

Acid/ Base, Surface Electron Donating Properties And Catalytic Activity Of Praseodymium - Zirconium Mixed Oxides

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Abstract - 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 are reported. The catalytic activities for liquid phase esterification of acetic acid with n-butanol and reduction of cyclohexanone in isopropanol have been correlated with surface acidity/basicity of the oxides.

Index terms - Electron donating properties, Zirconia, Praseodymia, acidity, esterification

I. INTRODUCTION

Zirconia is reported as an excellent catalyst, and a very good supporting material [1-8], for many reactions. It shows both acidic and basic properties. The addition of basic oxides (La) suppresses the acidic behaviour whereas addition of an acidic oxide promotes acidic property [9]. Sulfated Zirconia is known as a super acid and it is shown [10] 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 [11]. 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 [12] and a higher amount of chemisorbed oxygen on its surface. The lattice oxygen atoms in Pr₆O₁₁ play a major role in its catalytic activity [13]. So far no attempt has been made to study the effect of mixing of ZrO₂ with Pr₆O₁₁ on their surface properties. In this paper the acid/base properties, surface electron donor properties and the catalytic activity of praseodymium - zirconium mixed oxides at various compositions (*viz.* 20, 40, 60 and 80 weight % of the rare earth oxide) at an activation temperature of 500°C were reported and the data were compared with those for pure oxides.

II. EXPERIMENTAL

The mixed oxides were prepared through the hydroxide route. The hydroxides were precipitated by adding 1:1 ammonia to a boiling solution containing calculated quantities of Praseodymium Nitrate and Zirconyl Nitrate. The precipitate was then thoroughly washed free from Nitrate ions and dried at 120°C. It was 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 500°C for two hours prior to each experiment. All the reagents were purified by standard methods before use. 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 were used: (electron affinity values in eV are given in brackets) 7,7,8,8-tetracyanoquinodimethane (TCNQ) {2.84}, 2,3,5,6-tetrachloro-1,4-benzoquinone (Chloranil) {2.40}, 1,4-dinitrobenzene (PDNB) {1.77} and 1,3-dinitrobenzene (MDNB) {1.26}. The adsorption studies were carried out by a procedure reported earlier [14]. 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 λ_{max} of the EA in Acetonitrile, i.e. at 393.5, 288, 262 and 237 nm for TCNQ, Chloranil, PDNB and MDNB respectively.

Surface area of the oxides were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The ESR spectra of the adsorbed samples were measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer. Radical concentrations were calculated by comparison of peak 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 reflectance spectra of the adsorbed samples were measured with a Hitachi 200-20 UV-visible spectrophotometer with a 200 - 0531 reflectance attachment. The surface acidity/ basicity of the oxides were determined by titration method using a set of Hammett indicators [15]; the pK_a values of the indicators are given in brackets. :-Crystal violet (0.8), Dimethyl yellow (3.3), Methyl red (4.8), Neutral red (6.8), Bromothymol blue (7.2) and 4-Nitroaniline (18.4). Of these 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 [16]. It was done by comparing the acidity/ basicity of the combination of the oxide with a white standard material. The catalytic activity of the mixed oxides for two reactions, viz. reduction of cyclohexanone and esterification of Acetic acid with Butyl alcohol were studied. The catalytic activity of the oxides for the reduction reaction were determined by the following method. 0.5 g of the oxide (100-200 mesh size) after activation, was placed in a 50 ml round bottomed flask equipped with a reflux condenser. 5 m mol cyclohexanone and 20 ml isopropanol were then added. The contents were heated under gentle reflux for 8 hours. The progress of the reaction was followed by noting the concentration of cyclohexanone before and after the reaction by absorbance measurements at the λ_{max} of cyclohexanone viz. 283 nm. The catalytic activity is expressed as the first order rate constant per m^2 of the oxide surface (Table 2). The esterification was carried out in a RB flask attached with a reflux condenser in which the catalyst (.5 g), acetic acid (2 m mol), n- butanol (32 m mol) and 2 drops of n-decane as an internal standard were added.

The contents of the flask were maintained at 98°C and stirred continuously on a magnetic stirrer for 4 hours. The progress

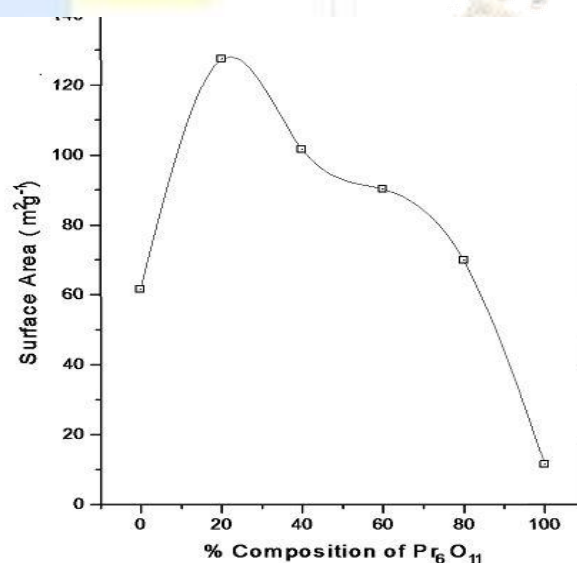


Figure1. Surface areas of Pr -Zr mixed oxides as a function of composition

of the reaction was studied by gas chromatographic analysis on a Chemito 8510 GC with an FID detector, by comparing the peak area of the product and the internal standard.

III. RESULTS AND DISCUSSION

Surface areas of Pr_6O_{11} is very small compared to that of ZrO_2 . On mixing the oxides the surface areas are increased. The surface area of ZrO_2 is almost doubled by addition of 20 % Pr_6O_{11} to it. For all the mixed oxides, the surface areas are more than the pure component oxides, it is maximum for 20 Pr.

On the surface of the oxides there will be a distribution of electron donor sites of various strengths. The electron donor strength of a metal oxide is the limiting electron affinity value of the electron acceptor for which free anion radical formation is not expected on the oxide surface. The distribution or the amount of electron donor sites of a particular strength is estimated by the amount of electron acceptor adsorbed on the oxide surface. For all the oxides studied, the amounts of PDNB and MDNB adsorbed were so negligible that the amount adsorbed could not be estimated by spectrophotometric method. For most of the oxides chloranil and TCNQ were adsorbed on the oxide surface and the electron donor strength lies in the range 1.77-2.40 eV in terms of the electron affinity of the acceptor. The adsorption isotherms are of Langmuir type, suggesting a chemical monolayer adsorption. It is verified by the linear plot of C_{eq}/C_{ad} against C_{eq} , where C_{eq} is the equilibrium concentration in mol dm^{-3} and C_{ad} is the amount adsorbed in mol per m^{-2} . The limiting amount of electron acceptors adsorbed, which corresponds to monolayer coverage, was determined from the Langmuir plots and are presented in Table 2.

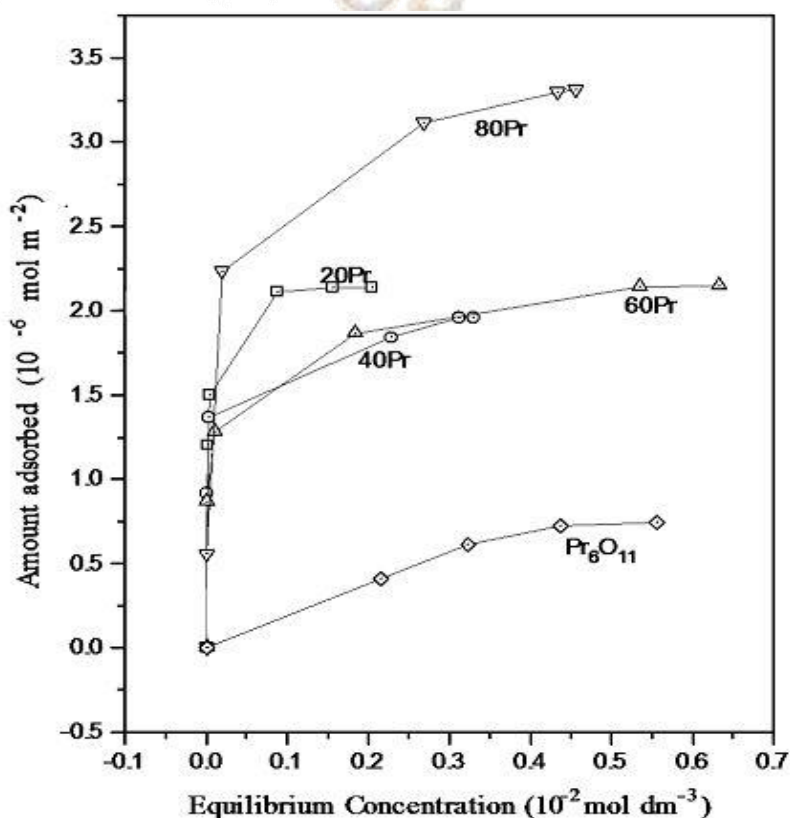


Figure 2 Adsorption Isotherms of TCNQ on Pr-Zr Mixed Oxides

When the electron acceptors were adsorbed on the oxide surface, the catalyst surface acquired a characteristic colouration owing to the interaction between electron acceptor adsorbed and the oxide surface [17]. Chloranil gave light to dark pink colour to the oxides and TCNQ gave dark green to bluish green colour to the oxides, the colour intensified with increase in zirconium content (for dark coloured oxides the colouration

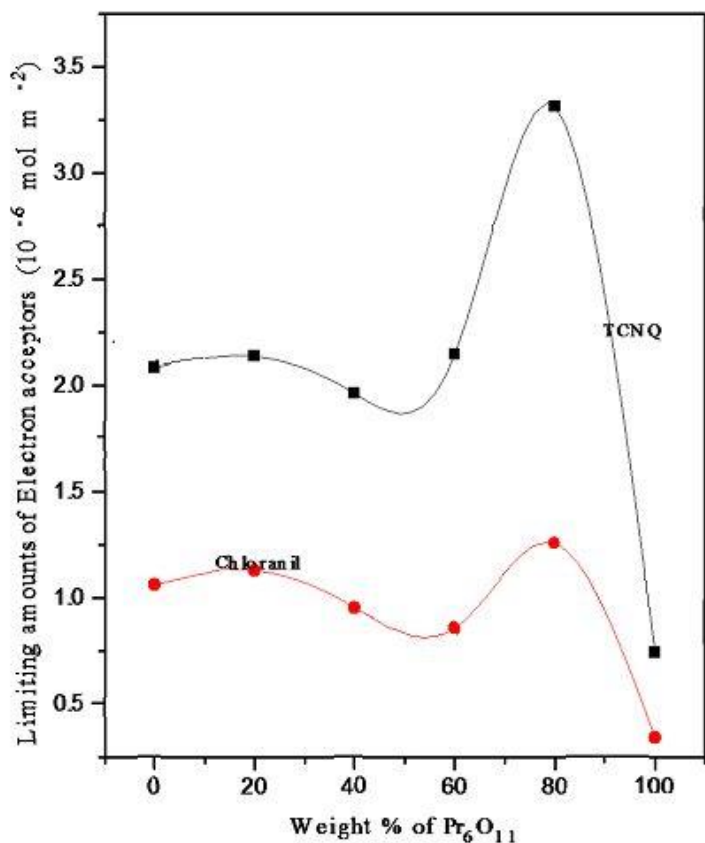


Figure 3 .Limiting amounts of TCNQ and Chloranil adsorbed on Pr -Zr mixed oxides as a function of composition

was not detectable by visual method). The ESR spectrum of these coloured samples gave unresolved spectral lines with g values of 2.003 and 2.011 for TCNQ [18] and chloranil [19] respectively, due to the hindered rotational freedom of the adsorbed species which obscures the hyperfine structure of the spectrum. The radical concentrations of TCNQ and chloranil adsorbed were calculated and plotted against equilibrium concentrations. The isotherms obtained were also of Langmuir type and of the same shape as the plot of the amount of electron acceptor adsorbed. The formation of radical species was also confirmed by reflectance spectra of the adsorbed samples.

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 an electron donating power in between the component oxides. In the case of chloranil adsorption again 80 Pr is having the highest value followed by 20 Pr. 60 Pr and 40 Pr are having values in between the component oxides, 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 limiting amount of TCNQ adsorbed on the surface is a measure of the total number of electron donor sites on the oxide surface. The amount adsorbed increases with increase in electron affinity of the electron acceptor. The strong electron acceptors like TCNQ and chloranil are capable of forming anion radicals even from weak donor sites whereas weak acceptor like MDNB are capable of forming anion radicals only at strong donor sites. Hence the limiting radical concentration and limiting amount of the weak acceptor adsorbed is a measure of the number of strong donor sites on the surface and that for a strong acceptor is the sum of all weak and strong donor sites on the surface. The extent of electron transfer depends on the electron affinity of the acceptor. It is found that the limiting radical concentration and the limiting amount adsorbed decrease with decrease in the electron affinity of the acceptor. The difference between the limiting amounts of TCNQ and Chloranil adsorbed on the metal oxides can serve as an indication of the number of weaker donor sites. Two possible electron sources exist on the oxide surface capable of electron transfer, namely electrons trapped in intrinsic defects and surface hydroxyl ions [14]. 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 [20]. The more basic the surface the higher is the number of O^{2-} which can transfer electrons to the EA.

The acid/ base strength distribution of the oxides were measured on a common H_0 scale [15] (Table 1). The acid/base strength distribution curves intersect at a point on the abscissa where acidity = basicity = 0 [21]. The point of intersection is defined as $H_{0,max}$, which can be regarded as a practical parameter to represent acid /base properties on solids. A solid with a large positive $H_{0,max}$ value has strong basic sites and weak acid sites and a solid with a large negative $H_{0,max}$ value has strong acid sites and weak basic sites. The acid-base properties of Pr-Zr mixed oxides change with composition of the mixed oxide. Pure ZrO_2 is having both acidic and basic sites. The acidity and basicity of the mixed oxides are intermediate between those of the pure component oxides. The surface acidity-basicity data revealed the presence of sites of different energies. It has been suggested that the acid-base sites on oxide surfaces are metal ions and O^{2-} ions on the surface and the site energy distribution is due to their presence in different coordinations. The lower coordinated ions are responsible for stronger acid/base sites [22]. The formation and annihilation of new acid-base sites on mixing oxides is attributed to the charge imbalance localized on $M_1 -O- M_2$ bonds formed in the mixed oxides, where M_1 is the host metal ion and M_2 is the added metal ion [20].

Table 1.

Acid-base strength distribution on Pr -Zr mixed oxides activated at 500°C

Weight % of Pr_6O_{11}	Basicity	Basicity	Basicity	Acidity	
	$(10^{-3} \text{ m mol m}^{-2})$				$H_{0,max}$
	$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 7.2$	
0	2.74	0.10	-	2.75	4.9
20	2.51	2.00	-	2.43	6.0
40	2.07	1.69	-	2.01	6.1
60	2.81	1.70	-	1.23	6.3
80	3.27	1.81	-	0.08	7.0
100	4.21	2.88	0.08	-	7.2

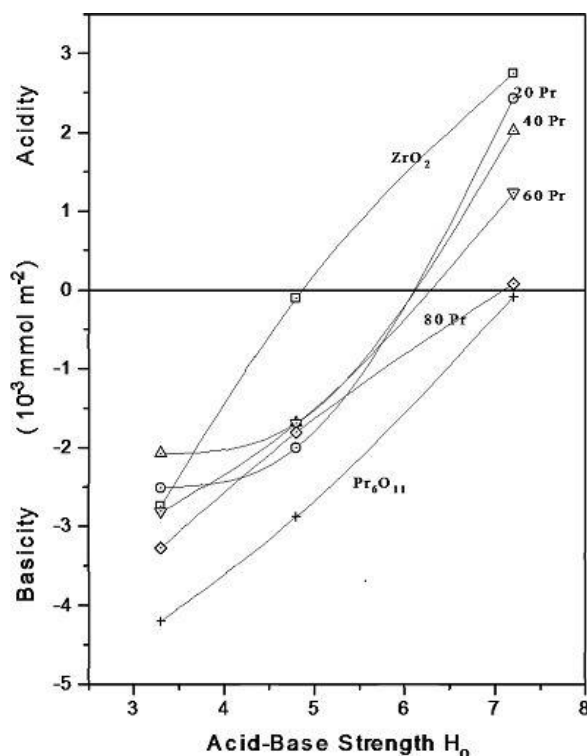


Figure 4. Strength and Distribution of Acid and base sites on Pr -Zr mixed oxides

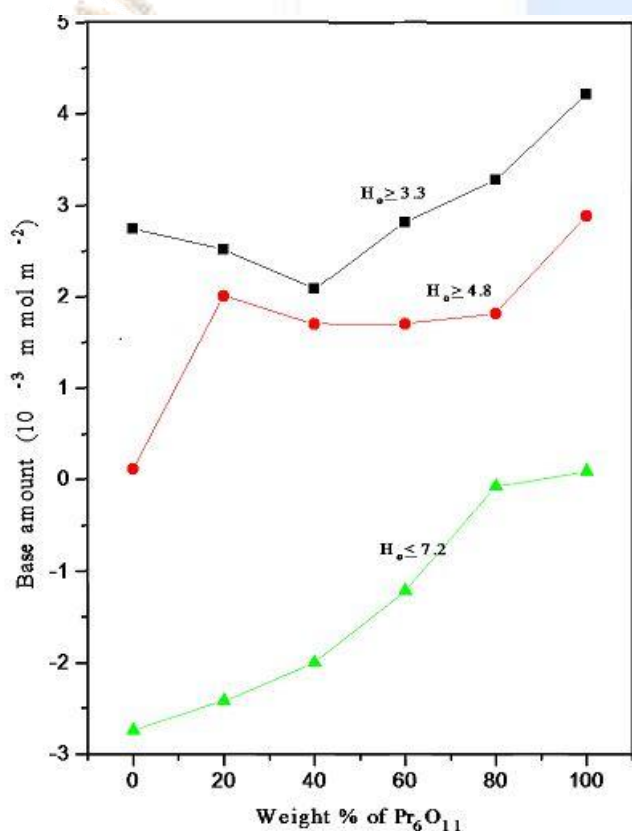


Figure 5. Catalytic activity of Pr -Zr mixed oxides towards reduction of cyclohexanone as a function of composition

According to Tanabe's hypothesis [24-26], acidity generation is by an excess of a positive or negative charge in the model structure of a binary oxide. The model structure is pictured according to the following two postulates. (1) The coordination number of the positive element of a metal oxide, C₁, and that of the second metal oxide, C₂, are maintained even when mixed; and (2) the coordination number of the negative element (oxygen) of the major component oxide is retained for all oxygens in the binary oxide.

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 [18]

The coordination numbers of Pr (Pr⁺³, Pr⁺⁴) is six and oxygen is three in the cubic form of pure Pr₆O₁₁. The coordination numbers of Zr is eight and oxygen is four in pure ZrO₂. When the two oxides are mixed with ZrO₂ as the major component, coordination numbers of the cations will remain as such but that of the anion will be 4 as by postulates 1 and 2. In its structure the positive charge of the Pr (the added cation) will be distributed along six bonds (+3/6 for Pr⁺³ and +4/6 for Pr⁺⁴ for each bond). The negative charge of the oxygen will be distributed along four bonds (-2/4 for each bond). The

charge imbalance produced at one $\text{Pr}^{+3}\text{-O}$ bond is $(+3/6 - 2/4 = 0)$ and the charge imbalance produced at one $\text{Pr}^{+4}\text{-O}$ bond is $(+4/6 - 2/4 = +1/6)$. The total charge difference produced by one Pr^{+3} cation is $(6 \times 0) = 0$ and that for Pr^{+4} is $(6 \times +1/6) = +1$. So Pr^{+3} cannot generate acidity on mixing with zirconia. In $\text{Pr}^{+4}\text{-Zr}^{+4}$ oxide mixtures Lewis acidity is assumed to appear upon the presence of an excess positive charge.

When the two oxides are mixed with Pr_6O_{11} in the cubic C form as the major component, the coordination number of cation will remain as such and that of the anion will be three (as in Pr_6O_{11}). In its structure the positive charge of the Zr (the added cation) will be distributed along eight bonds ($+4/8$ for each bond). The negative charge of the oxygen will be distributed along three bonds ($-2/3$ for each bond). The charge imbalance produced at one Zr-O bond is $(+4/8 - 2/3 = -1/6)$, and the total charge difference produced by one Zr cation is $(8 \times -1/6) = -8/6$. In this case Bronsted acidity is assumed to appear, because eight protons are considered to associate with six oxygens to keep electrical neutrality. Again according to Tanabe's model Pr^{+3} and Pr^{+4} in the A form when mixed with zirconia can generate acidity on mixing. A form is prominent at higher temperatures. Praseodymia itself is a mixture of Pr^{+3} and Pr^{+4} , and there will be intrinsic acidity in it due to the charge imbalance produced at $\text{Pr}^{+3}\text{-O}-\text{Pr}^{+4}$, 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.

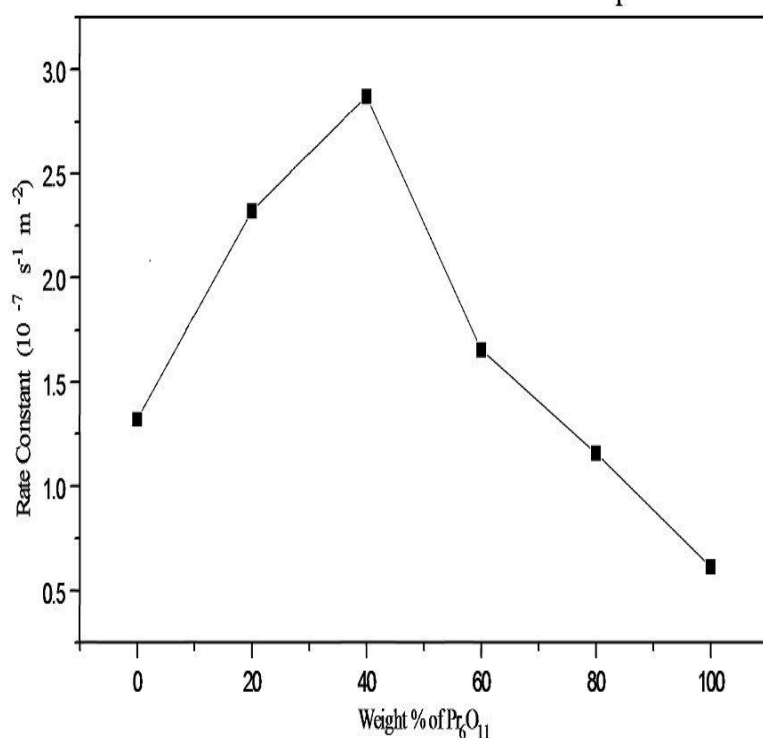


Figure 6. Catalytic activity of Pr -Zr mixed oxides towards esterification reaction as a function of composition

For a sufficiently basic oxide, the rate of reaction may depend on the amount of acid sites coexisting 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

The reduction reaction showed a first order dependence on the concentration of cyclohexanone and zero order dependence on isopropanol concentration under the experimental conditions adopted. 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 except 80 Pr are having higher activities than the pure oxides. The activity is the highest for 40 Pr.

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 that the availability of the particular

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

Table 2

Surface areas, catalytic activity & limiting amounts of electron acceptors adsorbed on praseodymium - zirconium mixed oxides activated at 500°C

Weight % of Pr ₆ O ₁₁	Surface Areas (m ² g ⁻¹)	Rate Constant (10 ⁻⁷ s ⁻¹ m ⁻²)		Limiting amount Adsorbed (10 ⁻⁶ mol m ⁻²)	
		Reduction	Esterificatio	TCNQ	Chloranil
0	61.5	1.32	2.51	2.08	1.06
20	127.6	2.32	0.08	2.14	1.13
40	101.6	2.87	0.95	1.96	0.95
60	90.2	1.65	1.02	2.15	0.86
80	69.9	1.16	0.24	3.31	1.25
100	11.4	0.61	-	0.74	0.34

the reaction, the exact nature being unknown [18]. The active sites for the reduction reaction is still uncertain. The proposed mechanism [1] involves the following steps.

1. The adsorption of the hydrogen source (isopropanol), as isopropoxide on an acid site through the oxygen atom, with the proton abstracted on an adjacent base site on the catalyst surface (both acid and base sites or acid-base pair sites are involved in it) .
2. Adsorption of the ketone on an adjacent acid site, attached through the carbonyl oxygen.
- 3 A hydride ion abstraction by the carbonyl carbon of the ketone from the isopropoxide species.
4. Subsequent bond rearrangement
5. Desorption of the alkoxide formed as the alcohol by accepting a proton either from a Bronsted acid site or from the medium.

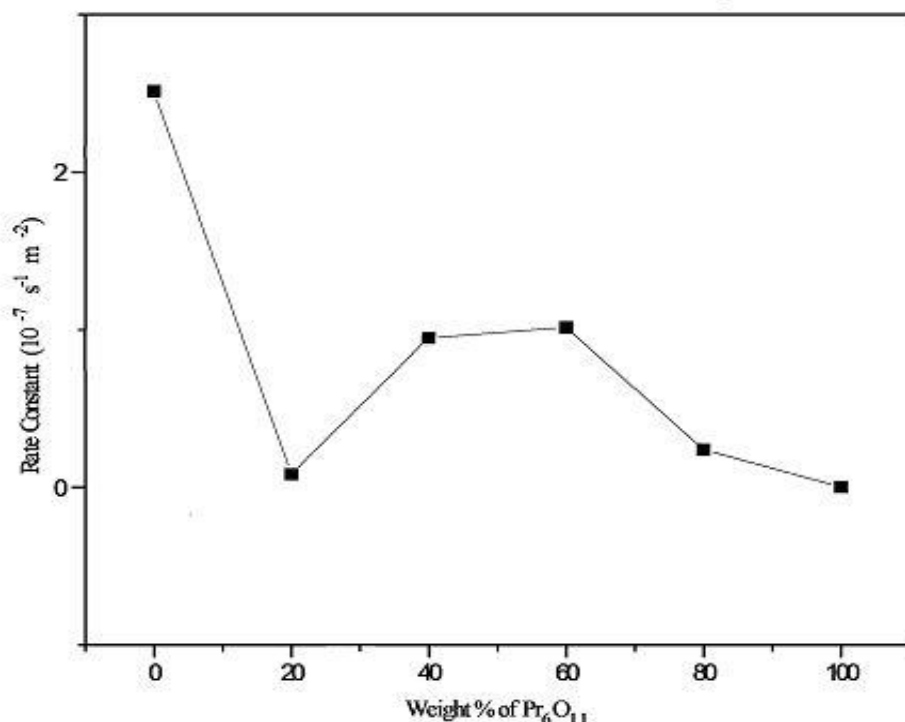


Figure 7. Catalytic activity of Pr -Zr mixed oxides towards esterification reaction as a function of composition

A plausible mechanism in which Bronsted acid sites are involved in the reaction is as follows. $\text{RCOOH} + \text{H}^+ + \text{R}^1\text{OH} \rightleftharpoons \text{RC}^+(\text{OH})_2 + \text{R}^1\text{OH} \rightleftharpoons \text{RC}(\text{OH})(\text{OH}_2^+)(\text{OR}^1) \rightleftharpoons \text{RCOOR}^1 + \text{H}_2\text{O} + \text{H}^+$

Esterification can also be catalysed by Lewis acid sites [27] (metal ions in low coordination). In this case esterification proceeds by combination of strongly adsorbed carboxylate ion and alkoxide ion on adjacent Lewis acid sites. This type of mechanism [28] is more prominent in vapour phase esterification. Esterification reaction is known to be catalysed by strong acid sites on the solid surface. Pure Pr₆O₁₁ does not possess strong acid sites on their surface to catalyse the esterification reaction. But ZrO₂ having a polyfunctional behaviour and possessing strong acid sites can catalyse the esterification reaction. 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.

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