CHAPTER 4.

ACID-BASE, SURFACE ELECTRON DONATING & CATALYTIC PROPERTIES OF PRASEODYMIUM - ZIRCONIUM MIXED OXIDES.
Zirconia is reported as an excellent catalyst [1,2], and very good supporting material [3], for many reactions. It shows both acidic and basic properties, the addition of basic oxides (La) suppress the acidic behaviour whereas addition of an acidic oxide promotes acidic property [4]. Sulfated zirconia is known as a superacid and it is shown [5] to be a better acid catalyst than Amberlyst-15. Rare earth oxides, are basic and can act as effective catalysts for a number of reactions [6]. Praseodymia, one among the rare earth oxides is a nonstoichiometric, paramagnetic oxide having Pr in +3 and +4 oxidation states in the ratio 1:2. Due to its nonstoichiometric nature it has intrinsic oxygen vacancies [7] and a higher amount of chemisorbed oxygen on its surface. The lattice oxygen atoms in Pr$_6$O$_{11}$ play a major role in its catalytic activity [8]. So far no attempt has been made to study the effect of mixing of ZrO$_2$ with Pr$_6$O$_{11}$ on their surface properties. In this chapter the acid/base properties, surface electron donor properties and the catalytic activity of Praseodymium - Zirconium mixed oxides are reported at various compositions at an activation temperature of 500°C.

The acid/base and surface electron donating properties and the catalytic activity of Praseodymium - Zirconium mixed oxides at various compositions at an activation temperature of 500°C were studied. The mixed oxides with various compositions, Viz. 20, 40, 60 and 80% of the rare earth oxide were studied. For comparison pure oxides were also incorporated in the study. The mixed oxides were
prepared through the hydroxide route. The hydroxides were precipitated by adding 1:1 ammonia to a solution containing calculated quantities of praseodymium nitrate and zirconyl nitrate. The precipitate is then thoroughly washed free from nitrate ions and dried at 120° C, then calcined at 300° C for two hours to get the oxide. The calcined samples were then sieved to get oxides with 100-200 mesh size. The mixed oxides with various compositions (Viz. 20, 40, 60 and 80 % (abbreviated as 20 Pr, 40 Pr, 60 Pr and 80 Pr) of the rare earth oxide were prepared. Pure oxides were also prepared in the same fashion. All the oxides were heat treated at a particular temperature, namely 500°C for two hours prior to each experiment. All the reagents were purified by standard methods (Ref. chapter 2) before use. The catalytic activities have been correlated with electron donating properties and surface acidity/basicity of the oxides.

4.1 Surface areas

Surface areas of Pr₆O₁₁ is very small compared to that of ZrO₂ (Table 4.1 and Figure 4.1). On mixing the oxides the surface areas are increased. The surface area of ZrO₂ is almost doubled by addition of 20 % Pr₆O₁₁ to it. For all the mixed oxides, the surface areas are more than the pure component oxides, it is maximum for 20 Pr.
4.2 Electron Donor Properties

The strength and distribution of electron donor sites are determined from the studies on the adsorption of electron acceptors (EA) of various electron affinity in acetonitrile, a solvent with low basicity. The following electron acceptors used are given in chapter 3, table 1.

The adsorption studies were carried out by a procedure reported earlier [9]. The amount of electron acceptor adsorbed was determined by noting the concentration of the electron acceptor before and after adsorption by means of a UV-Visible spectrophotometer at the \( \lambda_{\text{max}} \) of the EA in acetonitrile, i.e. at 393.5, 288, 262 and 237 nm for TCNQ, Chloranil, PDNB and MDNB respectively.

The adsorption of EA on the oxides were of Langmuir type. From the Langmuir plots (Figure 4.2 & 4.3) the limiting amount of EA adsorbed were determined (Table 4.1). In the case of PDNB and MDNB, adsorption was so negligible that the amount could not be detected by spectrophotometric method. When EA were adsorbed, the surface of the oxides showed characteristic coloration owing to the interaction between the EA adsorbed and the oxide surface, [9] (for dark colored oxides the coloration was not detectable by visual method). The electron donor property of pure praseodymia is less than that of zirconia. Highest value for electron donating capacity is shown by 80 Pr followed by 60 Pr and then 20 Pr, which are higher than that of the pure oxides. 40 Pr is having lower electron donating power than
the pure component oxides. In the case of chloranil adsorption also the same trend is followed, all the values being less than that for TCNQ. The extent of electron acceptor adsorption depends on the electron affinity of the electron acceptor and on the composition of the mixed oxide. The nature of the adsorbed species was studied by ESR and Reflectance spectra of the adsorbed samples.

The limiting amount of TCNQ adsorbed is a measure of the total number of electron donor sites on the surface. The extent of electron transfer depends on the electron affinity of the acceptor. Two possible electron sources exist on the oxide surface capable of electron transfer, namely electrons trapped in intrinsic defects and surface hydroxyl ions [10]. It has been reported at higher activation temperatures the donor sites consists of a co-ordinatively unsaturated $O^{2-}$ associated with a nearby OH group and the concentration of these sites is related to the base strength of the surface [11]. The more basic the surface the higher is the number of $O^{2-}$ which can transfer electrons to the EA.

4.3 Acid- Base Properties

The surface acidity/ basicity of the oxides were determined by titration method using the same set of Hammett indicators [12] given in chapter 3, table 2. The oxides under study responded only to dimethyl yellow, methyl red and bromothymol blue. The surface acidity/ basicity of the dark colored oxides were determined by a
modified procedure [13]. It was done by comparing the acidity/ basicity of the combination of the oxide with a white standard oxide material with the standard oxide.

The acid/ base strength distribution of the oxides were measured on a common H₀ scale [14] (Table 4.2). The acid-base properties of Pr-Zr mixed oxides change with composition of the mixed oxide. Pure ZrO₂ is having both acidic and basic sites. Praseodymia is having only basic sites. The acidity and basicity of the mixed oxides are intermediate between those of the pure component oxides. The acid/base strength distribution curves (Figure 4.5) intersect at a point on the abscissa where acidity = basicity = 0 [14]. The point of intersection is defined as H₀,max. It can be regarded as a practical parameter to represent acid/base properties on solids. A solid with a large positive H₀,max value has strong basic sites and weak acid sites and a solid with a large negative H₀,max value has strong acid sites and weak basic sites.

Pr₆O₁₁ is a mixture of two crystalline forms, the C (body centered cubic, coordination number of cation 6) and A (distorted hexagonal, coordination number of cation 7) forms which are prominent in the rare earth oxides, the amount of each form being varying [15]. According to Tanabe’s model [16], Pr³⁺ in cubic form when mixed with zirconia will not generate acidity, but in the A form it can generate acidity on mixing. The A form is prominent at higher temperatures. Praseodymia itself is a mixture of Pr³⁺ and Pr⁴⁺, and there will be a small amount of intrinsic acidity.
in it, which will not be much affected by the addition of Zr$^{4+}$. Acidities present in the mixed oxides are only the sum of their components or slightly more.

### 4.4 Catalytic activity measurements.

The catalytic activity of the mixed oxides for three reactions Viz. reduction of cyclohexanone, oxidation of cyclohexanol and esterification of acetic acid with n-butanol were studied (See Table 4.3). The catalytic activity is expressed as the first order rate constant per m$^2$ of the oxide surface.

The rate constant for the reduction is very small when catalysed by praseodymia. Zirconia is having a higher value for activity than praseodymia. All the mixed oxides are having higher activities than the pure oxides. The activity is the highest for 40 Pr. The active sites for the reduction reaction is still uncertain. Shibagaki et al proposed a mechanism involving the adsorption of ketone and alcohol on the oxide surface [17] (See section 3.2.4).

It is an acid-base bifunctional catalysis. The activity can depend on the amount of acid/base sites, if they are very small in number the availability of the particular type of site determine the rate of the reaction. For a sufficiently basic oxide, the rate of reaction may depend on the amount of acid sites coexisting with the basic sites and vice-versa. The active sites for the reaction may be surface OH$^-$, O$^{2-}$ or lattice disorders such as trapped electrons formed in the system. The latter two increase in concentration at high activation temperatures. Surface O$^{2-}$ are formed by
sintering of surface OH-. The catalytic activity showed dependence on both the surface acidity and basicity, however the relationship is not straight forward. The lack of a linear relationship between activity and basicity implies the involvement of acid sites also in the reaction, the exact nature being unknown [11].

Praseodymia is having a very high value of rate constant for the oxidation of cyclohexanol. This can be due to the availability of lattice oxygens [7] (high mobility through the intrinsic oxygen vacancies) to take part in the reaction or due to the presence of chemisorbed oxygen [8] on its surface. The activity is more for Pr6O11 than that for zirconia. The mixed oxides are having lower values of catalytic activity than pure praseodymia and zirconia. Sites which catalyse the oxidation reactions are not generated on mixing the two oxides.

Praseodymium oxide does not catalyse the esterification reaction while zirconia catalyses the same reaction. Esterification reaction is a typical acid catalysed reaction, zirconia having a polyfunctional behaviour, have acid sites on it. All the mixed oxides catalyse the esterification reaction but the activity is less than that for zirconia. Among the mixed oxides 40 Pr and 60 Pr are having higher activity than 20 Pr and 80 Pr. In 40 Pr and 60 Pr (both having the higher amount of Pr-O-Zr bonds than 20 Pr and 80 Pr) have higher amount of acidity associated with them and will catalyse the esterification reaction more effectively.
Table 4.1. Surface areas & Limiting Amounts of Electron Acceptors Adsorbed on Praseodymium-Zirconium Mixed Oxides activated at 500°C

<table>
<thead>
<tr>
<th>Weight % of Pr$<em>6$O$</em>{11}$</th>
<th>Surface Areas m$^2$ g$^{-1}$</th>
<th>Limiting amount Adsorbed 10$^{-6}$ mol /sq.m</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>TCNQ</td>
</tr>
<tr>
<td>0</td>
<td>61.50</td>
<td>2.081</td>
</tr>
<tr>
<td>20</td>
<td>127.56</td>
<td>2.138</td>
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<td>40</td>
<td>101.59</td>
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<tr>
<td>100</td>
<td>11.40</td>
<td>0.744</td>
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</table>
4.2. Acid-Base Strength Distribution on Praseodymium-Zirconium Mixed Oxides activated at 500°C

<table>
<thead>
<tr>
<th>Weight % of Pr₆O₁₁</th>
<th>Basicity $10^{-3}$ m mol m⁻²</th>
<th>Acidity $H_o$</th>
<th>$H_o \geq 3.3$</th>
<th>$H_o \geq 4.8$</th>
<th>$H_o \geq 7.2$</th>
<th>$H_o \leq 7.2$</th>
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<tr>
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<td>2.738</td>
<td>4.89</td>
<td>2.745</td>
<td>4.89</td>
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<td>4.89</td>
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<tr>
<td>20</td>
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<td>2.431</td>
<td>6.05</td>
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Table 4.3. Catalytic activity of Praseodymium-Zirconium mixed oxides Activated at 500°C

<table>
<thead>
<tr>
<th>Weight % of Pr$<em>6$O$</em>{11}$</th>
<th>Reduction of Cyclohexanone</th>
<th>Oxidation of Cyclohexanol</th>
<th>Esterification Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>% conversion</td>
<td>Rate Constant ($10^7$ s$^{-1}$ m$^{-2}$)</td>
<td>% conversion</td>
</tr>
<tr>
<td>0</td>
<td>11.05</td>
<td>1.320</td>
<td>87.24</td>
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<tr>
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<td>2.321</td>
<td>89.20</td>
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<td>34.25</td>
<td>2.867</td>
<td>91.75</td>
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<td>60</td>
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<td>1.653</td>
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<tr>
<td>100</td>
<td>1.10</td>
<td>0.612</td>
<td>95.59</td>
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</tbody>
</table>
Figure 4.1
Surface areas of Pr-Zr Mixed Oxides
Activated at 500°C

Figure 4.2
Adsorption isotherms of TCNQ on Pr-Zr
Mixed oxides activated at 500°C

Figure 4.3
Limiting Amounts of Electron acceptors
adsorbed on Pr-Zr mixed oxides activated
at 500°C as a function of composition

Figure 4.4
Adsorption isotherms of Chloranil on Pr-Zr
Mixed oxides activated at 500°C
Figure 4.5
Acid-Base Strength Distribution on Pr-Zr mixed oxides activated at 500°C as a function of composition

Figure 4.6
Acid-base strength distribution on Pr-Zr Mixed Oxides Activated at 500°C as a function of composition

Figure 4.7
$H_{o,max}$ Values of Pr-Zr mixed oxides activated at 500°C as a function of composition

Figure 4.8
Catalytic activity for Reduction of cyclohexanone on Pr-Zr mixed oxides activated at 500°C as a function of composition
Figure 4.9  
Catalytic activity for Oxidation of cyclohexanol on Pr-Zr mixed oxides activated at 500°C as a function of composition

Figure 4.10  
Catalytic activity for Esterification of n-Butanol on Pr-Zr mixed oxides activated at 500°C as a function of composition
REFERENCES


121


