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SURFACE ELECTRON DONOR PROPERTIES OF Dy_2O_3 , Y_2O_3 AND
THEIR MIXED OXIDES WITH ALUMINA CATALYST

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The limit of electron transfer in electron affinity from the oxide surface to the electron acceptor (EA) are reported from the adsorption of EA on Dy_2O_3 , mixed oxides of Dy_2O_3 with alumina and mixed oxides of Y_2O_3 with γ -alumina. The extent of electron transfer is understood from magnetic measurements.

The adsorption of electron acceptors (EA) on metal oxides has been investigated to estimate electron donor properties of metal oxides and their characterization [1]. The electron donor properties of some of the rare earth oxides have been reported [2-4]. Dy_2O_3 and Y_2O_3 have been used as catalyst for a variety of reactions [5]. In this paper we report surface electron donating properties and magnetic properties of Dy_2O_3 activated at various temperatures and its mixed oxides with alumina and mixed oxides of Y_2O_3 with γ -alumina.

EXPERIMENTAL

Dy_2O_3 and Y_2O_3 were obtained from Indian Rare Earths Ltd. Dy_2O_3 was regenerated by the hydroxide method [6] from its nitrate solution and activated by heating in air for 2 h, at

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300, 500 and 800°C were studied. Mixed oxides of Dy and Al were prepared by the co-precipitation method [7] for compositions of 5, 10, 20, 45, 60 and 75 wt.% Dy_2O_3 and were activated at a temperature of 500°C and mixed oxides of Y_2O_3 with γ -alumina were prepared by impregnation method [8] for compositions of 5, 10, 15 and 20 wt.% Y_2O_3 and activated at 500°C. The following EA 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. The specific surface areas of the catalysts were determined by the BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The purification of the adsorbates and the solvents and the details of the experimental techniques have been described elsewhere [2].

The ESR spectra of the adsorbed samples were measured at room temperature using a Varian E-112 X/Q band ESR spectrophotometer. Infrared spectra of oxides were taken on a Perkin Elmer PE-183 Infrared Spectrophotometer. The magnetic susceptibility of Dy_2O_3 before and after adsorption was measured using a simple Guoy type balance.

In the case of PDNB and MDNB the adsorption was so negligible that the amount was hardly estimated. The adsorption of EA has been studied in two solvents, acetonitrile, a very weak base, and 1,4-dioxan a moderately weak base. The adsorption isotherms of EA from these two solvents may be classified as Langmuir type. From the Langmuir plots the limiting amounts of EA adsorbed were obtained [2], Fig. 1.

Magnetic moment of Dy_2O_3 during adsorption decreases and reaches a minimum value at a concentration corresponding to the limiting amount of EA adsorbed (Fig. 2), indicating the extent of electron transfer from the oxide surface to the EA.

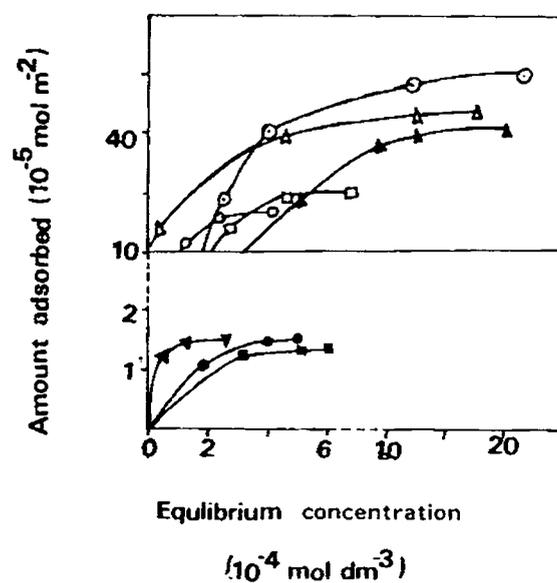


Fig. 1. Adsorption isotherms of Dy_2O_3

- TCNQ in acetonitrile 300°C
- Chloranil in dioxan 800°C
- ▼ TCNQ in dioxan 500°C
- TCNQ in dioxan 800°C
- Chloranil in acetonitrile 500°C
- ▲ TCNQ in acetonitrile 500°C
- △ Chloranil in acetonitrile 800°C
- ⊙ TCNQ in acetonitrile 800°C

RESULTS AND DISCUSSION

When TCNQ and chloranil were adsorbed from solutions, the surface of oxides showed remarkable coloration characteristics for the kind of acceptors like bluish green for TCNQ and light pink for chloranil due to the interaction between the EA adsorbed and the oxide surface [9]. The ESR spectrum of the sample colored with 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

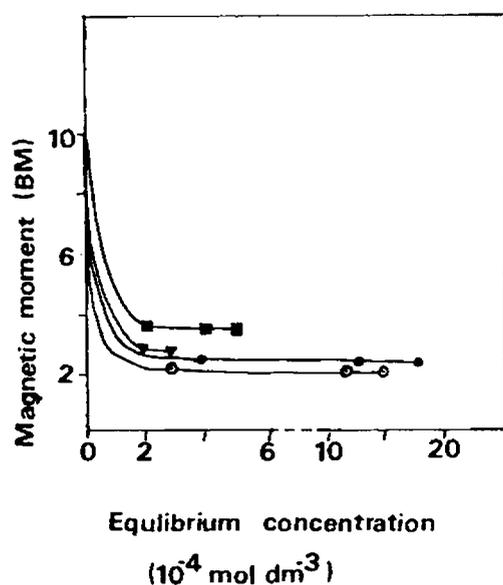


Fig. 2. Magnetic moment of Dy_2O_3 as a function of equilibrium concentration of electron acceptor
 ○ TCNQ in acetonitrile ▼ TCNQ in dioxan*
 ● Chloranil in acetonitrile ■ Chloranil in dioxan

surface. The electronic spectrum of the adsorbed sample gave bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ [4], dimeric TCNQ radical [10] and to chloranil anion radical [11]. In the case of oxides studied this assignment does not hold completely because these oxides have characteristic bands in the same region.

Figure 3 shows the effect of temperature on the limiting amount of EA adsorbed on Dy_2O_3 from acetonitrile and dioxan. It was reported that two possible electron sources exist on the metal oxide surface, responsible for the electron transfer [1]. One of these has electrons trapped in intrinsic defects and the other has hydroxide ions. It has been observed by IR spectroscopy that the surface of the oxides activated at 500°C

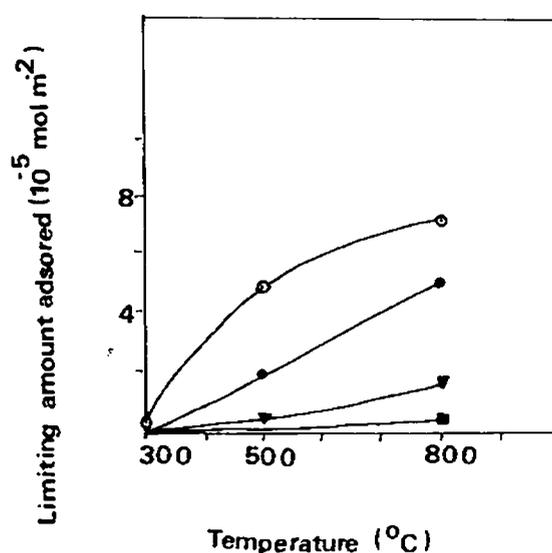


Fig. 3. Limiting amount of electron acceptors adsorbed on Dy_2O_3 as a function of activation temperature
 ○ TCNQ in acetonitrile ▼ TCNQ in dioxane
 ● Chloranil in acetonitrile ■ Chloranil in dioxane

contain hydroxy groups (peak near 3400 cm^{-1}). The free electron defect site on metal oxide surface was created at activation temperatures above 500°C [12], where the presence of surface hydroxide ions would be insignificant. The possible electron source responsible for electron transfer should be the electron donor defect site created on Dy_2O_3 at high temperature. The effect of increase in activation temperature is to increase the concentration of electron donor sites, as indicated by the data on the limiting amount of the EA adsorbed.

A weak EA like MDNB (1.26 eV) can accept electrons from strong electron donor sites, whereas a strong EA like TCNQ (2.84 eV) can accept electrons from both weak and strong donor sites. The strength of an electron donor site can be expressed in terms of the electron affinity of the acceptor which can

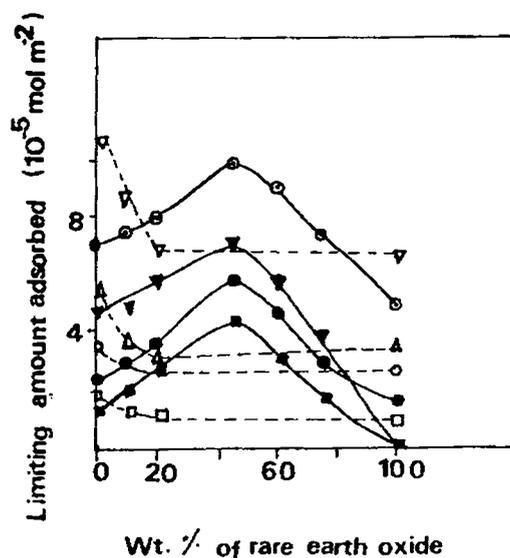


Fig. 4. Limiting amount of electron acceptors adsorbed as a function of composition of $\text{Dy}_2\text{O}_3\text{-Al}_2\text{O}_3$ (thick lines) and $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ (dotted lines)
 ∇ , \circ TCNQ in acetonitrile
 \circ , \bullet Chloranil in acetonitrile
 Δ , \blacktriangledown TCNQ in dioxan
 \square , \blacksquare Chloranil in dioxan

form anion radicals on the adsorption site. Hence the limit of electron transfer of the catalysts should be between 2.40 and 1.77 eV. Limiting amount for the various EA adsorbed is a measure of the number and donor strength of electrons on oxide surface. 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 Dy_2O_3 .

Figure 4 shows the change in surface electron properties of the catalyst as a function of composition. The limiting amounts of the EA adsorbed increases with increase in percentage of Dy_2O_3 in the mixed oxide, goes to a maximum and then

decreases with further increase in concentration of Dy_2O_3 in Al_2O_3 . The surface electron properties of alumina are promoted by Dy_2O_3 in the mixed oxide without changing the limit of electron transfer, as a consequence of the increase in concentration of Al-O-Dy bonds. Further addition of Dy_2O_3 decreases the limiting amount due to the increase in concentration of Dy_2O_3 in the oxide lattice because Dy_2O_3 has lower electron donocity than Al_2O_3 . The relative decrease in electron donor properties of Y_2O_3 in γ -alumina can be understood along the same line.

The decrease in adsorption of EA with increase in basicity of solvents shows the competition between the solvent and the electron donor site of metal oxide surface for EA.

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