Basicity of the electron donating properties of La_2O_3 activated at 300, 500, and 800 C and its mixed oxides with alumina compound

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Abstract

The electron donating properties of **La_2O_3** activated at 300, 500 and 800 C and its mixed oxides with alumina are reported from the studies on adsorption of electron acceptors of varying electron affinity on **La_2O_3**. The electron acceptors with their electron affinity values given in parenthesis are: 7,7,8,8-tetracyanoquinodimethane (2.84 eV), 2,3,5,6-tetrachloro-1,4-benzoquinone (2.40 eV) and p-dinitrobenzene (1.77 eV). The basicity of the oxide has been determined by titration with n-butylamine and $H_{o,max}$ values are reported. The limit of electron transfer from the oxide to the electron acceptor is between 2.40 and 1.77 eV. It is observed that **La_2O_3** promotes the surface electron properties of alumina without changing its limit of electron transfer.

Introduction

Although investigations on the catalytic properties of rare earth sesquioxides have multiplied in recent years, the primary mode of surface interactions on these materials remains largely undefined. Details of adsorption/desorption **processes,** for example, and of the nature of adsorbed species on La_2O_3 surface are sparse. Esumi et al. studied the acid-base (electron donor-acceptor) interactions of electron acceptors like 7,7,8,8-tetracyanoquinodimethane, 2, 3, 5, 6 - tetrachloride- 1,4-benzoquinone, 2,5-dichloro- p - benzoquinone, p-dinitrobenzene and m-dinitrobenzene with MgO, Al_2O_3 SiO_2, TiO_2, ZnO and NiO[1]. The adsorption of electron acceptors on Y_3O_3 and on its mixed oxides with alumina have been investigated as a function of activation temperature to study and characterize their electronic properties.

Supported rare earth oxides are quite often used as catalysts for polymerization and for carbon monoxide hydrogenation'. Rare earth oxides have already been recognized as solid

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base catalysts°". In this paper we report surface electron donating properties and acid-base nature of Lab 3 activated at various temperatures and its mixed oxide with alumina. Since the electron donating properties depend on the nature of the medium, studies were carried out in two solvents; acetonitrile a very weak base and 1,4-dioxan a moderately weak base.

Materials and Methods

Lanthanum oxide (purity 99.9%) was obtained from Indian Rare Earths Ltd. Since the oxide was already heat treated at higher temperature, it was regenerated by the hydroxide method from its chloride solution. The oxide was activated by **heating** in air for 2hr at 300, 500 and 800'C.

The electron acceptors used were 7, 7, 8, 8-tetracyanoquinodimethane **(TCNQ),** 2,3,5,6- tetrachloro-1,4- benzoquinone (chloranil), and p-dinitrobenzene (PDNB) with electron affinity values 2.84, 2.40 and 1.77 eV respectively. The solvents, acetonitrile and 1,4-dioxan used, were obtained from Merck. The purification of the adsorbates and the solvents have been described elsewhere.

The mixed oxide of lanthanum with aluminum was prepared for different weight percentages of La_2O_3 by the co-precipitation method with aluminum nitrate solution. The following mixed oxides were prepared, 10,20,45,60 and 75 (% by wt. of La_2O_3) and were activated at 500'C. Alumina and La_2O_3 were also prepared by the hydroxide method from the respective nitrate solutions. The specific surface area of the oxides were determined by the BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The values in m^2g^{-1} were as follows (activation temperature is given in brackets): La_2O_3 (300'C) 39.8, Lab La_2O_3 (500°C) 38.28 and La_2O_3 (800'C) 29.75. The specific surface area of the mixed oxides at 500°C were Al_2O_3 193.91; 10% La_2O_3/Al_2O_3, 169.12; 20% La_2O_3/Al_2O_3 157.47; 45% La_2O_3/Al_2O_3 , 149.70; 60% La_2O_3/Al_2O_3, 144.65 and 75% La_2O_3/Al_2O_3, 81 m^2g^{-1}.

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The oxides were activated at a particular temperature for 2hr prior to each experiment. The oxide (0.5g) was placed in a 25ml test tube which was fitted with a mercury sealed stirrer. It was outgassed at 10^{-5} Torr for 1hr. Solution of an electron acceptor (20 ml) in organic solvent was then admitted into the test tube. After stirring the solution for 3hr at 28'C in a thermostatic bath, the oxide was collected by centrifuging the. solution and dried at room temperature in vacuum. The reflectance spectra of the dried 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 Varian E-112 X/Q band ESR spectrophotometer. The amount of electron acceptor adsorbed was determined from the difference in concentration before and after adsorption.

The absorbance of electron acceptors was measured at the tax of the electron acceptor in the solvent. The y_{max} were 393 and 403nm for TCNQ, 288 and 286nm for chloranil and 262 and 26lnm for PDNB in acetonitrile and 1,4-dioxan. respectively. The concentration and strength of acidic and basic sites on the surface were measured by titration method[10] using the following indicators (the *pKa* values are given in brackets): crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroani1ine (18.4). The acidity was determined by titration with n-butylamine and basicity with trichloroacetic acid.

Results

In the case of PDNB the adsorption was so negligible that the amount was hardly estimated. The adsorption isotherms of TCNQ and chloranil from these two basic solvents may be classified as Langmuir type. From the Langmuir plots of these isotherms, the limiting amounts of TCNQ and chloranil adsorbed were obtained. Visible colour change was obtained only for dimethyl yellow, methyl red, neutral red and bromothymol blue.

Discussion

When electron acceptors were adsorbed from solvents on the surface of the oxides, the surface showed remarkable coloration characteristic for the kind of acceptors like bluish

green for TCNQ and light pink for chloranil. These colorations were due to the interaction between the acceptor adsorbed and the oxide surface.

The ESR spectrum of the sample colored with adsorption of TCNQ and chloranil gave unresolved spectral line with a g-value of 2.003 and 2.01 I respectively with a width of approximately 30 G indicating the presence of anion radicals on the surface. The electronic spectrum of the adsorbed sample gave bands near 400, 600 and 700nm corresponding to physically adsorbed state of neutral TCNQ[1], dimeric TCNQ radical and to chloranil anion radical. In the case of oxides studied this assignment does not hold completely because these oxides have characteristic bands in the same region.

The following Figure shows the increase in the limiting amounts of TCNQ and chloranil adsorbed from both solvents. It was reported that two possible electron sources exist on the metal oxide surface responsible for the electron transfer". One of these has electrons trapped in intrinsic defects and the other has hydroxide ions. The free electron defect site on metal oxide surface was created at activation tempratures above 500°C. The ionization potential of the hydroxide ion is comparatively small (2.6 eV in the gas phase). Hence the other site may be the surface hydroxide ion and the participation in oxidation-reduction process of the type

$$OH + A = OH + A$$
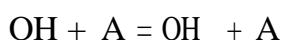
(where A is an electron acceptor) can be included. Electron transfer from hydroxide ions occurs in certain solvent systems provided a suitable acceptor molecule is present.

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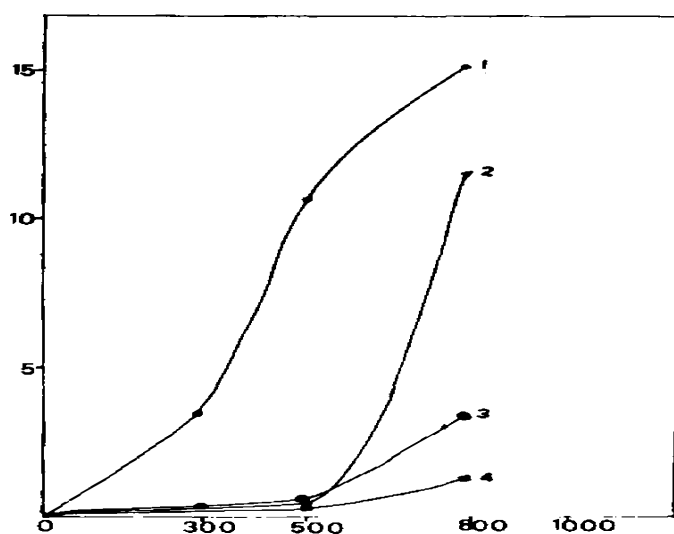
Temperature 1 ° Cl

Figure: Limiting amount of electron acceptors adsorbed on La$_2$O$_3$ as a function of activation temperature. (1, TCNQ in acetonitrile; 2, TCNQ in dioxan; 3, chloranil in acetonitrile; 4, chloranil in dioxan.)

When La$_2$O$_3$is activated at 800'C, the presence of surface hydroxide ions cannot be expected. The possible electron source responsible for electron transfer should be the electron donor defect site created on La$_2$O$_3$ at this temperature.

Electron donor properties of La$_2$O$_3$ & its mixed Oxides

It has been reported that La$_2$O$_3$ is catalytically inactive unless calcined at temperature p> 400ºC. La (OH)$_3$ undergoes thermal decomposition in two stages. A well defined oxyhydroxide LaOOH intermediate formed at 200'C, decomposes in a second stage at 300'C. Above 400'C the dehydration or the oxyhydroxide is complete and exposed La^{3+} and/or basic O^{2-} ions in various normal or defective surface environments become available for participation as components of active sites. The change in limiting amount 1ºC the electron acceptor adsorbed as a function of the activation temperature can thus be understood.

The increase in limiting amount of electron acceptors adsorbed is small at activation temperatures below 50t1'C. Above 500'C the limiting amount of electron acceptors increases appreciably with increasing activation temperature. This trend can be understood as the decrease in concentration of surface hydroxyl ions and the increase in concentration of trapped electron centers with increasing temperature. It might be expected that the trapped electron centers are solely responsible for the adsorption of electron acceptors on the surface of La$_2$O$_3$ activated at higher temperatures and the concentration of such trapped electron centers increases with increase in temperature above 500'C. A weak electron acceptor like PDNB (1.77 eV) can accept electrons from strong electron donor sites whereas a strong electron acceptor like TCNQ (2.84 eV) can accept electrons from both weak and strong

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sites. The strength of an e) electron donor site can be expressed in terms of the electron affinity of the acceptor which can form anion radical on the adsorption site. Hence the limit of electron transfer of La_2O_3 is between 2.40 and 1.77 eV. Limiting value of the electron acceptor adsorbed shows the concentration and distribution of electron donor sites on La_2O_3. From the data it must be inferred that the effect of temperature is to increase the concentration of both weak and strong donor sites on La_2O_3.

The following Figure shows the increase in limiting amount of electron acceptor adsorbed as a reaction of the composition of the mixed oxide. The limiting amount of the electron acceptor adsorbed increases with increase in percentage of La_2O_3 in the mixed oxide, as a consequence of the increase in concentration of $Al-O-La$ bonds. Further addition of La_2O_3 decreases the limiting amount without changing the limit of electron transfer due to the increase in concentration of La_2O_3 in the oxide lattice because La_2O_3 has lower electron donating capacity Al^2O^3.
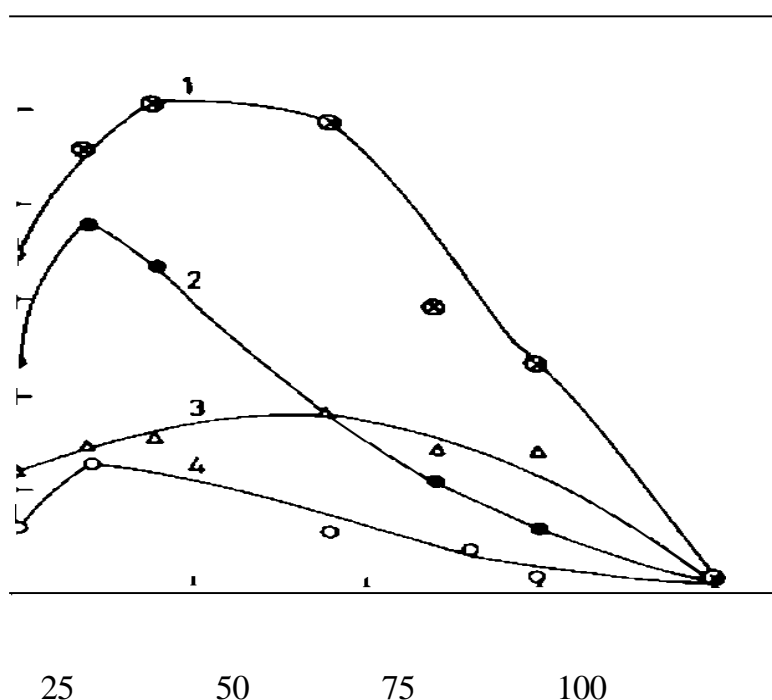

Fig. Limiting amount of electron acceptors adsorbed as a function of composition of La_2O_3.

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The following figure shows the basicity of La_2O_3 and its mixed oxides with alumina. For all these oxides only basic sites could be observed. The $H_{o,max}$ value of the oxides was determined by the extrapolation of the basicity curve to the abscissa where acidity = basicity = 0. It is known that a solid with a large positive $H_{o,max}$ value has strong basic sites and that with a large negative $H_{o,max}$ value has weak sites. $H_{o,max}$ values increase with increase in temperature which parallel the electron donating properties of the oxide.
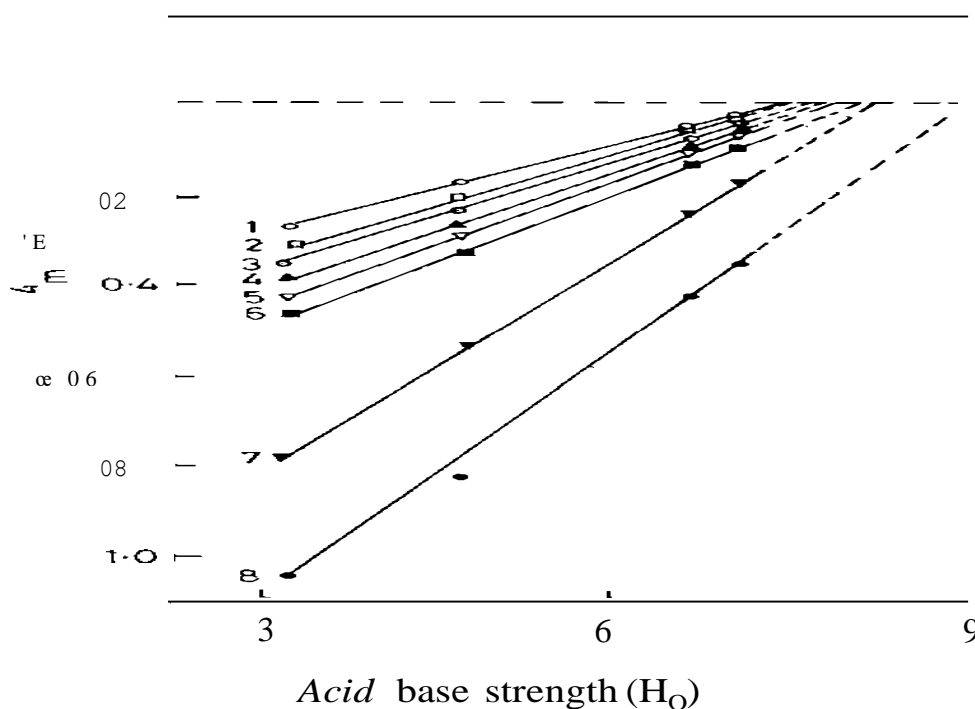

Fig. Acid-base strength distribution or La_2O_3 and its mixed oxides with alumina.

Hence it can be concluded that the amount of electron acceptors adsorbed depends on the activation temperature of the oxide, basicity of the solvent, the electron affinity of the electron acceptor and the electron donor power of the oxide surface. The limit of electron transfer of La_2O_3 and its mixed oxides with alumina lies between 1.77 and 2.40 eV gratitude to the CSIR, New Delhi, for the award of a junior research fellowship to KBS.

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