

Acidity/basicity, electron donor properties and catalytic activity of sulphate modified ceria

S Sugunan* & C R Kumaree Seena

Department of Applied Chemistry, Cochin University of Science and Technology,
Kochi 682 022, India

Received 9 June 1999; revised 27 August 1999

The changes in surface acidity/basicity and catalytic activity of cerium oxide due to surface modification by sulphate ion have been investigated. Electron donor properties of both the modified and unmodified oxides have been studied using electron acceptors of various electron affinity values, viz. 7,7,8,8-tetracyanoquinodimethane, 2,3,5,6-tetrachloro-1,4-benzoquinone, *p*-dinitrobenzene and *m*-dinitrobenzene in order to find out whether the increase in acidity on sulphation is due to the generation of new acidic sites or they are formed at the expense of some of the basic sites. The surface acidity/basicity has been determined using a set of Hammett indicators. The data have been correlated with the catalytic activity of the oxides for esterification of acetic acid using 1-butanol, reduction of cyclohexanone with 2-propanol and oxidation of cyclohexanol using benzophenone.

The study of sulphate modified metal oxides first reported in 1976^{1,2}, has become an active area of research because of the high catalytic activity for carbocation reactions. The significantly higher activity over that of untreated metal oxides has been ascribed to the presence of sulphur(VI) species. It is well known that some sulphate modified metal oxides lead to superacid materials with surface acidity and surface areas much larger than those oxides without sulphate³. Among solid superacids studied so far^{3,4} sulphated zirconia is the highest in acid strength. Studies on γ -alumina modified by the introduction of small amount of SO_4^{2-} , PO_4^{3-} , Cl⁻, F⁻, Mg^{+2} and Na⁺ are also reported⁵. Seiyama *et al*⁶ found that the surface acidity of bismuth and tin oxide increased upon introduction of more electronegative elements into their lattices.

Though a number of studies have so far been reported about sulphate modified metal oxides, no studies have been made to gain information about the electron donor properties of sulphate modified rare earth oxides. The electron donor properties of some rare earth oxides have been reported^{7,9}. The effect of sulphate modification on the acid and catalytic properties of samarium oxide was also reported¹⁰. In this paper, we report on the electron donor properties and surface acidity/basicity of SO_4^{2-} /

CeO_2 and CeO_2 for the esterification of acetic acid using *n*-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone.

Materials and Methods

Cerium oxide was prepared by hydroxide method¹¹ from nitrate salt. To the boiling nitrate solution, 1:1 ammonium hydroxide was added dropwise with stirring until the precipitation was complete. Concentrated ammonium hydroxide solution (an amount equal to one tenth of volume of solution) was then added with stirring, allowed to digest on a steam bath until the precipitate was flocculated and settled, the precipitate was filtered off on a whatmann No.41 filter paper, washed until the precipitate was free from NO_3^- , kept in an air oven at 110°C for overnight and was calcined at 300°C for 2 hours. It was then powdered and sieved to get samples below 75 microns mesh size. Sulphated catalysts were prepared by a previously published procedure¹². Sulphation was carried out by impregnation of the sieved oxide with a 0.2 N ammonium sulphate solution for 4 hours using a magnetic stirrer. The precipitate was filtered without washing and dried and sieved as above.

The samples activated by heating in CO_2 free air for 2 hours at various activation temperatures viz. 573, 773

and 973K were studied. The amount of electron acceptor adsorbed was determined by means of a Shimadzu 160A UV-visible spectrophotometer. The radical concentration of EA adsorbed on the oxides were determined based on the ESR spectra measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer. The reflectance spectra of the adsorbed samples were determined using a 160A UV-visible spectrophotometer with a 200-0531 reflectance attachment. The IR spectra of both modified and unmodified samples were measured using a Shimadzu IR-470 spectrophotometer. The surface area of the samples were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800.

The acidity/basicity of the oxides was determined by using the following set of Hammett indicators, (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) and 4-nitro aniline (18.4). A visible colour change was only observed with three indicators, viz. bromothymol blue, methyl red and dimethyl yellow. Acidity and basicity were determined by titration with *n*-butyl amine and trichloroacetic acid respectively.

The adsorption properties were studied with the following electron acceptors (EA), (electron affinity values are given in parenthesis): 7,7, 8, 8-tetracyanoquinodimethane [TCNQ (2.80eV)], 2,3,5,6-tetrachloro-1,4-benzoquinone [chloranil(2.40eV)] *p*-dinitrobenzene [PDNB (1.77eV)] and *m*-dinitrobenzene [MDNB(1.26eV)]. The adsorption of electron acceptors was conducted in acetonitrile, a very weak base. The activated sample was placed in a 25 ml test tube and outgassed at 1.3×10^{-3} Pa for an hour. Subsequently 10 ml of a solution of electron acceptor of choice in the organic solvent was added and the solution was stirred at 28°C for 4 hours in a thermostated bath. The sample was then collected by centrifuging the solution and dried at room temperature *in vacuo*. All the reagents were purified prior to use.

The catalytic activity of both modified and unmodified ceria were determined by the following procedures.

Esterification

In a round bottomed flask equipped with a reflux condenser were placed 1 g catalyst, 2 mmol acetic acid, and 32 mmol *n*-butanol and *n*-decane (0.20 mmol) was

used as the internal standard. The reaction temperature was maintained at 98°C and stirred continuously using a magnetic stirrer for 5 hours.

Oxidation

In a round bottomed flask equipped with a reflux condenser, were placed 0.5 g catalyst, 10 ml of a toluene solution of cyclohexanol (0.25 mmol), benzophenone (14.6 mmol) and *n*-decane (0.20 mmol) as an internal standard. The contents were heated under gentle reflux for 2 hours.

Reduction

To 0.5 g of the catalyst placed in an R.B. flask equipped with reflux condenser, 5 mmol of cyclohexanone, 10 ml 2-propanol and 0.5 mmol of xylene (internal standard) were added. The contents were heated under gentle reflux for 10 hours.

The reaction products were analyzed by CHEMITO 8510 Gas Chromatograph. The reactions showed a first order dependence on the concentration of the reactants.

Results and Discussion

The strength of an acid or base site can be expressed in terms of the Hammett acidity function, H_o , which is measured by using indicators adsorbed on the solid surface¹³. If acid sites with a H_o value, which is lower than or equal to the pK_a of the indicator exist on the solid surface, the colour of the indicator changes to that of its conjugate acid. If a neutral acid indicator is adsorbed on the solid base, the colour of the indicator changes to that of its conjugate base, provided that the solid has a significantly high basic strength. The acidity and basicity were described on a common H_o scale. The acidity measured with acidic sites whose acid strength $H_o < pK_a^{ind}$, whereas the basicity shows the number of basic sites whose base strength $H_o > pK_a^{ind}$. The acid base distribution curves meet at a point on the abscissa, H_o,max , where acidity = basicity = 0. The H_o,max value represents the acid base properties of solids which is sensitive to the surface structure. A solid with a large positive H_o,max has strong basic sites and weak acidic sites and vice versa. The acidity/basicity and the H_o,max values determined from the points of intersection of acid-base distribution curves with abscissa, at different activation temperatures are given in Table 1. The acid-base strength distribution curves are shown in Fig. 1.

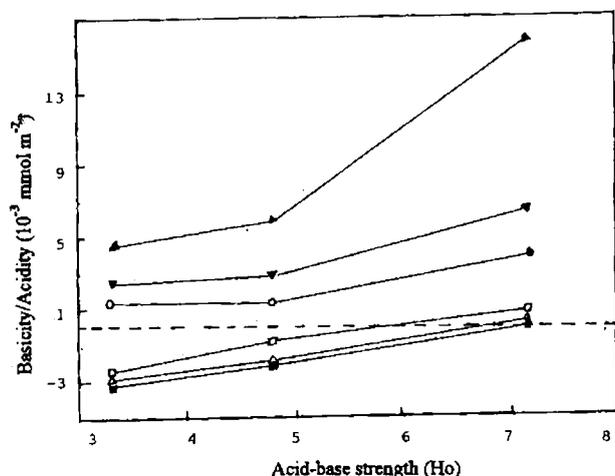


Fig. 1 - Acid-base strength distribution curves for ceria & sulphated ceria at different activation temperatures (K).

■ CeO₂ 573 ; ○ SO₄²⁻/CeO₂ 573 ; △ CeO₂ 773 ;
▼ SO₄²⁻/CeO₂ 773 ; □ CeO₂ 973 and ▲ SO₄²⁻/CeO₂ 973

The adsorption of PDNB and MDNB on CeO₂ and SO₄²⁻/CeO₂ was so low that the amount could hardly be estimated in the solvents. TCNQ and chloranil gave adsorption with characteristic results. Figures 2 and 3 shows the adsorption isotherms (Langmuir type) of the electron acceptors for CeO₂ and SO₄²⁻/CeO₂ at different activation temperatures. From that, the limiting amount of the electron acceptors adsorbed were determined. The limit of electron transfer in terms of the electron affinity (eV) of the acceptors is between 1.77 and 2.40 for both CeO₂ and SO₄²⁻/CeO₂. The limiting amount of electron acceptor adsorbed are given in Table 2.

The reflectance spectra of the samples were measured in order to gain insight into the nature of interaction during the adsorption. The spectra gave bands appearing at 400 nm (corresponding to the physically adsorbed state of neutral TCNQ, which displays¹⁴ an absorption band at 395 nm), near 600 nm (corresponding to the dimeric TCNQ radical, which has an absorption band¹⁵ at 643 nm) and a broad band extending up to 700 nm (corresponding to the chloranil anion radical)¹⁶. The samples analyzed after chloranil adsorption showed unresolved ESR spectra with a *g* value of 2.011 attributed to chloranil anion radicals¹⁷, and the samples after TCNQ adsorption gave unresolved ESR spectra with a *g* value of 2.003 identified as being those of TCNQ anion radicals¹⁸.

The radical concentrations were calculated by comparing the area obtained by double integration of the first

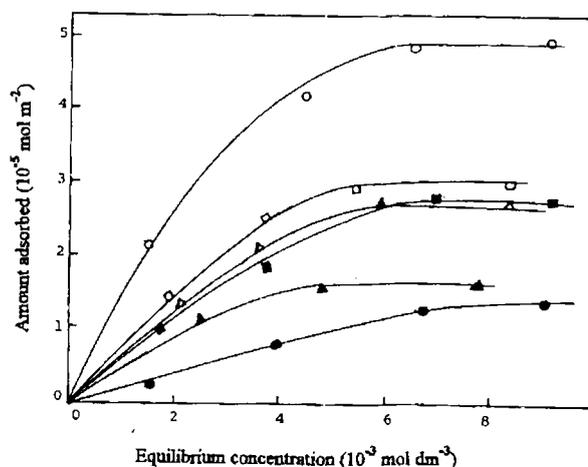


Fig. 2 - Langmuir adsorption isotherms of chloranil adsorbed on ceria & sulphated ceria at different activation temperatures (K.)

○ CeO₂ 573 ; △ SO₄²⁻/CeO₂ 573 ; □ CeO₂ 773 ;
▲ SO₄²⁻/CeO₂ 773 ; ■ CeO₂ 973 and ● SO₄²⁻/CeO₂ 973

derivative curve for the sample and standard solution of 2,2-diphenyl-1-picryl hydrazyl in benzene. The plot of radical concentration against equilibrium concentration of electron acceptor in the solution, also corresponds to the Langmuir adsorption isotherms and are of the same shape as shown in Figs. 2 and 3. The limiting radical concentrations, calculated from those plots are given in Table 2.

From the data given in Table 1, it was observed that, unmodified cerium oxide is weakly acidic as acidic sites are present only at *Ho* value of 7.2. But for sulphate modified CeO₂ acidity is generated at *Ho* values of 3.3 and 4.8 in addition to that at 7.2, which prove that the presence of sulphate ion increases both the acidity and acid strength of cerium oxide. Though acid strength of cerium oxide increases on modification with sulphate ion, it is not considered as a superacid (a surface site with acid strength more than that of H₂SO₄). Depending upon the methods used for preparation, the nature and relative concentration of surface sulphate, the surface acidic sites also change¹⁹.

Electron donor properties arise from surface O²⁻, electrons trapped in intrinsic defect sites and surface hydroxyl groups⁷⁻⁹. The data in Table 2 shows that as temperature increases, electron donating capacity decreases for both ceria and sulphated ceria. Therefore, it is inferred that surface hydroxyl groups are responsible for electron donating capacity in the case of ceria and sulphated ce-

Table 1- Acid-base strength distribution of CeO₂ and SO₄²⁻ / CeO₂ at different activation temperatures

Catalyst	Activation temp. (K)	Surface area (m ² g ⁻¹)	Basicity (10 ⁻³ mmol m ⁻²)		Acidity (10 ⁻³ mmol m ⁻²)			Ho,max
			Ho >3.3	Ho >4.8	Ho < 3.3	Ho < 4.8	Ho < 7.2	
CeO ₂	573	49.48	3.27	2.18	--	--	0.14	7.3
CeO ₂	773	44.81	3.01	1.81	--	--	0.34	6.8
CeO ₂	973	31.18	2.60	0.86	--	--	0.87	6.1
SO ₄ ²⁻ / CeO ₂	573	40.64	--	--	1.34	1.33	4.01	--
SO ₄ ²⁻ / CeO ₂	773	30.15	--	--	2.26	2.72	6.30	--
SO ₄ ²⁻ / CeO ₂	973	18.68	--	--	4.39	5.84	16.01	--

Table 2- Limiting amount and limiting radical concentration of adsorbed electron acceptors and catalytic activity of CeO₂ & SO₄²⁻ / CeO₂ for the esterification, reduction and oxidation

Catalyst	Act. temp. (K)	Limiting amount of EA adsorbed (10 ⁻⁵ mol m ⁻²)		Limiting radical conc. of EA adsorbed (10 ¹⁸ spins m ⁻²)		Catalytic activity		
		Chloranil	TCNQ	Chloranil	TCNQ	Esterification (10 ⁻⁷ s ⁻¹ m ⁻²)	Reduction (10 ⁻⁷ s ⁻¹ m ⁻²)	Oxidation (10 ⁻⁶ s ⁻¹ m ⁻²)
CeO ₂	573	4.89	8.31	0.15	3.26	1.61	17.10	5.40
CeO ₂	773	3.03	6.40	0.09	2.85	2.26	15.60	4.55
CeO ₂	973	2.81	4.48	0.08	2.31	3.34	10.20	2.92
SO ₄ ²⁻ / CeO ₂	573	2.76	4.18	0.08	2.16	7.05	0.22	1.83
SO ₄ ²⁻ / CeO ₂	773	1.59	3.53	0.05	1.82	8.53	0.16	1.56
SO ₄ ²⁻ / CeO ₂	973	1.44	3.34	0.04	1.72	10.09	0.03	1.26

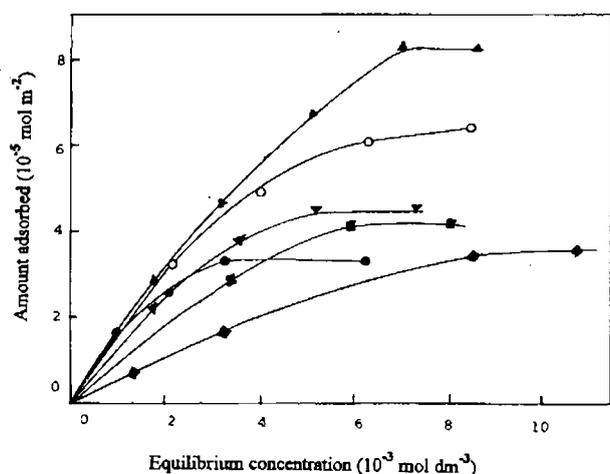


Fig. 3 - Langmuir adsorption isotherms of TCNQ adsorbed on ceria & sulphated ceria at different activation temperatures (K.)

▲ CeO₂ 573 ; ■ SO₄²⁻ / CeO₂ 573 ; ○ CeO₂ 773 ;
◆ SO₄²⁻ / CeO₂ 773 ; ▼ CeO₂ 973 and ● SO₄²⁻ / CeO₂ 973

ria. As the temperature increases, the number of hydroxyl groups decreases due to the desorption of water molecules by the dehydroxylation process from adjacent hydroxyl groups. According to Bluementhal *et al*²⁰ as activation temperature increases, electronic mobility is decreased for ceria. The decrease in electron donating capacity on increasing activation temperature may be attributed to the decrease in the number of OH groups and electron mobility. For sulphated ceria, the electron donating ability is further decreased. The decrease may be attributed to the increase in acidic strength on modification with sulphate ion. The study of electron donor properties revealed that, by sulphate modification, acidic sites are enhanced at the expense of basic sites. The nature of surface acidity in anion modified oxides remains controversial. The data in Table 2 clearly reveal the strong effect of surface modification of ceria by sulphate ion on their catalytic activity (esterification, reduction & oxidation).

The data in Table 2 indicate that sulphate modified cerium oxide catalyses the esterification reaction more effectively than the unmodified ones. On modification with sulphate ions both acidity and acidic strength increase resulting in high catalytic activity for esterification, which is found to be in agreement with the acid-base properties. The data also indicate that reduction and oxidation reactions proceed effectively over unmodified CeO₂, owing to its higher basicity. The data have been

correlated with surface electron donor properties of the oxides, which are in agreement with the acid-base properties. As activation temperature increases, catalytic activity decreases for both modified and unmodified oxides which parallels the electron donor properties. The mechanisms for both oxidation and reduction reactions involve hydride ion transfer. Lewis basicity of catalyst surface favours the hydride ion transfer. Unmodified ceria owing to its high basicity, favours both oxidation and reduction reactions. Superacidity is considered to be generated by the interaction between the oxide and sulphate ion. The strong acidity was attributed to the electron-withdrawing anion groups, which leads to coordinatively unsaturated and electron deficient metal centres that behave as strong Lewis acid sites²¹.

Infra red spectra of sulphate modified ceria show a strong absorption band at 1400 cm⁻¹ like other sulphate modified metal oxides, which correspond to the asymmetric stretching frequency of S=O double bond and is regarded as a characteristic bond of SO₄²⁻ (ref.22). High catalytic activity for esterification can be attributed to the enhanced acidic properties, which originate from the inductive effect of S=O double bond of the complex formed by the interaction of oxides with the sulphate ion. Both Lewis and Bronsted acid strengths increase due to inductive effect of S=O double bond in the complex²³.

On modification with sulphate ion, some of the basic sites are converted to acidic sites which is in agreement with the acid-base properties. Navarrete *et al*²⁴ found that the mechanism of sulphate modification is an anion exchange between SO₄²⁻ and OH⁻ species, which gives an additional proof for the enhancement of acidity at the expense of basicity. *H_{0,max}* values of the oxides are also consistent with this result.

References

1. Tanabe K, Itoh M & Hattori H, *Stud Surf Sci Catal*, 1 (1976) 65.
2. Kurosaki A & Okasaki S, *Nippon Kagaku Kaishi*, (1976) 1816.
3. Arata K, *Adv Catal*, 37 (1990) 165.
4. Hino M & Arata K, *Bull chem Soc Japan*, 67 (1994) 1472.
5. Berteau P & Delmon B, *Catal Today*, 5 (1989) 121.
6. Seiyama T, Egashira M, Sakamoto T & Aso I, *J Catal*, 24 (1972) 76.
7. Sugunan S, Devika Rani G & Sherly K B, *React Kinet Catal Lett*, 43 (1991) 375.
8. Sugunan S & Devika Rani G, *J mater Sci Lett*, 10 (1991) 887.
9. Sugunan S & Devika Rani G, *J mater Sci Lett*, 10 (1992) 1269.

10. Sugunan S & Kumaree Seena C R, *Indian J Chem*, 37A (1998) 438.
11. *Encyclopaedia of Industrial Chemical Analysis*, edited by F D Snell & L S Etire, vol 17, (Interscience, New York, 1973) P 475.
12. Jatia A, Chang C, Macleod J D, Okube T & Davis M E, *Catal Lett*, 2 (1994) 25.
13. Yamanaka T & Tanabe K, *J phys Chem*, 74 (1975) 91.
14. Acker D S & Hertler W R, *J Am chem Soc*, 84 (1962) 328.
15. Boyd R H & Phillips W D, *J chem Phys*, 43 (1965) 2927.
16. Foster R & Thomson T J, *Trans Faraday Soc*, 58 (1962) 860.
17. Esumi K & Meguro K, *Japan Colour Mater*, 48 (1975) 539.
18. Hosaka H, Fujiwara T & Meguro K, *Bull chem Soc Japan*, 44 (1971) 2626.
19. Morterra C, Cerrato G, Emanuel C & Bolis V, *J Catal*, 142 (1993) 342.
20. Bluementhal R, Lee P W & Panlener R J, *J electrochem Soc*, 118 (1971) 123.
21. Jin T, Yamaguchi T & Tanabe K, *J phys Chem*, 90 (1986) 4794.
22. Changxi Maio, Weiming Hur, Jiannum Chen & Zi Gao, *Catal Letters*, 37 (1996) 187.
23. John J R & Kim H J, *J catal.*, 101 (1986) 428.
24. Navarrete J, Lopez T & Gomez R, *Langumir*, 12 (1996) 4385.