

ELECTRON DONATING AND ACID-BASE PROPERTIES OF CERIUM OXIDE AND ITS MIXED OXIDES WITH ALUMINA

Sankaran SUGUNAN* and Jacob M. JALAJA

Department of Applied Chemistry,

Cochin University of Science and Technology, Kochi 682 022, S. India

Received February 11, 1994

Accepted August 12, 1994

The electron donating properties of ceria activated at 300, 500 and 800 °C and its mixed oxides with alumina are reported from the studies on adsorption of electron acceptors of various electron affinity. The surface acidity/basicity of the oxides have been determined by titration method and $H_{0,max}$ values are reported. The limit of electron transfer from oxide surface is between 1.77 and 2.40 eV in terms of the electron affinity of the electron acceptor. Ceria promotes the electron donating of alumina without changing the limit of electron transfer.

Acid-base properties of some of the metal oxides have been studied extensively and correlated with their catalytic properties^{1,2}. The semiconducting behaviour³, high structural and thermal stability⁴ and catalytic activity of ceria towards the decomposition of alcohols⁵ are reported. Supported rare earth oxides are quite often used as catalysts for reactions such as polymerization⁶, carbon monoxide hydrogenation⁷ etc. However, no effort has so far been made to study their surface properties. In this paper we report the electron donating properties and acid-base nature of CeO₂ and its mixed oxides with alumina for various composition. Since these properties depend on the activation temperature of the oxide, studies were carried out at different temperatures.

EXPERIMENTAL

Cerium oxide was prepared by hydroxide method⁸ from nitrate salt (purity 99.9%) obtained from Indian Rare Earths Ltd., Udyogamandal. Carbon dioxide contamination during the precipitation was prevented by a method reported earlier⁹. The oxide activated by heating in CO₂ free air atmosphere for 2 h at various activation temperatures viz. 300, 500 and 800 °C were studied.

The electron acceptors used were 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-1,4-benzoquinone (Chloranil), *p*-dinitrobenzene (PDNB) and *m*-dinitrobenzene (MDNB) with electron affinity values 2.84, 2.40, 1.77 and 1.26 eV, respectively. Since the electron donating properties

* The author to whom correspondence should be addressed.

depend on the basicity of the medium, studies were carried out in solvents of various basicity; acetonitrile, ethyl acetate and 1,4-dioxane. The purification of the adsorbates and the solvents have been described elsewhere¹⁰.

Mixed oxides of Ce and Al were prepared by co-precipitation from their nitrate solutions¹¹. 10, 20, 40, 60 and 80 wt.% of CeO₂ in alumina were prepared and activated at 500 °C. Elemental analysis of the samples with a Perkin-Elmer 23-80 Atomic Absorption Spectrometer gave results within 1% of the composition reported. The specific surface area of the oxides were determined using Carlo-Erba Strumentazione Sorptomatic series 1800. The values in m² g⁻¹ were as follows (activation temperature is given in brackets): CeO₂ (300 °C) 66.42, CeO₂ (500 °C) 200.35, CeO₂ (800 °C) 210.17. The specific surface area of the mixed oxides at 500 °C were: Al₂O₃ 193.91, 10% CeO₂/Al₂O₃ 217.02, 20% CeO₂/Al₂O₃ 216.85, 40% CeO₂/Al₂O₃ 160.14, 60% CeO₂/Al₂O₃ 143.70, 80% CeO₂/Al₂O₃ 125.24.

The oxides were activated at a particular temperature for 2 h prior to each experiment. The oxide (0.5 g) was placed in a 25 ml test tube and outgassed at 10⁻³ Pa for 1 h. To the test tube fitted with a mercury sealed stirrer 20 ml of a solution of the electron acceptor dissolved in the organic solvent was then admitted in. After the solution had subsequently been stirred for 3 h at 25 °C in a thermostated water bath the oxide was collected by centrifuging the solution and dried the solid obtained at room temperature in vacuo.

The reflectance spectra of dried samples were recorded on a Hitachi 200-20 UV Visible spectrophotometer with a 200-0531 reflectance attachment. The electron spin resonance spectra (ESR) were measured at room temperature using a Varian E-112 X/Q band ESR Spectrophotometer. The formation of TCNQ and chloranil anion radicals as a result of electron transfer from adsorbate to adsorbent was confirmed by electronic and ESR spectral data. The concentration of radical anions were calculated by comparison of area obtained by double integration of the first derivative curve for the sample and standard solutions of 1,1-diphenyl-2-picrylhydrazyl in benzene. Infrared spectra of samples were taken on a Perkin-Elmer PE-983 infrared spectrophotometer.

The amount of electron acceptor adsorbed was determined from the difference in concentration of electron acceptor in solution before and after adsorption. The adsorption of PDNB and MDNB were negligible. The absorbance of electron acceptor was measured by means of a UV Visible Spectrophotometer at the λ_{\max} of the electron acceptor in the solvent: 393.5, 393 and 403 nm for TCNQ, 288, 287 and 286 nm for chloranil in acetonitrile, ethyl acetate and 1,4 dioxane, respectively.

Tanabe's method¹² was used for the measurement of acid-base strength of oxides. Activated samples were ground and sieved to prepare powders of 100 – 200 mesh size. The following Hammett Indicators were used, (pK_a values are given in parenthesis) crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2), 4-nitroaniline (18.4). A 0.1 wt.% of the indicator in benzene was used in each experiment. The acidity was determined by titration with n-butylamine and basicity with trichloroacetic acid.

RESULTS AND DISCUSSION

Adsorption studies were carried out on a pure oxide in three solvents; acetonitrile, ethyl acetate and 1,4-dioxane. Basicity of the solvents were in the order, acetonitrile < ethyl acetate < 1,4-dioxane. Adsorption isotherms (Fig. 1) were drawn by plotting the amount of electron acceptor adsorbed against the equilibrium concentration of the electron acceptor. The isotherms obtained were of Langmuir type. From these isotherms the limiting amount of electron acceptor adsorbed was determined.

When electron acceptor was adsorbed, the surface of the oxide showed remarkable colouration characteristic of the kind of acceptor, like bluish green for TCNQ and light

pink for chloranil. This is due to the interaction between electron acceptor adsorbed on the surface with the oxide. Figure 2 shows radical concentration of TCNQ adsorbed against the equilibrium concentration of TCNQ in solution for CeO_2 activated at 300°C . The isotherm (Fig. 2) obtained is of Langmuir type and is of the same shape as those given in Fig. 1. The ESR spectrum of the sample coloured after adsorption of TCNQ and chloranil gave unresolved spectral line with a g value of 2.003 and 2.011, respectively, with a width of approximately 30 G indicating the presence of anion radicals on the surface.

The limiting amount of electron acceptor adsorbed on the oxide surface decreases with increase in basicity of the solvent. The heat of mixing of substances with acid-base interaction are expressed by Drago equation,

$$-\Delta H^{\text{ab}} = C_A C_B + E_A E_B, \quad (1)$$

where E and C are the Drago constants for acidic compound (A) and basic compound (B) (ref.¹³). The basicity of solvent was estimated by the heat of interaction with electron acceptor and the values obtained in kJ mol^{-1} are: acetonitrile 14.7, ethyl acetate 17.8 and dioxane 21.9. The limiting amount of TCNQ adsorbed on ceria as a function

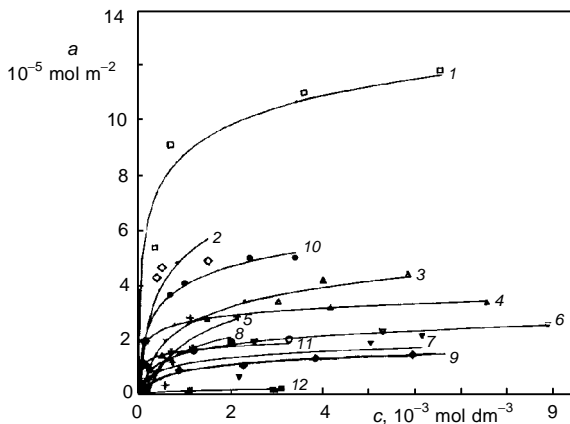


FIG. 1

Amount of electron acceptor, a , vs equilibrium concentration of electron acceptor, c , on CeO_2 . 1 TCNQ in acetonitrile on ceria activated at 300°C , 2 TCNQ in ethyl acetate on ceria activated at 300°C , 3 TCNQ in dioxane on ceria activated at 300°C , 4 TCNQ in acetonitrile on ceria activated at 500°C , 5 TCNQ in ethyl acetate on ceria activated at 500°C , 6 TCNQ in dioxane on ceria activated at 500°C , 7 TCNQ in acetonitrile on ceria activated at 800°C , 8 TCNQ in ethyl acetate on ceria activated at 800°C , 9 TCNQ in dioxane on ceria activated at 800°C , 10 chloranil in acetonitrile on ceria activated at 300°C , 11 chloranil in acetonitrile on ceria activated at 500°C , 12 chloranil in acetonitrile on ceria activated at 800°C

of acid-base interaction enthalpy are shown in Fig. 3. The limiting amount decreases with increase of acid-base interaction between solvent and TCNQ. The limiting amount adsorbed is higher for CeO_2 activated at 300 °C implying that it has higher electron donating capacity compared to those activated at higher temperatures. It was reported² that at lower activation temperature unsolvated hydroxyl ions are responsible for electron transfer. The presence of hydroxyl group on CeO_2 activated at 300 °C and 500 °C was confirmed from IR spectral data (peak near 3 400 cm^{-1}). A weak electron acceptor like PDNB (1.77 eV) can accept electrons from strong donor sites, whereas a strong electron acceptor like TCNQ (2.84 eV) can accept electrons from both weak and strong donor sites. The strength of an electron donor site can be expressed in terms of the electron affinity of the electron acceptor which can form anion radicals on the adsorption site. Hence the limit of electron transfer of CeO_2 is between 2.40 and 1.77 eV in acetonitrile. As the basicity of the solvent increases the limit of electron transfer shifts from 2.40 – 1.77 to 2.84 – 2.40 eV (in ethyl acetate and 1,4-dioxane).

The electron donicity increases with increase in percentage of CeO_2 in the mixed oxide, as a consequence of the increase in concentration of Al–O–Ce bonds. Further addition of CeO_2 decreases the limiting amount due to increase in concentration of CeO_2 in the oxide lattice, because CeO_2 has lower electron donicity than Al_2O_3 . The limiting amount of electron acceptor adsorbed as a function of composition of mixed oxide are given in Table I. The limit of electron transfer of mixed oxide is between 2.40 and 1.77 eV.

Figure 4 shows the acid-base strength distribution on the surface of ceria at different activation temperatures. Visible colour change was obtained only for three indicators: dimethyl

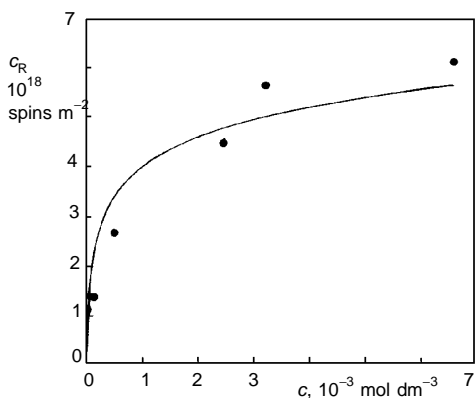


FIG. 2

Radical concentration of TCNQ on CeO_2 , c_R , vs equilibrium concentration of TCNQ, c

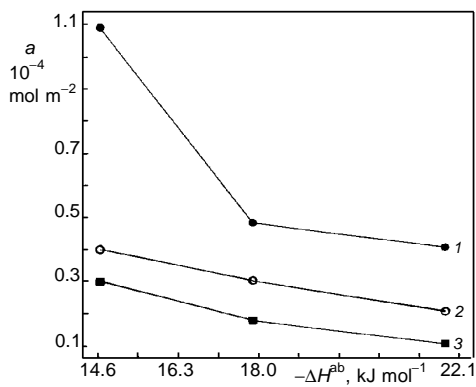


FIG. 3

Limiting amount of TCNQ, a , adsorbed on CeO_2 activated at various temperatures as a function of acid-base interaction enthalpy (1 kJ = 4.18 kcal). 1 300 °C, 2 500 °C, 3 800 °C

TABLE I
Limiting amount of electron acceptors adsorbed on mixed oxides

Catalyst	Solvent	Electron acceptor	Limiting amount adsorbed (10^{-5} mol m ⁻²)
CeO ₂	acetonitrile	TCNQ	3.37
	acetonitrile	chloranil	2.05
	dioxane	TCNQ	2.54
10% CeO ₂ /Al ₂ O ₃	acetonitrile	TCNQ	8.64
	acetonitrile	chloranil	3.56
	dioxane	TCNQ	4.92
	dioxane	chloranil	1.37
20% CeO ₂ /Al ₂ O ₃	acetonitrile	TCNQ	10.83
	acetonitrile	chloranil	3.87
	dioxane	TCNQ	5.33
	dioxane	chloranil	2.93
40% CeO ₂ /Al ₂ O ₃	acetonitrile	TCNQ	13.48
	acetonitrile	chloranil	5.32
	dioxane	TCNQ	5.53
	dioxane	chloranil	4.49
60% CeO ₂ /Al ₂ O ₃	acetonitrile	TCNQ	11.23
	acetonitrile	chloranil	4.43
	dioxane	TCNQ	4.58
	dioxane	chloranil	3.72
80% CeO ₂ /Al ₂ O ₃	acetonitrile	TCNQ	8.96
	acetonitrile	chloranil	4.08
	dioxane	TCNQ	3.67
	dioxane	chloranil	2.68
Al ₂ O ₃	acetonitrile	TCNQ	6.65
	acetonitrile	chloranil	2.21
	dioxane	TCNQ	4.52
	dioxane	chloranil	1.10

yellow, methyl red and bromothymol blue. The acid-base strength¹¹ (H_0) distribution curves intersect at a point on the abscissa ($H_{0,\max}$). For CeO_2 as activation temperature increases $H_{0,\max}$ value decreases which in turn shows the decrease in basic sites on the oxide. The data are given in Table II. Basicity values parallel the order of electron transfer.

TABLE II
Acidity (A) and basicity (B) of CeO_2 and its mixed oxides

Oxides	$B, 10^{-3} \text{ meq m}^{-2}$			$A, 10^{-3} \text{ meq m}^{-2}$			$H_{0,\max}$
	$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 7.2$	
CeO_2 (300 °C) ^a	1.08	0.52	–	–	–	1.02	5.5
CeO_2 (500 °C)	0.23	0.10	–	–	–	1.59	5.0
CeO_2 (800 °C)	0.12	–	–	–	0.12	1.79	4.3
10% CeO_2 ^b	0.91	0.14	0.06	–	–	–	8.4
20% CeO_2	1.41	0.21	0.09	–	–	–	8.4
40% CeO_2	1.57	0.28	0.12	–	–	–	8.5
60% CeO_2	1.16	0.21	0.09	–	–	–	8.4
80% CeO_2	1.10	0.15	–	–	–	0.35	5.4
Al_2O_3	0.04	0.03	0.01	–	–	–	7.5

^a Activation temperature. ^b Composition of the mixed oxide is reported as per cent by weight of CeO_2 in alumina. The mixed oxides are activated at 500 °C.

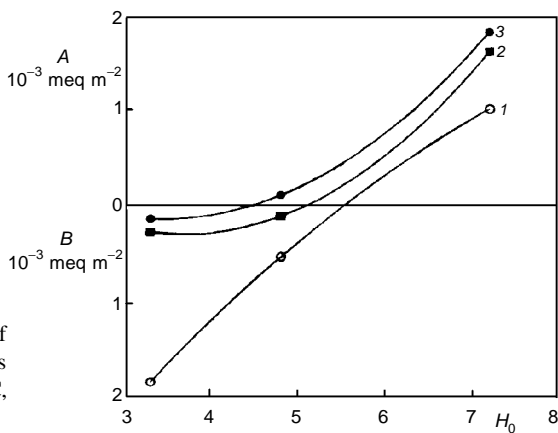


FIG. 4
Acid-base strength (H_0) distribution of CeO_2 activated at different temperatures (A acidity, B basicity). 1 300 °C, 2 500 °C, 3 800 °C

The amount of electron acceptor adsorbed depends on the activation temperature of the oxide, basicity of the solvent, the electron affinity of the electron acceptor and the electron donor properties of the oxide catalyst.

The authors wish to acknowledge their sincere gratitude to the University Grants Commission, New Delhi, India for the award of a Senior Research fellowship to J. M. J.

REFERENCES

1. Esumi K., Magara K.: *J. Jap. Color. Mater.* 58, 9 (1985).
2. Meguro K., Esumi K.: *J. Adhes. Sci. Technol.* 4, 393 (1990).
3. Bluementhal R., Lee P. W., Panlener R. J.: *J. Electrochem. Soc.* 118, 123 (1971).
4. Meller J. W.: *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, Vol. V, p. 625. Longmans, London 1960.
5. Fahim R. B., Zaki M. I., Gabr R. M.: *J. Chem. Technol. Biotechnol.* 30, 535 (1980).
6. Johnson O.: *J. Phys. Chem.* 59, 827 (1955).
7. Toru A., Kenich M., Kazunen D., Tokahara O.: *Bull. Chem. Soc. Jpn.* 62, 349 (1989).
8. Foster D. S., Leslie S. E. in: *The Encyclopedia of Industrial Chemical Analysis*, Vol. 15, p. 152. Interscience, New York 1972.
9. Peri J. B.: *J. Phys. Chem.* 69, 212 (1965).
10. Sugunan S., Devika R. G., Sherly K. B.: *React. Kinet. Catal. Lett.* 43, 372 (1991).
11. Rodenase E., Hattori H., Toyoshima I.: *React. Kinet. Catal. Lett.* 16, 73 (1981).
12. Yamanaka T., Tanabe K.: *J. Phys. Chem.* 74, 2409 (1973).
13. Esumi K., Miyata K., Waki F., Meguro K.: *Bull. Chem. Soc. Jpn.* 59, 3363 (1986).