

Acid-base, electron-donating and magnetic properties of Nd_2O_3 and its mixed oxides with alumina catalysts

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The electron donor properties of Nd_2O_3 activated at 300, 500 and 800 °C were investigated through studies on the adsorption of electron acceptors of various electron affinities – 7, 7, 8, 8-tetracyanoquinodimethane (2.84 eV), 2, 3, 5, 6-tetrachloro-1, 4-benzoquinone (2.40 eV), *p*-dinitrobenzene (1.77 eV), and *m*-dinitrobenzene (1.26 eV) in solvents acetonitrile and 1, 4-dioxan. The extent of electron transfer during adsorption has been found from magnetic measurements and electronic spectral data. The corresponding data on mixed oxides of neodymium and aluminium are reported for various compositions. The acid-base properties of catalysts were also determined using a set of Hammett indicators.

1. Introduction

Acid-base properties of metal oxides have been studied extensively and correlated with their catalytic activities [1, 2]. It has been observed that when an electron acceptor is adsorbed on a metal oxide, a corresponding anion radical is formed on the metal-oxide surface [3-6]. The adsorption of electron acceptors with varying electron affinities on some of the rare-earth oxides has been reported [7-9]. It is well known that the basic sites in metal oxides play an important role in catalytic reactions [10]. The determination of basicity of metal oxides by titration using Hammett indicators has been used to characterize the acid-base nature of metal oxide surfaces [11]. In the present paper we report the surface electron properties, acid-base nature and magnetic properties of Nd_2O_3 activated at 300, 500 and 800 °C.

2. Experimental Procedure

Nd_2O_3 (99.99% pure, Indian Rare Earths Ltd, Udyogamandal) was regenerated by the hydroxide method [8]. Mixed oxides of neodymium and aluminium (5, 10, 15 and 20% by weight) were prepared by co-hydrolysis from their sulphate solutions [12].

The following electron acceptors were used; the electron affinity values are given in parentheses: 7, 7, 8, 8-tetracyanoquinodimethane (TCNQ) (2.84 eV), 2, 3, 5, 6-tetra-chloro-*p*-benzoquinone (Chloranil) (2.40 eV), *p*-dinitrobenzene (PDNB) (1.77 eV) and *m*-dinitrobenzene (MDNB) (1.26 eV). The purification of electron acceptors and solvents has been described elsewhere [8].

The following Hammett indicators were used; $\text{p}K_a$ values are given 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). 0.1%

by weight of the indicator in benzene was used in each experiment.

2.1. Adsorption studies

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 fitted with a mercury-sealed stirrer and outgassed at 10^{-5} torr (1 torr = 133.322 Pa) for 1 h. A solution of electron acceptor (20 ml) in the organic solvent was then admitted into the test tube. After the solution had subsequently been stirred for 3 h at 28 °C in a thermostatted bath, the oxide was collected by centrifuging the solution and dried 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 (ESR) spectra were measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer.

The amount of electron acceptors adsorbed was determined from the difference in concentration of electron acceptors before and after adsorption. The absorbance of electron acceptors was measured using a UV-visible spectrophotometer (Hitachi 200-20) at the λ_{max} of the electron acceptor in the solvent: 393.5 and 403 nm for TCNQ, 288 and 286 nm for chloranil and 262 and 261 nm for PDNB in acetonitrile and 1,4-dioxane respectively.

Infrared spectra of oxides were taken on a Perkin Elmer PE-983 infrared spectrophotometer. The surface areas of oxides were determined by the BET method using a Carlo-Erba Strumentazione sorptomatic series 1800.

Tanabe's method was used for measurement of acid base strength of the oxides [13]. Activated

samples were ground and sieved to prepare powders of 100–200 mesh size. Acidity at various acid strengths of the solid was measured by titrating the solid suspended in benzene with a 0.1 N solution of *n*-butylamine in benzene using the chosen Hammet indicators [12]. Basicity was determined by titrating the oxide suspended in benzene with a 0.1 N solution of trichloroacetic acid in benzene using the same indicators as those used for acidity measurement. The magnetic susceptibility measurements were done at room temperature on a simple Gouy-type balance.

3. Results and discussion

The adsorption of PDNB and MDNB were negligible on all the systems studied. Adsorption was studied using two solvents – acetonitrile and 1,4-dioxane. The isotherms obtained are of Langmuir type and are shown in Fig. 1. The limiting amount of electron acceptors adsorbed was obtained from the Langmuir plot. The reflectance spectra of coloured samples showed bands appearing below 400 nm corresponding to the physically adsorbed state of neutral TCNQ and a band near 600 nm which was attributed to dimeric TCNQ radical which absorbs at 643 nm [14]. A broad band extending up to 700 nm corresponds to the chloranil anion radical [15]. In the case of the oxides studied, this assignment does not hold completely,

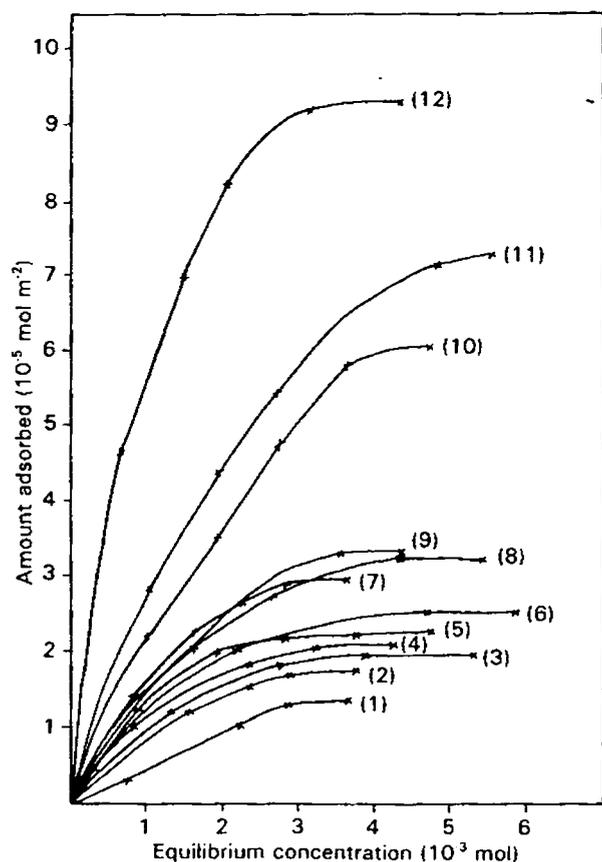


Figure 1 Adsorption isotherms on Nd_2O_3 . (1) Chloranil in dioxan at 300 C, (2) chloranil in dioxan at 500 C, (3) chloranil in dioxan at 800 C, (4) chloranil in acetonitrile at 300 C, (5) TCNQ in dioxan at 300 C, (6) TCNQ in dioxan at 500 C, (7) chloranil in acetonitrile at 500 C, (8) TCNQ in dioxan at 800 C, (9) chloranil in acetonitrile at 800 C, (10) TCNQ in acetonitrile at 300 C, (11) TCNQ in acetonitrile at 500 C, (12) TCNQ in acetonitrile at 800 C.

because they have characteristic bands in the same region. The samples coloured by TCNQ adsorption gave unresolved ESR spectra with a g value of 2.001 and coloured samples obtained by adsorption of chloranil gave unresolved spectra with a g value of 2.001 which are in agreement with those reported earlier [16]. Thus ESR and electronic spectra provide evidence that anion radicals are formed as a result of electron transfer.

The limiting amount of electron acceptors adsorbed on the oxide surface depends on activation temperature (Fig. 2). Data are given in Table I.

The dual nature of electron donor sites has been postulated previously [2]. At lower activation temperature, surface sites are associated with hydroxyl ion and at higher activation temperatures, an electron defect site is responsible for electron transfer. Infrared spectral data of Nd_2O_3 activated at 300 and 500°C confirm the presence of hydroxyl ions (peak near 3400 cm^{-1}). Because the concentration of surface hydroxyl ions decreases with increase in activation temperature it might be expected that trapped electrons are solely responsible for electron transfer at higher activation

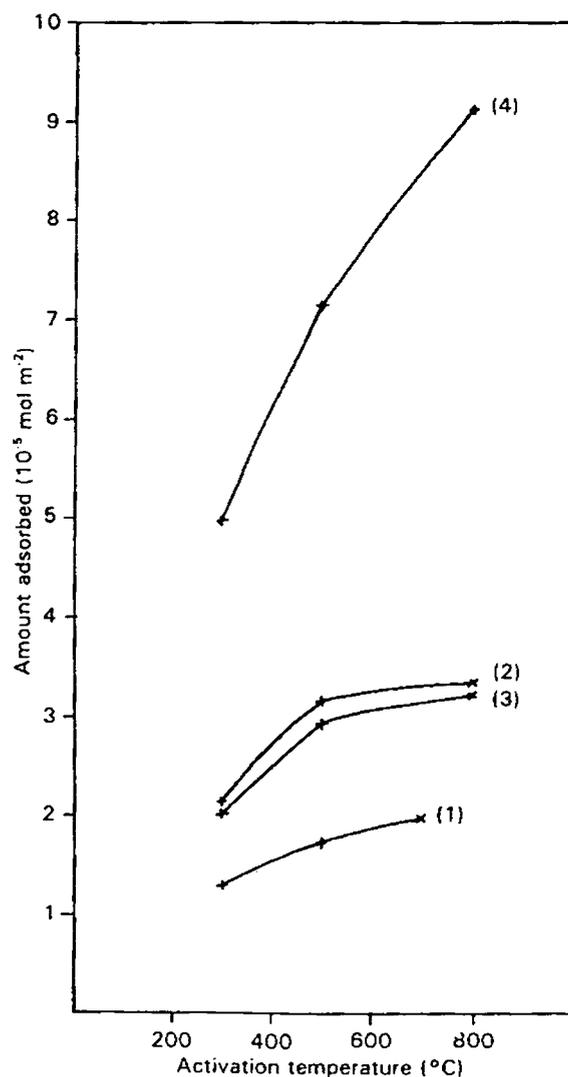


Figure 2 Effect of activation temperature on the limiting amount of electron acceptor adsorbed on Nd_2O_3 . (1) Chloranil in dioxan, (2) TCNQ in dioxan, (3) chloranil in acetonitrile, (4) TCNQ in acetonitrile.

TABLE III Magnetic moments of Nd_2O_3 after adsorption of electron acceptors

Temperature (°C)	TCNQ		Chloranil	
	Equilibrium conc. (mol^{-2})	Magnetic moment (BM)	Equilibrium conc. (mol^{-2})	Magnetic moment (BM)
300	1.07×10^{-3}	1.72	8.34×10^{-4}	2.85
	1.95×10^{-3}	1.11	1.71×10^{-3}	1.85
	2.69×10^{-3}	0.83	2.37×10^{-3}	1.61
	3.6×10^{-3}	0.7	3.2×10^{-3}	1.50
	4.7×10^{-3}	0.65	4.1×10^{-3}	1.45
500	0	3.52	0	3.52
	1.09×10^{-3}	2.4	7.94×10^{-4}	2.85
	1.99×10^{-3}	1.55	1.61×10^{-3}	1.84
	2.76×10^{-3}	1.01	2.26×10^{-3}	1.72
	2.32×10^{-3}	0.84	2.8×10^{-3}	1.60
800	4.48×10^{-6}	0.81	3.68×10^{-3}	1.61
	0	3.61	0	3.61
	7.58×10^{-4}	2.7	7.89×10^{-4}	3.2
	1.58×10^{-3}	1.81	1.65×10^{-3}	2.41
	2.3×10^{-3}	1.41	2.3×10^{-3}	2.01
	3.16×10^{-3}	0.92	2.89×10^{-3}	1.73
	4.38×10^{-3}	0.91	3.76×10^{-3}	1.71

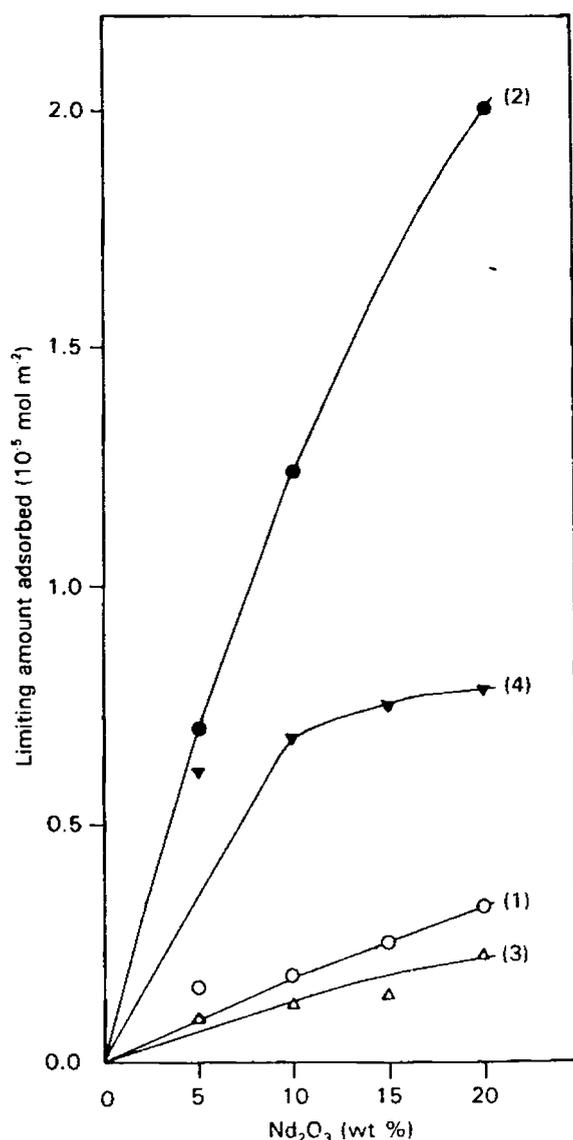


Figure 5 Limiting amount of electron acceptor adsorbed as a function of composition of $\text{Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$. (1) Chloranil in acetonitrile, (2) TCNQ in acetonitrile, (3) chloranil in dioxan, (4) TCNQ in dioxan

TABLE IV Limiting amount of electron acceptors adsorbed on mixed oxides

Nd_2O_3 (wt %)	Solvent	Electron acceptor	Limiting amount ($10^{-6} \text{ mol m}^{-2}$)
5	Acetonitrile	Chloranil	1.69
		TCNQ	7.07
10	Dioxan	Chloranil	0.91
		TCNQ	6.17
15	Acetonitrile	Chloranil	1.78
		TCNQ	12.4
		Dioxan	1.13
20	Acetonitrile	Chloranil	6.86
		TCNQ	2.51
		Dioxan	13.0
20	Dioxan	Chloranil	1.34
		TCNQ	7.41
		Chloranil	3.27
20	Dioxan	TCNQ	19.2
		Chloranil	2.15
20	Dioxan	TCNQ	7.83

and reaches a limiting value at the same concentration corresponding to the limiting amount of electron acceptor. The mixed oxide system $\text{Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$ prepared by co-hydrolysis from their sulphate solutions, showed much lower electron donicity than the single oxide Nd_2O_3 . The limiting amounts of electron acceptors adsorbed on mixed oxides of various compositions determined from Langmuir plots are shown as a function of composition of mixed oxide in Fig. 5. Data are given in Table IV.

The electron donicity increases with increase in concentration of Nd_2O_3 in the mixed oxide and decreases with increase in basicity of the solvent. Al_2O_3 prepared from aluminium sulphate had a much lower electron donicity and basicity compared to Nd_2O_3 or its mixed oxide. For mixed oxides, electron donicity increases with increasing concentration of Nd_2O_3 without changing the limit of electron transfer. Fig. 6 shows the acid base strength distribution curves of

temperature. The data show that the concentration of both weak and strong donor sites increases with increasing activation temperature.

Visible colour change was obtained for four indicators: dimethyl yellow, methyl red, neutral red and bromothymol blue. The acid-base strength distribution curves of Nd_2O_3 activated at different temperatures are shown in Fig. 3. Data are given in Table II. The acid-base strength distribution curves intersect at a point on the abscissa, ($H_{0, \text{max}}$) where acidity = basicity = 0 [13]. For Nd_2O_3 activated at 300 and 500°C, acidic and basic sites were present, while at 800°C only basic sites were present and the $H_{0, \text{max}}$ value was determined by extrapolating the basicity curve. It is known that a solid with a large positive $H_{0, \text{max}}$ value has strong basic sites and that, with a large negative $H_{0, \text{max}}$, has weak basic sites [13]. For Nd_2O_3 as activation temperature increases, $H_{0, \text{max}}$ value increases which, in turn, shows the increase in basic sites on the oxide. The donicity of the Nd_2O_3 surface increases with the basic strength of the surface itself; the more basic the surface, the higher is the number of oxygen ions which can transfer the electrons to the acceptor molecules. As the activation temperature increases, the basicity and electron donicity of Nd_2O_3 increase.

The electron donicity of Nd_2O_3 was found to decrease with increase in basicity of the solvent and the limit of electron transfer from electron donor sites of

Nd_2O_3 to the electron acceptor is located between 1.77 and 2.40 eV. Fig. 4 shows the change in magnetic moment of Nd_2O_3 as a function of equilibrium concentration of electron acceptors in solution. Data are given in Table III. The magnetic moment decreases

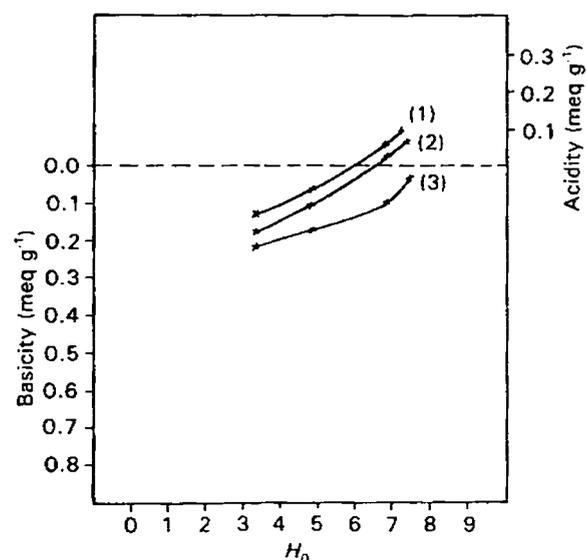


Figure 3 Acid-base strength distributions of Nd_2O_3 . Activation temperature: (1) 300°C, (2) 500°C, (3) 800°C.

TABLE I Limiting amounts adsorbed on Nd_2O_3 as a function of activation temperature

Activation temp. (°C)	Solvent	e Acceptor	Limiting amount ($10^{-5} \times \text{mol m}^{-2}$)
300	Acetonitrile	Chloranil	2.03
		TCNQ	6.01
	Dioxan	Chloranil	1.375
		TCNQ	2.27
500	Acetonitrile	Chloranil	2.94
		TCNQ	7.36
	Dioxan	Chloranil	1.74
		TCNQ	2.49
800	Acetonitrile	Chloranil	3.35
		TCNQ	9.34
	Dioxan	Chloranil	1.99
		TCNQ	3.33

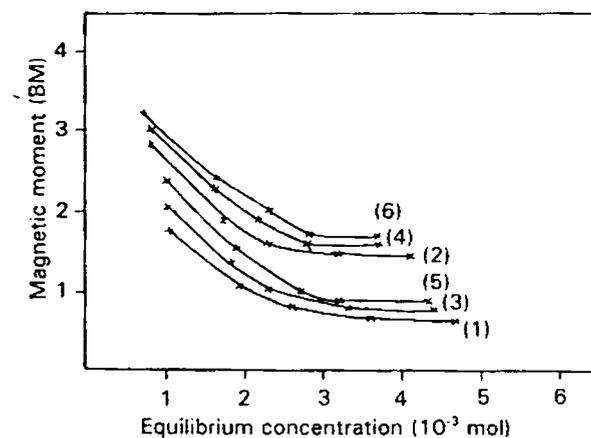


Figure 4 Effect of adsorption of electron acceptor on the magnetic moment of Nd_2O_3 . (1) TCNQ at 300°C, (2) chloranil at 300°C, (3) TCNQ at 500°C, (4) chloranil at 500°C, (5) TCNQ at 800°C, (6) chloranil at 800°C.

TABLE II Acidity and basicity of Nd_2O_3 and its mixed oxides^a

Oxide	Surface area ($\text{m}^2 \text{g}^{-1}$)	Basicity ($10^{-4} \text{ meq m}^{-2}$)				Acidity ($10^{-4} \text{ meq m}^{-2}$)				$H_{0, \text{max}}$
		$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 6.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 6.8$	$H_0 \leq 7.2$	
Nd_2O_3 (300)	39.7	3.37	1.51	-	-	-	-	1.25	2.51	6.0
Nd_2O_3 (500)	42.4	4.0	2.35	-	-	-	-	0.70	1.65	6.4
Nd_2O_3 (800)	37.9	4.21	3.82	1.51	0.25	-	-	-	-	7.3
Al_2O_3 (500)	41.2	0.58	0.82	0.17	-	-	-	-	-	7.4
5% Nd_2O_3	142.45	1.31	0.66	0.19	0.11	-	-	-	-	7.5
10% Nd_2O_3	151.50	1.64	0.87	0.35	0.15	-	-	-	-	7.6
15% Nd_2O_3	149.75	1.85	1.07	0.42	0.18	-	-	-	-	7.6
20% Nd_2O_3	154.50	2.08	1.12	0.68	0.31	-	-	-	-	7.7

^a Activation temperature (°C) is given in brackets.

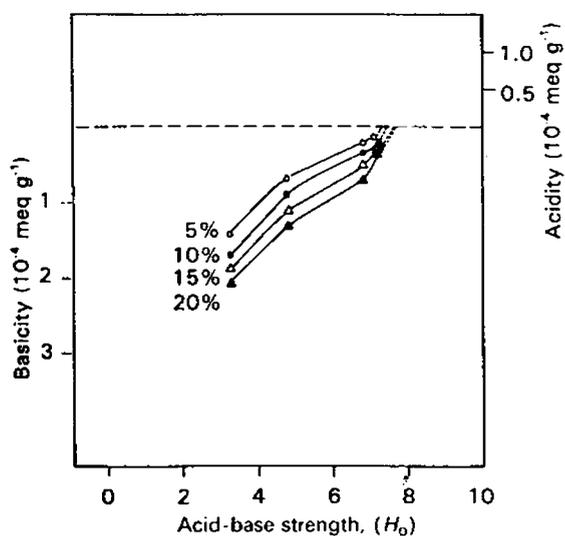


Figure 6 Acid-base strength distribution of $\text{Nd}_2\text{O}_3\text{-Al}_2\text{O}_3$.

mixed oxides. Data are given in Table II. Basicity increases with increase in concentration of Nd_2O_3 and basicity values parallel the order of electron donicity.

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