

Electron donating properties and catalytic activity of cerium oxide and its mixed oxides with alumina

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The electron donating properties of CeO_2 and its mixed oxides with alumina have been determined from the studies of adsorption of electron acceptors of various electron affinities on the surface of these oxides. The catalytic activity of these oxides towards some reactions such as oxidation of alcohols and reduction of ketones have been correlated with their surface electron donor properties. The surface acidity/basicity of these oxides have also been determined by titration method using a set of Hammett indicators.

The electron donating properties of some of the rare earth oxides have already been reported^{1,2} and the catalytic activities of lanthana and its mixed oxides with alumina have been correlated with their electron donor properties³. Rare earth oxides have been classified as solid base catalysts^{4,5} and CeO_2 is quite often used as catalyst for a number of reactions^{6,7}. So far no effort has been made to correlate its catalytic activity with surface electron donor properties. Reduction of ketones and aldehydes by metal alkoxides and alcohol is known as Meerwein-Ponndorf-Verley (MPV) reduction and the reverse reaction which is known as Oppenauer oxidation has been used for the oxidation of alcohols with carbonyl compounds by metal alkoxides. Heterogeneous catalysts for such reaction are reported⁸. With metal oxides as catalysts the oxidation of primary and secondary alcohols^{9,10} proceeds efficiently using benzophenone as the hydrogen acceptor. It has the high ability for oxidising the alcohols and to resist aldol condensation. In this note we report the catalytic activity of CeO_2 and its mixed oxides with alumina towards some of the reactions such as oxidation of a secondary alcohol and reduction of a ketone. The data have been correlated with their surface electron donor properties which have been determined from the studies on the adsorption of electron acceptors of various electron affinities. The acid-base properties

of the oxides have been determined by titration method using a set of Hammett indicators.

Experimental

All the reagents were purified by standard procedures before use. Cerium oxide was obtained from Indian Rare Earths Ltd. Udyogamandal and was regenerated by hydroxide method¹¹. CO_2 contamination during the precipitation was prevented by a method reported earlier¹². The oxide activated by heating in CO_2 free air for 2 h at various activation temperatures viz 300, 500 and 800°C were studied. Mixed oxides of various compositions were prepared by co-precipitation from their nitrate solutions¹³. 10, 20, 40, 60 and 80% by weight of CeO_2 in alumina were studied.

The following electron acceptors were used to determine the electron donor properties of the oxides: (the electron affinity values are given in parentheses) 7,7,8,8-tetracyanoquinodimethane [TCNQ (2.84eV)], 2,3,5,6-tetrachloro-1,4-benzoquinone [chloranil (2.40eV)] and *p*-dinitrobenzene [PDNB (1.77eV)]. Adsorption studies were carried out in acetonitrile, a very weak base. The methods adopted for adsorption studies have been described elsewhere¹⁴. Specific Surface area of the oxides were determined by BET method using Carlo Erba Strumentazione Sorptomatic series 1800.

When electron acceptors were adsorbed on the surface of the oxides corresponding anion radicals were formed on the surface. The anion radicals were detected by ESR spectra using Varian E-112 X/Q band ESR spectrophotometer. The samples coloured with the adsorption of electron acceptors gave unresolved ESR spectra with *g* values of 2.003 and 2.011 corresponding to TCNQ and chloranil anion radicals respectively. Radical concentrations were calculated by comparing the 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 following Hammett indicators were used for the acidity/basicity measurement (*pK_a* values in parentheses) 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 only dimethyl yellow, methyl red and bromothymol blue responded to acidity/basicity of these oxides. A 0.1% solution of the indicator in benzene was used. The basicity was determined by titration with trichloroacetic acid and

acidity with *n*-butylamine. Data are given in Table 1. The $H_{o,max}$ values¹⁵ of these oxides were determined from the acid base distribution curves. The acid-base distribution curves intersect at a point on the abscissa ($H_{o,max}$) were acidity = basicity = 0, $H_{o,max}$ can be regarded as a practical parameter to represent acid base properties of solids which is sensitive to surface structure. It is known that a solid with a large positive $H_{o,max}$ has strong basic sites and that with a large negative value has weak basic sites.

In a round bottomed flask (20 cm³) equipped with a reflux condenser were placed catalyst (100-200 mesh, 0.5 gm), 10 cm³ 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 h at 110°C.

To 1 gm of the catalyst placed in a round bottomed flask (20 cm³) equipped with a reflux condenser, 5 mmol of cyclohexanone, 10 cm³ of 2-propanol and 0.5 mmol of xylene were added. The contents were heated under gentle reflux.

The reaction products were analyzed by CHEMITO 8510 gas chromatograph. No byproducts were detected. The reaction showed a first order dependence on the concentration of the reactant. The activity is expressed as the first order rate coefficient per unit area of the catalyst surface.

Results and discussion

The adsorption of PDNB from solution on these oxides was so negligible that the amount could not be measured. On plotting radical concentration of the electron acceptors adsorbed on these oxides against equilibrium concentration of electron acceptor the isotherms obtained were of Langmuir type. Similar isotherms were obtained in the case of plots of amount

of electron acceptor adsorbed on the oxide surface against the equilibrium concentration of electron acceptor. From these plots the limiting radical concentration of the corresponding electron acceptor was calculated. A weak electron acceptor like PDNB can accept electrons only from strong electron donor sites whereas a strong electron acceptor like TCNQ can accept electrons from both weak and strong electron donor sites. The strength of an electron acceptor can be expressed in terms of the electron affinity of the acceptor which can form anion radicals on the adsorption site. Thus the surface electron donor strength on ceria and its mixed oxides with alumina should be between 2.40-1.77 eV.

Catalytic activity and electron donor capacity as a function of activation temperature and composition are shown in Table 2 and Figs 1 and 2. In contrast to the results with lanthana^{1,3} the limiting amount of radical concentration formed on ceria decreases with

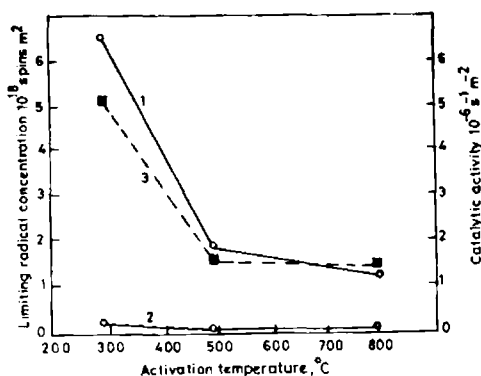


Fig. 1—Limiting radical concentration of electron acceptor adsorbed and catalytic activity for oxidation as a function of activation temperature of CeO₂, (1, TCNQ in acetonitrile; 2, Chloranil acetonitrile; 3, Rate constant)

Table 1—Acidity and basicity of CeO₂ and its mixed oxides

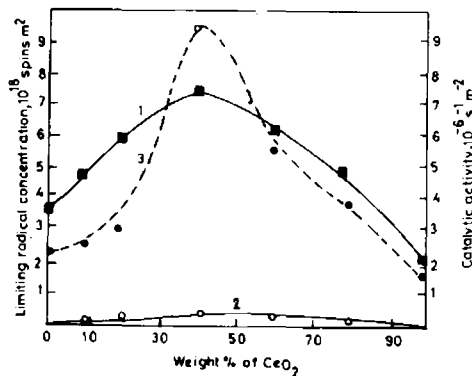
Oxides	Basicity(10 ⁻³ meq m ⁻²)			Acidity(10 ⁻³ meq m ⁻²)			$H_{o,max}$
	H_o ≥ 3.3	H_o ≥ 4.8	H_o ≥ 7.2	H_o ≤ 3.3	H_o ≤ 4.8	H_o ≤ 7.2	
CeO ₂ (300°C)†	1.08	0.52	—	—	—	1.02	5.5
CeO ₂ (500°C)	0.23	0.10	—	—	—	1.59	5.0
CeO ₂ (800°C)	0.12	—	—	—	0.12	1.79	4.3
10%CeO ₂ ‡	0.91	0.14	0.06	—	—	—	8.4
20%CeO ₂	1.41	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 ₂ O ₃	0.04	0.03	0.01	—	—	—	7.5

†Activation temperature(°C) is given in brackets.

‡Composition of the mixed oxide is reported as per cent by weight of CeO₂ in alumina. The mixed oxides are activated at 500°C.

Table 2—Surface area, catalytic activity and limiting radical concentration of CeO₂ and its mixed oxides and alumina (activation temperature in °C is given in brackets)

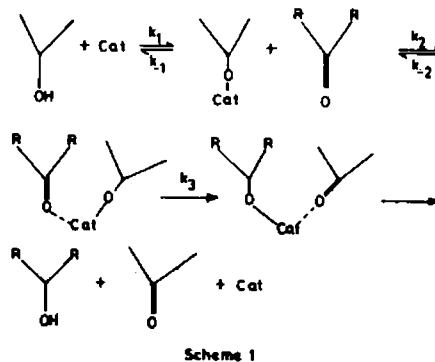
Catalyst	Surface area (m ² g ⁻¹)	Rate constant		Electron Acceptor	[Limiting Radical] (10 ¹⁸ m ⁻² spins)
		Red. (10 ⁻⁸ s ⁻¹ m ⁻²)	Oxid. (10 ⁻⁶ s ⁻¹ m ⁻²)		
CeO ₂ (300)	66.42	15.110	5.113	TCNQ	6.495
				Chloranil	0.160
CeO ₂ (500)	200.35	0.197	1.593	TCNQ	1.854
				Chloranil	0.061
CeO ₂ (800)	210.17	0.041	1.453	TCNQ	1.277
				Chloranil	0.009
Al ₂ O ₃ (500)	193.91	2.085	2.306	TCNQ	3.657
				Chloranil	0.066
10% CeO ₂ / Al ₂ O ₃ (500)	217.05	2.879	2.505	TCNQ	4.752
				Chloranil	0.106
20% CeO ₂ / Al ₂ O ₃ (500)	216.85	3.703	2.631	TCNQ	5.956
				Chloranil	0.116
40% CeO ₂ / Al ₂ O ₃ (500)	160.14	5.532	9.470	TCNQ	7.414
				Chloranil	0.159
60% CeO ₂ / Al ₂ O ₃ (500)	143.70	7.738	5.468	TCNQ	6.176
				Chloranil	0.138
80% CeO ₂ / Al ₂ O ₃ (500)	125.24	5.338	3.173	TCNQ	4.928
				Chloranil	0.122

Fig. 2—Limiting radical concentration of electron acceptor adsorbed and catalytic activity for oxidation as a function of composition of CeO₂/Al₂O₃. (1. TCNQ in acetonitrile; 2. Chloranil in acetonitrile; 3. Rate constant)

CeO₂ activated at lower temperatures (300°C) was found to be effective in both oxidation and reduction. Figs. 1 and 2 show that the catalytic activity varies in the same way as the limiting radical concentration varies as a function of activation temperature/composition.

The catalytic activity of these oxides can be rationalised in terms of the mechanism (Scheme 1) proposed by Shibagaki *et al.*¹⁸ for oxidation and reduction using ZrO₂ as catalyst. It has already been established from primary kinetic isotope effect studies¹⁸ that k_3 is the rate determining step. The basic sites play a very important role at this step. The mechanism involves hydride transfer from alcohol to the carbonyl carbon of the ketone. Lewis basicity of the catalyst surface favours the hydride transfer.

increase in activation temperature. At lower activation temperature surface hydroxyl ions are responsible for the electron transfer. At higher activation temperature free electrons derived from intrinsic defects are responsible for the electron transfer¹⁶. In ceria electrical conductivity measurements showed¹⁷ that as activation temperature increases electronic mobility is decreased. The $H_{0,max}$ value also decreases with increase in activation temperature which in turn shows the decrease in basic sites on the oxide surface.



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