

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

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ANTO PAUL


DEPARTMENT OF APPLIED CHEMISTRY
COCHIN UNIVERSITY OF SCIENCE AND TECHNOLOGY
KOCHI - 682 022, INDIA

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*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.



Dr. S .Sugunan
(Supervising Teacher)
Professor in Physical Chemistry
Department of Applied Chemistry
Cochin University of Science and Technology

Kochi -22.
27-11-'97.

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.

Anto Paul

ANTO PAUL

Kochi
27-11-'97

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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 recognised 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 exist simultaneously on the surface. It was argued that these dual acid-base sites could provide new routes for reactions involving a dual site mechanism. In addition, considerable interest has been directed to the possible correlation between catalytic activity and acidic/or basic properties of 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 of 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
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6. Cyclohexanol conversion as a measure of strength of basicity of ZrO_2 - Y_2O_3 mixed oxides.
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7. Basicity and catalytic activity of ZrO_2 - Dy_2O_3 mixed oxide systems.
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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.

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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.

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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
-

ZrO₂ 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 ZrO₂ 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 [Al₂O₃ and SiO₂). The advent of partially and fully stabilised ZrO₂ 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_{1s} 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+} (1.06\AA) to Lu^{3+} (0.85\AA) 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 promoters or supports in catalytic reactions has grown extensively in past few years, due to its interesting properties encountered 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 opportunity 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 valence 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 valence 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_0 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.

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CHAPTER 2

REVIEW

2.1. ELECTRON DONOR-ACCEPTOR PROPERTIES

The formation of radical ions on the surface by electron 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 from 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

