

Electron-donating, acid–base, and magnetic properties of samaria catalyst

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Revised version received 2 July 1994

Abstract—The electron-donor properties of Sm_2O_3 activated at 300, 500, and 800°C are reported from studies on the adsorption of electron acceptors of various electron affinities (electron affinity values in eV are given in parentheses): 7,7,8,8-tetracyanoquino-dimethane (2.84), 2,3,5,6-tetrachloro-1,4-benzoquinone (2.40), *p*-dinitrobenzene (1.77), and *m*-dinitrobenzene (1.26) in acetonitrile and 1,4-dioxane. The extent of electron transfer during the adsorption was determined from magnetic measurements. The acid–base properties of Sm_2O_3 at different activation temperatures are reported using a set of Hammett indicators. Electron donor–acceptor interactions at interfaces are important in elucidating the adhesion forces.

Keywords: Rare earth oxides; solid acids and bases; surface acidity and basicity; electron-donor properties; metal oxides; heterogeneous catalysts; adhesion.

1. INTRODUCTION

Acid–base interactions during the adsorption of acidic and basic molecules on inorganic powders such as iron oxides, silica, and titania have been studied by Fowkes *et al.* [1–3]. Fowkes has also extended the acid–base interaction theory to polymer–powder interfaces [4]. When strong electron acceptors or donors are adsorbed on metal oxides, the corresponding radicals are formed as a result of electron transfer between the adsorbate and metal oxide surface [5–8]. Flockhart *et al.* associated the electron-donor sites with unsolvated hydroxyl ions and defect centres involving oxide ions [9]. Such electron donor–acceptor interactions at surfaces are quite important in elucidating the adhesion forces at these interfaces. Oxides of metals such as Cr, Al, and Cu are commonly of interest in the field of adhesion. In this paper we report on the surface electronic properties, magnetic properties, and acid–base nature of a rare earth oxide, but this approach can be extended to other metal oxides. For this purpose, Sm_2O_3 samples activated at 300°C, 500°C, and 800°C were stud-

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ied. The electron-donating property was evaluated using the adsorption of electron acceptors of various electron affinities on the surface of the oxide. The acid–base properties were determined by the titration method using Hammett indicators [10]. It is well known that acidic and basic sites on metal oxides play an important role in adhesion.

2. EXPERIMENTAL

Samarium oxide was prepared by the hydroxide method [11] from the chloride salt obtained from Indian Rare Earths Ltd., Udyogamandal, India. The hydroxide was washed with dilute ammonia solution until free from chloride ions as determined by the silver nitrate test. The oxide was activated by heating it in CO₂-free air for 2 h at different activation temperatures. Activated samples were ground and sieved to prepare powders of 100–200 mesh size.

The following electron acceptors were used: 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 of 2.84, 2.40, 1.77, and 1.26 eV, respectively. Since the electron-donating properties of an adsorbent depend on the basicity of the medium, adsorption studies were carried out in two solvents: acetonitrile and 1,4-dioxane. The solvents were obtained from Merck. The purification of the adsorbate and the solvents has been described elsewhere [12].

The oxide was activated at the desired temperature for 2 h before each experiment. It was placed in a 25 ml test-tube and outgassed at 10⁻⁵ Torr for 1 h. A solution of the electron acceptor (20 ml) in an organic solvent was then added to the test-tube. After the solution had been stirred with a mercury-sealed stirrer for 3 h at 25°C in a thermostated bath, the oxide was collected by centrifuging the solution and dried at room temperature in a vacuum. The magnetic susceptibility measurements were done at room temperature on a simple Gouy-type magnetic balance. The effective magnetic moment was calculated using the general equation [13].

The reflectance spectra of adsorbed samples were recorded on a Hitachi 200-20 UV–visible spectrophotometer with a 200-0531 reflectance attachment. The ESR spectra of the adsorbed samples were measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer.

The amount of electron acceptor adsorbed was determined from the concentration difference of the electron acceptor before and after adsorption. The absorbance of the electron acceptor was measured by means of a UV–visible spectrophotometer (Hitachi 200-20) at the λ_{\max} value of the electron acceptor in the solvent, i.e. 393.5 and 403 nm for TCNQ, 288 and 286 nm for chloranil, 262 and 261 nm for PDNB, and 237 and 218 nm for MDNB in acetonitrile and in 1,4-dioxane, respectively.

Surface areas of oxides were determined by the BET method by adsorption of N₂ gas using a Carlo Erba Strumentazione Sorptomatic series 1800. The specific surface areas of the samples were 65.84, 47.97, and 30.2 m² g⁻¹ at 300, 500, and 800°C, respectively.

The following Hammett indicators were used for the acid–base strength distribution studies (the pK_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). A visible colour change was observed only for dimethyl yellow, methyl red, neutral red, and bromothymol blue. Acidity was determined by titration with *n*-butyl amine, and basicity with trichloroacetic acid.

3. RESULTS AND DISCUSSION

The adsorption of both PDNB and MDNB was so low that the amount could hardly be estimated. The adsorption isotherms of an electron acceptor from these two solvents (i.e. acetonitrile, a very weak base and 1,4-dioxane, a moderately weak base) may be classified as Langmuir type. The adsorption isotherms were drawn by plotting the amount of electron acceptor adsorbed against its equilibrium concentration. From the Langmuir plots (Fig. 1), the limiting amounts of electron acceptor adsorbed were determined. A weak electron acceptor like MDNB (electron affinity 1.26 eV) can accept electrons from strong electron-donor sites, whereas a strong electron acceptor like TCNQ (electron affinity 2.84 eV) can accept electrons from both weak and strong electron-donor sites. The strength of an electron-donor site can be expressed in terms of the electron affinity of the acceptor which can form anion radicals on the adsorption site. Hence the strength of the electron-donor sites on the Sm_2O_3 surface should be between 2.40 and 1.77 eV.

When TCNQ and chloranil were adsorbed from solutions, the surface of the oxide showed a remarkable coloration, namely bluish green for TCNQ and light pink for chloranil due to the interaction between the adsorbed electron acceptor and the oxide surface [14]. The reflectance spectra of adsorbed samples showed bands at 400, 600, and 700 nm, corresponding to the physically adsorbed state of neutral TCNQ, dimeric TCNQ radical, and chloranil anion radical, respectively [15, 16]. The ESR spectra of the samples coloured due to the adsorption of TCNQ and chloranil gave unresolved spectral lines with a g value of 2.003 and 2.011, respectively, indicating the presence of anion radicals on the surface. The concentration of radicals formed on the surface was estimated by comparing the area under the peak for the adsorbed sample and for the standard solutions of 2,2-diphenyl-1-picrylhydrazyl in benzene. Radical concentrations were plotted against the corresponding equilibrium concentration of the electron acceptor. The isotherms obtained were also of the Langmuir type. From these plots the limiting radical concentration was calculated and the data are given in Table 1.

The limiting amount of electron acceptor adsorbed on the oxide surface depends on the activation temperature. The temperature effect on the limiting amount of electron acceptor adsorbed is shown in Fig. 2. From the data it is inferred that the effect of temperature is to increase the concentration of both weak and strong donor sites on Sm_2O_3 .

During the adsorption of the electron acceptor on Sm_2O_3 , the magnetic moment of the oxide decreases and reaches a limiting value at the same concentration at which

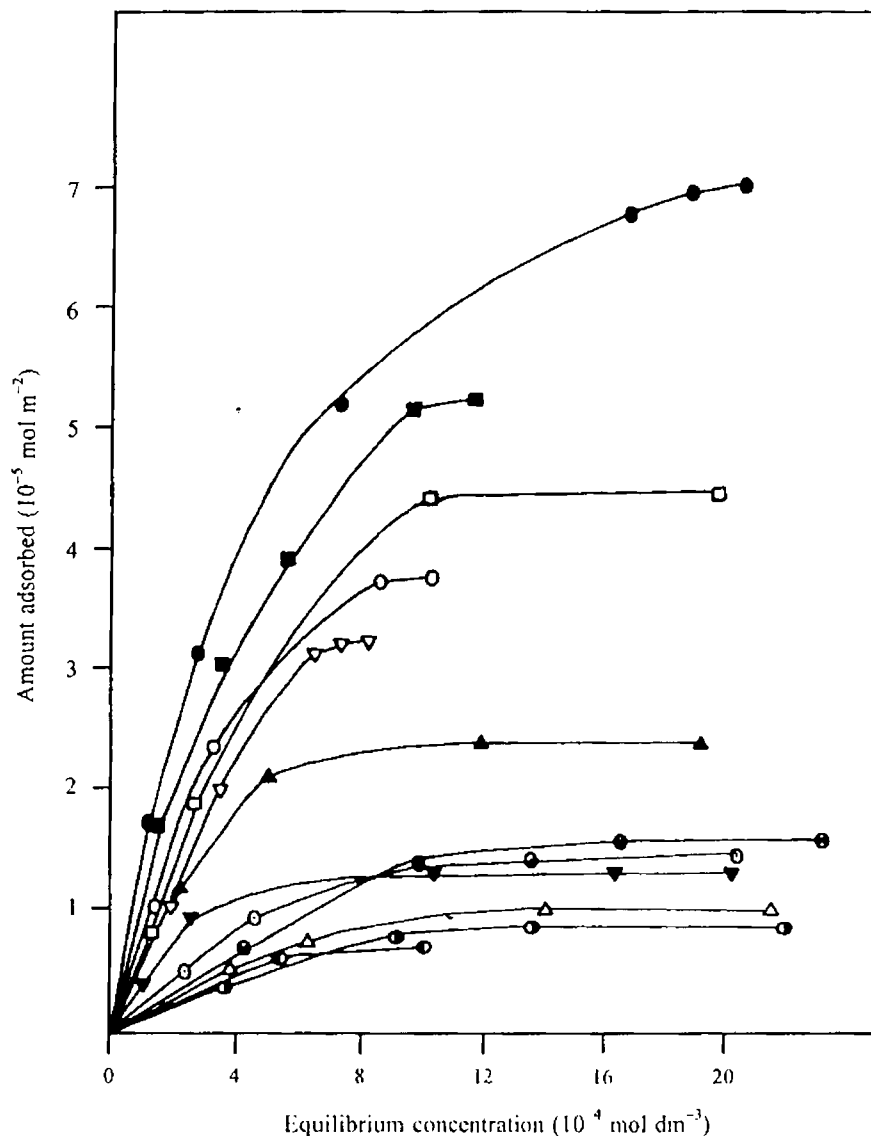


Figure 1. Adsorption isotherms on Sm_2O_3 . (●) Chloranil in dioxan at 300°C; (○) TCNQ in dioxan at 300°C; (△) chloranil in acetonitrile at 300°C; (▼) chloranil in dioxan at 500°C; (⊙) TCNQ in acetonitrile at 300°C; (⊗) chloranil in acetonitrile at 500°C; (▲) TCNQ in dioxan at 500°C; (▽) chloranil in dioxan at 800°C; (○) TCNQ in dioxan at 800°C; (□) TCNQ in acetonitrile at 500°C; (■) chloranil in acetonitrile at 800°C; (●) TCNQ in acetonitrile at 800°C.

the limiting amount of electron acceptor was adsorbed (Fig. 3). This shows the extent of electron transfer from the oxide surface to the electron acceptor. Moreover, the radical concentration also reaches a maximum at this concentration.

Table 2 shows the acidity and basicity of Sm_2O_3 activated at different temperatures. The strength of an acidic or basic site can be expressed in terms of the Hammett

Table 1.
Limiting amounts of electron acceptors adsorbed on Sm_2O_3

Temp. (°C)	Surface area ($\text{m}^2 \text{g}^{-1}$)	Solvent	Electron acceptor	Electron affinity (eV)	Limiting amount adsorbed ($10^{-5} \text{ mol m}^{-2}$)	Radical conc. ($10^{18} \text{ spins m}^{-2}$)
300	65.84	Acetonitrile	Chloranil	2.40	0.99	0.03
		Acetonitrile	TCNQ	2.84	1.46	0.79
		1,4-Dioxane	Chloranil	2.40	0.73	0.02
		1,4-Dioxane	TCNQ	2.84	0.85	0.44
500	47.97	Acetonitrile	Chloranil	2.40	1.63	0.05
		Acetonitrile	TCNQ	2.84	4.44	2.42
		1,4-Dioxane	Chloranil	2.40	1.36	0.04
		1,4-Dioxane	TCNQ	2.84	2.46	1.34
800	30.2	Acetonitrile	Chloranil	2.40	5.70	0.18
		Acetonitrile	TCNQ	2.84	7.04	3.82
		1,4-Dioxane	Chloranil	2.40	3.16	0.10
		1,4-Dioxane	TCNQ	2.84	3.68	1.90

Table 2.
Acid–base strength of Sm_2O_3 at various activation temperatures, using different Hammett indicators

Temp. (°C)	Basicity ($10^{-5} \text{ eq m}^{-2}$)				Acidity ($10^{-5} \text{ eq m}^{-2}$)				$H_{0,\text{max}}$
	$H_0 \geq 3.3$	$H_0 \geq 4.8$	$H_0 \geq 6.8$	$H_0 \geq 7.2$	$H_0 \leq 3.3$	$H_0 \leq 4.8$	$H_0 \leq 6.8$	$H_0 \leq 7.2$	
300	0.37	0.04	0.04	—	—	—	—	0.11	6.9
500	0.62	0.10	0.05	—	—	—	—	0.10	7.0
800	1.1	4.49	0.16	0.11	—	—	—	—	8.0

acidity function H_0 . It is measured by using indicators that are adsorbed on the solid surface. If acidic sites of $H_0 \leq \text{p}K_a$ of the indicator exist on a solid surface, the colour of the indicator changes to that of its conjugate acid. When a neutral or acidic indicator is adsorbed on a basic solid, the colour of the indicator changes to that of its conjugate base, provided the solid has a sufficient basic strength. Both acidity and basicity were determined on a common H_0 scale. The acidity measured with an indicator shows the number of acidic sites whose acid strength $H_0 \leq \text{p}K_a$ of the indicator, and the basicity shows the number of basic sites whose base strength $H_0 \geq \text{p}K_a$ of the indicator. The acid–base strength distribution curves meet at a point on the abscissa, $H_{0,\text{max}}$, where acidity = basicity = 0. $H_{0,\text{max}}$ can be regarded as a practical parameter to represent the acid–base properties of solids, which is sensitive to the surface structure. It was found that for Sm_2O_3 activated at 800°C only basic sites were present, while at activation temperatures of 300 and 500°C , both acidic and basic sites were present. It is known that a solid with a large negative $H_{0,\text{max}}$ value has weak basic sites and that a solid with a large positive $H_{0,\text{max}}$ value has strong basic sites [17]. The data for Sm_2O_3 show that as the activation temperature increases, the $H_{0,\text{max}}$ value increases, which, in turn, shows an increase in basic sites on the oxide.

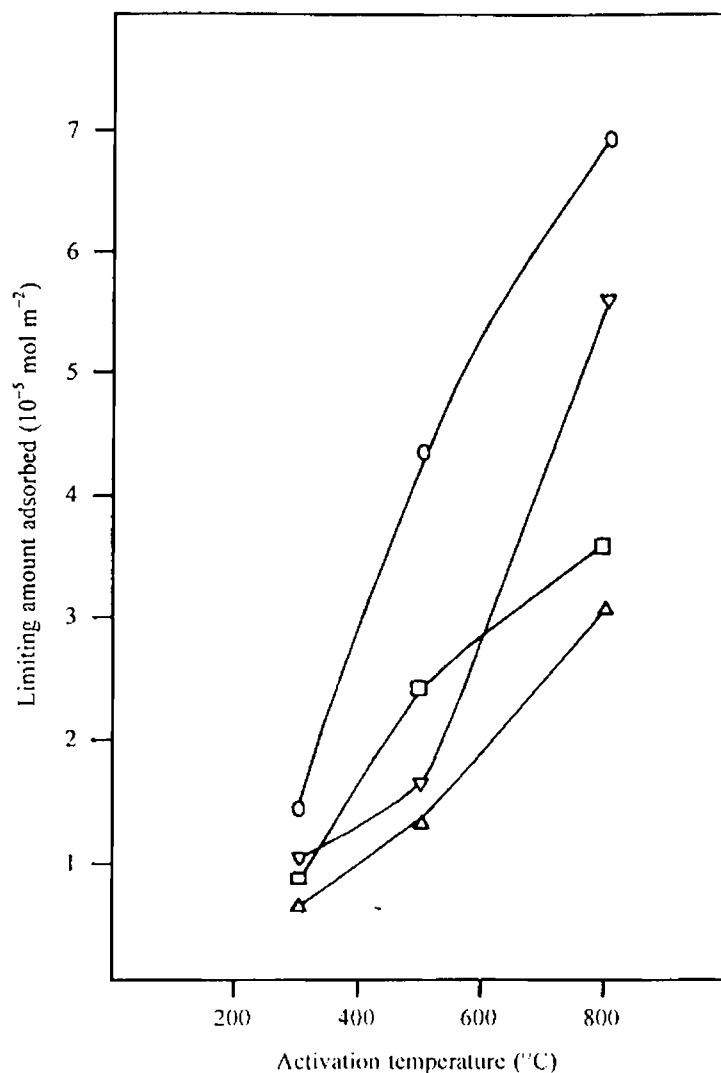


Figure 2. Effect of the activation temperature on the limiting amount of electron acceptor adsorbed on Sm_2O_3 . (Δ) Chloranil in dioxan; (\square) TCNQ in dioxan; (∇) chloranil in acetonitrile; (\circ) TCNQ in acetonitrile.

The limiting amount of electron acceptor adsorbed decreases with increasing basicity of the solvent. It shows the competition between basic solvents and basic sites (electron-donor sites) of the metal oxide for electron acceptors. The adsorption on the metal oxide has been shown to be strongly influenced by the interaction between basic solvents and electron acceptors [18].

It has been reported that two possible electron sources exist on a metal oxide surface responsible for electron transfer: one of these is associated with electrons trapped in the intrinsic defects and the other is OH groups present on the surfaces of the solids at activation temperatures lower than 500°C [19]. At higher activation temperatures, free

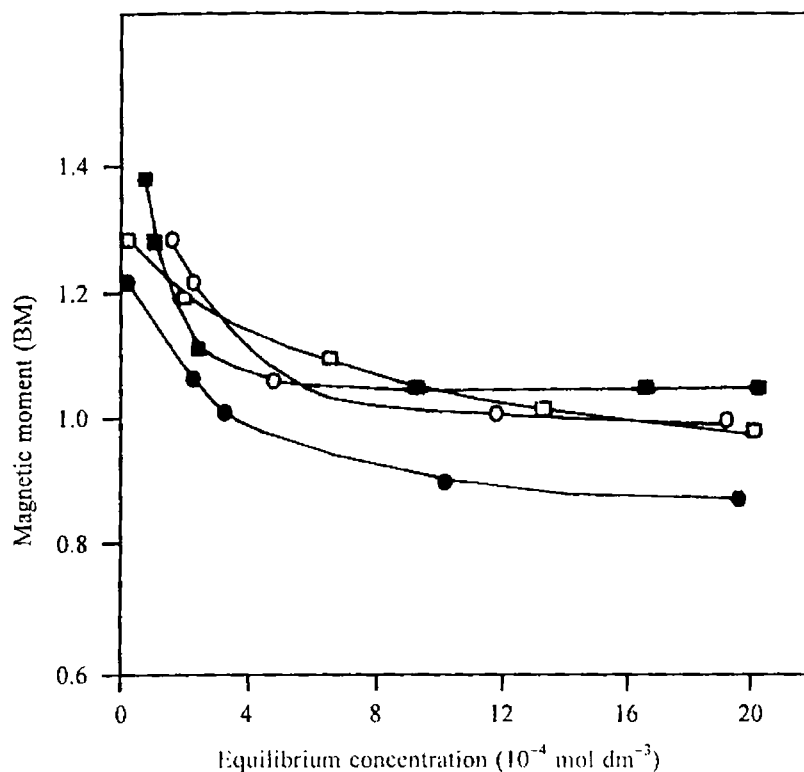


Figure 3. Effect of adsorption of the electron acceptor on the magnetic moment of Sm_2O_3 . (●) TCNQ in acetonitrile; (□) chloranil in acetonitrile; (○) TCNQ in dioxan; (■) chloranil in dioxan.

electrons originating from the intrinsic defects are responsible for the electron-donor properties of the oxide [9]. It might be expected that the trapped electron centres are solely responsible for the adsorption of electron acceptors on the surface of Sm_2O_3 activated at higher temperatures and that the concentration of such trapped electron centres increases with increasing temperature above 500°C .

4. CONCLUSION

The electron-donating properties of Sm_2O_3 have been determined by the adsorption of electron acceptors of various electron affinities in solvents of different basicities. The extent of electron transfer from the oxide surface to the electron acceptor was determined from magnetic susceptibility measurements. Anion radicals of the corresponding electron acceptors are formed due to electron transfer from the oxide surface. The electron donicity increases with increasing activation temperature of the oxide. The adsorption of electron acceptors on the oxide surface is influenced by the basicity of the solvent. The surface acidity and basicity of the oxide were also determined by the titration method using a set of Hammett indicators.

Acknowledgement

We are grateful to the University Grants Commission, New Delhi for the award of a Junior Research Fellowship to J.J.M.

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