



# EFFECT OF ACTIVATION TEMPERATURE ON THE SURFACE ELECTRON DONATING PROPERTIES OF CERIUM -ZIRCONIUM MIXED OXIDES

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**Abstract:** The electron donating properties of Cerium - Zirconium mixed oxides at various compositions have been reported at three activation temperatures of 300°C, 500°C & 800°C. The strength and distribution of electron donor sites are determined from the studies of the adsorption of electron acceptors (EA) of various electron affinities from acetonitrile solvent.

**Index Terms:** Electron donocity, Electron acceptors, Electron affinity, TCNQ, Chloranil, PDNB, MDNB

## INTRODUCTION

The thermochemistry of rare earth metal doped Zirconia indicates that the addition of rare earth metal increases the thermal stability of the host oxide and stabilised it in a high surface area form [Sun and Sermon 1996]. The catalytic property of metal oxides depend on many factors. Attempts are now being done to establish valid correlations between the catalytic activity and other surface properties

A detailed review of the literature revealed that no attempts were made to study the surface electron donating property of mixed oxides of zirconium with cerium. Zirconium is a transition element and zirconia is unique in exhibiting acid, base, oxidising and reducing properties. Further zirconia based materials are now attracting much attention because of their promising potential as catalysts for use in combustion and hydrogenation [Marcos,Lili Luis 2020], Piezo electric ceramics and thermal barriers. Anions vacancies can be created in CeO<sub>2</sub> extrincically by the reduction process. It can be considered as nonstoichiometric oxide. CeO<sub>2</sub> 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<sub>2</sub> with zirconia is expected to be different from other rare earth oxides. Strength and distribution of acid and base sites on the Ce- Zr mixed oxides are reported earlier [Sugunan and Binsy, 1998]. So far no attempt was made to study the effect of mixing of CeO<sub>2</sub> with zirconia on its surface electron donating properties.

In this paper we report the surface electron donating properties of cerium - zirconium mixed oxides at various compositions at three activation temperatures (300°C, 500 °C and 800 °C). 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.

## EXPERIMENTAL

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 is added slowly with constant stirring. The precipitate after aging at 80°C for 1 hour was then thoroughly washed free from nitrate ions and dried at 120°C. It was calcined at 300°C for two hours and sieved to get the oxide with 100-200 mesh size. The mixed oxides with various compositions, viz. 20, 40, 60 and 80 % (abbreviated as 20 Ce, 40 Ce, 60 Ce and 80 Ce) of the rare earth oxide were prepared. Pure oxides were also prepared in the same fashion and incorporated in the study for comparison. All the oxides were heat treated at a particular temperature viz 300°C, 500°C & 800°C, for two hours prior to each experiment. All the reagents were purified by standard methods before use. The adsorption studies were carried out by a procedure reported earlier [Sugunan and Binsy, 1996]. The amount of electron acceptors adsorbed were determined by noting the concentrations of the electron acceptors before and after adsorption by means of a UV-Visible spectrophotometer at the  $\lambda_{\max}$  of the EA

**Table 1. Electron Acceptors used**

Electron Acceptor	Electron Affinity	$\lambda_{\max}$ of the EA in acetonitrile(nm)
7,7,8,8 Tetracyanoquinodimethane (TCNQ)	2.84 eV	393.5
2,3,5,6 Tetrachloro-p-benzoquinone (Chloranil)	2.40 eV	288
1,4 Dinitrobenzene (PDNB)	1.77 eV	262
1,3 Dinitrobenzene (MDNB)	1.26eV	237

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.

## RESULTS AND DISCUSSION

The strength and distribution of electron donor sites on the oxide surface were studied by adsorption of various electron acceptors with a range of electron affinities. The electron donor properties of some of the oxides as a function of the basic nature of the medium were reported by many authors [Sugunan, Rani and Unnikrishnan, 1994]. It was found that the amount of electron acceptor adsorbed decreases with the increase in the basicity of the medium, due to the competition between the solid base and the solvent base for electron acceptor interaction. In this study the electron acceptor adsorption on the oxide surfaces were done from acetonitrile, which is a very weak base [Esumi, Miyata, Waki and Meguro 1986].

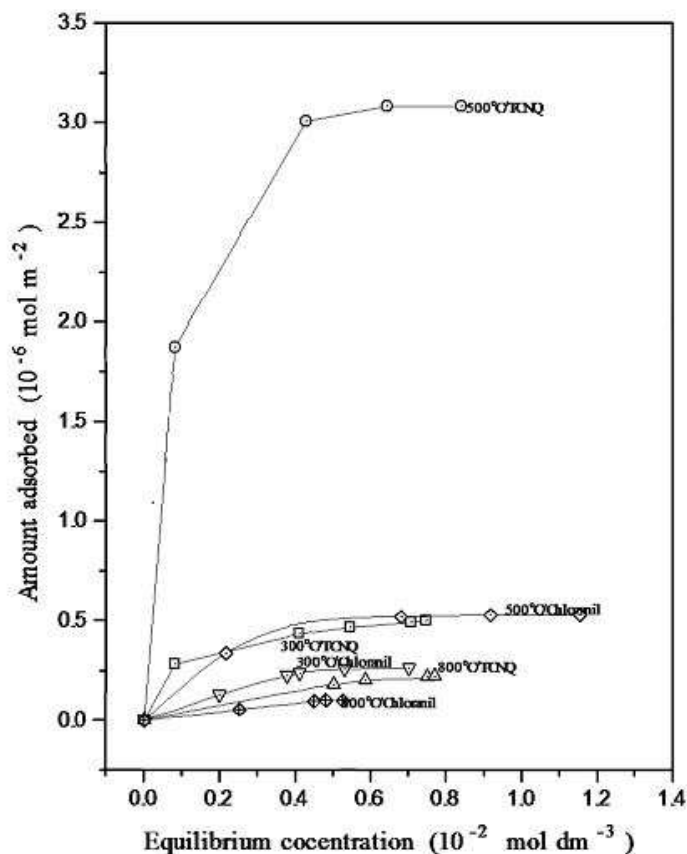


Figure 1. Langmuir adsorption isotherms of TCNQ and chloranil at different activation temperatures on 40Ce

On the surface of the oxides there will be a distribution of electron donor sites of various strength. 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. To study the strength and distribution of electron donor sites on the catalysts, electron acceptors of various electron affinity were used. They are listed in Table. 1 with their respective electron affinities. For all the oxides studied the amount of PDNB and MDNB adsorbed was so negligible that the

amount adsorbed could not be estimated by

**Table 2.** Surface areas and monolayer coverage of EA of cerium -zirconium mixed oxides activated at different temperatures.

Weight % of CeO <sub>2</sub> Activation temp.300°C	Surface area (m <sup>2</sup> g <sup>-1</sup> )	Limiting amount of Electron acceptor adsorbed 10 <sup>-6</sup> mol /sq.m	
		TCNQ	Chloranil
0	200.30	0.9656	0.6933
20	193.29	0.6833	0.4861
40	173.32	0.4964	0.2603
60	124.30	0.3133	0.2454
80	99.44	1.4137	0.8401
100	200.35	1.1910	0.5201
Activation temp.500 °C			
0	61.50	2.0814	1.0613
20	30.72	2.4141	0.8984
40	11.36	3.081	0.5282
60	45.92	0.245	0
80	66.54	1.7399	0.8452
100	66.42	0.3372	0.2050
Activation			

temp.800 °C			
0	29.75	2.2064	0.6835
20	46.34	0.5243	0
40	45.15	0.2182	0.0974
60	33.39	0.4306	0.3078
80	32.90	1.0358	0
100	29.00	0.2323	0.0301

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 mole  $dm^{-3}$  and  $C_{ad}$  is the amount adsorbed in mole per square metre (Fig. 1). The limiting amount of electron acceptors adsorbed, which corresponds to monolayer coverage were determined from the Langmuir plots and presented in Table. 2.

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 [Che, Naccache and Imelik 1982]. Chloranil gave light to dark pink colour to the oxides and TCNQ gave dark green to bluish green colour to the oxides, the colour intensifies with increase in zirconium content.

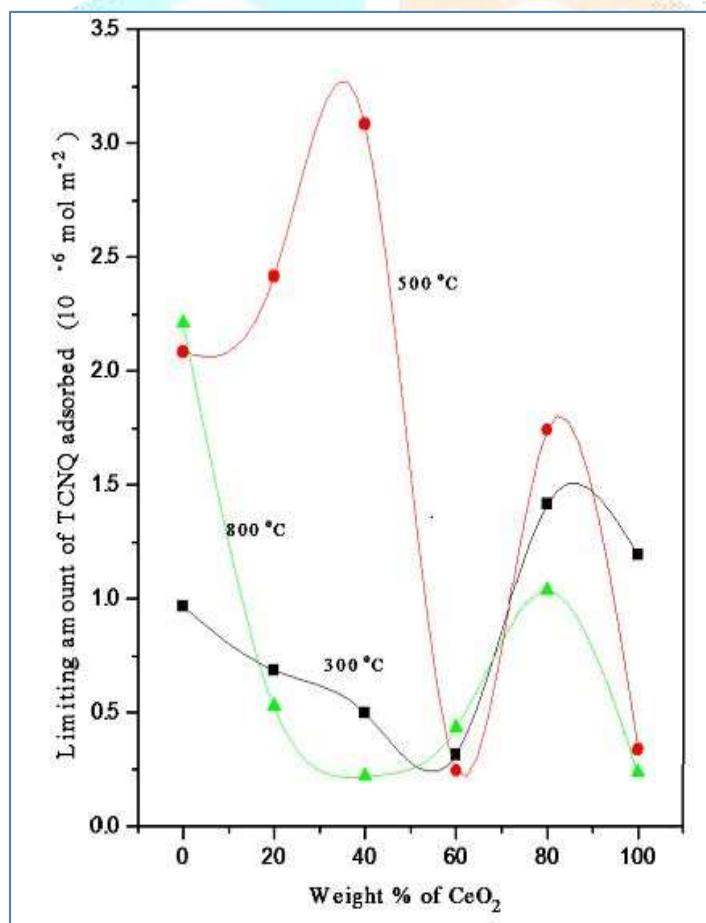


Figure 2. Limiting amount of TCNQ adsorbed as a function of Composition

The nature of interaction of electron acceptor with the oxide surface was studied by reflectance spectra of the solid after adsorption. The spectra of adsorbed TCNQ on solid oxide gave bands below 400 nm and near 600 nm. The first one corresponds to physically adsorbed state of neutral TCNQ which has an absorption band at 395 nm [Meguro and Esumi 1990]. The band near 600 nm corresponds to dimeric TCNQ radical which absorbs at 643 nm [Boyd and Philips 1965]. In the case of chloranil the broad band extending up to 700 nm corresponds to chloranil anion radical [Foster and Thomson 1962]. In the case of oxides under study these assignments do not hold completely because these oxides have characteristic band in the same region.

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The nature of interaction of the electron acceptor with the oxide surface was also investigated by esr spectra. The esr spectra indicated the presence of radical species. The samples after TCNQ adsorption gave unresolved esr spectra with a g value of 2.003, due to the hindered rotational freedom of the adsorbed species which obscures the hyperfine structure of the spectrum. These spectra have been identified as being those of TCNQ anion radicals [Hosaka, Fujiwara and meguro 1971]. The coloured samples obtained by the adsorption chloranil gave an unresolved esr spectra with a g value of 2.011 [Esumi and Meguro 1975]. 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 limiting amount of radical concentration of TCNQ 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 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 of the weak acceptor 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 decreases with decrease in the electron affinity of the acceptor.

CeO<sub>2</sub> and ZrO<sub>2</sub> have comparable surface areas and their surface areas decrease with increase in activation temperature (Table 2). The rate of decrease also appears to be same for the two oxides. For the mixed oxides the surface areas are less than the pure components at the activation temperatures of 300°C and 500°C. At 300°C the decrease is more for the cerium rich oxides (60 Ce and 80 Ce). At 500°C the decrease in surface areas is more for zirconium rich samples (20 Ce and 40 Ce). At 800°C a different trend is observed, the surface areas of mixed oxides are found to have higher values than the pure component oxides. The increment is very small and is more for the zirconium rich samples. In general surface areas are found to be improved by mixing of the oxides only at higher temperatures even though the increment is small.

The electron donor properties of Ce - Zr mixed oxides depend both on activation temperature and composition of the mixed oxides as well as on the electron affinity of the electron acceptor (Table 2, Figures 3, 4). In the case of pure ZrO<sub>2</sub>, the limiting amount of TCNQ adsorbed increase with

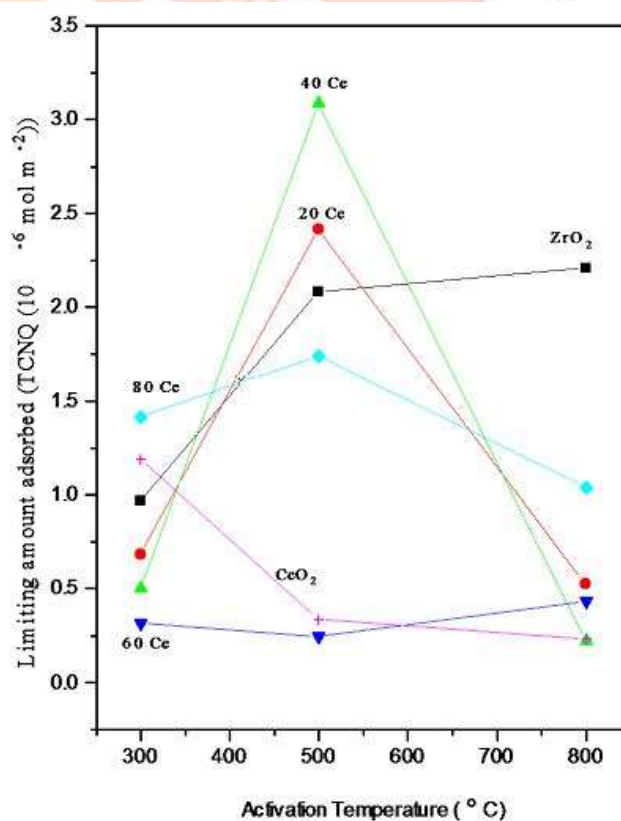


Figure 3. Limiting amounts of TCNQ adsorbed as a function of activation temperature

activation temperature and the rate of increase is more in between 300°C to 500°C than between 500°C to 800°C. In the case of ceria the trend is just reversed. The limiting amount decreased with increase in activation temperature. The decrease is more steep between 300 to 500°C than between 500 to 800°C. In the case of 60 Ce the limiting amount first decreased from 300 to 500°C and then increased, however, the increase is very small. For all other mixed oxides (20 Ce, 40 Ce, 80 Ce), the limiting amount is maximum at 500°C. In the case of 20 Ce and 40 Ce they have high electron donor properties than the pure component oxides at 500°C. For 80 Ce the limiting amount of TCNQ adsorbed is large at 300°C and is greater than both the pure oxides. At 800°C pure ZrO<sub>2</sub> is having the highest value for limiting amount of TCNQ adsorbed, CeO<sub>2</sub> having the lowest value and all the mixed oxides have intermediate values.

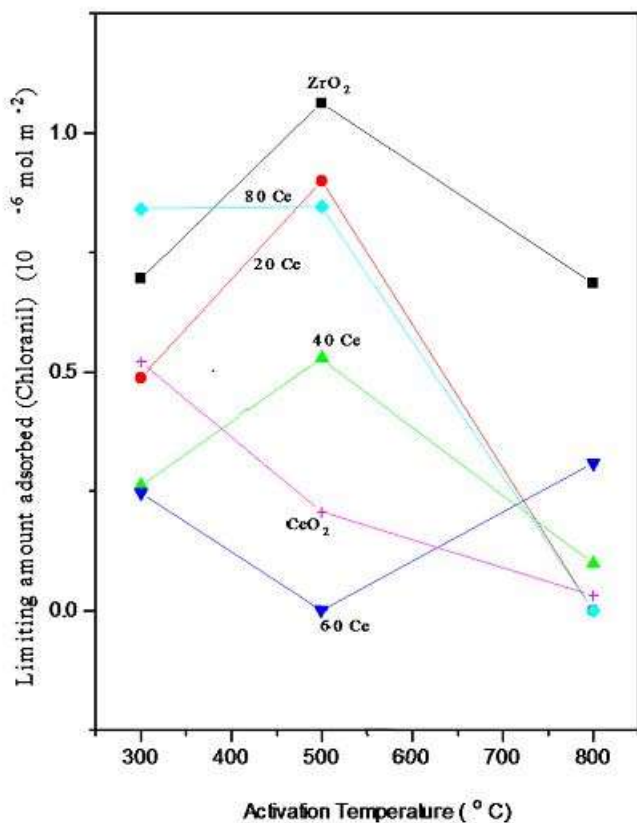


Figure 4. limiting amounts of Chloranil adsorbed on Ce -Zr mixed oxides as a function of activation temperature

For chloranil adsorption all the limiting amounts are found to be less than that for TCNQ. The limiting amounts adsorbed on ZrO<sub>2</sub> increased first from 300 to 500°C and then decreased. In the case of ceria the limiting amount adsorbed gradually decreased with increase in activation temperature. For 80 Ce the limiting amount adsorbed at 300°C is greater than the pure component oxides. All the remaining compositions have lower values than the component oxides, 60 Ce having the lowest value. At 500°C ZrO<sub>2</sub> is having the highest value for limiting amount adsorbed. 80 Ce, 40 Ce and 20 Ce have intermediate values between the component oxides. For 60 Ce it does not give chloranil adsorption. At 800°C, 20 Ce and 80 Ce do not give chloranil adsorption, 40 Ce and 60 Ce having values in between those of component oxides. For 20 Ce and 40 Ce the limiting amount adsorbed is maximum at 500°C. For 60 Ce the maximum value is at 800°C. For 80 Ce the value does not differ much from 300 to 500°C. At 800°C it does not give chloranil adsorption.

Two possible electron sources exist on the metal oxide surface responsible for electron transfer. One of these has electrons trapped in intrinsic defect and other has hydroxyl ions [Flockhart, Leigh and Pink 1969]. At lower temperatures electron donor sites are associated with unsolvated hydroxyl ions and at higher activation temperatures an electron defect centre is produced. It is reported that free electron defect site on metal oxide surface is created at activation temperatures above 500°C. It has been suggested that at higher activation temperatures the donor site consists of a co-ordinatively unsaturated doubly charged oxygen ion ( $O_{CUS}^{2-}$ ) associated with a nearby  $OH^-$  group and the concentration of this donor site

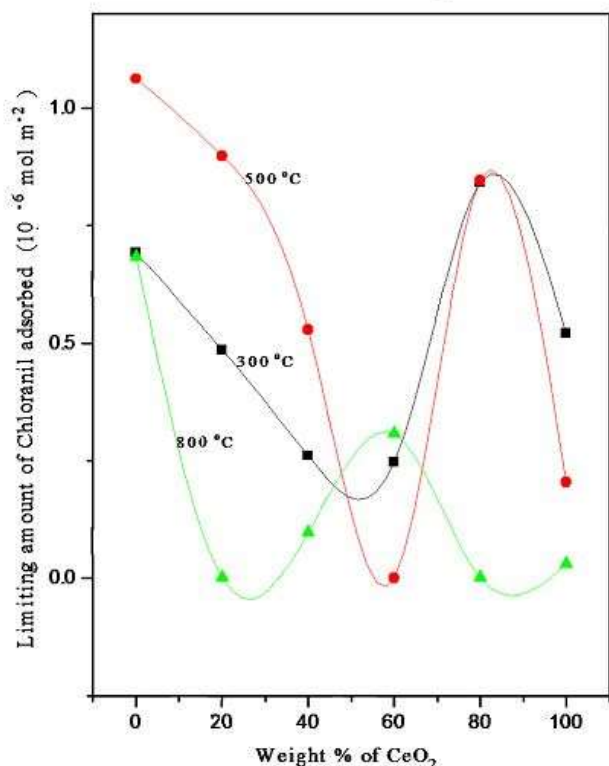


Figure 5. Limiting amounts of Chloranil adsorbed on Ce-Zr mixed oxides as a function of composition

is related to the base strength of the surface [Choudhary and Rane 1991]. The more basic the surface, the higher is the number of oxygen ions which can transfer the electron to the acceptor molecule.

### CONCLUSIONS

Amount of electron acceptor adsorbed depend on the composition of the mixed oxide, activation temperature and electron affinity of the electron acceptor. The limit of electron transfer is between 1.77- 2.40 eV for all oxides under study except for some 60Ce (500°C) and 20Ce, 80Ce (800°C) mixed oxides. Electron donor power increases with basicity of the oxide. CeO<sub>2</sub> and its mixed oxides with zirconium are found to be more acidic than others. Acidity is generated on mixing cerium oxide with zirconium oxide.

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