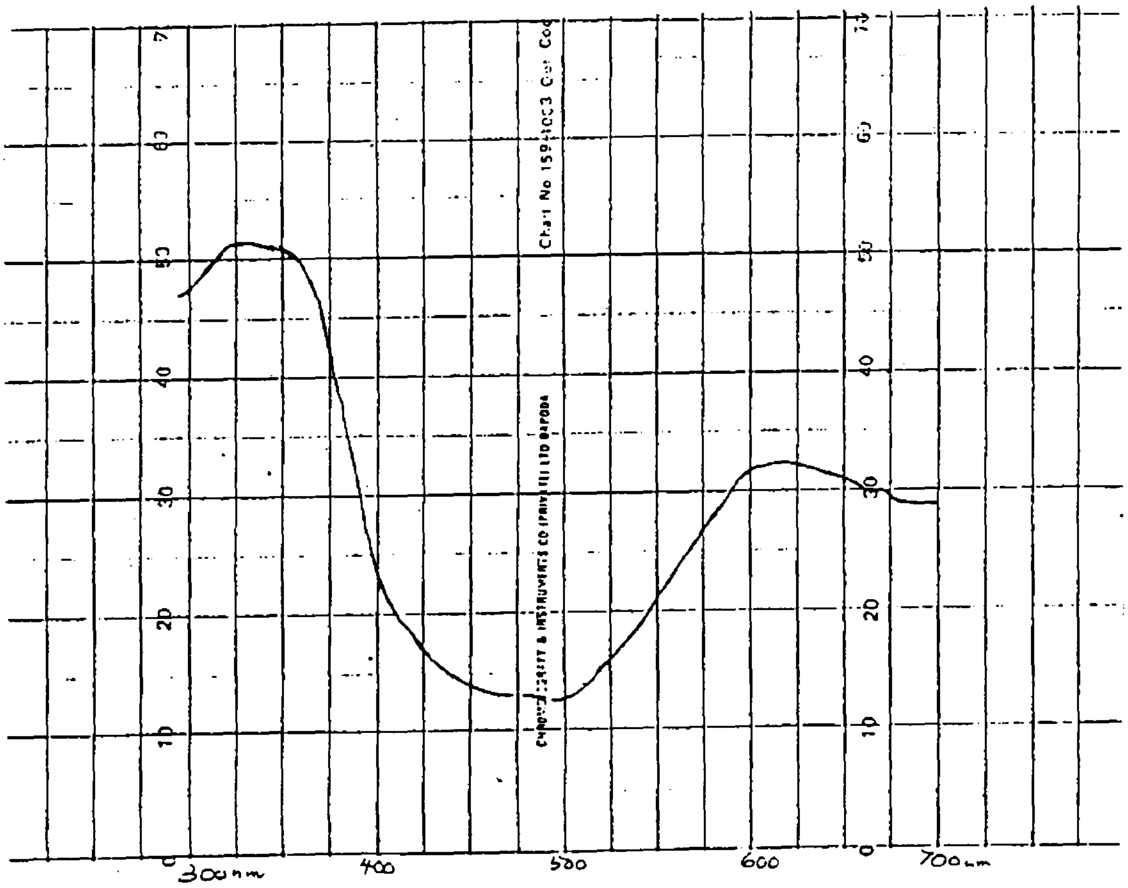


Fig. 4.13 Electronic spectra of the adsorbed samples

Table 4.7. Limiting radical concentration of chloranil adsorbed on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures (10^{18} spins m^{-2})

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	0.200	0.340	0.240
20	0.190	0.190	0.060
40	0.230	0.220	0.020
60	0.150	0.270	0.220
80	0.230	0.380	0.220
100	0.050	0 .075	0.140

Table 4.8. Limiting radical concentrations of TCNQ adsorbed on ZrO_2-Y_2O_3 mixed oxides at different activation temperatures (10^{18} spins m^{-2})

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	0.420	1.748	0.551
20	0.470	0.460	0.136
40	0.617	0.577	0.359
60	0.359	0.709	0.425
80	0.478	0.823	0.408
100	0.295	0.373	0.486

Table 4.9. Limiting radical concentration of chloranil adsorbed on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures (10^{18} spins m^{-2})

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	0.020	0.340	0.240
20	0.190	0.200	0.080
40	0.180	0.200	0.170
60	0.280	0.240	0.200
80	0.610	0.420	0.190
100	-	0.050	0.140

Table.4.10. Limiting radical concentration of TCNQ adsorbed on ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures. (10^{18} spins m^{-2})

Catalyst (% of Dy_2O_3)	Activation temperature(° C)		
	300	500	800
0	0.420	1.073	0.073
20	0.459	0.656	0.359
40	0.445	0.697	0.302
60	0.773	0.903	0.489
80	1.143	1.539	0.449
100	0.007	0.210	0.311

Table 4.11. Limiting radical concentration of chloranil and TCNQ adsorbed on ZrO_2-Gd_2O_3 mixed oxides (10^{18} spins m^{-2})

Catalyst (% of Gd_2O_3)	Activation temperature (° C))	Electron acceptor	
		Chloranil	TCNQ
0	300	0.020	0.420
0	500	0.340	1.073
0	800	0.240	0.557
20	500	0.130	0.831
40	500	0.201	0.633
60	500	0.210	1.029
80	500	0.471	1.658
100	300	-	0.189
100	500	0.104	0.182
100	800	0.591	2.470

TCNQ can form anion radicals even at weak donor sites. But very weak electron acceptors like MDNB and PDNB are incapable of forming anion radicals only at strong electron donor sites. Hence the limiting radical concentration of the weak electron acceptor is a measure of the total number of stronger donor sites on the surface and that for a strong electron acceptor is the measure of both weak and strong donor sites on the surface. It isfound that the limiting amount and limiting radical concentration of electron acceptors adsorbed decreased with decreasing electron affinity values for all oxides. Thus the electron donor strength or capacity of a metal oxide surface can be expressed as the limiting electron affinity value at which free anion radical formation is not observed at the surface

The limiting amount of electron acceptor adsorbed decreased steeply between chloranil and PDNB. This suggest that the adsorption sites on the surface of oxides can act as electron donors to the adsorbed molecule with the electron affinity greater than 2.4 eV but not below with 1.77 eV in acetonitrile. Accordingly the limit of electron transfer from surface to electron acceptor is between 2.4 to 1.77 eV in terms of electron affinity of the acceptor.

The electron donor property of the mixed oxides obtained by the incorporation of rare earth metal oxides varies with pretreatment temperature in every system studied, the electron donocity is higher at lower temperatures. and at high temperature (800°C) the donor capacity decreases. It is also found that at 800°C there is not much variation in electron donor property except in composition with 20 % of rare earth metal oxide in the case of mixed oxides of zirconia-dysprosia systems. The electron donocity increases with increase in percentage composition of Dy. But for mixed oxides of ZrO_2-Y_2O_3 catalysts the electron donor property first increases up to composition with 40 % by weight of Y and then decreases and finally increases.

Mixed oxides showed characteristic electron donor property which are not quantitatively predictable from the consideration of the independent properties of component oxides. The electron donor strength of pure oxides follows the order $Gd_2O_3 > ZrO_2 > Y_2O_3 > Dy_2O_3$. The electron donor property of zirconia decreases after 500°C, but for rare earth oxides the electron donor property increases with increasing activation temperature. The change in electron donor property for ZrO_2 is ascribed to the change in crystallinity from amorphous to monoclinic at about 500°C and it is confirmed by DSC experiment [19-20] (figure 4.14). In the case of rare earth oxides the number of electron donor sites increase with increasing temperature due to desorption of trapped ions and dehydration process [21]. The variation of limiting value of electron acceptor adsorbed with activation temperature for metal oxides are shown in figures 4.15 and 4.16.

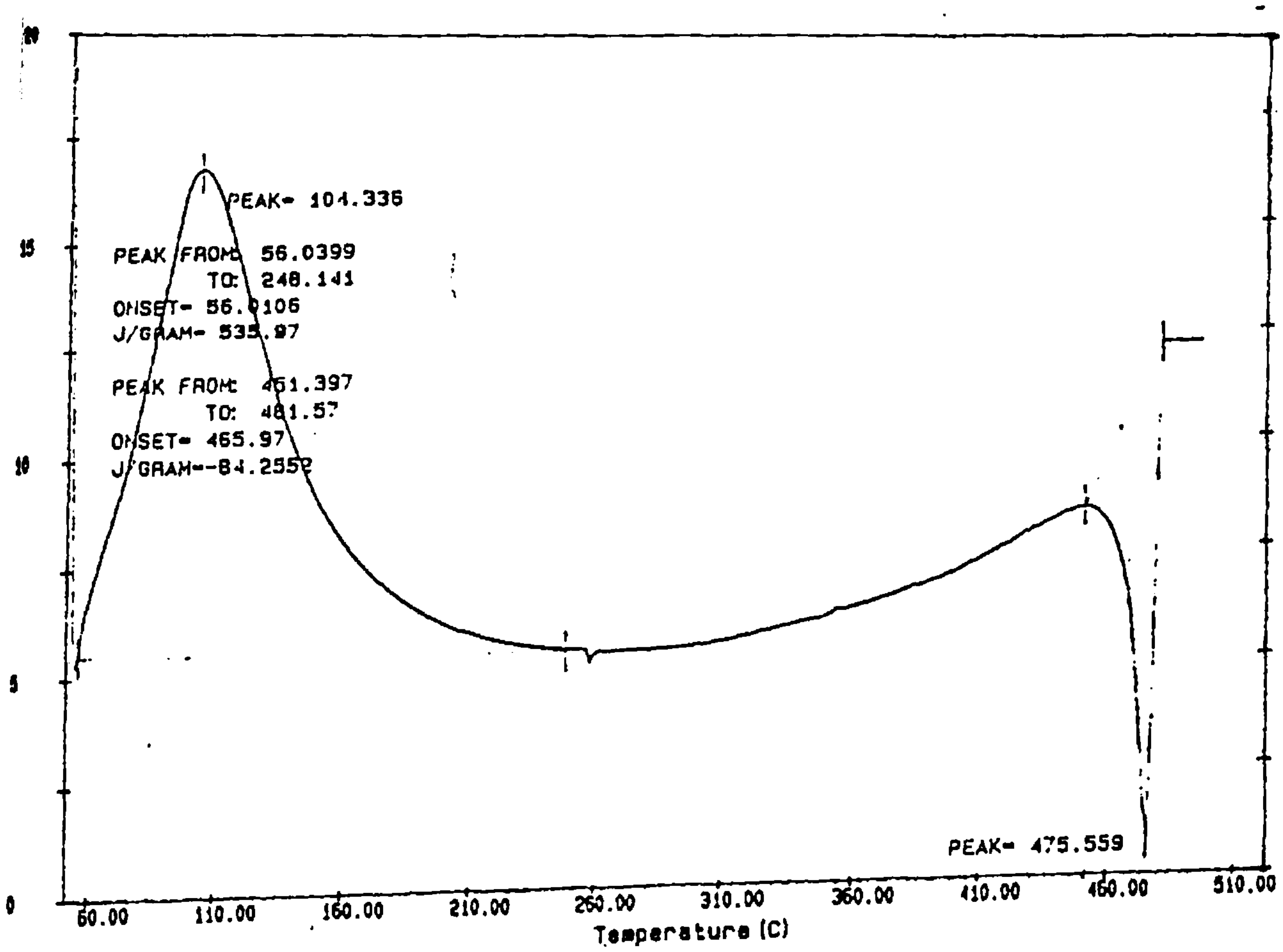


Fig. 4.14 DSC of ZrO_2

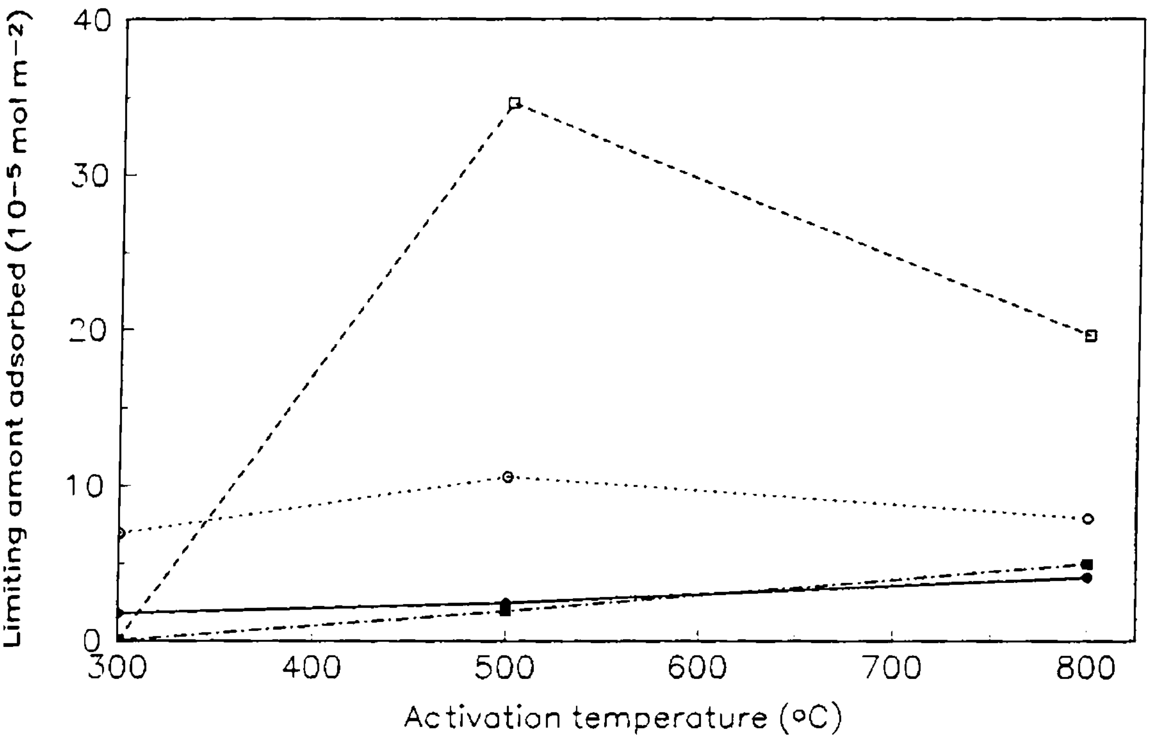


Fig. 4.15 Variation of limiting amount of chloranil adsorbed on metal oxides as a function of activation temperature.

[●]]	ZrO_2-300°C	[■]	Y_2O_3-300°C
[○]	Dy_2O_3-300°C	[□]	Gd_2O_3-300°C

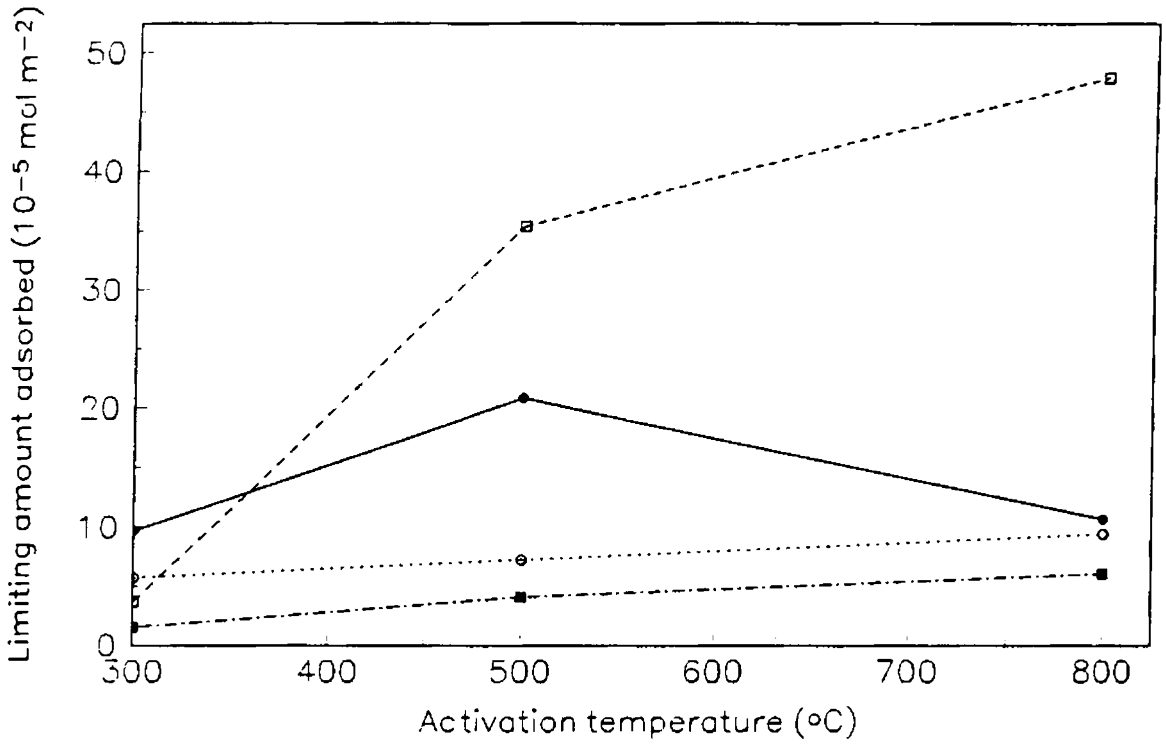


Fig. 4.16 Variation of limiting amount of TCNQ adsorbed on metal oxides as a function of activation temperature.

[●]	ZrO_2-300°C	[■]	Y_2O_3-300°C
[○]	Dy_2O_3-300°C	[□]	Gd_2O_3-300°C

The incorporation of rare earth oxides into ZrO_2 increases the electron donor capacity. As the percentage composition of rare earth oxide increases the limiting amount of electron acceptors adsorbed also increases. ZrO_2 is a refractory oxide containing both acidic and basic sites [22]. But rare earth oxides were classified as basic metal oxides [23]. The increasing electron donor property by the substitution of rare earth metals into ZrO_2 can be attributed to the increasing concentration of Zr-O-M bonds were M is the rare earth metal. The electron donor property depends upon the charge imbalance localized on Zr-O-M bondings. The maximum electron donocity for mixed oxides with compositioncontaining 80 % by weight of rare earth oxide shows that, the difference in oxidation state of zirconium and rare earth metal may give rise to a limiting concentration of Zr-O-M bonds at this composition. If larger the charge imbalance, the higher acidic character is generated [24]. The variation of electron donor properties of mixed oxides with the composition are given in figures 4.17 to 4.21.

The nature of the sites responsible for the electron transfer process is not well understood. Che et. al have carried out a systematic study of the adsorption of TCNQ on metal oxides and showed that electron donor sites are associated with the surface hydroxyl ions for the samples activated at lower temperatures but the oxide ions on the surface played an important role at higher temperatures [13]. This was also supported by Flockhart et. al [25]. Free electrons derived from the intrinsic defects on the surface of the oxides would also be expected to participate in electron transfer process [26].

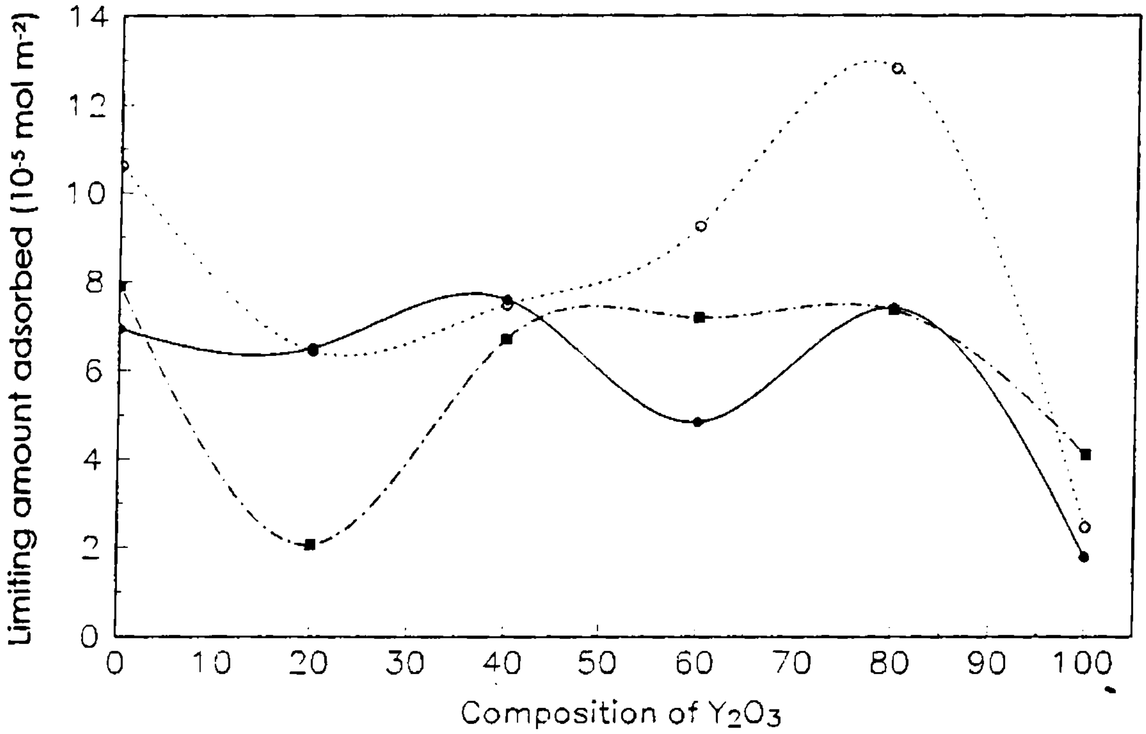


Fig. 4.17 Limiting amount of chloranil adsorbed as a function of composition of ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

[●]] 300°C [○] 500°C [■] 800°C

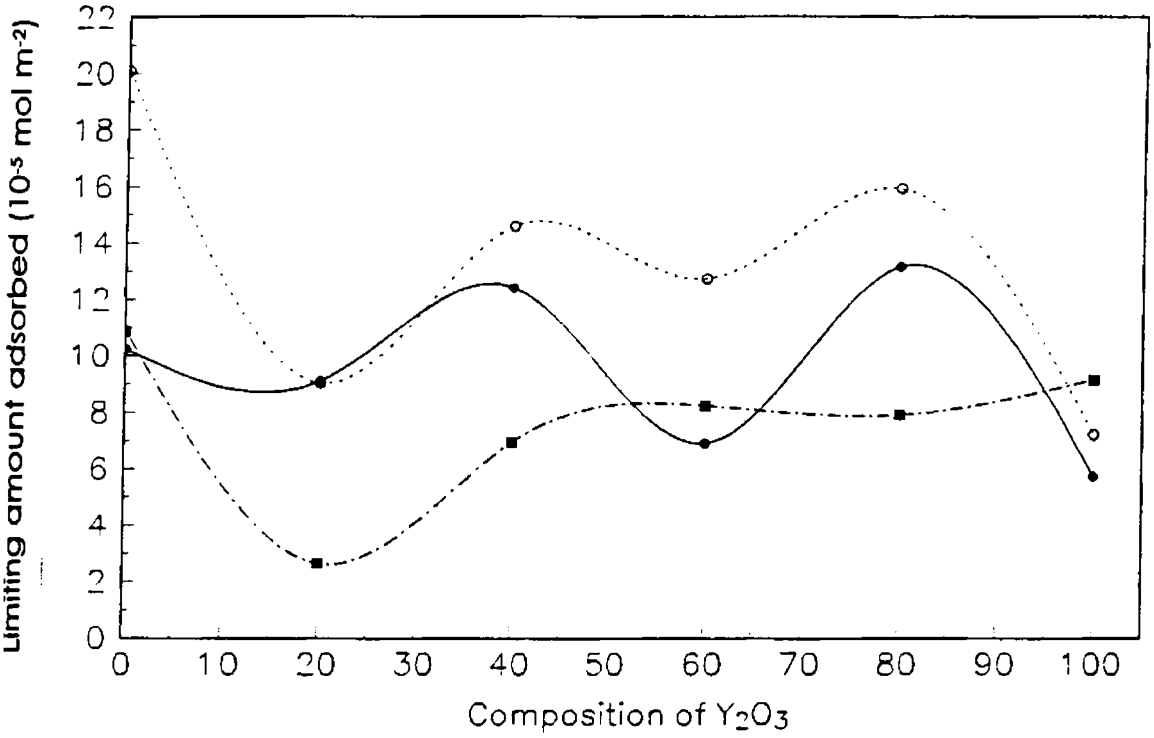


Fig. 4.18 Limiting amount of TCNQ adsorbed as a function of composition of ZrO_2- Y_2O_3 mixed oxides at different activation temperatures.

[●]] 300°C [○] 500°C [■] 800°C

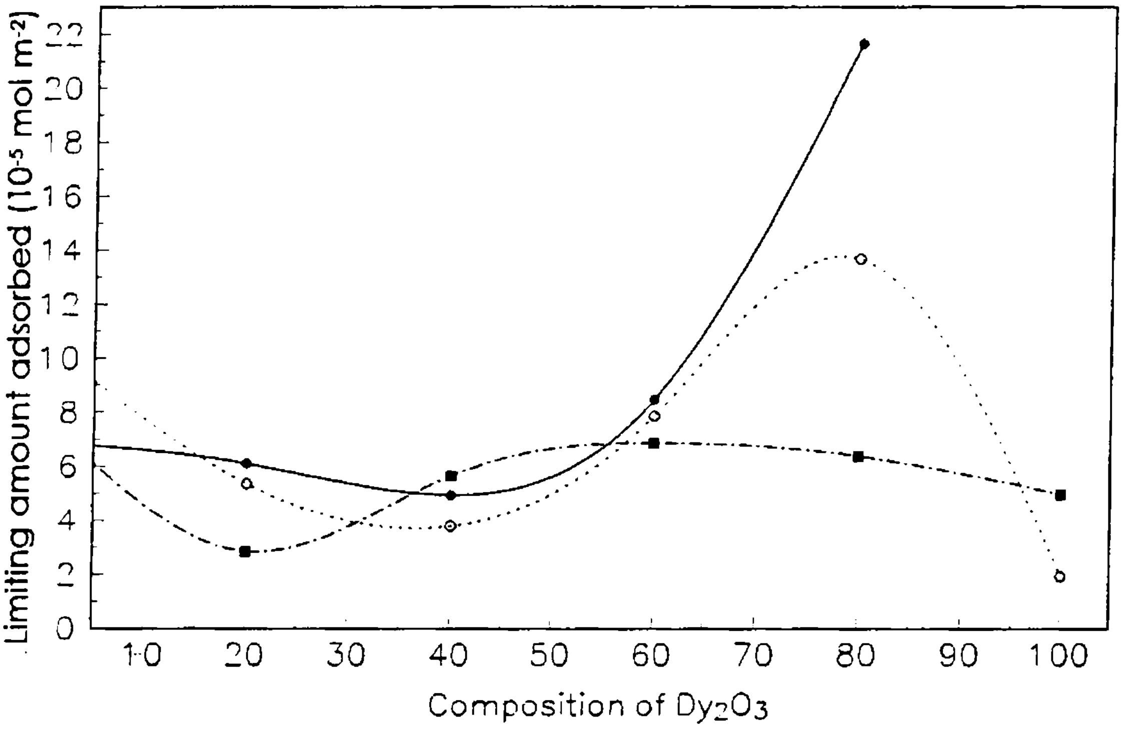


Fig. 4.19 Limiting amount of chloranil adsorbed as a function of composition of ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

[●] 300°C [o] ·500°C [■] 800°C

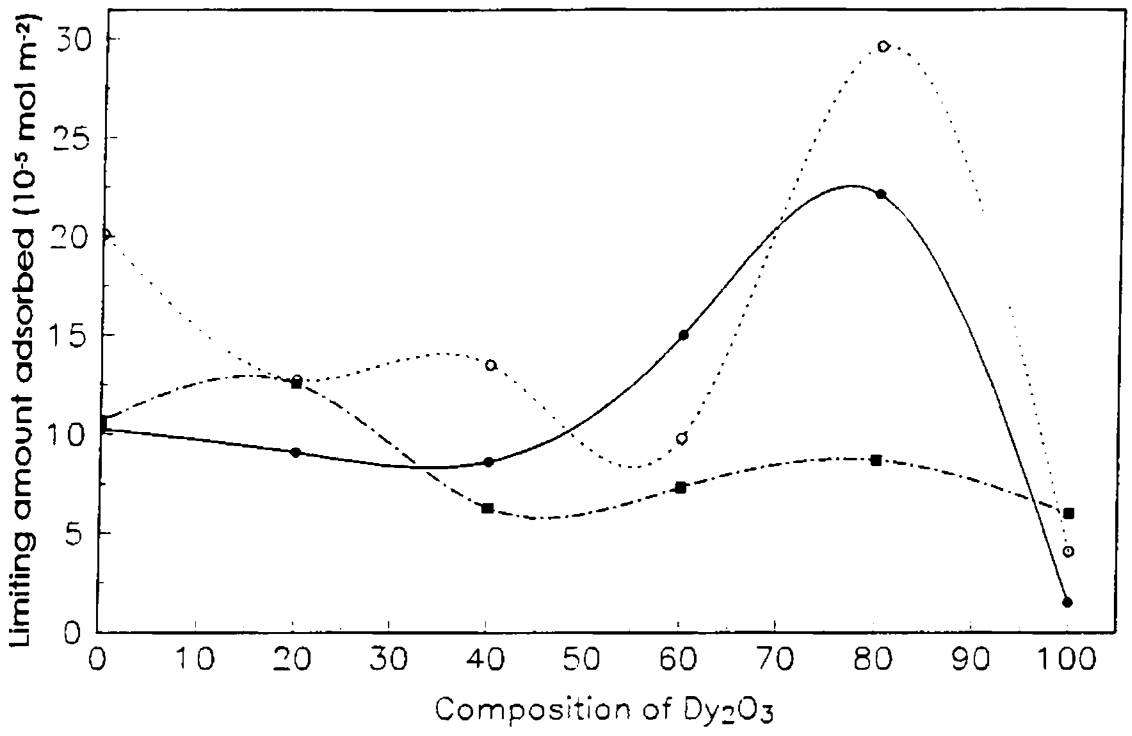


Fig. 4.20 Limiting amount of TCNQ adsorbed as a function of composition of ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

[•]] 300°C [o] 500°C [■] 800°C

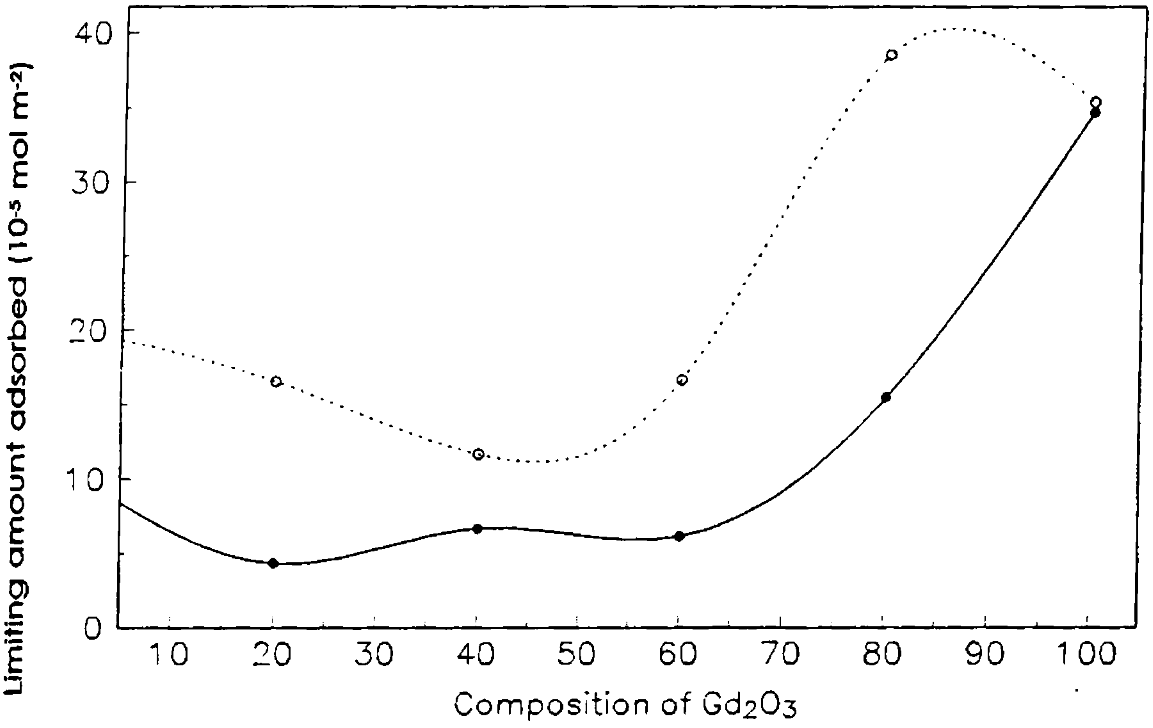


Fig. 4.21 Limiting amount of chloranil and TCNQ adsorbed as a function of composition of ZrO_2-Gd_2O_3 mixed oxides at 500° C

[●] Chloranil [o] TCNQ

IR study has shown that ZrO_2 is associated with the surface hydroxyl ions at low temperature [27,28]. The presence of two types of sites have also been observed by IR spectroscopy [29]. Rare earth oxides give the peak at near 3400 cm^{-1} in IR study which reveals the presence of hydroxyl groups (figure 4. 22)

The electron transfer adsorption of electron acceptor on zirconia rare earth oxide systems may result from surface hydroxyl ions and electrons trapped in intrinsic effects and oxide ions at higher temperature. At lower activation temperatures major electron donor sites are surface OH groups whereas the oxide ions and trapped electrons at defect sites predominates at higher temperatures. Fomin et. al [30] have shown that electron transfer from OH ions does occur in certain solvent systems provided a suitable acceptor is present. It is well known that as the temperature increases the number of OH groups decreases due to desorption of water molecules by the dehydroxylation process from adjacent OH groups. The oxide ions and trapped electrons are solely responsible for electron transfer at higher temperatures. The change in radical concentration depends upon the amount of pure ZrO_2 phase or rare earth oxide phase present on the surface of the mixed oxides.

The electron donor property of the oxide depends upon the basicity of the solvent used. The electron donocity depend upon the interaction between the solvent and adsorbent, solvent and electron acceptor and adsorbent and electron acceptor [31-32]. A strong interaction between electron acceptor and solvent and that between solvent and

Fig. 4.22 I R spectra of Dy_2O_3 at 500°C.

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------------------------- PARAMETERS OF SPECTRUM -- 1993/10/19 04:18:21 ---
            MEASURING MODE :  %T
                RESOLUTION :  4.0 cm-1
              ACCUMULATION :  40
                  AMP GAIN :  AUTO
                  DETECTOR :  DETECTOR 1 (2.8 mm/sec)
              APODIZATION  :  HAPP-GENZEL
                   REMARKS :
                   ANALYST :
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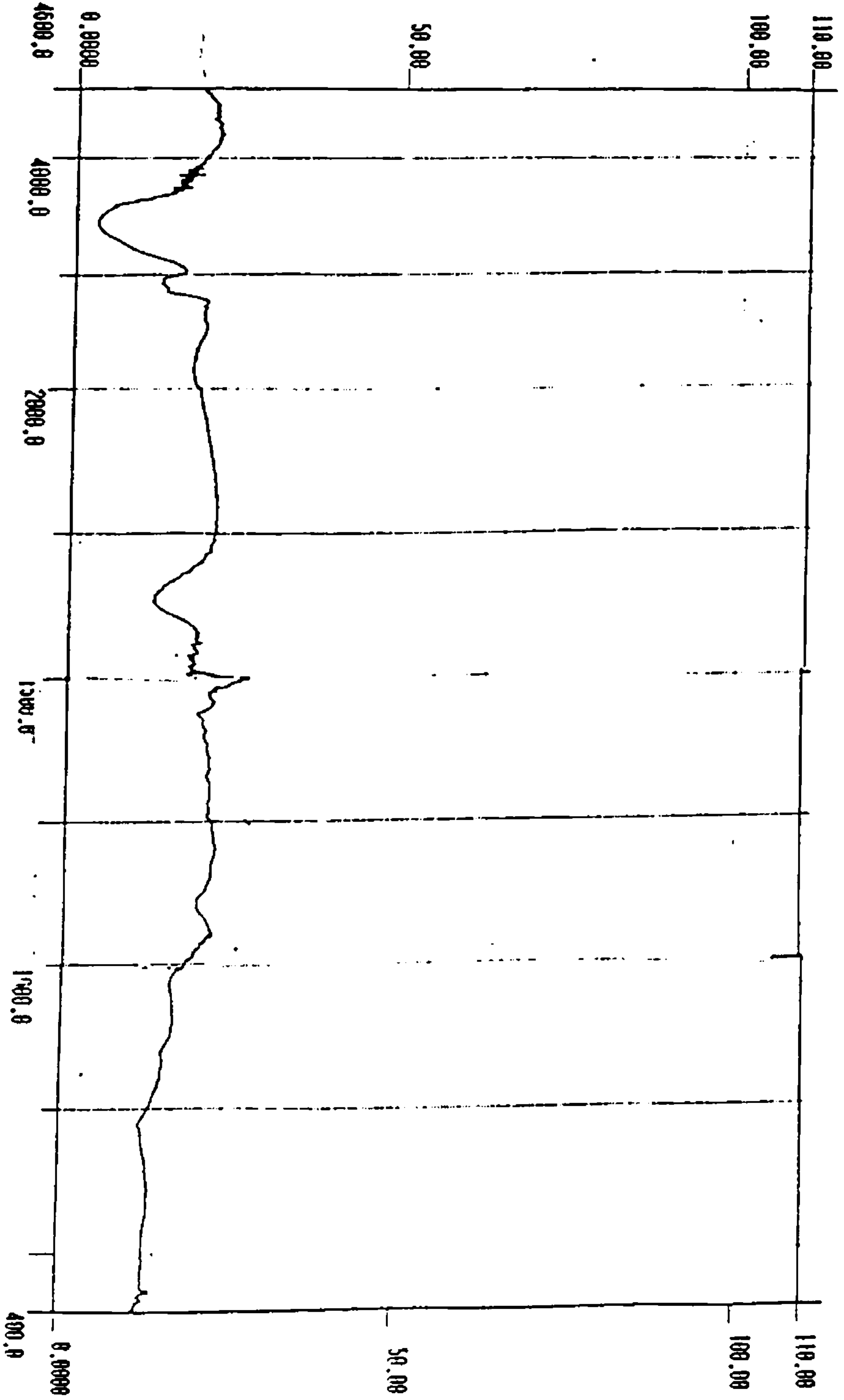


oxide will reduce the adsorption of electron acceptors on the surface. We used acetonitrile, a very weak base to reduce the interaction between electron acceptor and solvent

The ratio of the transformation from the electron acceptor adsorbed into the anion radical on the surface of the oxide is important to understand the strength of electron donor sites. Larger the ratio, the stronger the donor sites. This ratio can be estimated by dividing anion radical concentration by half value of the limiting amount of electron acceptor adsorbed. The values are given in Tables 4.11 to 4.16. The ratio is almost constant in all mixed oxides. But for ZrO_2 the ratio decreases after 500°C and for rare earth oxides the ratio increases with increase in temperature. These results suggests that the strength of electron donor sites of mixed oxides is almost the same irrespective of temperature and composition. But the electron donor capacity of ZrO_2 decreases at higher temperature, which is in agreement with reported results. The strength of electron donor sites of rare earth oxides increases with increase in activation temperature. But the number and concentration of electron donor sites varies.

Thus, the electron donor properties of the oxide surfaces increases with basic strength of the surface itself. The basic strength of a surface is considered as the ability of surface (S) possessing an electron pair to transfer it to an acceptor molecule (A).

Table 4.12.Ratio of chloranil radical concentration to half value of adsorbed amount for ZrO_2-Y_2O_3 Mixed oxides (Spin mol^{-1})

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	5.78	6.45	6.09
20	5.84	5.90	5.83
40	6.07	5.89	5.96
60	6.19	6.21	6.11
80	6.13	5.93	5.98
100	5.62	6.09	6.82

Table 4.13. Ratio of TCNQ radical concentration to half value of adsorbed amount for ZrO_2-Y_2O_3 Mixed oxides. (Spin mol^{-1})

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	0.872	1.093	1.032
20	1.030	1.037	1.024
40	1.030	0.907	1.001
60	1.030	1.032	1.032
80	1.032	1.032	1.032
100	1.031	1.032	1.302

Table 4.14.Ratio of TCNQ radical concentration to half value of adsorbed amount for ZrO_2-Dy_2O_3 Mixed oxides. (Spin mol^{-1})

Catalyst (% of Dy_2O_3)	Activation temperature (°C)		
	300	500	800
0	5.78	6.42	6.09
20	6.28	6.30	5.62
40	6.06	5.89	5.98
60	6.17	6.11	5.84
80	6.05	6.15	5.97
100	-	5.18	5.65

Table 4.15. Ratio of TCNQ radical concentration to half value of adsorbed amount for ZrO_2-Dy_2O_3 Mixed oxides. (Spin mol^{-1})

Catalyst (of Dy_2O_3)	Activation temperature (°C)		
0	0.872	1.093	1.032
20	1.432	1.030	1.045
40	1.032	1.030	0.971
60	1.037	1.038	1.031
80	1.037	1.037	1.023
100	0.920	1.030	1.032

Table 4.16. Ratio of TCNQ and chloranil radical concentrations to half value of adsorbed amount for ZrO_2-Gd_2O_3mixed oxides (Spin mol^{-1}).

Catalyst (% of Gd_2O_3)	Activation temperature (°C)	Electron acceptor	
		Chloranil	TCNQ
0	300	5.780	0.873
0	500	6.415	1.093
0	800	6.09	1.032
20	500	6.01	1.05
40	500	6.03	1.030
60	500	6.02	1.030
80	500	6.02	1.020
100	300	-	1.03
100	500	6.01	1.03
100	800	6.01	1.03

$$S{:} + A \rightarrow S^{\cdot} + A$$

From the results obtained by the adsorption of electron acceptors on oxides ,it can be concluded that the surface can act as electron donor sites to the adsorbed molecules with electron affinity of 2.40 eV or above , but not below that of 1.77 eV. That is to say, the limit of electron acceptor is between 2.40 eV and 1.77 eV in terms of electron affinity of the electron acceptor and the electron donor sites of mixed oxides have more or less same basic strength.

REFERENCES

1. M.E.Labib, *Colloids Surf.*, 29 293 (1988).
2. K.Esumi and K.Meguro, *J.Colloid Int.Sci.*, 66, 192 (1978).
3. K.Esumi, K.Miyata, F.Waki and K.Meguro, *Colloid Surf.*, 20, 81 (1986).
4. K.Esumi, K.Magara and K.Meguro, *J. Colloid Inter. Sci.*, 141, 578 (1991).
5. S.Sugunan and G.D.Rani, *J. Mat. Sci. Lett.*, 43, 375 (1991).
6. S.Sugunan and G.D.Rani, *J. Mat. Sci. Lett.*, 10, 887 (1991).
7. S.Sugunan and K.B.Sherly, *India J. Che.*, 32A, 489 9193).
8. S.Sugunan and G.D.Rani, *J. Mat. Sci.*, 28, 4811 (1993).
9. K.Esumi and K.Meguro, *J. Jpn. Soc. Col. Mat.*, 58, 9 (1985).
10. F.M.Fowkes, "*Physico Chemical Aspects of Polymer Surface*", Vol.2, Plenum Press, (1983).
11. K.Meguro and K.Esumi, *J. Colloid Int. Sci.*, 59 3693 (1977).
12. B.D Flockhart, K.Y.Liew and R.C.Pink, *J. Chem. Soc. Faraday*, 1**(76),** 2026 (1980)., **65**, 542 (1969).
13. M.Che, C.Naccache and B.Imelik, *J. Cat.*, 24, 328 (1970).
14. H.Hosaka, T.Fujiwara and K.Meguro, *Bull. Chem. Soc. Jpn.*, 44, 2616 (1971).
15. K.Esumi and K.Meguro, *J. Jpn. Color Mat.*, 48, 539 (1975).
16. D.S.Acker and W.R.Hertler, *J. Ame. Chem. Soc.*, 84, 328 (1962).
17. R.H.Boyd and W.D.Philips, *J. Che. Phy.*, 43, 2927 (1965).

18. R.Foster and T.J.Thomson, *Trans. Faraday Soc.*, **58**, 860 (1962).

19. K.Esumi and K.Meguro, *Bull. Chem. Soc. Jpn.*, **55**, 315 (1982).

20. G.V.Chemparathy, *M.Phil Thesis*, p. 49, 1993.

21. T.Hattori, J.Inoko and Y.Murakami, *J. Cat.*, **42**, 60 (1976).

22. C.Morterra, C.Lerralo, C.Emmanuel and V.Bolis, *J. Cat.*, **142**, 349 (1993).,

23. V.H.Rane and V.R.Choudhary, *J. Cat.*, **130**, 417 (1991).

24. K.Tanabe, "*Solid Acids and Bases*", Academic Press, Kodansha, New York (1970)

25. B.D.Flockhart, L.R.Leith and R.C.Pink, *Trans. Far. Soc.*, **66**, 469 (1970).

26. B.D.Flockhart, J.A.N. Scott and R.C.Pink, *Trans. Far. Soc.*, **62**, 730 (166).

27. P.A.Argon, E.L.Fuller jr and R.A.Beh, *J. Colloid. Int. Sci.*, **52**, 553 (1975).

28. H.F.Holmes, E.L.Fuller Jr and R.A.Beh, *J. Colloid. Inte. Sci.*, **47**, 365 (1974).

29. A.J.Tench and R.L.Nelson, *Trans. Farad. Soc.*, **63**, 2254 (1967).

30. G.L.Fomin, L.A.Blyumentfield and V.I.Sukhorukov, *Pro. Acad. Sci.*, USSR, **157**, 819 (1964).

31. K.Esumi, K.Miyata and K.Meguro, *Bull. Chem. Soc. Jpn.*, **58**, 3524 (1985).

32. K.Esumi, K.Miyata, F.Waki and K.Meguro, *Bull. Chem. Soc. Jpn.*, **59**, 3362 (1986) .

CHAPTER 5

ACID/BASE PROPERTIES OF MIXED OXIDES OF ZrO_2 WITH RARE EARTH OXIDES.

5.1. INTRODUCTION

The surface acidity/basicity of solid catalysts has been subject of considerable study to investigate the acid/base strength distribution among acid base centers and how this distribution varies with the type of the catalysts. The method introduced by Johnson [1] and Benesi [2] for the determination of the acidity and basicity and acid strength on a solid surface by titration with n-butylamine, using a series of Hammett indicators have been widely used to characterise the nature of the solid acid catalyst [3,4]. The basicity and base strength on a solid surface by titration with benzoic acid or acetic acid using bromothimol blue and series of nitroaniline derivatives has also been introduced [5-7]. To determine the acid -base strength distribution on a common scale T.Yamanaka and K.Tanabe attempted a titration method using a series of Hammett indicators [8]. Acidity and basicity were determined by titration of the solid sample suspended in nonaqueous solvents by using a set of Hammett indicators having different pKa values with n-butylamine and trichloroacetic acid respectively. Colour of the adsorbed indicator can give the measure of the acid-base strength of the used oxides at a particular temperature.

This chapter deals with the acid-base strength distribution of mixed oxides of zirconia with rare earth oxides determined by titration method on a common H_o scale. By this method, the basicity at relatively weak basic strength can also be determined. This method makes it possible to determine the basic strength expressed by a Hammett acidity function as analogous to acid strength (H_o -Hammett acidity function) and hence the acid base strength distribution on a common H_o scale. The acid-base properties of the oxides are reported in terms of $H_{o,\ max}$. The usefulness and validity of $H_{o,max}$ as a practical parameter to represent an acid-base property of solids have been reported [9]. The strength of acid sites was expressed by H_o as usual and that of basic sites by the H_o of the their conjugate acids.

5.2. EXPERIMENTAL

The acidity/basicity at various acid-base strength of the mixed oxides were determined by titration method using a series of Hammett indicators. The details of procedure adopted was discussed in chapter.3. Benzene was used as the non aqueous solvent.

5.3. RESULTS AND DISCUSSION

The colour of the adsorbed indicators can give the measure of the acid base strength. The indicators used are given in the Table 5.1. Among them, oxides under study responded only to three indicators. They are dimethyl yellow, methyl red and bromothymol blue. The acidity and basicity were determined on a common H_o scale. The results of acid-base strength distributions at different activation temperature are given in Tables 5.2 to 5.4. No acid-base sites of equal strength have been found on the solid surface on the same mixed oxide. Acidity at an H_o value shows the number of acid sites whose acid strength is equal to or less than the H_o value and the basicity at an H_o value shows the number of basic sites whose conjugate acid has strength equal to or greater than the H_o value. Basic sites for which H_o greater than or equal to pK_{BH^+} value do not exist together with acid sites for which $H_o < pK_{BH^+}$ of the indicator used [8].

Table 5.1: Hammett indicators used

Indicator	pKa Value	Colour change	
		Acid	Basic
Crystal violet	0.8	white	blue
Dimethyl yellow	3.3	yellow	red
Methyl red	4.8	yellow	red
Neutral red	6.8	yellow	red
Bromothymol blue	7.2	yellow	blue
4-nitroaniline	18.4	yellow	red

The acid-base strength of the oxides are expressed by $H_{o,max}$ values. It is found that the strongest H_o values of acid sites was approximately equal to the strongest H_o value of the basic sites and this equal strongest H_o value is termed $H_{o,max}$. It is obtained from the point of intersection of acid-base strength distribution curve at a point on the

Table 5.2. Acid-base strength distribution of ZrO_2-Y_2O_3 mixed oxides systems.

Catalyst (% of Y_2O_3)	Act. Temp. (°C)	Basicity (mmol g^{-1})			Acidity (mmol g^{-1})		
		Ho ≥3.3	Ho ≥4.8	Ho ≥7.2	Ho ≤3.3	Ho ≤4.8	Ho ≤7.2
0	300	0.1913	0.0473	-	-	-	0.3363
	500	0.1684	0.0659	-	-	-	0.1688
	800	0.0729	0.1190	-	-	-	0.1129
20	300	0.1625	0.0375	-	-	-	0.0365
	500	0.2126	0.0625	-	-	-	0.0365
	800	0.0501	-	-	-	0.1095	0.1814
40	300	0.2251	0.1126	0.0625	-	-	-
	500	0.1376	0.0876	0.0251	-	-	-
	800	0.0625	-	-	-	0.0365	0.0730
60	300	0.2251	0.0751	0.0609	-	-	-
	500	0.1252	-	0.0626	-	0.0365	-
	800	0.2502	0.5003	-	-	-	0.0244
80	300	0.1934	0.0473	-	-	-	0.3363
	500	0.1684	0.0659	-	-	-	0.1688
	800	0.0729	0.1190	-	-	-	0.1129
100	0.1500	-	-	-	-	0.0500	0.1400
	0.2500	0.1500	-	-	-	-	0.0200
	0.4001	0.0240	0.0500	-	-	-	

Table 5.3. Acid-base strength distribution of ZrO_2-Dy_2O_3 mixed oxides systems.

Catalyst (% of Dy_2O_3)	Act. Temp. (°C)	Basicity (mmol g^{-1})			Acidity (mmol g^{-1})		
		Ho ≥3.3	Ho ≥4.8	Ho ≥7.2	Ho ≤3.3	Ho ≤4.8	Ho ≤7.2
0	300	0.1913	0.0473	-	-	-	0.3363
	500	0.1684	0.0659	-	-	-	0.1688
	800	0.0729	0.1190	-	-	-	0.1129
20	300	0.3002	0.1751	-	-	-	0.0243
	500	0.1876	0.0876	-	-	-	0.0486
	800	0.0503	-	-	-	0.0487	0.0976
40	300	0.3671	0.1501	-	-	-	0.0365
	500	0.1251	0.0375	-	-	-	0.0365
	800	0.0751	0.0375	-	-	-	0.0609
60	300	0.1626	0.1001	0.0503	-	-	-
	500	0.1251	0.0503	-	-	-	0.0365
	800	0.1379	0.0250	-	-	-	0.0487
80	300	0.3252	0.1626	0.1001	-	-	-
	500	0.2502	0.0876	-	-	-	0.0487
	800	0.1876	0.0375	-	-	-	0.0243
100	300	0.1517	-	-	-	0.1724	0.2956
	500	0.1949	0.0649	0.0283	-	-	-
	800	0.1949	0.0868	0.0434	-	-	-

Table 5.4. Acid-base strength distribution of ZrO_2-Gd_2O_3 mixed oxides systems.

Catalyst (% of Gd_2O_3)	Act. Temp. (°C)	Basicity (mmol g^{-1})			Acidity (mmol g^{-1})		
		Ho ≥3.3	Ho ≥4.8	Ho ≥7.2	Ho ≤3.3	Ho ≤4.8	Ho ≤7.2
0	300	0.1913	0.0473	-	-	-	0.3363
	500	0.1684	0.0659	-	-	-	0.1688
	800	0.0729	0.1190	-	-	-	0.1129
20	300	0.1876	0.0473	-	-	-	0.1217
	500	0.1684	0.0659	-	-	-	0.1583
	800	0.0729	0.1190	-	-	-	0.1339
40	300	0.1626	0.0625	-	-	-	0.0243
	500	0.0625	0.0250	-	-	-	0.0487
	800	0.0501	-	-	-	0.0698	0.1582
60	300	0.1501	0.0250	0.0250	-	-	-
	500	0.1126	0.0250	0.0250	-	-	-
	800	0.0625	0.0122	0.0487	-	-	-
80	300	0.1375	0.0501	0.0375	-	-	-
	500	0.0876	0.0375	0.0501	-	-	-
	800	0.1751	-	-	-	0.0122	0.0365
100	300	0.0433	0.0216	-	-	-	0.0251
	500	0.2163	0.0648	-	-	-	0.0433
	800	0.3250	0.0433	0.0493	-	-	-

abscissa where acidity = basicity = 0. Each solid surface exhibits its own characteristic $H_{o,max}$ values at a particular temperature. $H_{o,max}$ value can be considered as a practical parameter to represent the acid-base properties of a solid surface [9], which is very sensitive to the surface structure. $H_{o,max}$ value expresses the equal strongest H_o value of both acidic and basic sites. A solid with a high $H_{o,max}$ values possess strong basic sites and weak acidic sites and vice versa. The $H_{o,max}$ values obtained at different activation temperatures are given in Tables 5.5 to 5.7. The acid-base distribution curves are given in figures 5.1 to 5.9.

ZrO_2 shows both acidic and basic behavior. The maximum number of acid sites is at $H_o = 7.2$ and maximum basicity is at $H_o = 3.3$. This implies the presence of weak acidic and basic sites on ZrO_2. The acid sites were reported as Lewis acid and partially Bronsted sites [10]. It has already been reported that ZrO_2 possess a low but definite basicity and is confirmed by the studies on the adsorption of CO [11]. ZrO_2 itself has both weakly acidic and basic properties which sometimes results in intriguing acid base bifunctional catalysis [12-13]. The basicity of ZrO_2 decreases with increase in temperature after 500°C. $H_{o,max}$ value also decreases with increase in temperature above 500°C. This may be considered as due to the change in crystallinity from amorphous to monoclinic and has been confirmed by DSC measurements [14-15].

Rare earth metal oxides showed the increasing basicity as follows: $Gd_2O_3 > Dy_2O_3 > Y_2O_3$. This is in accordance with the order of basicity along the lanthanide series from

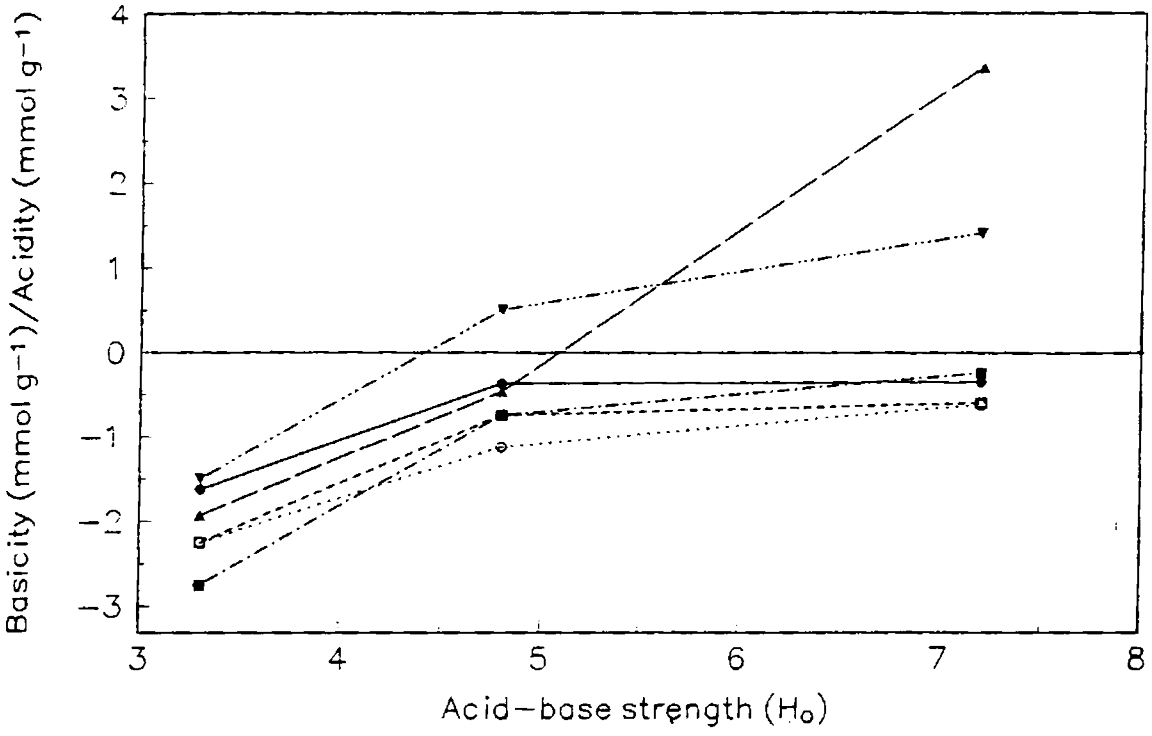


Fig. 5.1 Acid-base strength distribution of ZrO_2-Y_2O_3 mixed oxides at 300° C

[ZY_1 - (80 %ZrO_2 & 20 % Y_2O_3) ZY$_2$ - (60 % ZrO_2 & 40 % Y_2O_3)
ZY_3 - (40 % ZrO_2 & 60 % Y_2O_3) ZY$_4$ - (20 % ZrO_2 & 80 % Y_2O_3)]

[●] ZrO_2-300°C [▼] Y_2O_3-300°C [○] ZY_1-300°C
[■] ZY_2-300°C [□] ZY_3-300°C [▲] ZY_4-300°C

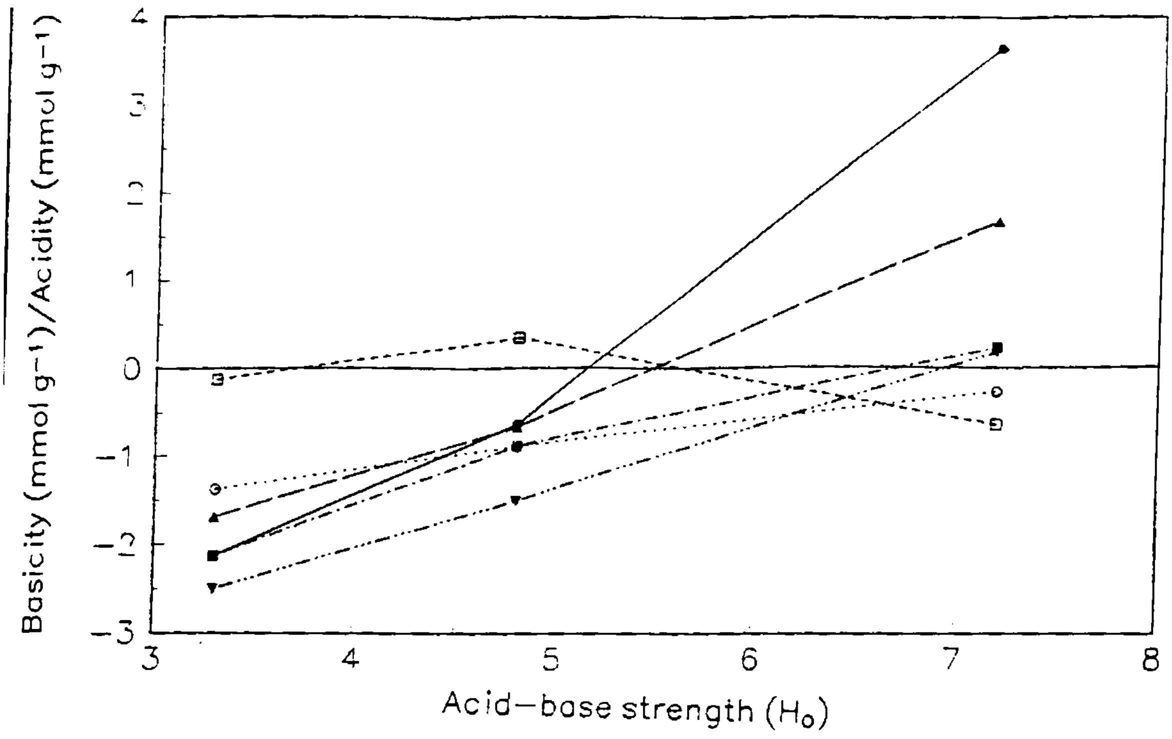


Fig. 5.2 Acid-base strength distribution of ZrO_2-Y_2O_3 mixed oxides at 500°C

[ZY_1- (80 %ZrO_2 & 20 % Y_2O_3)
ZY_2 - (60 % ZrO_2 & 40 % Y_2O_3)
ZY_3 - (40 % ZrO_2 & 60 % Y_2O_3)
ZY_4 - (20 % ZrO_2 & 80 % Y_2O_3)]

[●]	ZrO_2-300°C	[▼]	Y_2O_3-300°C	[○]	ZY_1-300°C
[■]	ZY_2-300°C	[□]	ZY_3-300°C	[▲]	ZY_4-300°C

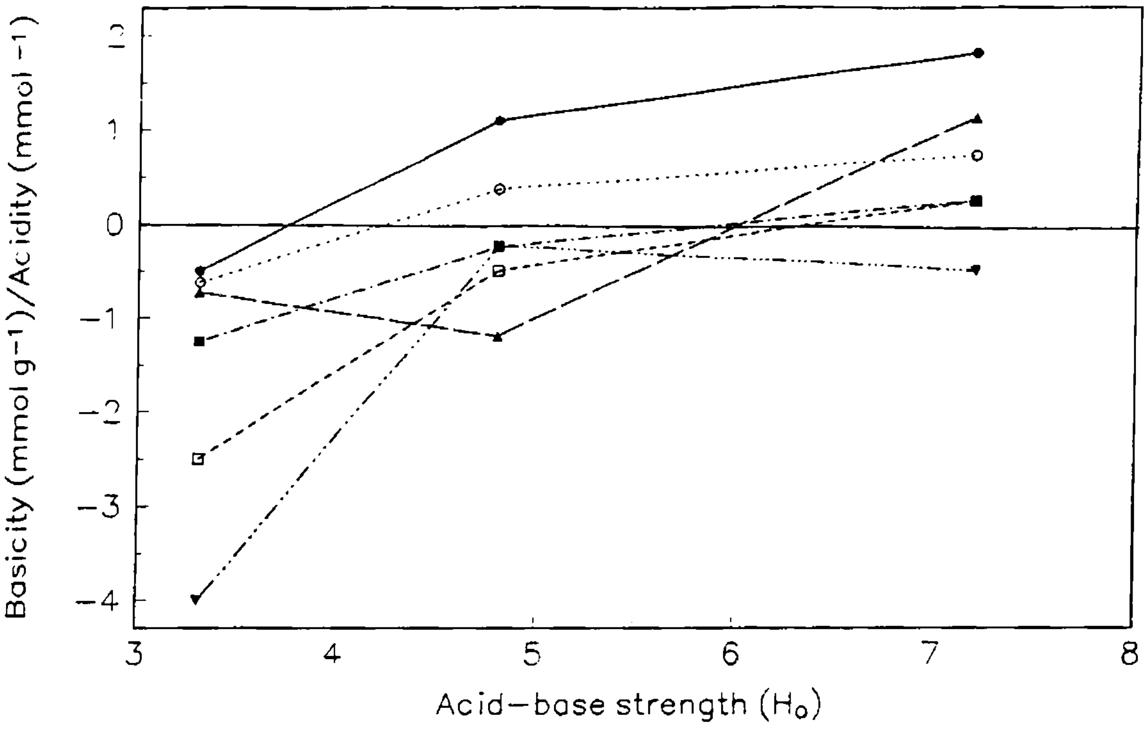


Fig.5.3 Acid-base strength distribution of ZrO_2-Y_2O_3 mixed oxides at 800°C

[ZY_1- (80 %ZrO_2& 20 % Y_2O_3) ZY_2 - (60 % ZrO_2& 40 % Y_2O_3)
ZY_3 - (40 % ZrO_2& 60 % Y_2O_3) ZY_4 - (20 % ZrO_2& 80 % Y_2O_3)]

[●]	ZrO_2-300°C	[▼]	Y_2O_3-300°C	[○]	ZY_1-300°C
[■]	ZY_2-300°C	[□]	ZY_3-300°C	[▲]	ZY_4-300°C

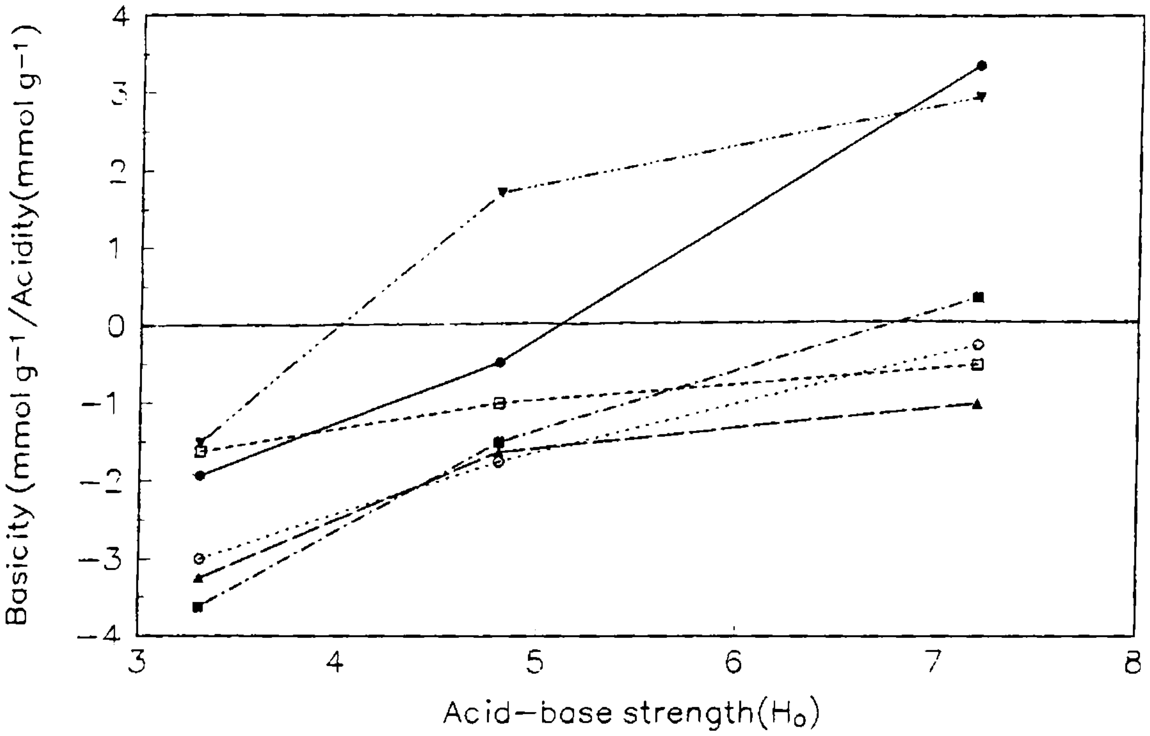


Fig.5.4 Acid-base strength distribution of ZrO$_2$-Dy$_2$O$_3$ mixed oxides at 300°C

[ZD$_1$- (80 % ZrO$_2$ & 20 % Dy$_2$O$_3$)   ZD$_2$ - (60 % ZrO$_2$ & 40 % Dy$_2$O$_3$)
ZD$_3$ - (40 % ZrO$_2$ & 60 % Dy$_2$O$_3$)   ZD$_4$ - (20 % ZrO$_2$ & 80 % Dy$_2$O$_3$)]

[●]	ZrO$_2$-300°C	[▼]	Dy$_2$O$_3$-300°C	[o]	ZD$_1$-300°C
[■]]	ZD$_2$-300°C	[□]]	ZD$_3$-300°C	[▲]	ZD$_4$-300°C

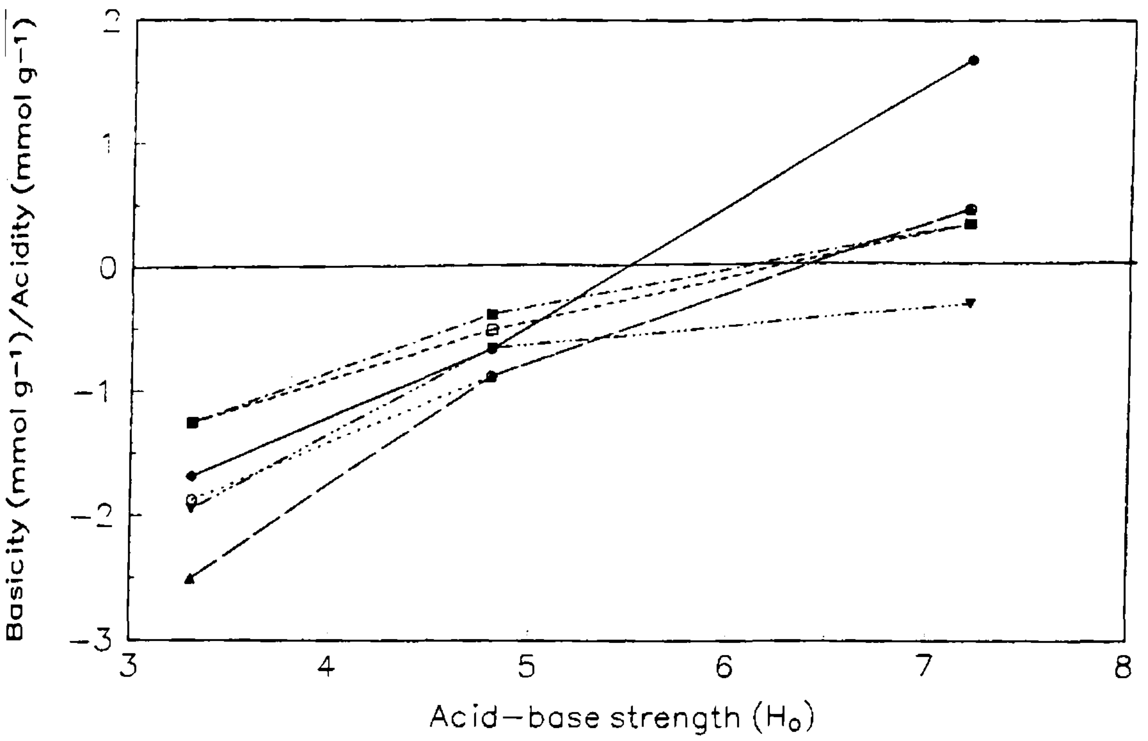


Fig. 5.5 Acid-base strength distribution of ZrO_2-Dy_2O_3 mixed oxides at 500°C

[ZD₁- (80 % ZrO_2 & 20 % Dy_2O_3) ZD₂ - (60 % ZrO_2 & 40 % Dy_2O_3)
ZD₃ - (40 % ZrO_2 & 60 % Dy_2O_3) ZD₄ - (20 % ZrO_2 & 80 % Dy_2O_3)]

[●]	ZrO_2-500°C	[▼]	Dy_2O_3-500°C	[○]	ZD₁-500°C
[■]]	ZD₂-500°C	[□]]	ZD₃-500°C	[▲]	ZD₄-500°C

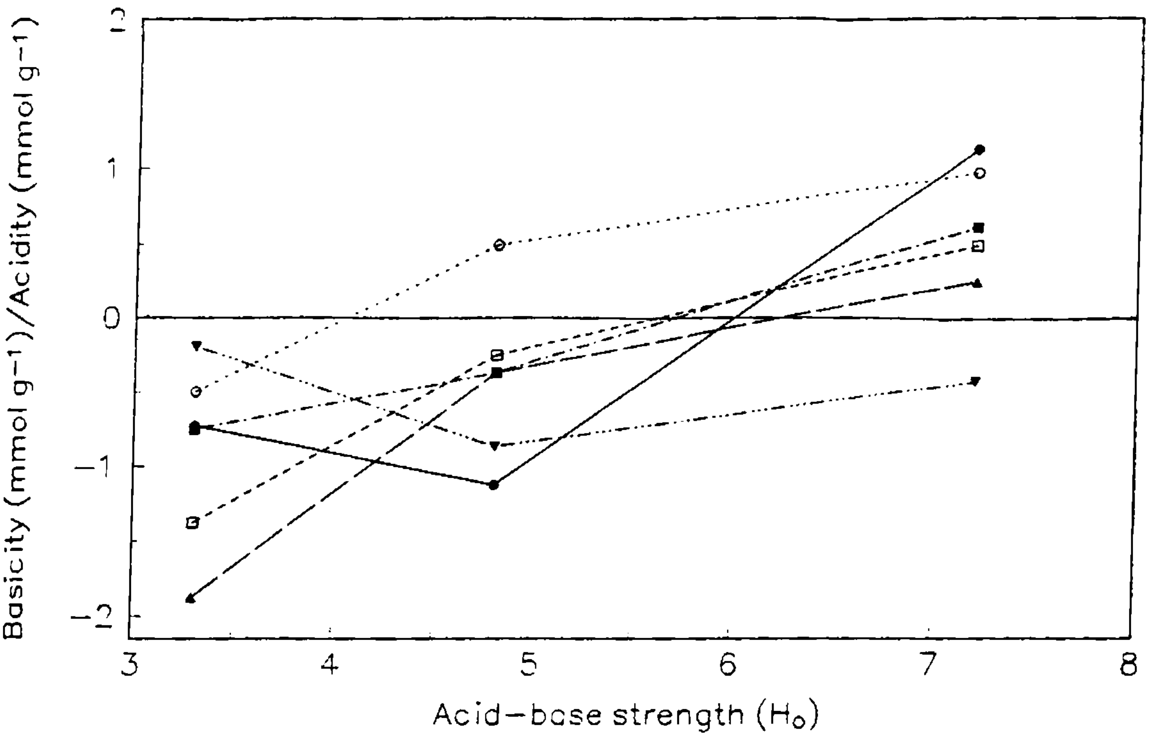


Fig. 5.6 Acid-base strength distribution of ZrO_2-Dy_2O_3 mixed oxides at 800°C

[ZD_1- (80 % ZrO_2 & 20 % Dy_2O_3) ZD_2 - (60 % ZrO_2 & 40 % Dy_2O_3)
ZD_3 - (40 % ZrO_2 & 60 % Dy_2O_3) ZD_4 - (20 % ZrO_2 & 80 % Dy_2O_3)]

[●]	ZrO_2-800°C	[▼]	Dy_2O_3-800°C	[○]	ZD_1-800°C
[■]]	ZD_2-800°C	[□]]	ZD_3-800°C	[▲]	ZD_4-800°C

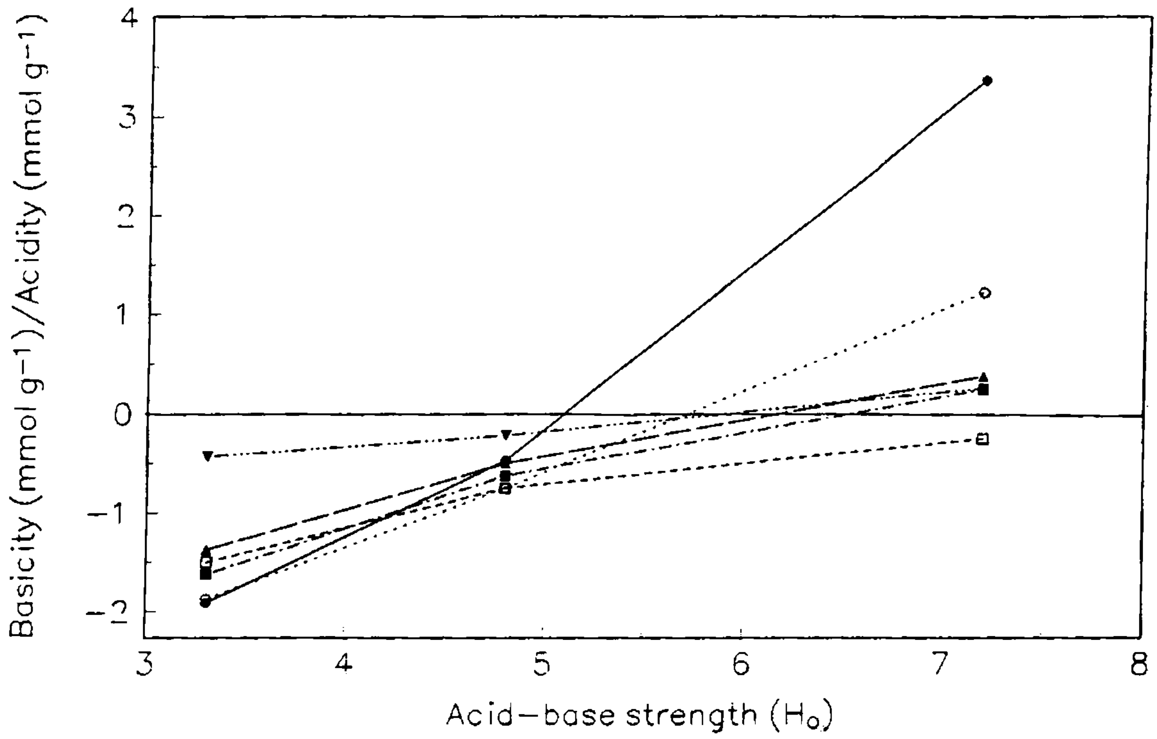


Fig. 5.7 Acid-base strength distribution of ZrO_2-Gd_2O_3 mixed oxides at 300°C

[ZG$_1$- (80 % ZrO_2 & 20 % Gd_2O_3) ZG$_2$ - (60 % ZrO_2 & 40 % Gd_2O_3)
ZG$_3$ - (40 % ZrO_2 & 60 % Gd_2O_3) ZG$_4$ - (20 % ZrO_2 & 80 % Gd_2O_3)]

[●]	ZrO_2-300°C	[▽]	Gd_2O_3-300°C	[○]	ZG$_1$-300°C
[■]]	ZG$_2$-300°C	[□]]	ZG$_3$-300°C	[▲]	ZG$_4$-300°C

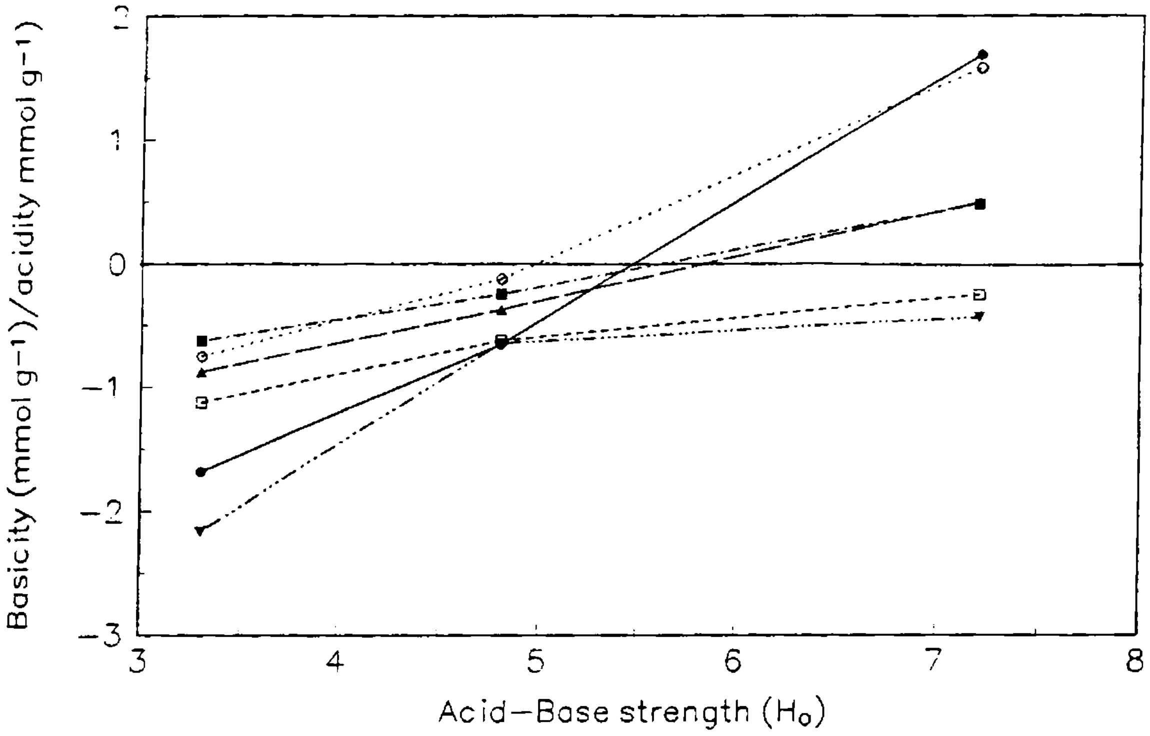


Fig. 5.8 Acid-base strength distribution of ZrO_2-Gd_2O_3 mixed oxides at 500°C

[ZG_1- (80 % ZrO_2 & 20 % Gd_2O_3) ZG_2 - (60 % ZrO_2 & 40 % Gd_2O_3)
ZG_3 - (40 % ZrO_2 & 60 % Gd_2O_3) ZG_4 - (20 % ZrO_2 & 80 % Gd_2O_3)]

[●] ZrO_2-500°C   [▼] Gd_2O_3-500°C   [○] ZG_1-500°C
[■]] ZG_2-500°C   [□]] ZG_3-500°C   [▲] ZG_4-500°C

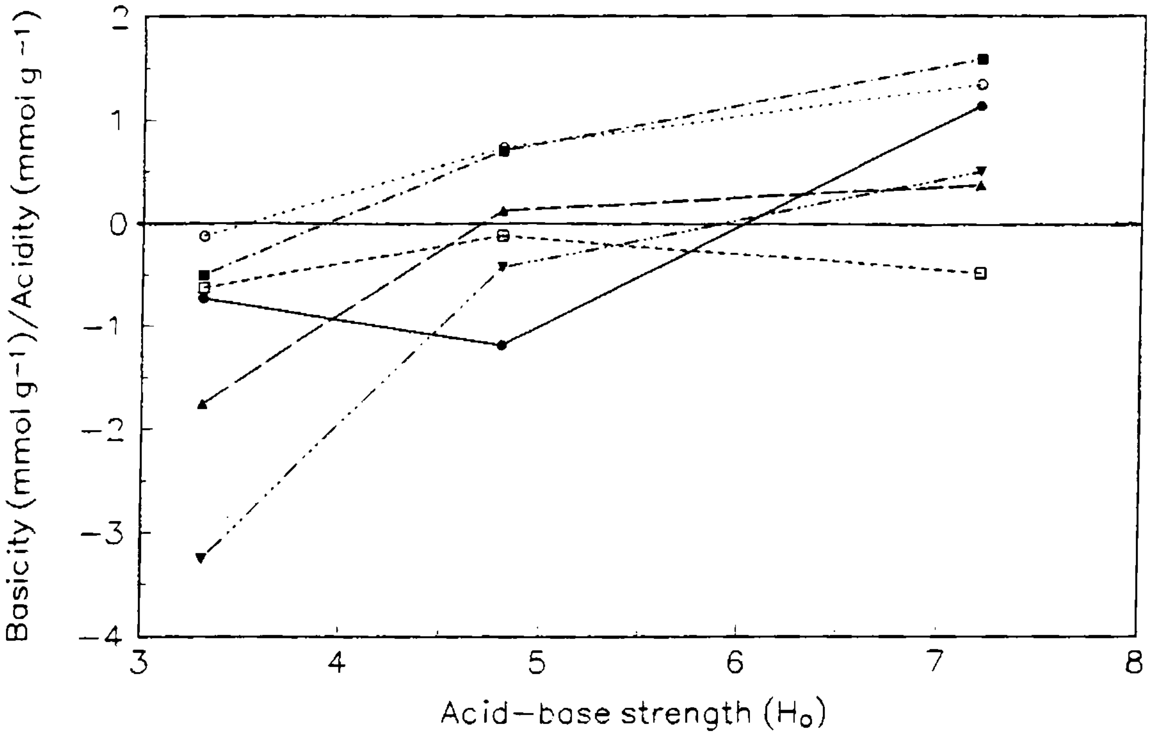


Fig. 5.9 Acid-base strength distribution of ZrO_2-Gd_2O_3 mixed oxides at 800°C

[ZG_1- (80 % ZrO_2 & 20 % Gd_2O_3) ZG_2 - (60 % ZrO_2 & 40 % Gd_2O_3)
ZG_3 - (40 % ZrO_2 & 60 % Gd_2O_3) ZG_4 - (20 % ZrO_2 & 80 % Gd_2O_3)]

[●]	ZrO_2-800°C	[▽]	Gd_2O_3-800°C	[○]	ZG_1-800°C
[■]]	ZG_2-800°C	[□]]	ZG_3-800°C	[▲]	ZG_4-800°C

Table 5.5. $H_{o,max}$ values of ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	5.1	5.6	5.2
20	6.4	6.4	3.8.
40	10.2	8.2	4.3
60	8.0	8.1	6.1
80	6.1	4.5	4.5
100	6.1	7.2	7.9

Table 5.6. $H_{o,max}$ values of ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	5.1	5.6	5.2
20	6.7	6.3	4.0
40	5.6	5.1	4.0
60	8.4	5.6	5.2
80	10.3	6.6	5.1
100	3.9	8.6	9.9

Table 5.8. $H_{o,max}$ values of ZrO_2-Gd_2O_3 mixed oxides at different activation temperatures.

Catalyst (% of Y_2O_3)	Activation temperature (°C)		
	300	500	800
0	5.1	5.6	5.2
20	5.7	4.9	3.5
40	6.5	5.5	3.9
60	8.7	8.4	4.6
80	9.5	8.4	4.7
100	5.9	6.3	6.0

La to Lu. The basicity of the rare earth oxide increases with the activation temperature. This increase has been ascribed to the increasing removal of trace surface contaminants such as carbonate ion, OH species or adsorbed water [16] and to the generation of stoichiometric and/or structural defects such as anion vaccancies and exposed metal ions that serves as catalytic sites [17]. Increasing temperature undoubtedly leads to the formation of various surface defect structures on rare earth oxides.

Regarding the binary oxides, all mixed oxides gave independent behavior compared to component oxides. All mixed oxides irrespective of composition showed maximum basicity at 300°C and with increasing temperature basicity decreases. The variation of $H_{o,max}$ with composition is given in figures 5.10 to 5.12. Even though the Y_2O_3 has less basicity than Dy_2O_3 and Gd_2O_3, the mixed oxides of ZrO_2 with Y_2O_3 exhibit higher basicity. This is due to the formation of the stabilised ZrO_2. It has been already reported that when small ions like Ca^{2+}, Mg^{2+}, Y^{3+} are substituted into ZrO_2 it gets stabilised [18]. Yttrium ions have ionic radius comparable to with Zr^{4+} ions and substitution of yttrium can makes more stabilised forms of oxides.

Preactivation temperature is crucial for acid site generation. For all mixed oxides the acidity was generated at 800°C at H_o value of 4.8 and 7.2. No acid sites are reported at H_o value of 3.3. It indicates that for mixed oxides, there were no acid sites whose strength is equal to or less than the pK_{BH^+} value of the indicator (H_o=3.3). Absence of no

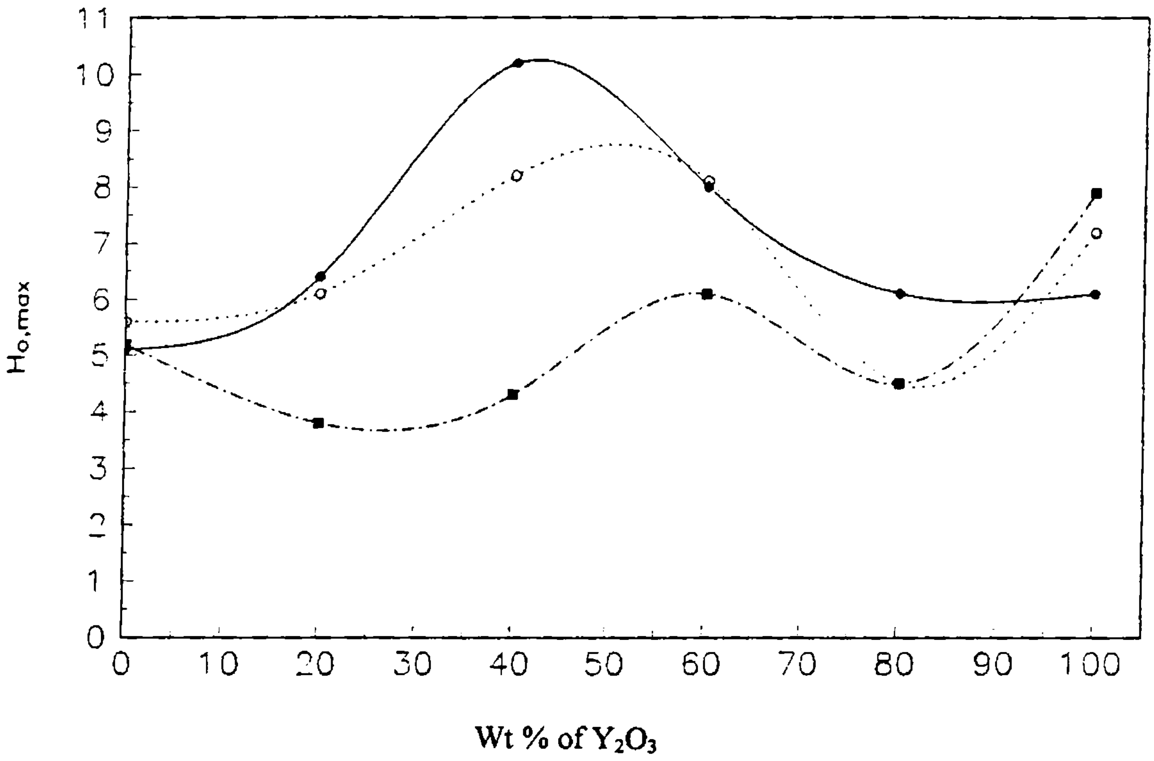


Fig. 5.10 $H_{o,max}$ as a function of composition of ZrO_2-Y_2O_3 mixed oxides at different activation temperatures

[●] 300°C [o] 500°C [■] 800°C

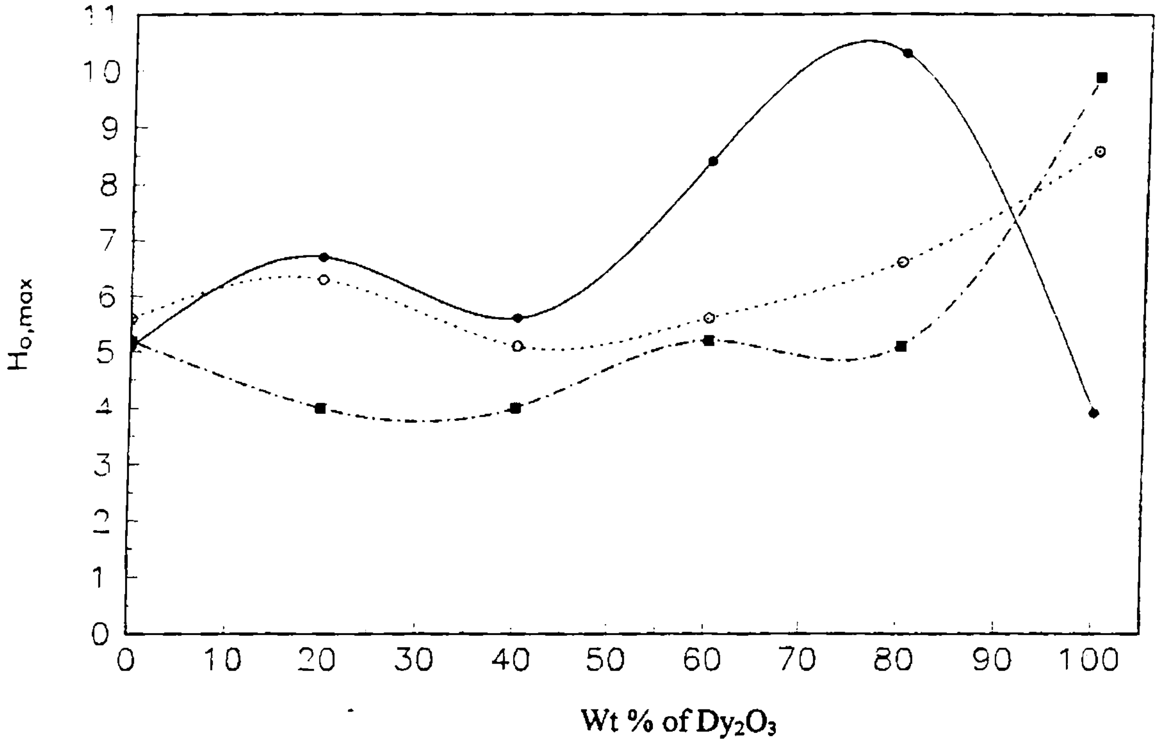


Fig. 5.11 $H_{o,max}$ as a function of composition of ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

[●] 300°C [○] 500°C [■] 800°C

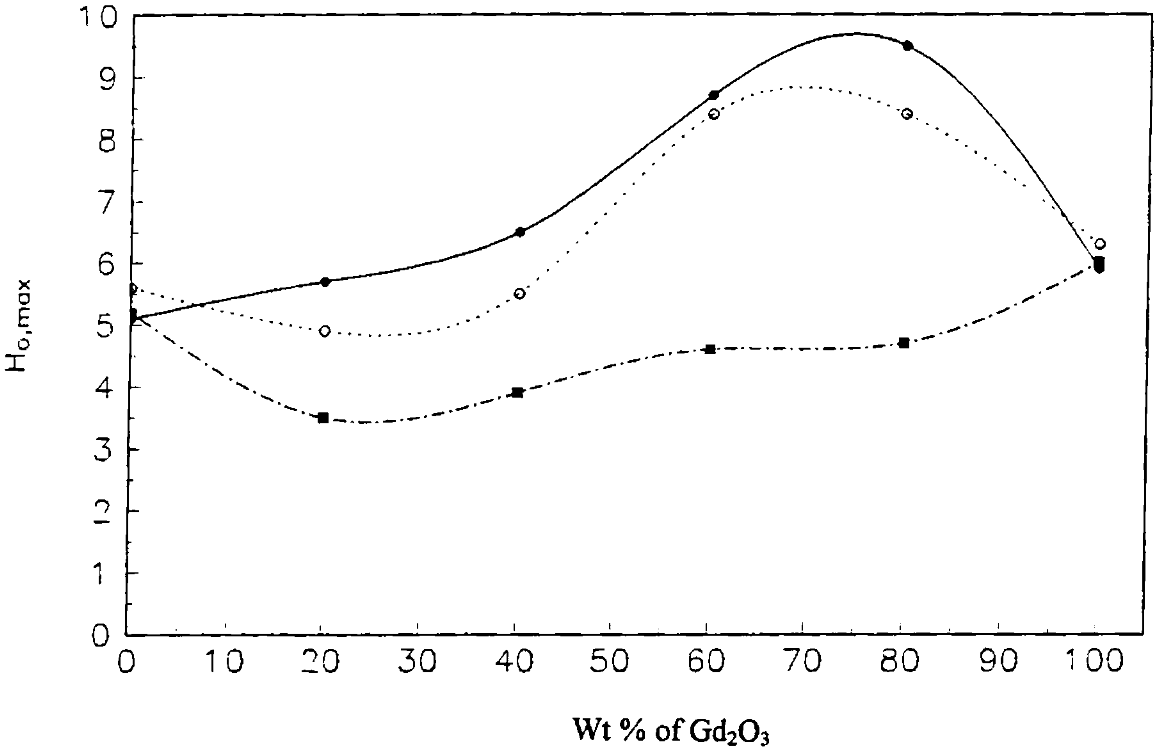


Fig. 5.12 $H_{o,max}$ as a function of composition of ZrO_2-Gd_2O_3 mixed oxides at different activation temperatures.

[●] 300°C [○] 500°C [■] 800°C

acidic and basic sites of equal strength on the surface shows significant acid-base strength distribution on the surface of the oxides.

For a mixed oxide the number of basic and acid sites generated depend upon the composition of the oxides [19]. As the % of earth oxide increases the basicity increases. The surface properties of mixed oxides depend on the amount of zirconia and/or rare earth oxide phase that is predominantly present on the surface. Two types of electron sources are available for basicity on mixed oxide surface [20-21]. One of these associated with the surface hydroxyl ions and the other is trapped electrons at intrinsic defect sites. Coordinately unsaturated ions can also contribute to the basicity at higher temperature. Surface hydroxyl ions are solely responsible for basicity at low temperature. As the temperature increases the number and strength of OH ions decreases. Therefore the surface oxide ions and the trapped electrons at intrinsic defects are major sources for the basicity at higher temperature.

In all mixed oxides irrespective of the composition, acid sites are generated at higher temperatures especially at 800°C . The generation of new and strong acid sites on mixed oxides has been ascribed to a charge imbalance localized in M_1-O-M_2 bondings where M_1 and M_2 are metal ions [22-26]. M_1 is the host metal ion (Zr^{4+}) and M_2 is the dopant metal ion (Y^{3+}, Dy^{3+} and Gd^{3+}). The charge imbalance might emerge however even on the simple component metal oxides comprising small particles [23,27]. This is partially attributed to the surface imperfections in small crystallites. The typical imperfections in small crystallites are metal or oxygen vacancies which cause a local charge imbalance. The existence of a coordinatively unsaturated cations were responsible for the Lewis acidity. A coordinatively unsaturated cation can chemisorb a molecule of water resulting in the formation of the Bronsted acid site [3]. At low temperature Bronsted acid sites are probable and at high activation temperature because of desorption of chemisorbed water molecules, Lewis sites are probably formed.

The acid-base properties also depend upon the method of preparation. It is found that even traces of impurities can greatly increase the acid strength of the oxides, the extent of the increase depending on the nature and amount of the acidic impurity [2]. At much higher activation temperature the lattice distortion can also contribute to an increase in acid sites. The acidity-basicity also depend on the nature of the oxide charges and the radius of the metal ion, M-O bonds and the coordination number, the filling of the d orbitals and the nature of the ligands. By the substitution of rare earths into zirconia whose ionic radii are nearly close to each other, Zr ions are replaced from lattice. This replacement results in a deformed lattice and the unbalanced electron charge distribution which increases the basicity. The charge imbalance makes more acidic sites. The acidity of a solid is also determined by the electronegativity of the compound. As the electronegativity increases , the covalency of the bonding increases along with the acidic character.

The surface acidity/basicity studies reveal the presence of groups of sites of different energies. It has been suggested that the acid base sites are metal ions and O_2^- ions on the surface and the site energy distribution was attributed to the presence of metal ions and O_2^- ions in different coordinations. The lower coordinated ion sites are considered as responsible for strong acid-base properties [28]. It was suggested that there are more than one kind of acid-base pair sites which differ in acid-base properties.

It can be concluded that the titration method provides the quantitative determination of acid- base sites of different strength. Since the actual amount of surface acid-base sites in a given H_o range is given by the difference between the acid -base amounts at pKa values of the indicators bracketing that H_o range it may be said that the characteristics of basicity distribution over mixed oxides at all temperatures is fairly large in amount in the range of base strength $H_o \geq 3.3$ especially at lower temperatures. The acid sites are relatively weak. The surfaces of mixed oxides of zirconia are associated with the acid - base sites of different strength, amount and energy distribution which can be used for selective reactions. Thus use of a series of Hammett indicators enabled to quantify the differentiation of the acid - base strength of mixed oxides in terms of pKa values of the indicators.

REFERENCES

1. O.Johnson, *J. Phy. Chem.*, 59, 827 (19 55).
2. H.A.Benesi, *J. Phy. Chem.*, 61, 970 (1957).
3. K.Tanabe , " *Solids and Bases*", Kodansha, Academic press, New York, (1970).
4. H.Hattori, T.Ono, M.Misono and K.Tanabe, "*New Solid acids and Bases*", Kodansha, Academic press, New York, (1989).
5. K.Tanabe and T.Yamaguchi, *J. Res. Inst. Cat.* Hokkaido Univ., 11, 179 (1964).
6. J.Take, N.Nikuchi and Y.Yoneda, *J.Cat.*, 21, 164 (1971).
7. Z.G.Szabo and B.Jover, *Proc. Int. Cong. Catal. 5th*, 57, 833 (1972).
8. T.Yamanaka and K.Tanabe, *Bull. Chem. Soc. Jpn.*, 79, 2409 (1975).
9. T.Yamanaka and K.Tanabe, *Bull. Chem. Soc. Jpn.*, 80, 1723 (1976)
10. Y.Nakano, T.Iizuka, H.Hattori and K.Tanabe, *J. Cat.*, 57, 1 91978).
11. C.Morterra, R.Aschieri and M.Volante, *Mat. Chem. Phy.*, **20**, 539 (1988).
12. T.Yamguchi, Y.Nakano, T.Iizuka and K.Tanabe, *Chem. Lett.*, 677 (1976).
13. T.Yamaguchi, H.Sasaki and K.Tanabe, *Chem. Lett.* 1017 (1973).
14. K.Esumi and K.Meguro, *Bull. Chem. Soc. Jpn.*, 55 315 (1982).
15. G.V.Chemparathy, *M.Phil Thesis*, p. 49, 1993.
16. H.Hattori, K.Murayama and K.Tanabe, *J. Cat.*, 44, 50 (1974).
17. M.Itoh, H.Hattori and K.Tanabe, *J. Cat.* 43, 192 91976).

18. R.Stevens, *"In Zirconia and Zirconia Ceramics"*, 2nd ed., Magnesium Electron Ltd., Manchester (1986).

19. H.Hattori, T.Ono, M.Misono and K.Tanabe, *"New Solids and Bases"*, Kodansha, Academic press, New Yok, (1989).

20. M.Che, C.Nccache and B.Imelik, *J. Cat.*, 24, 328 (1970).

21. S.Sugunan and G.D.Rani, *J. Mat. Sci. Lett.*, **28**, 4811 (1983)., **10**, 887 (1991)., **11**, 1269 (1992).

22. K.Nishiwaki, N.Kakuta , A.Ueno and H.Nakabayashi, *J. Cat.* **118**, 498 (1989).

23. H.Nakabayashi, N.Kakuta and A.Ueno, *Bull. Chem. Soc. Jpn.*, **64**, 2420 (1991).

24. K.Tanabe, T.Sumiyoshi, K.Shibata, T.Kiyora and J.Kitagawa, *J.Bull. Chem. Soc. Jpn.*, **47**, 1064 (1974).

25. K.R.P Sabu, K.V.C.Rao and C.G.R Nair, *Bull. Chem. Soc. Jpn.*, **64**, 1926 (1991).

26. K.Tanabe and T.Takashita, *"Adavnces in Catalysis"*, Vol.**17**, p.315, Academic Press, New York,(1967).

27. J.R.Anderson, " *Structure of Metallic Catalysts*", Academic Press, New York, (1975).

28. V.R.Choudhari and V.H.Rane, *J.Cat.*, **130**, 417 (1991).

CHAPTER 6

CATALYTIC ACTIVITY OF MIXED OXIDES OF ZrO_2 WITH RARE EARTH OXIDES

6.1. INTRODUCTION

Oxidation reduction reactions are important in organic chemistry. The reduction of multiple bonds using an organic molecule instead of hydrogen gas or metal hydride is known as hydrogen transfer reaction [1]. Reduction of carbonyl group is one of the most fundamental operation in organic chemistry and Meerwin Pondorf Verly reduction is one of the best example where the ketones and aldehydes are reduced with metal alkoxides and 2- propanol. Reverse reaction is known as Oppenauer oxidation. The reduction of aldehydes and ketones over anhydrous ZrO_2 to give corresponding alcohols has been reported [2,3]. MPV reduction is prominent in terms of compatibility with many different types of functional group, selectivity for reduction and low cost of 2-propanol [4]. Oxidation of secondary alcohols with ketones has also been carried out by catalysis with hydrous Zr (IV) oxide [5,6]. Shibagaki et al [2] found that the reduction with hydrous zirconia has the following advantages.

1. The reduction does not call for strong acid treatment.

.2 Products are easily isolated by filtering off catalyst and subsequent evaporation of solvent, because the catalyst is insoluble in any solvent.

3. It is stable at room temperature in air for seven years and can be used for repeated reductions.

4. It is insensitive to air or water and the reaction does not require water free conditions.

The reduction of aldehydes and ketones and oxidation of alcohols are considered to be catalysed by basic sites. It has been found that mixed oxides of zirconia are associated predominantly with basic sites by titration methods (Chapter. 5). We have studied the catalytic activities for reduction of cyclohexanone and oxidation of cyclohexanol over mixed oxides. In order to evaluate the presence of acidic sites esterification reaction has also been carried out which is considered as a Bronsted acid catalysed reaction. The heterogeneous catalysis for esterification of the carboxylic acids have also been reported [7]. The mixed oxides of zirconia with rare earth oxides constitutes predominantly basic sites. Only at higher temperatures new and strong acid sites are generated. To evaluate the activity of acid sites the esterification of acetic acid with n-butanol has been selected as a model reaction .

$$CH_3COOH + C_4H_9OH \rightleftharpoons CH_3COOC_4H_9 + H_2O$$

6.2 EXPERIMENTAL

The catalytic activities of mixed oxides for the oxidation, reduction and esterification reactions are done in liquid phase. The descriptive procedures for these reactions are given in chapter.3. The reduction of cyclohexanone is followed by means of UV-vis spectrophotometer, while oxidation and reduction reactions are followed by means of gas chromatography. The activity is expressed as the first order rate constant for the conversion of reactant per m^2 of the catalyst.

6.3 RESULTS AND DISCUSSIONS

6.3.1. Reduction of cyclohexanone

The liquid phase reduction of cyclohexanone in isopropanol proceeded very well over the catalysts. Data are given in Tables 6.1 to 6.5. It is an analogous reaction to well known Meerwin Pondorf Verly (MPV) reaction. The heterogeneous catalysis has over come the tedious work ups to be encountered in the conventional reaction. The reaction shows a first order kinetics with respect to the ketone, isopropanol and the catalyst. Kibby et. al [8] proposed a reaction mechanism for the heterogeneous catalysis which is similar to the original MPV reduction. Shibagaki et. al [2] have also reported a reaction mechanism for the reduction of cyclohexanone over ZrO_2 which follows the conventional mechanism of MPV reduction. An observation of kinetic isotopic effect has suggested

Table 6.1. % conversion of cyclohexanone using ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

catalyst (% of Y_2O_3)	Activation temperatures(°C).		
	300	500	800
0	25.19	11.05	3
20	55.81	13.13	2.41
40	58.13	43.73	-
60	61.07	36.33	5.01
80	50.51	9.3	-
100	-	50.15	-

Table 6.2. Catalytic activity for reduction of cyclohexanone using ZrO_2-Y_2O_3 mixed oxides at different activation temperatures.

catalyst (% of Y_2O_3)	Rate constant (10^{-5} min^{-1} m^{-2})		
	300	500	800
0	0.3019	0.3967	0.2453
20	0.8076	0.2397	0.0892
40	0.9657	1.0119	-
60	0.9148	0.7638	0.2232
80	1.113	0.1876	-
100	-	1.7798	-

Table 6.3. % conversion of cyclohexanone using ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

catalyst (% of Dy_2O_3)	Activation temperatures		
	300°C	500°C	800°C
0	25.19	11.05	3
20	36.58	15.	3.9
40	36.28	18.66	-
60	11.50	32.93	-
80	33.33	39.27	-
100	-	34.33	-

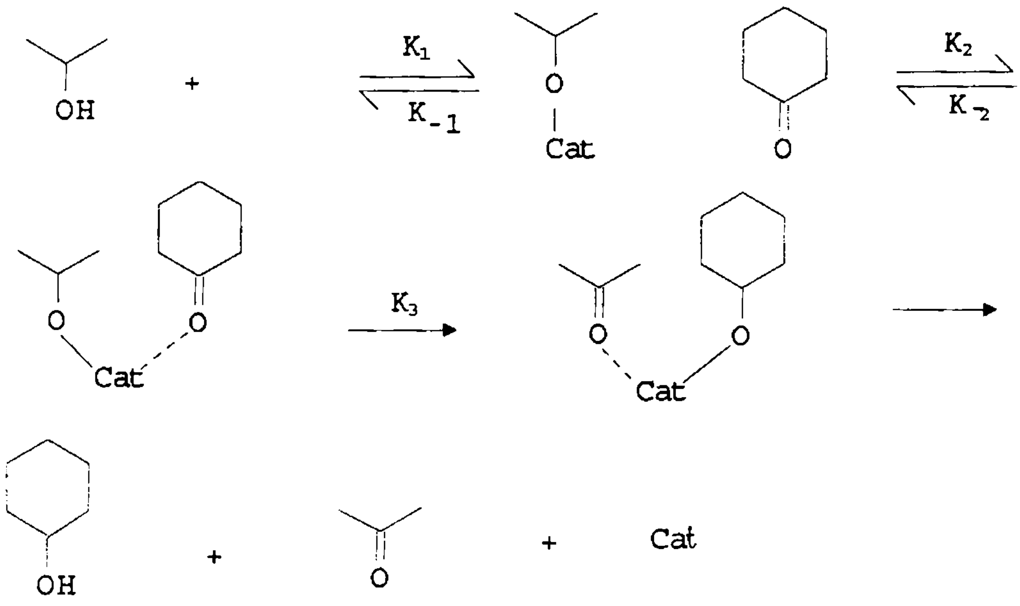
Table 6.4. Catalytic activity for reduction of cyclohexanone using ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

catalyst (% of Dy_2O_3)	Rate constant (10^{-5} min^{-1} m^{-2})		
	300	500	800
0	0.3019	0.3967	0.2453
20	0.4325	0.2888	0.2085
40	0.4869	0.3957	-
60	0.1981	1.117	-
80	1.694	2.463	-
100	-	3.589	-

Table 6.5. Catalytic activity for reduction of cyclohexanone using ZrO_2-Gd_2O_3 mixed oxides at different activation temperatures.

Catalyst (% of Gd_2O_3)	activation temperature (°C)	% conversion	Rate constant (10^{-5} m^{-1} m^{-2})
0	300	25.19	0.3019
0	500	11.05	0.3967
0	800	3.00	0.2453
20	500	23.55	0.5268
40	500	33.14	0.8289
60	500	28.17	0.9799
80	500	30.52	1.7600
100	300	-	-
100	500	-	-
100	800	-	-

that a step of hydride ion transfer from adsorbed isopropanol to the adsorbed carbonyl group constitute the rate determining step for the reduction of cyclohexanone. The catalytic activity of the mixed oxides of ZrO_2 can be rationalised in terms of the mechanism (Scheme. 1) proposed by Shibagaki et. al for the reduction. It has already been suggested that K_3 is the rate determining step. That is the step subsequent to the adsorptionof 2-propanol and carbonyl compound on the catalyst. A Hammett relationship was found in the reduction of carbonyl compounds [9]. The mechanism of the reaction involves the hydride ion transfer from alcohol to the carbonyl carbon of the ketone. Basic sites favors the hydride transfer.



(Scheme 1)

The activity parallels with the basicity of the oxides. Lewis basic sites of the catalyst surface favors the reaction. It is found that even the very weak basic sites which possess the basic strength greater than or equal to the H_o value of 3.3 are active for the reaction. No acidic sites are reported at H_o value of 3.3 at all temperatures studied. As the temperature is increased the number of basic sites decreases, the activity of reaction also decreases at higher temperatures. The variation in activity of oxides for the reduction of cyclohexanone with basicity at H_o of 3.3 as a function of composition is given in figures 6.1 to 6.3..Again there is a direct parallelism with the limiting amount of chloranil adsorbed. Compared to TCNQ, being a weak electron acceptor chloranil is capable of forming anion radical with strong basic sites. The variation in activity of oxides for the reduction of cyclohexanone with limiting amount of chloranil adsorbed as a function of composition has been given in figures 6.4 to 6.6. This itself indicates that the reduction of cyclohexanone is catalysed by strong donor sites, especially the sites which possess maximum number of basic sites. The electron donor properties of oxides are discussed in detail in chapter.4.

The nature of the basic sites available for electron transfer process is discussed in chapter 5. At lower temperatures, the surface hydroxyl ions favors the reaction and at higher temperatures the surface oxides ions and trapped electrons in the intrinsic defect sites take part in the reaction. As the temperature is increased, due to the desorption and dehydroxylation of surface hydroxyl groups from adjacent sites, the number and concentration of hydroxyl groups decrease and surface oxides ions are exposed. At higher temperatures due to surface lattice distortion, the defect sites may also be generated. It

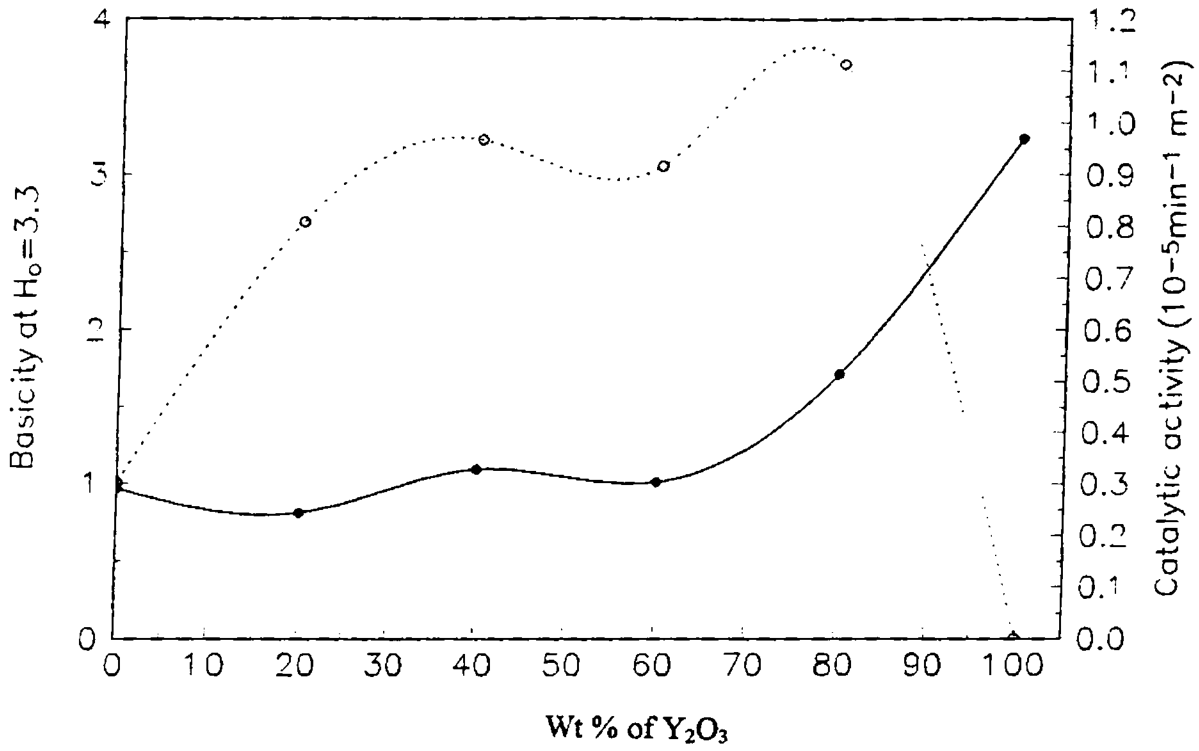


Fig 6.1 Catalytic activity of ZrO_2-Y_2O_3 mixed oxides for the reduction of cyclohexanone and basicity at Ho =3.3 as a composition of Y_2O_3.

[o]	Activity	[●]	Basicity

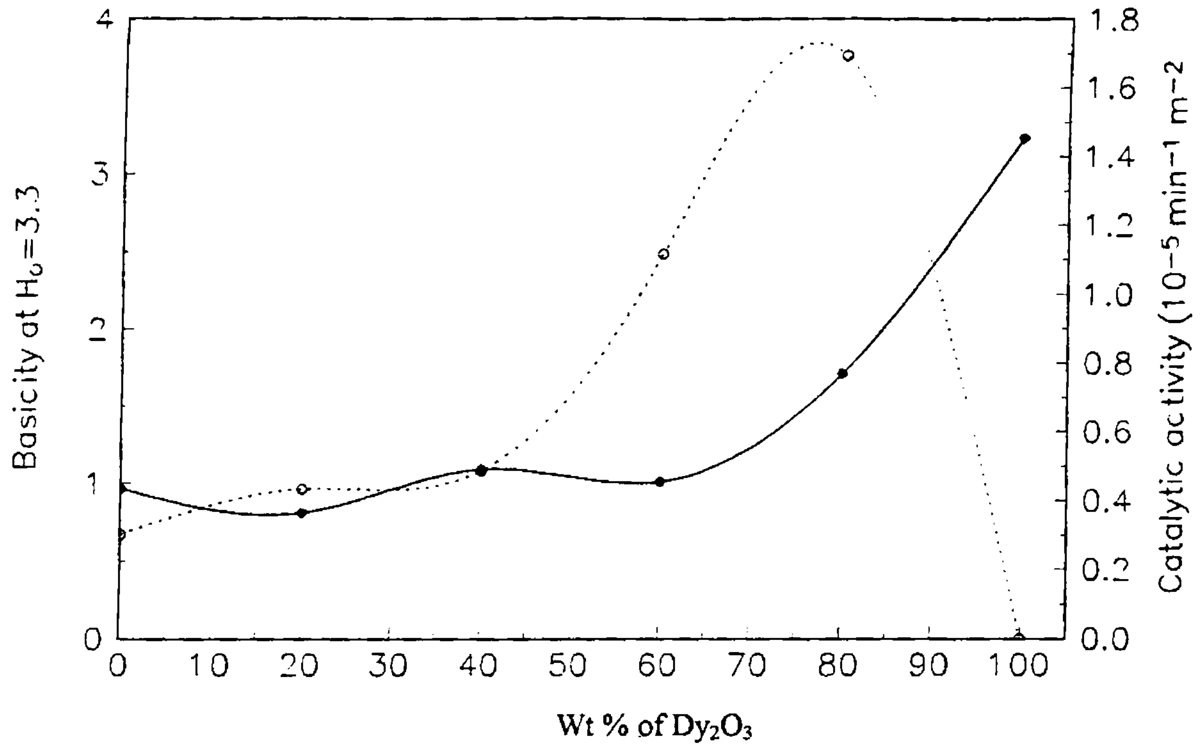


Fig 6.2 Catalytic activity of ZrO_2-Dy_2O_3 mixed oxides for the reduction of cyclohexanone and basicity at Ho =3.3 as a composition of Dy_2O_3.

[●] Basicity at H_o=3.3 [o] Catalytic activity

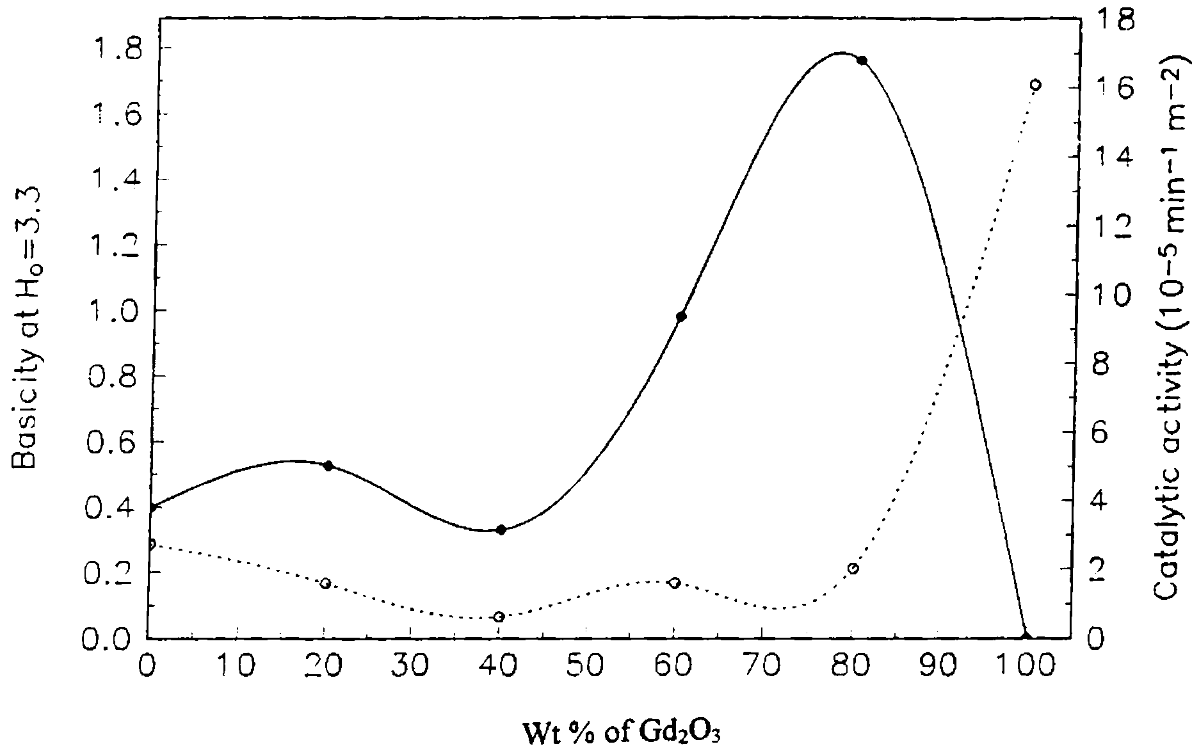


Fig 6.3 Catalytic activity of ZrO_2-Gd_2O_3 mixed oxides for the reduction of cyclohexanone and basicity at Ho =3.3 as a composition of Gd_2O_3.

[●] Activity [○] Basicity

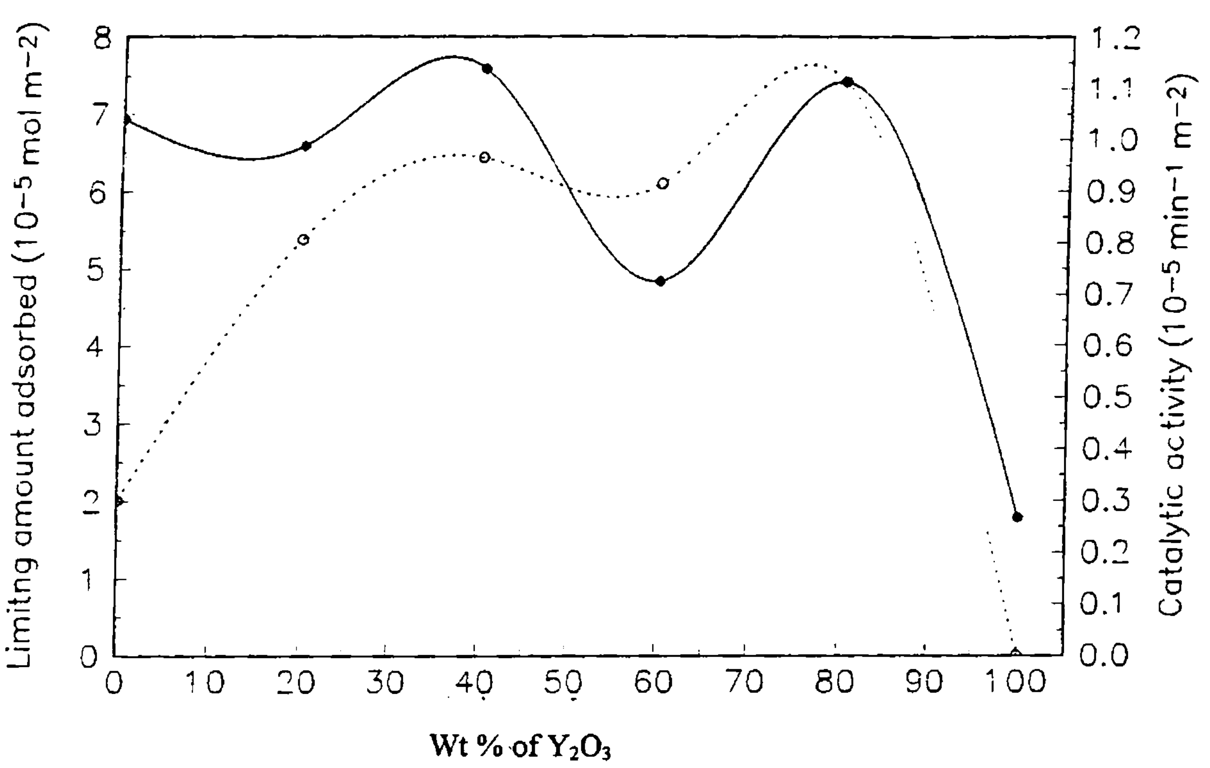


Fig 6.4 Catalytic activity of ZrO_2-Y_2O_3 mixed oxides for the reduction of clohexanone and limiting amount of chloranil adsorbed as a composition of Y_2O_3.

[●] Limiting amount adsorbed [○] Catalytic activity

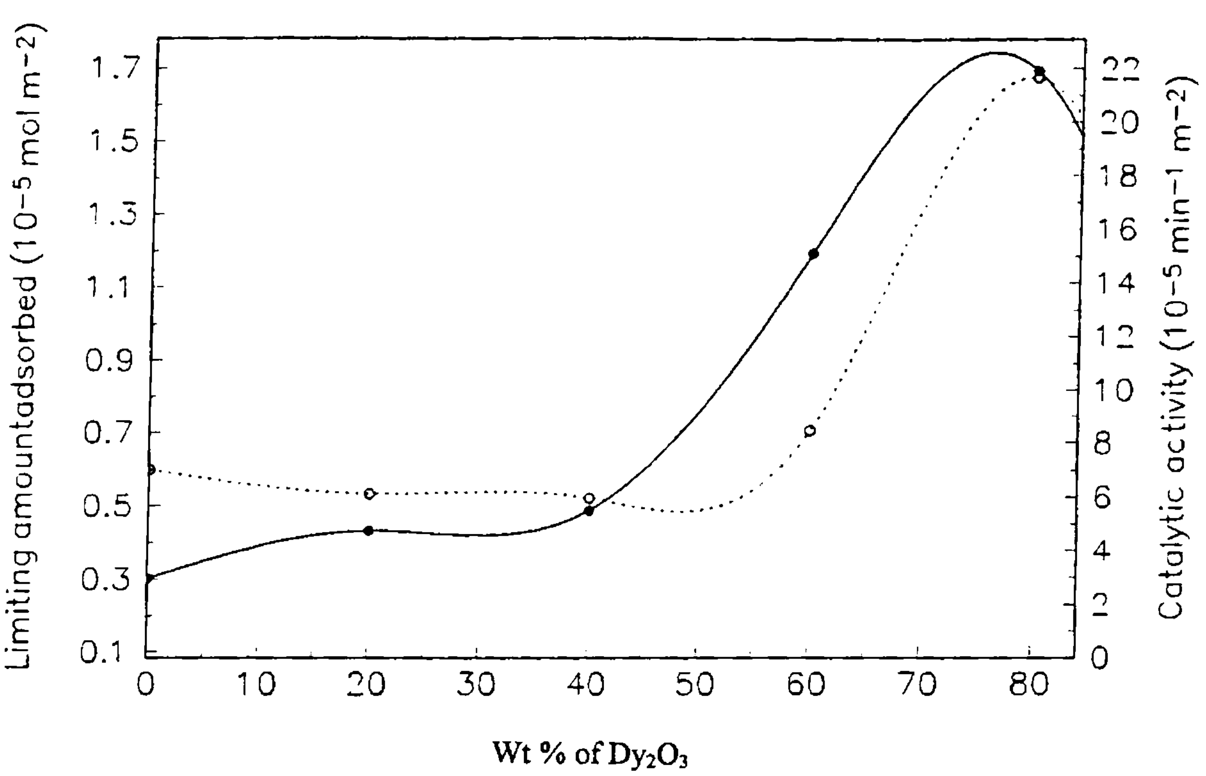


Fig 6.5 Catalytic activity of ZrO_2-Dy_2O_3 mixed oxides for the reduction of cyclohexanone and limiting amount of chloranil adsorbed as a composition of Dy_2O_3.

[•] Limiting amount adsorbed [o] Catalytic activity

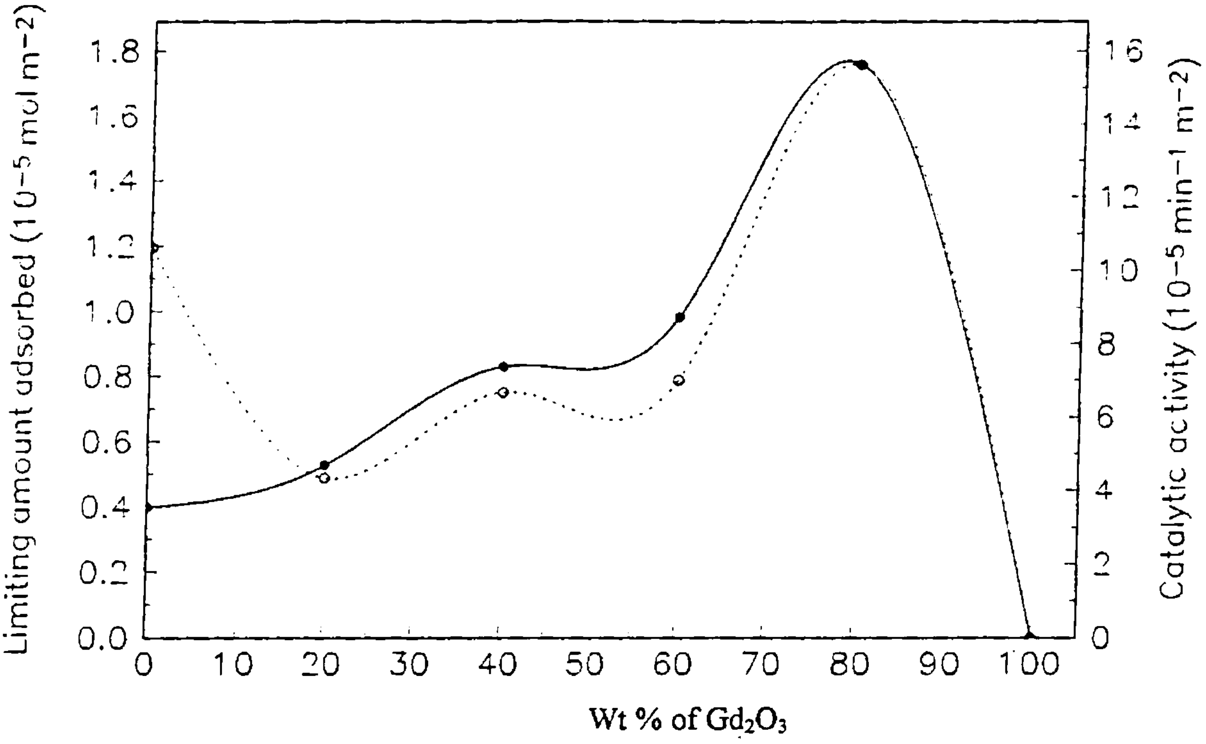


Fig 6.6 Catalytic activity of ZrO_2-Gd_2O_3 mixed oxides for the reduction of cyclohexanone and limiting amount of chloranil adsorbed as a composition of Gd_2O_3

[●] Limiting amount adsorbed [o] Basicity

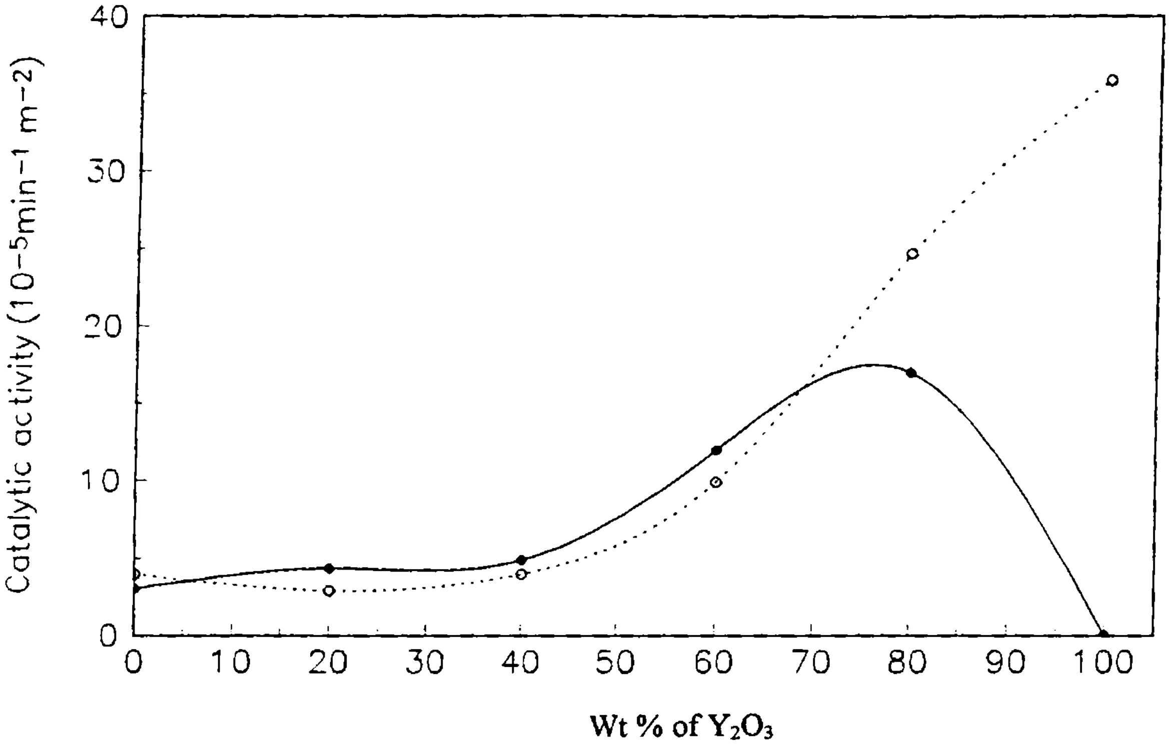


Fig 6.7 Catalytic activity of ZrO_2-Y_2O_3 mixed oxides for the reduction of cyclohexanone as a composition of Y_2O_3.

[●] 300°C [○] 500°C

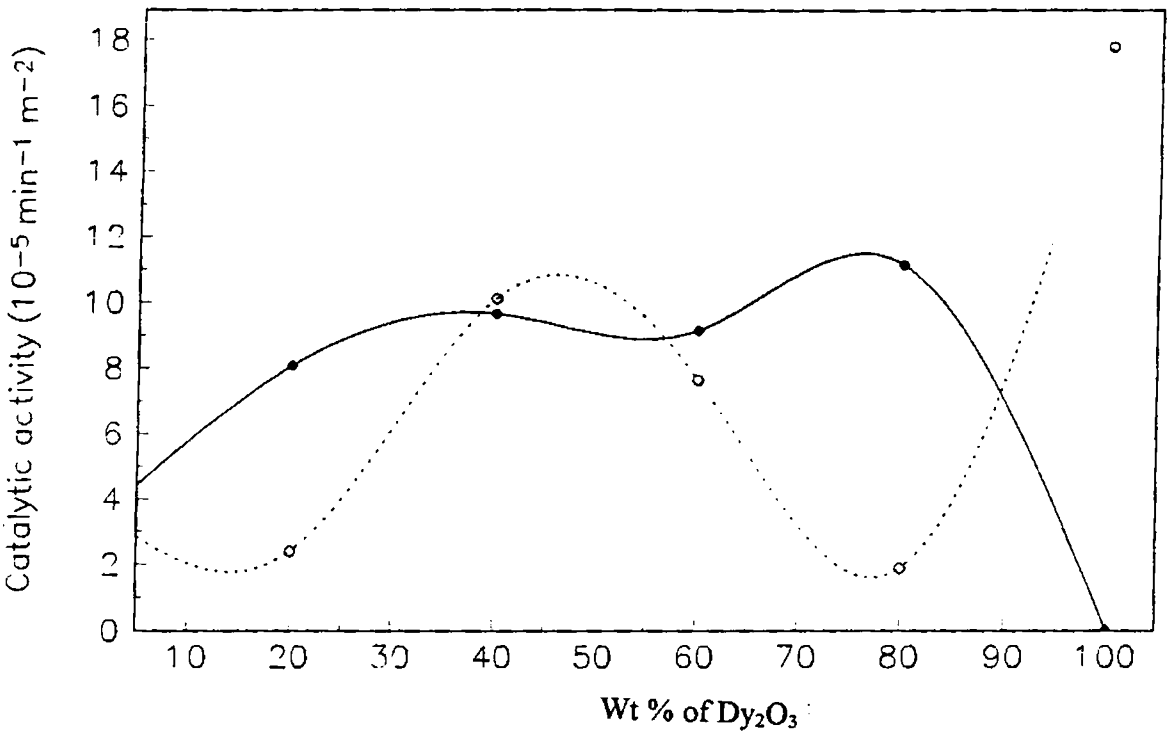


Fig 6.8 Catalytic activity of ZrO_2-Dy_2O_3 mixed oxides for the reduction of cyclohexanone as a composition of Dy_2O_3.

[●] 300°C [○] 500°C

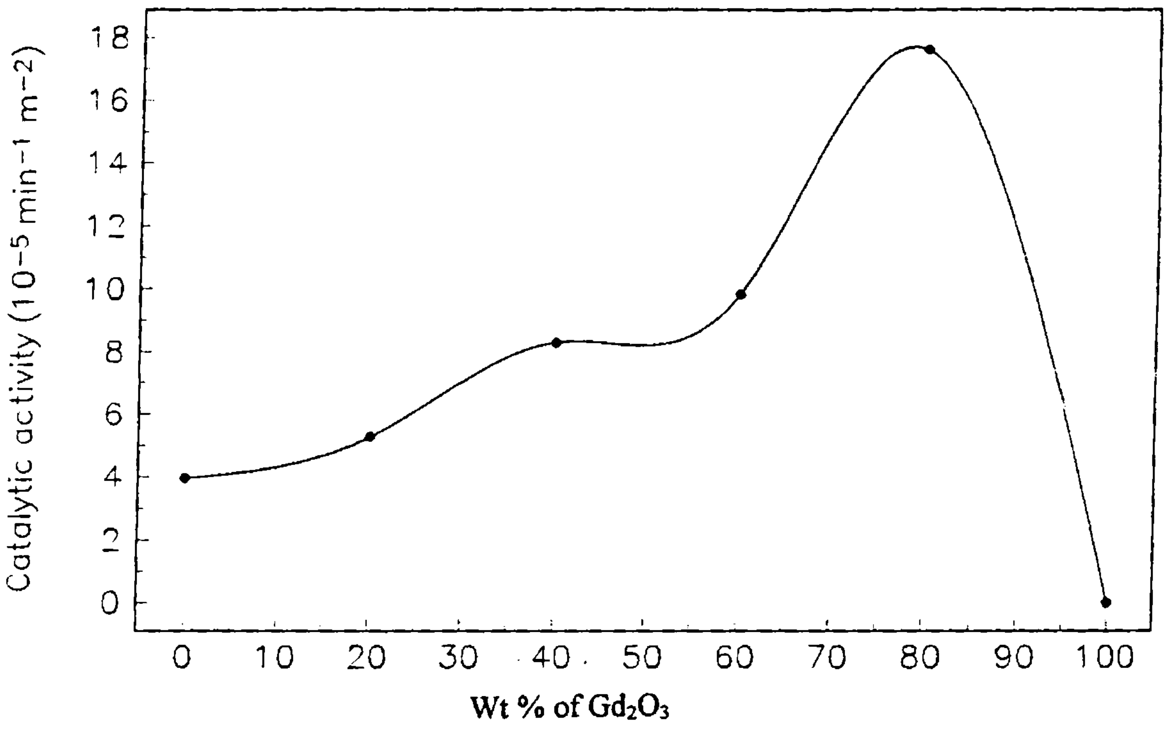


Fig 6.9 Catalytic activity of ZrO_2-Gd_2O_3 mixed oxides for the reduction of cyclohexanone as a composition of Gd_2O_3

has been reported that for most of the metal oxides the surface hydroxyl ion are evacuated above 500°C and at higher temperature surface anions and trapped electrons are created. The heat treatment at higher temperatures facilitates the crystallisation, resulting in the stabilised surface states and decreasing the surface area, resulting in a decrease in number and strength of the active sites.

The variation of catalytic activity with composition for the reduction of cyclohexanone are given in figure 6.7 to 6.9. The oxides show negligible activity for the reduction of cyclohexanone at 800°C. This is due to the generation of new and strong acid sites, the formation of acid sites have been confirmed by titration method (in chapter 5). The highest activity is found at 300°C. The addition of rare earth oxides increased the activity. Mixed oxides of ZrO_2 with Y_2O_3 showed higher activity compared to other oxides. ZrO_2 shows maximum activity 300°C and it has been already reported that the ZrO_2 exhibits highest activity at 300°C [10]. Rare earth oxides gave activity only at 500°C.

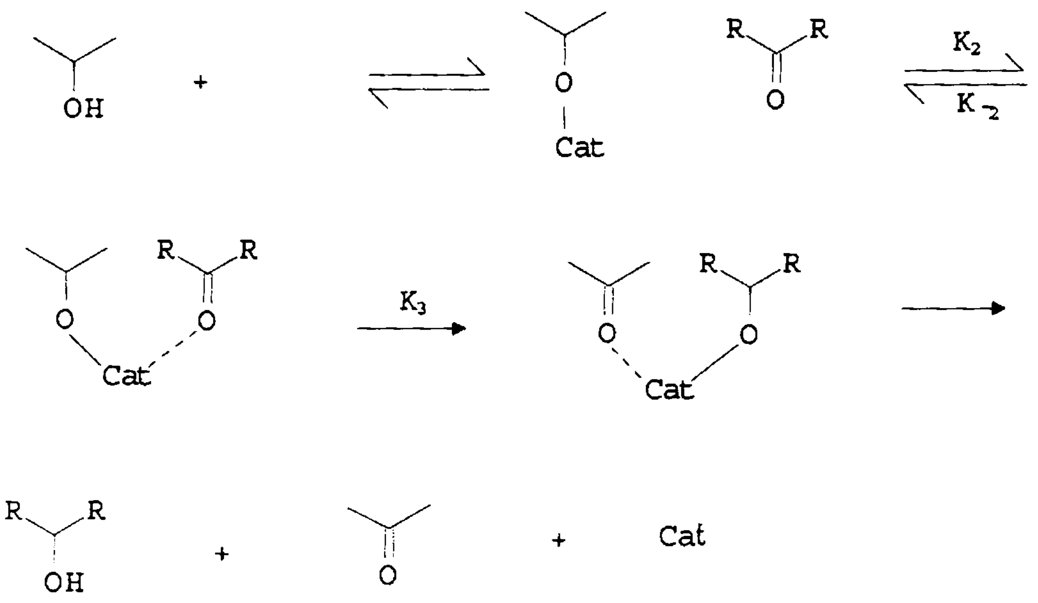
6.3.2. Oxidation of cyclohexanol with benzophenone

When a ketone in the presence of a base is used as the oxidising agent the reaction is known as Oppenauer oxidation, which is considered as the reverse reaction of the MPV reduction. The acidic and basic properties of oxides are very important for the development of scientific criteria in catalytic applications. As a measure of the base strength of metal oxide catalyst Davis [11] suggested the alcohol conversion selectivity. The amphoteric character of alcohol permits their interaction with the acids and bases. The ability of oxide catalysts to dehydrogenation activity has also been reported.

Cyclohexanol is the key intermediate in the manufacture of nylon-6 and nylon-66 which are largely used for fiber and tyre cord industry [12]. Present industrial practice of cyclohexanone manufacture involves the dehydrogenation of cyclohexanol over commercially available ZnO catalyst and copper on MgO catalyst. These catalyst systems require an operating temperature of 200-450°C range to give 75 % conversion and 99 % selectivity to cyclohexanone. The reaction however has been a subject of intensive research by major caprolactum and adipic acid producing industries with a view to achieving higher conversion and selectivity, a improved catalyst life and lower operating temperatures [13]. Improvements in thermal stability, mechanical strength and selectivity can be brought about by selected additives, changes in thermal treatment and reduction procedures [14].

The oxidation of cyclohexanol over mixed oxides is analogous to Oppenauer oxidation where alcohols are oxidised using metal alkoxides in presence of a hydrogen acceptor. This is an example for hydrogen transfer reaction. The reaction is prominent in terms of compatibility with selective oxidation of functional groups and mild oxidation conditions. The Oppenauer oxidation of cyclohexanol proceeded very well over mixed oxides of ZrO_2. Benzophenone is used as the hydrogen acceptor. Benzophenone is selected as the hydrogen acceptor due to the low electron density at carbonyl carbon. It has ability for oxidising the alcohol and to resist aldol condensation [5]. The oxidation of secondary alcohols with benzophenone as hydrogen acceptor over other commonly available ketones has also been reported [15]. As a reverse reaction of the MPV reduction the same mechanism (scheme) has also been suggested for the oxidation of alcoholes.

The reaction finds high activity and selectivity. The reaction is assumed to be catalysed by lattice oxygen ions. Data are given in Tables 6.6 to 6.10. The mechanism of



(Scheme 2)

Table 6.6. % conversion of cyclohexanol using ZrO_2-Y_2O_3 mixed oxides at different activation temperatures

catalyst (% of Y_2O_3)	Activation temperatures (°C)		
	300°C	500°C	800°C
0	95.97	87.24	83.90
20	100	100	45.01
40	100	94.54	89.30
60	100	93.50	90.90
80	100	95.67	94.00
100	29.3	87.42	86.00

Table 6.7. Catalytic activity for oxidation of cyclohexanol using ZrO_2-Y_2O_3 mixed oxides at different activation temperatures

catalyst (% of Y_2O_3)	Rate constant (10^{-5} min^{-1})		
	300°C	500°C	800°C
0	13.362	27.90	58.84
20	24.56	26.41	8.260
40	39.06	20.47	41.65
60	32.94	18.10	41.64
80	46.88	24.14	37.95
100	6.241	21.20	43.12

Table 6.8. % conversion of cyclohexanol using ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures

Catalyst (% of Dy_2O_3)	Activation temperatures		
	300°C	500°C	800°C
0	95.97	87.24	83.90
20	79.72	75.88	70.81
40	89.67	82.80	72.7
60	85.65	63.75	93.00
80	82.64	84.00	83.90
100	63.68	88.47	88.64

Table 6.9. Catalytic activity for oxidation of cyclohexanol using ZrO_2-Dy_2O_3 mixed oxides at different activation temperatures.

catalyst (Dy_2O_3)	Rate constant (10^{-5} min^{-1} m^{-2})		
	300°C	500°C	800°C
0	13.362	27.90	58.84
20	6.063	10.11	25.82
40	9.81	13.48	39.01
60	12.60	29.34	84.56
80	29.28	36.20	61.94
100	34.67	73.75	61.39

Table 6.10. Catalytic activity for oxidation of cyclohexanol using ZrO_2-Gd_2O_3 mixed oxides.

Catalyst	Activation temperature (°C)	% conversion	Rate constant (10^{-5} m^{-1} m^{-2})
0	300	95.97	13.36
0	500	87.24	27.90
0	800	83.90	83.90
20	500	92.06	16.27
40	500	92.00	20.80
60	500	95.00	35.48
80	500	91.80	48.38
100	300	45.70	44.50
100	500	89.78	141.40
100	800	78.79	101.50

dehydrogenation of alcohol, has been examined [16]. According to the proposed scheme, the adsorption of alcohol which leads to dehydrogenation occurs on an electronegative atom with a participation of free electron where the rate determining step is the desorption of ketone. In the case of solid bases dehydrogenation can take place without the participation of free carriers of semiconductors owing to the presence of the large effective charges of oxygen and metal surface atoms. The ability of the oxide catalysts to dehydrogenation activity has also been related to the existence of basic sites originating from the oxygen in the oxide lattice [17]. The activity is reported as the first order rate coefficient for the conversion of cyclohexanol per unit area of the catalyst surface. The mixed oxides of zirconia with rareearth oxides exhibit good catalytic activity for the oxidation of cyclohexanol compared to reduction of cyclohexanone, where both reactions are favoured by basic sites. High activity is found in the case of oxidation. As in the case of reduction of cyclohexanone, there is no direct relationship for the activity of oxidation of cyclohexanol with basicity of the oxides. The presence of acid sites are very significant in determining activity. The maximum number of basic sites are those which possess the basic strength of H_o value of 3.3. No acidic sites were detected at H_o value of 3.3. No acid-base sites of equal strength has been reported on any surface which implies the presence of significant acid-base pair sites with difference in strength. The variation of catalytic activity with composition at different temperatures are given in figures 6.10 to 6.12.

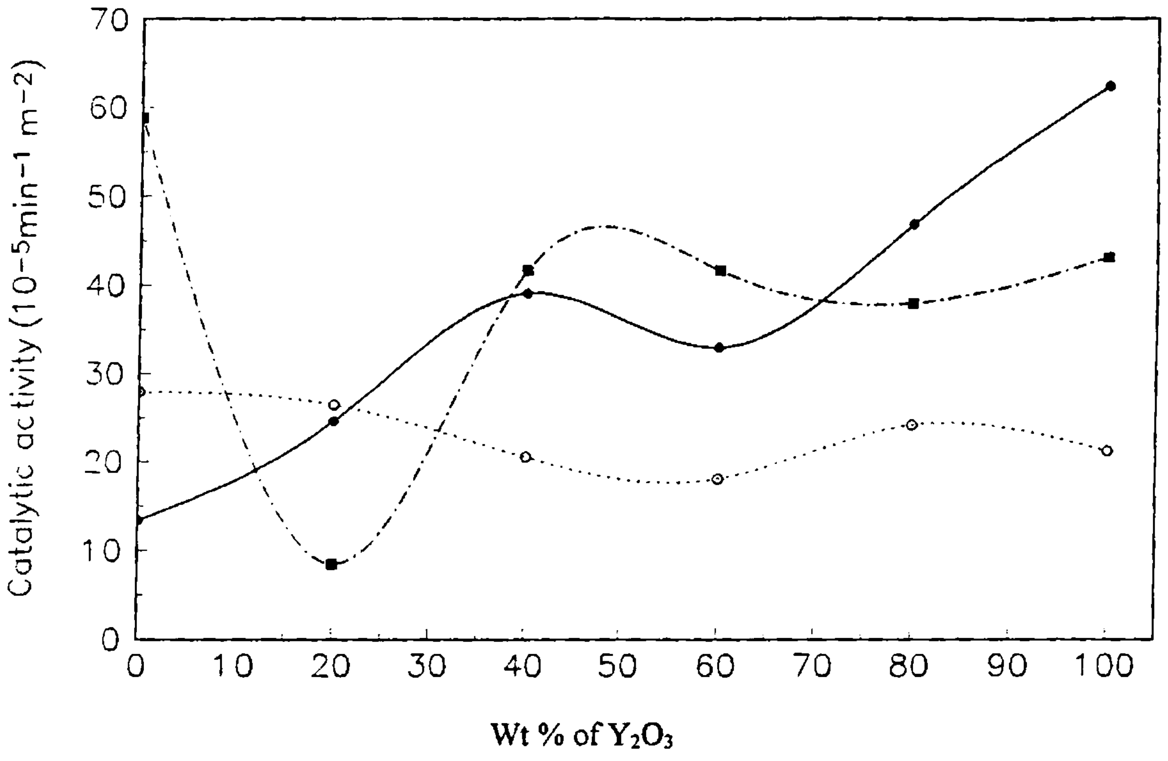


Fig 6.10 Catalytic activity of ZrO_2-Y_2O_3 mixed oxides for the oxidation of cyclohexanol as a composition of Y_2O_3

[●] 300°C [○] 500°C [■] 800°C

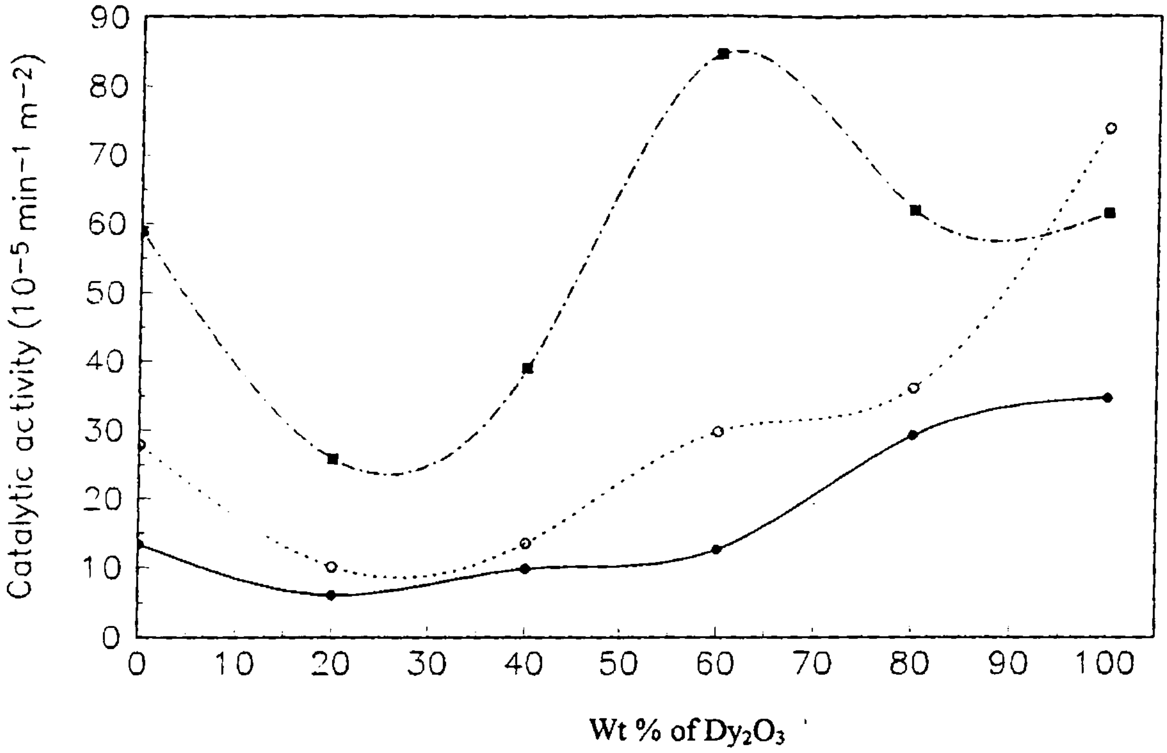


Fig 6.11 Catalytic activity of ZrO_2-Dy_2O_3 mixed oxides for the oxidation of cyclohexanol as a composition of Dy_2O_3

[•] 300°C [o] 500°C [■] 800°C

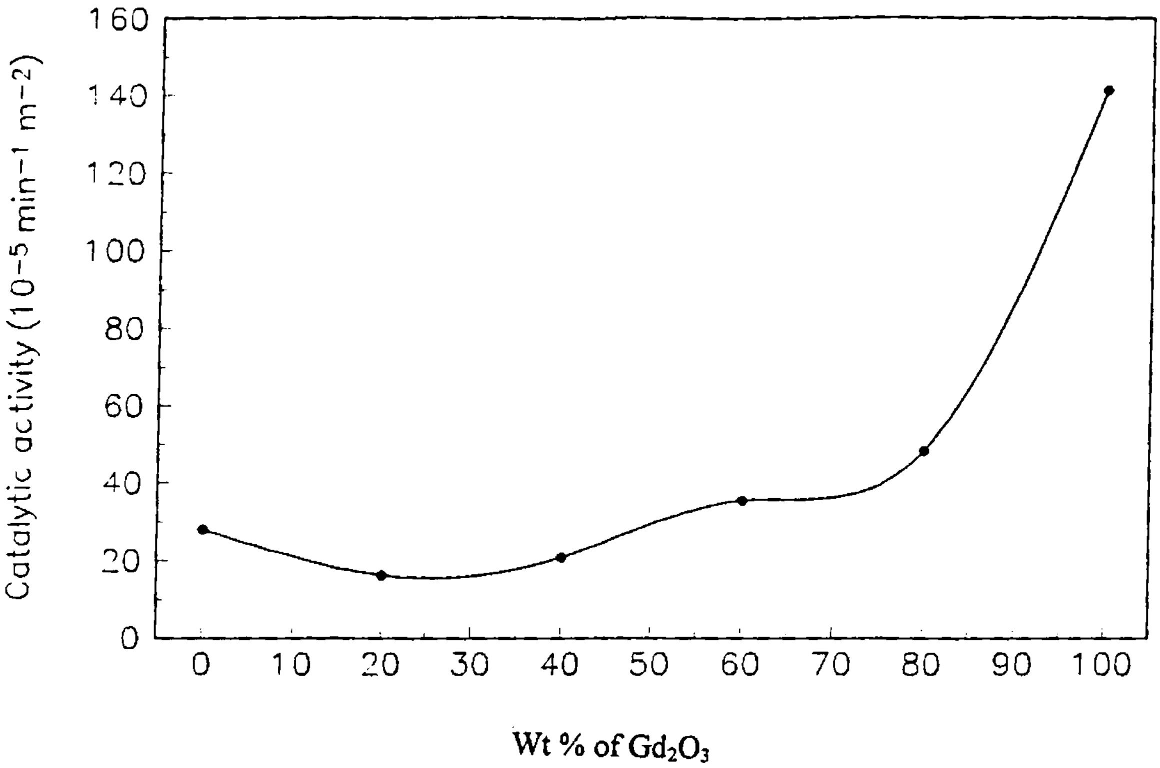


Fig 6.12 Catalytic activity of ZrO_2-Gd_2O_3 mixed oxides for the oxidation of cyclohexanol as a composition of Gd_2O_3

The presence of acid-base sites have been confirmed by the titration method. The high activity for oxidation can be attributed to the acid-base bifunctional catalysis. Even though oxidation is a base catalysed reaction, the presence of acid sites could be a factor of importance. The increase in catalytic activity of several transition metal oxides for the selective oxidation reactions have been considered in the light of their acid-base properties. High valent incompletely coordinated metal ions or anionic vacancies on oxide surface can be considered as acidic sites and oxygen ion (O_2^-) as basic sites. A significant influence of the acid-base properties of the transition metal oxides in their selectivity in the oxidation reactions have been reported in several studies [18,19]. It has been reported that the presence of acid sites of moderate strength fovour the deep oxidation of acrolien [20]. The influence of acidity exhibited by the metal ions in determining the rate of reaction has also been explained [21]. The role of acid-base properties of the reactants, products and catalyst in the partial oxidation of C_4 hydrocarbons has been studied by Ai and coworkers [22, 23], where the acid-base properties of the catalysts were determined by various physico chemical methods. The interaction between reactant with catalyst can be considered as a weak base-strong acid or weak base-weak acid interaction [24,25]..Since the bond between a strong acid and weak base cannot be strong , it seems that an increase in the acidic properties of a cation leads to a weakening of the interaction with the reactant and the selectivity of the oxidation thus likely to be improved. The exposed oxide ions adjacent to the metal ions constitute the acid base pair sites.

In the case of zirconia-yttria mixed oxide systems, all oxides irrespective of composition gave 100 % conversion at 300°C. In the case of these oxides the reaction is found to completed within one hour. This itself indicates the high activity of basic sites as a decisive property for determining the catalytic activity. The data are given in Table 6.7a Mixed oxides gave higher activity compared to component oxides. The catalytic properties of a metal oxide combination depend up on the acid base property, composition and activation temperature[26]. It has been reported that [27] the acid base property of mixed oxides can be varied by encapsulating the metal oxides with different constituents at different concentrations and by changing the pretreatment of the sample. The change in activity with increase in temperature seems to be partially due to small amount of basic site and partially due to basic strength being weakened by the electron shift to the neighboring

Table 6.7a. Activity of the oxides

Catalyst (% of Y_2O_3)	Activation temperature	Conversion (%)	Activity 10^{-5} min m^{-2}
20	300	58.41	2.456
20	500	84.00	2.301
40	300	83.00	4.316
60	300	78.63	3.291
80	300	58.64	4.262

Catalyst 0.5g, Time 25 min., Temperature 110°C.

strong acid site. The sensitivity of the oxidation reaction rate with the change in catalyst pretreatment temperature indicates that the surface concentration or relative activity of sites utilized during the pathway are affected appreciably by variation in thermal treatment.

The pronounced changes in activity rates suggest that the number/or activity of most active sites used for the reaction changed with the activation temperature. The observed effect may be caused by one or more of several possible thermally induced phenomenon including crystallographic transformation of residual surface hydroxyl or fundamental alterations in the chemical or structural nature of the active sites.

6.3.3. ESTERIFICATION OF BUTANOL

The esterification of carboxylic acids is a straight forward reaction subjected to Bronsted acid catalysis. Conventional method used sulfuric acid as a catalyst. The yields are high but traces of sulfuric acid is detected along with the ester, which finds tedious work procedures in the isolation of products. The use of heterogeneous catalysts for the esterification have been reported [28]. The presence of acid sites in the catalyst are good potential for the application in Bronsted catalysis for esterification. The use of solid acid catalysts such as α-zirconium molibdate has been reported to be a selective catalyst for esterification [29].

Table 6.11. Catalytic activity for esterification of n-butanol using ZrO_2-Y_2O_3 mixed oxides.

Catalyst (Y_2O_3)	Activation temperature (°C)	% conversion	Rate constant (10^{-5} m^{-1} m^{-2})
0	300	2.80	-
0	500	10.53	0.6032
0	800	13.00	-
20	500	8.54	0.2432
40	500	8.80	0.2593
60	500	28.40	0.9119
80	500	7.80	0.2497
100	300	6.30	0.4673
100	500	1.34	0.0512
100	800	-	-

Table 6.12. Catalytic activity for esterification of n-butanol using ZrO_2-Dy_2O_3 mixed oxides

Catalyst (% of Dy_2O_3)	Activation temperature (°C)	% conversion	Rate constant (10^{-5} m^{-1} m^{-2})
0	300	2.8	0.0456
0	500	10.53	0.6032
0	800	-	1.7800
20	500	7.40	0.2186
40	500	13.14	0.4318
60	500	0.28	0.9348
80	500	4.90	0.3936
100	300	3.17	0.5194
100	500	1	0.0235
100	800	-	-

Table 6.13. Catalytic activity for esterification of n-butanol using ZrO_2-Gd_2O_3 mixed oxides

Catalyst (% of Gd_2O_3)	activation temperature (°C)	% conversion	Rate constant (10^{-5} m^{-1} m^{-2})
0	300	2.8	0.0456
0	500	10.53	0.6032
0	800	13.00	1.7800
20	500	3.6	0.7498
40	500	8.11	0.2785
60	500	8.10	0.4003
80	500	5.16	0.4096
100	300	-	-
100	500	-	-
100	800	-	-

ZrO_2 has been recognized as a refractory oxide which possess both acidic and basic sites. It has been reported that surface of ZrO_2 is associated with strong acid sites and weak basic sites [30]. Incorporation of rare earth oxides into zirconia increased the basic character. The mixed oxides are more basic at lower activation temperatures. The acidic sites are generated only at higher temperature due to the charge imbalance localized on M_1-O-M_2 bonds. The esterification data of oxides are given in Tables 6.11 to 6.13

The reaction parallels with the acid base properties. The reverse order of the basicity is found in the reaction. The order of activity of esterification is $ZrO_2 > Y_2O_3 > Dy_2O_3 > Gd_2O_3$. In the case of Gd_2O_3 the reaction is negligible and there is no reaction at higher temperatures. The variation of activity with composition is given in figure 6.13.

For the metal oxides, the activity parallels with the activation temperature and acidity. In the case of ZrO_2 the activity increases with increase in temperature while for rare earth oxides the activity decreases. In the case of rare earth oxides the activity is higher at lower temperature. As the temperature is increased the basicity of rare earth oxides increased whereas the acidity of ZrO_2 also increases with increase in temperature. The variation of catalytic activity of the oxides for esterification reaction is given in figure 6.14.

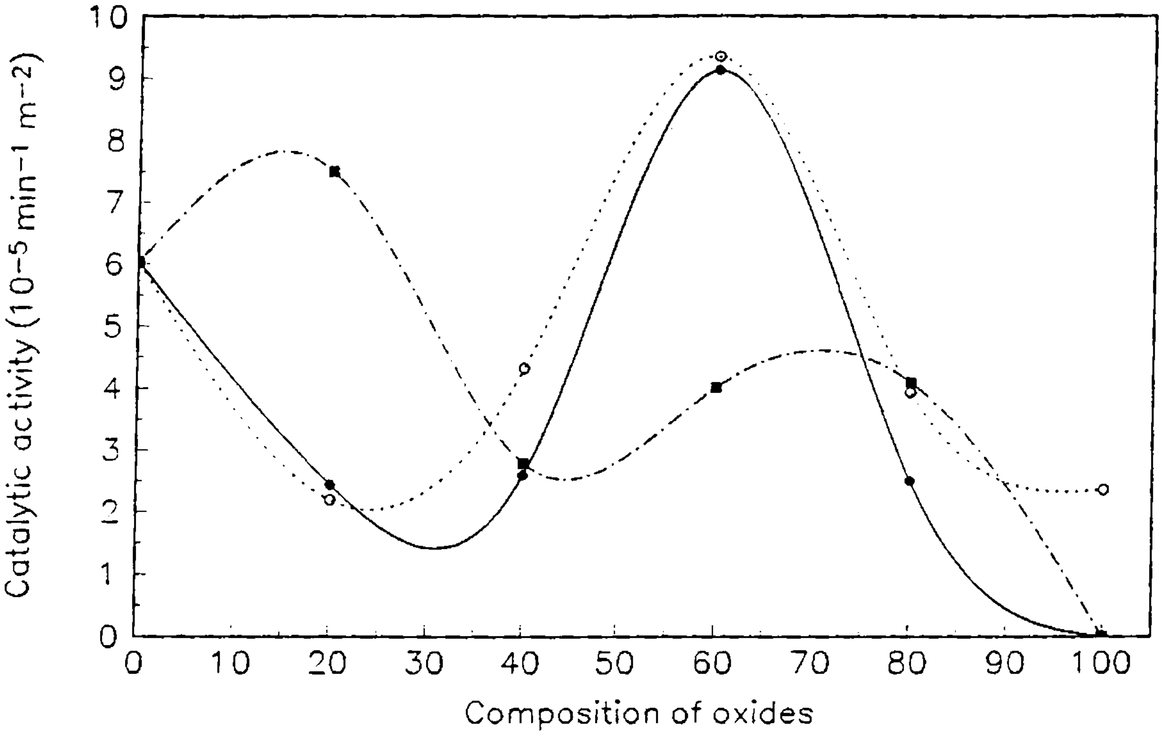


Fig 6.13 Catalytic activity of mixed oxides for the esterification of n-butanol with acetic acid as a composition at 500 °C

[ZY-ZrO_2-Y_2O_3 mixed oxides, ZG-ZrO_2-Gd_2O_3 mixed oxides] ZD- ZrO_2-Dy_2O_3 mixed oxides

[●] ZY -500°C [○] ZD-500°C [■] ZG-500°C

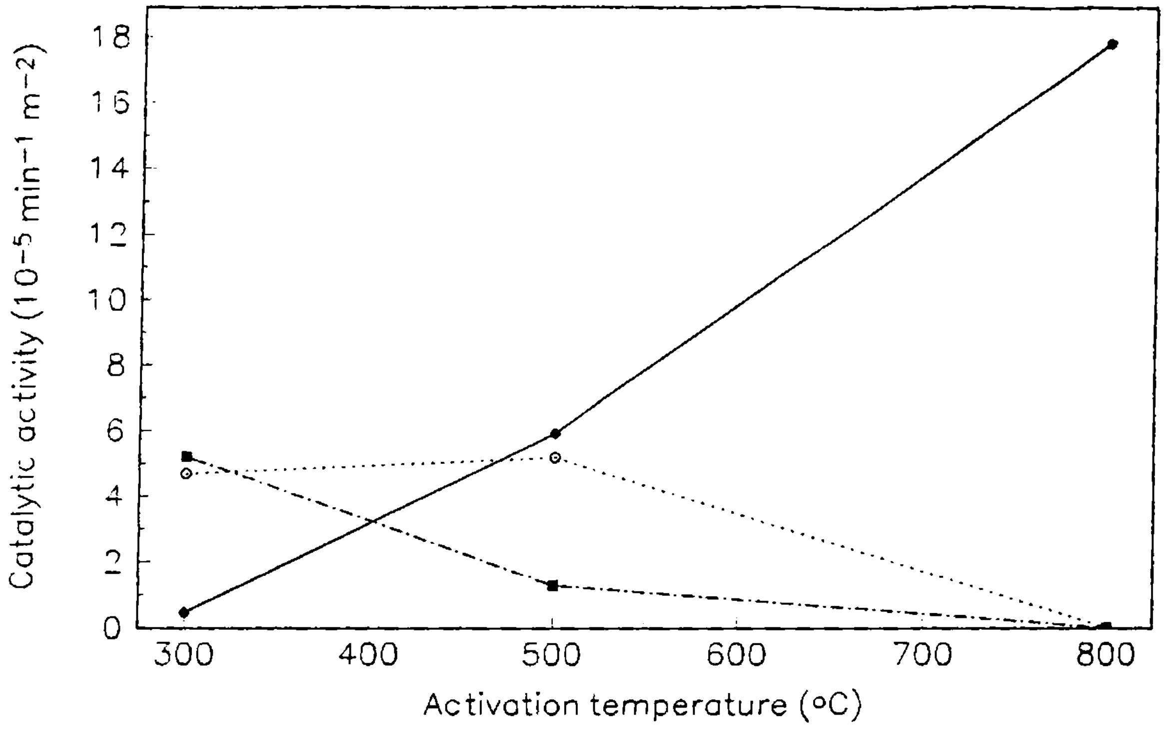
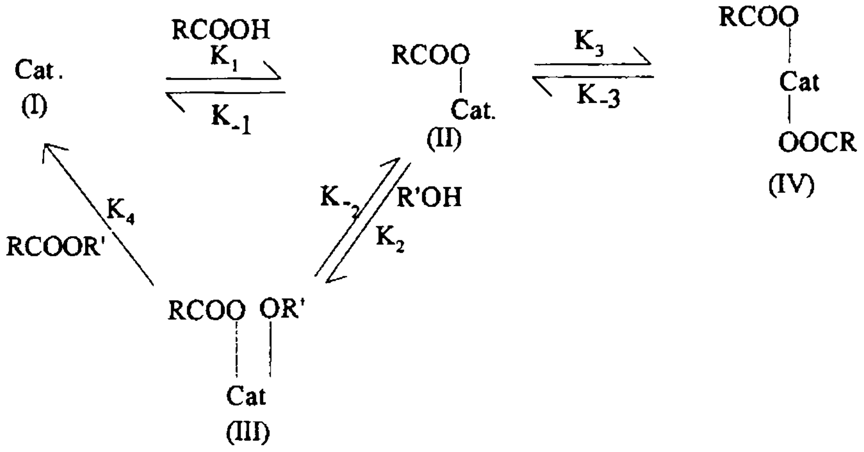


Fig 6.14 Catalytic activity of metal oxides for the esterification of n-butanol

[●] ZrO_2 [■] Y_2O_3

[○] Dy_2O_3

The low activity of esterification suggests that the surface of oxides is preferably associated with basic sites. Acid sites are scarcely formed at Ho value of 7.2. The mechanism proposed for the esterification reaction is given in scheme 3. [31]. The rate determining step is the step subsequent to the adsorption of the carboxylic acid and alcohol on the surface. The kinetic result shows the last step constitutes the rate determining step.



The increase in basicity of rare earth oxides is due to the generation of new basic sites as a result of desorption of trapped ions like nitrate, carbonate etc. formed during preparation and handling of catalyst and dehydroxylation at high temperatures [32]. But ZrO_2 being acidic oxide is incapable of forming basic nitrates and carbonates and no effects due to the decomposition of these ions have been expected.

REFERENCES

1. G.Brieger and J.J.Nectric, *Chem. Rev.*, **74**, 567 (1974).
2. M.Shibagaki, K.Takahashi and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **61**, 3283 (1988).
3. S.Sugunan, S.Kurur and A.Paul, *Indian J. Chem.*, **33A**, 1096,(1994).
5. H.Kuno, K.Takahashi, M.Shibagaki and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **64**, 312 (1991).
6. Ibid, **63**, 1943 (1990).
7. K.Takahashi, M.Shibagaki, H.Kuno and H.Matsushita, *Chem. Lett.*, 1141 (1989).
8. C.L.Kibby and W.Keithhall, *J. Cat.*, **31**, 65 (1973).
9. M.Shibagaki, H.Kuno, K.takahashi and H.Hattori, *Bull. Chem. Soc. Jpn.*, **61**, 4153 (1988).
10. M.Shibagaki, K.Takahashi H.Kuno and H.Matsushita, *Bull. Chem. Soc. Jpn.*, **63**, 258 (1990).
11. Davis "*In adsorption and Catalysis on oxide surface*", ed., M.Che and G.C.Bond, *Stud. Surf. Sci. Catal.*, Amstrdam, Vol.**21**, p. 309 (1985).
12. Kirk Othmer, *Encyclopeadia of Chemical Technology*, Johnwiley and Sons, Interscince, Vol.7, p.410, (1979)
13. S.Reddy, B.M.Rao and P.K.Rao, *Appl. Catal.*, 45 (**1**), L-11 14, (1988).

14. S.B.Oake, A.K.Varshney, M.A.Sidddique and M.H.Mehita, "*in Recent Developments in Catalysis*", theory and practicals, ed., B.Viswanathan and C.N.Pilli, Narosa Pubn, p. 373 (1990).

15. S.Sugunan and J.J.Malayan, *React. Kinet. Cat. Lett.*, **55(2),** 3283 (1995).

16 O.V.Krylov and E.A.Fokina, *Proceedings of the ivth international congress on catalysis*, Moscow (1968).

17. C.P.Bezouhanove and E.Echiyoga, *Bull. Chem. Soc. Jpn.*, **45**, 245 (1991).

18. D.B.Dadyburjor, S.S.Jewus and E.Ruckenstair, *Cat. Rev. Sci. Eng.*, **19**, 293 (1979)

19. B.Grzybowska, in B.Imlelik, C.Naccache, G.Coudenser, Y.B.Taant and J.C.Vendrin, (eds), *Catalysis by acids and bases*, Elsevier, Amsterdam, p.45 (1985).

20. Yu.Belokopytov, K.M.Kholyyovalent and M.Ya. Rubanik, *Kin. I Katalysis* (Russian),**14**, 1280 (1973).

21. T.Seiyama, M.Egashira, T.Sakamoto and I.Aso, *J. Cat.* **24**, 76 (1972).

22. M.Ai, *Bull. Chem. Soc. Jpn.*, **44**,761 (1971)., **49**, 1328 (1976).

23. M.Ai and S.Susuki, Bull. Chem. Soc. Jpn., **46**, 321 (1971), **46**, 1208 (1973)., **43**, 3074 (1974).

24. J.E.Germain, *Intra-Science Chem. Report*, **6** 101 (1972)

25. L.Ya. Margulus, and A.A.Firsowa, *Prob. Kinet. Catal. Russ.*, **16**, 98 (1975).

26. H.Hattori, M.Misono. N.Ono. and K.Tanabe, "*New Solid Acids and Bases*" Kodansha, New York (1989) .

27. K.Tanabe *"In catalytic Sci. And Technology,* Springer Verley, New York, 231 (1989).

28. A.Sivasankar and U.Chadasamma, in B.Viswanathan and C.N.Pilli,*"in recent development in catalysis," Theory and Practicals,* Narosa Pubn., New Delhi, p.489 (1990).

29. T.Hattori, A.Ishigura and Y.Muragakami, *J. Inorg. Nucl. Chem.,* **40**, 1107 (1978).

30. T.Yamaguchi and K.Tanabe, Chem. Lett., 1017 (1973).

31. S.Sugunan and V.Meera, *Colle. Czech. Chem. Comm.,* **59**, 2604 (1994).

32. H.Hattori, K.Murayama and K.Tanabe, *J.Cat.*, 44, 50 (1974)

CHAPTER 7

SUMMARY AND CONCLUSIONS

SUMMARY

The contents of the thesis has been divided into six chapters.

Chapter 1 of the thesis deals with the general introduction of ZrO_2 and rare earth oxide systems. Their relevance in catalysis field has been reviewed.

Chapter 2 of the thesis aim at the review of the important surface properties of the oxides namely, electron donor/acceptor properties, acid-base properties and catalytic activity of oxides. The detailed review of each properties have been given with corresponding references at the end of the chapter. In addition to these, the consequences of ZrO_2 and rare earth oxides as catalysts have been also included in this chapter.

Chapter 3 deals with the experimental methods adopted for the thesis works. Experimental part contain the preparation of oxides and characterisation of the oxides by using different techniques. The oxides were prepared by hydroxide method at constant pH. The experimental details used for the detrmination of electron donor, acid/base and catalytic properties of the oxides have also been discussed.

Chapter 4 deals with the results of surface electron donor properties of the mixed oxides of ZrO_2 with rare earth oxides. The electron donor properties were studied by the adsorption of different electron acceptors with various electron affinity values ranging from 1.26 to 2.84 eV. The adsorption of electron acceptors were confirmed by the esr studies and electronic spectral studies of the electron acceptor adsorbed on samples. The adsorption of electron acceptors on the surface of the oxides were correspond to the Langmuir adsorption isotherms and verified by the linear form of Langmuir plots. The mixed oxides were found to be possessed by electron donor sites of varying strength and showed variation with activation temperatures.

Chapter 5 deals with the quantitative determination of acid-base properties of metal oxides and mixed metal oxides by titration methods using Hammett indicators. Non aqueous titration method was employed. The colour of the adsorbed indicators can give the measure of acid-base strength of the sites on the surface of the solids. Titration methods provide differentiation of acid -base site of different strength, energy and amount. With this titration methods weak sites can be detected.

Chapter 6 deals with the catalytic activity of oxides for different organic reactions namely, reduction of cyclohexanone in 2-propanol, oxidation of cyclohexanol with benzophenone and esterification of acetic acid with butanol. The oxides were found to be effective for reduction and oxidation, but not for esterification reaction. The former reactions were favoured by the presence of basic sites, especially reduction of cyclohexanone. The three reactions were carried out in liquid phase. The reduction of cyclohexanone was followed by means of UV-visible spectrophotometer and oxidation and esterification reactions were analysed by gas chromatograph. The activity has been reported as the first order rate coefficient of reaction. The mechanisms of the reactions have been discussed. The activity of the oxides parallel with the acid - base properties.

CONCLUSIONS

Results and discussions of the thesis work can be concluded as:

1. The surface of the oxides are associated with electron donor sites of different strength. The electron donor property of oxides depend upon the activation temperature, electron affinity values of the electron acceptors, basicity of the solvent and composition of the oxides. The surface electron donor properties of the oxides depend upon the amount of ZrO_2 phase or rare earth oxide phase present on the surface at a particular activation temperature. The limit of electron transfer is between

1.77 eV and 2.40 eV. That is the surface can act as electron donor sites to the adsorbed electron acceptor molecules with electron affinity value of above 2.40 eV and not below 1.77 eV. The electron donor power of the oxides increases with basic strength of the surface. The electron donor sites of the mixed oxides have the same strength at all temperatures and the number of sites decreases. But the strength of rare earth oxides increases with increase in temperature.

2. Acidity/basicity of oxides determined at different strengths gives an idea of significant distribution of acid-base sites on the surface. No acid-base sites of equal strength has been reported. The maximum number of basic sites is found at H_o value of 3.3. Pretreatment temperature is a factor of importance for the generation of acidic sites. As the temperature is increased, the basicity decreases due to the generation of acidic sites. No acid sites were reported at H_o value of 3.3. $H_{o,max}$ values parallel with the electron donor strength of the oxides, i.e. the order of basic strength parallels with the order of electron donor strength.

3. The mixed oxides obtained by the incorporation of rare earth oxides into zirconia gave good results for the activity towards different reactions. Activity of the oxides for oxidation of cyclohexanol is found high compared to the reduction of cyclohexanone. Both reactions are preferentially favoured by basic sites. Reduction of cyclohexanone is a fully base catalysed reaction while the presence of acid sites are enhancing the activity of oxidation reaction. Oxidation of cyclohexanol can be considered as a bifunctionally catalysed reaction of strong basic sites and weak acidic sites. Low activity of oxides for esterification of acetic acid with butanol which is a perfectly Bronsted acid catalysed reaction, infers the lack of strong donor sites. The potentiality of the oxides for the base catalysed reactions (reduction and oxidation) indicates that most of the surface sites of the oxides are basic in character.

Thus incorporation of rare earth oxides into zirconia increased the basic character which is reflected in the catalytic activity of oxides.