Surface electron properties and catalytic activity of cerium-zirconium mixed oxides

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The electron donating properties, surface acidity/ basicity and catalytic activity of cerium - zirconium mixed oxides at various compositions have been reported at an activation temperature of 500°C. The catalytic activity for the esterification of acetic acid with n-butanol has been correlated with electron donating properties and surface acidity/basicity of the 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) suppresses the acidic behaviour whereas addition of an acidic oxide promotes acidic property[4]. Sulphated 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 in nature and can act as effective catalysts for a number of reactions[6]. CeO_2 shows acidic nature and Ce is in the +4 stable oxidation state unlike other rare earth elements which have stable +3 oxidation states. So the effect of mixing of CeO_2 with zirconia is expected to be different from other rare earth oxides. So far no attempt was made to study the effect of mixing of CeO_2 with zirconia on its surface properties. In this paper we report the acid/base properties, surface electron donor properties and the catalytic activity of cerium - zirconium mixed oxides at various compositions at an activation temperature of 500°C towards the liquid phase esterification of acetic acid with n-butanol.

Materials and Methods

The mixed oxides were prepared by the hydroxide route. To the boiling solution containing calculated quantities of cerium nitrate and zirconyl nitrate, a 1:1 solution of ammonia was added slowly with constant stirring . The precipitate after aging at 80°C for 1 h was then thoroughly washed free from nitrate ions and dried at 120°C. It was calcined at 300°C for 2 h and sieved to get the oxide with 100-200 mesh size. All the oxides were heat treated at a temperature of 500°C for 2 h 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[7]. 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-p-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[8]. 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. The surface acidity / basicity of the oxides was determined by titration method[9] using the following Hammett indicators; 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). Oxides under study responded only to dimethyl yellow, methyl red and bromothymol blue.

Surface area of the oxides were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The reflectance spectra of the adsorbed samples were measured with a Hitachi 200-20 UV-visible spectrophotometer with a 200 -

Table 1 — Surface areas, limiting amounts of electron acceptors adsorbed and catalytic activity of cerium -zirconium mixed oxides activated at 500°C

Weight % of CeO_2	Surface area (m^2g^{-1})	Limiting amount adsorbed $(10^{-6} mol\ m^{-2})$		Esterification reaction	
		TCNQ	Chloranil	% conversion	Rate constant $(10^{-7}s^{-1}m^{-2})$
0	61.50	2.0814	1.0613	10.53	2.513
20	30.72	2.4141	0.8984	30.99	16.773
40	11.36	3.0810	0.5282	26.46	37.583
60	45.92	0.2450	0.0000	38.86	14.884
80	66.54	1.7399	0.8452	55.19	16.759
100	66.42	0.3372	0.2050	0.00	—

0531 reflectance attachment. The radical concentration of the electron acceptors adsorbed on the oxides were determined from the ESR spectra measured at room temperature using a Varian E-112 X/ Q band ESR spectrometer. 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 esterification was carried out in a Round bottomed flask attached with a reflux condenser in which the catalyst (.5g), 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 h. The progress 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. The catalytic activity is expressed as the first order rate constant per m^2 of the oxide surface. The mixed oxides with various compositions ,viz. 20, 40, 60 and 80% of the rare earth oxide were studied and the data were compared with those for pure oxides.

Results and Discussion

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 amount of PDNB and MDNB adsorbed was 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. 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 1.

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[10]. 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. The ESR spectrum of these coloured samples gave unresolved spectral lines with *g* values of 2.003 and 2.011 for TCNQ and chloranil 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

Table 2 — Acid-base strength distribution on cerium-zirconium mixed oxides activated at 500°C

Weight % of CeO$_2$	Basicity $H_o \geq 3.3$	Basicity $H_o \geq 4.8$	Acidity $H_o \leq 4.8$	Acidity $H_o \leq 7.2$	$H_{o,max}$
		10^{-3} m mol m^{-2}			
0	2.738	0.107	-	2.745	5.6
20	1.400	-	4.492	9.993	3.7
40	2.113	-	8.363	14.080	3.6
60	0.740	-	1.851	5.226	3.6
80	0.346	-	0.842	0.255	4.3
100	0.557	0.271	-	5.063	5.8

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 nature of interaction of electron acceptor with the oxide surface was studied by reflectance spectra of the solid after adsorption. The electronic spectrum of the adsorbed samples gave bands near 400, 600 and 700nm corresponding to physically adsorbed state of neutral TCNQ[11], dimeric TCNQ radical[12], and to chloranil anion radical[13] respectively.

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. Strong electron acceptors like TCNQ are capable of forming anion radicals even from weak donor sites whereas weak acceptors 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. It is found that the limiting radical concentration and the limiting amount adsorbed decrease with decrease in 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[7]. It has been reported that at higher activation temperatures the donor sites consist 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[15]. The more basic the surface, the higher is the number of O^{2-} which can transfer electrons to the EA.

The acid/base strength of the oxides were measured on a common H_o scale[8]. The acid/base strength distribution curves intersect at a point on the abcissa where acidity = basicity = 0 (ref.14). The point of intersection is defined as $H_{0,max}$. Table 2 contains the data on acidity/basicity distribution. $H_{0,max}$ value 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 surface acidity-basicity data revealed the presence of sites of different energies. It has been suggested[15] that the acid, base sites on oxide surfaces are metal ions and O^{2-} ions respectively 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[15]. Acidity measurement show the formation and annihilation of new acid-basic sites on mixing oxides. This 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[16].

The CeO$_2$ is found to have a normal rutile structure in which the Ce^{4+} ion is six coordinated with no paramagnetic susceptibility[17]. As the covalency (charge to radius ratio) of the oxide is greater, the oxide will be more acidic[18]. Cerium is having +4 charge and the ionic radius will be less than the trivalent ions and so the covalency of the metal ion in the

oxide will be higher and CeO$_2$ is found to be more acidic than the other rare earth oxides.

According to Tanabe's hypothesis[19], 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, C$_1$, and that of the second metal oxide, C$_2$, 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.

The coordination numbers of Ce is six and oxygen is three in pure CeO$_2$. The coordination numbers of Zr is eight and oxygen is four in pure ZrO$_2$. When the two oxides are mixed with ZrO$_2$ 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 Ce (the added cation) will be distributed along six bonds (+4/6 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 Ce-O bond is (+ 4/6 − 2/4 = +1/6) +1/6, and the total charge difference produced by one Ce cation is (6 × +1/6) +1. In this case Lewis acidity is assumed to appear upon the presence of an excess positive charge.

When the two oxides are mixed with CeO$_2$ as the major component, the coordination number of cation will remain as such and that of the anion will be three (as in CeO$_2$). 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) − 1/6, and the total charge difference produced by one Zr cation is (8 × −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. In all the cases of Ce- Zr mixed oxides acidity is generated and it agrees well with our studies.

The esterification reaction showed a first order dependence on the concentration of acetic acid under the experimental conditions adopted. Pure CeO$_2$ does not catalyse the esterification reaction of acetic acid with *n*-butanol. But ZrO$_2$ catalyses the esterification reaction to a certain extent. The mixed
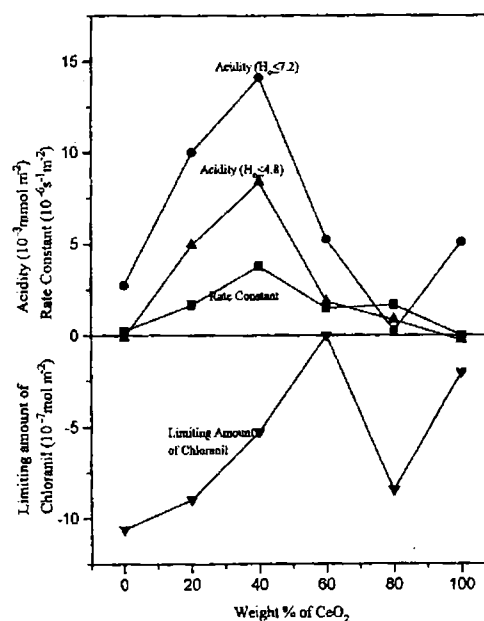

Fig. 1 — Rate constant for esterification reaction, acidity and limiting amount of electron acceptor adsorbed as a function of composition of the mixed oxide.

oxides show very high activity for the esterification reaction, 40Ce exhibiting the highest value. The mixing of CeO$_2$ and ZrO$_2$ generates a number of sites which are active in the esterification reaction.

The reaction of acetic acid and *n*-butanol in the liquid phase catalysed by solid acids proceeds according to a rate equation which is first order with respect to acetic acid and zeroth order with respect to *n*-butanol[20,21].

A plausible mechanism in which Bronsted acid sites are involved in the reaction is as follows.

$$RCOOH + H^+ \Leftrightarrow RC^+(OH)_2 + R'OH \Leftrightarrow$$
$$RC(OH)(OH_2^+)(OR^1) \Leftrightarrow RCOOR^1 + H_2O + H^+$$
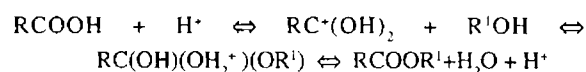
Esterification can also be catalysed by Lewis acid sites (metal ions in low coordination)[22]. In this case esterification proceeds by combination of strongly adsorbed carboxylate ion and alkoxide ion on adjacent Lewis acid sites. This type of mechanism[23] is more prominent in vapour phase esterification.

Esterification reaction is known to be catalysed by strong acid sites on the solid surface. Pure CeO$_2$ does not posses strong acid sites on their surface to catalyse the esterification reaction. But ZrO$_2$ having a polyfunctional behaviour can catalyse esterification reaction. On mixing ZrO$_2$ with rare earth oxides, strong acid sites are generated in the case of Ce-Zr mixed oxides which can catalyse the esterifi-

cation reaction. So Ce-Zr mixed oxides have very high values for rate constant . Figure 1 shows the change in acidity, electron donating properties and catalytic activity as a function of composition of the oxides activated at 500° C . This shows that acidic sites having strength $H_o \leq 4.8$ and $H_o \leq 7.2$ play an important role in the reaction and these may be the catalytically active sites for this reaction. Electron donating property does have an invert parallel relationship to the activity. The strong basic sites or electron donor sites with the limit of electron transfer between 1.77eV -2.40eV inhibit the reaction. It can be seen from the data that highest esterification activity is obtained for zirconium oxide by incorporating 40 weight% of CeO_2 in it, which may be due to the highest density of acid sites on its surface.

Acknowledgement

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