Electron donor strength of rare earth oxides

S Sugunan* & G Devika Rani
Department of Applied Chemistry, Cochin University of Science & Technology, Kochi 682 022
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The adsorption of electron acceptors, viz., 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-
P-benzoquinone (chloranil) and p-dinitrobenzene (PDNB) on the surface of three rare earth oxides Y2O3, Nd2O3 and Pr6O11 has been studied in acetonitrile and dioxan. From the radical concentration on the surface determined using ESR spectral data, the electron donor strength of the rare earth oxides are reported.

The utility of electron acceptor adsorption for the study of electron donor properties of metal oxides has been well established. Esumi et al. studied the electron donor properties of some metal oxides and they found that difference in electron donor properties among metal oxide systems can be characterized by the change in electron acceptor radicals formed. Comparing the radical forming activity of metal oxides, their electron donor properties have been evaluated. The adsorption of electron acceptors on some of the rare earth oxides have been reported. The present note describes an investigation of the electron donor strength of three rare earth oxides Y2O3, Nd2O3 and Pr6O11 by comparing their radical forming tendencies.

Experimental

The rare earth oxides, viz., Y2O3, Nd2O3 and Pr6O11 were prepared by hydroxide method from the salts obtained from Indian Rare Earths Ltd., Udyogamandal. The electron acceptors employed for the study are TCNQ, chloranil and PDNB. The purification of these reagents and solvents have been described elsewhere. The oxides were activated at 500°C for 2h prior to each experiment. The oxide (0.5 g) was placed in a 25 ml test tube fitted with a mercury sealed stirrer and was outgassed at 10⁻¹³ Torr for 1h. A solution of electron acceptor in acetonitrile (20 ml) was then admitted into the tube. After the solution had subsequently been stirred for 3h at 28°C in a thermostated bath, the oxide was collected by centrifuging and dried at room temperature in vacuo. 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 were measured at room temperature using Varian E-122 X/Q band ESR spectrophotometer. The radical concentrations were calculated by comparison of areas obtained by double integration of first derivative curves for the sample and standard solutions of 1,1-diphenyl-2-picrylhydrazyl in benzene.

The amount of electron acceptor adsorbed was determined from the difference in concentration of electron acceptor in solution before and after adsorption. The absorbance of electron acceptor was measured by means of a Hitachi 200-20 UV-vis spectrophotometer at the λmax of electron acceptor in the solvent: 393 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. The infrared spectra of oxides were taken on a Perkin Elmer PE-983 Infrared spectrophotometer. The surface area of oxides was determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800.
Table I—Data of electron acceptor adsorption on rare earth oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Surface area m² g⁻¹</th>
<th>Electron acceptor</th>
<th>Colour</th>
<th>Limiting amount absorbed mol m⁻²</th>
<th>Limiting-radical concentration spin m⁻²</th>
<th>Radical concentration Amount adsorbed spin mol⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y₂O₃</td>
<td>81.5</td>
<td>Chloranil light pink</td>
<td></td>
<td>2.46 × 10⁻³</td>
<td>1.38 × 10¹⁶</td>
<td>5.22 × 10²⁰</td>
</tr>
<tr>
<td>Y₂O₅</td>
<td>81.5</td>
<td>TCNQ green</td>
<td></td>
<td>7.21 × 10⁻³</td>
<td>3.98 × 10¹⁸</td>
<td>5.26 × 10²²</td>
</tr>
<tr>
<td>Nd₂O₃</td>
<td>42.4</td>
<td>Chloranil</td>
<td></td>
<td>2.94 × 10⁻⁵</td>
<td>1.65 × 10¹⁶</td>
<td>5.30 × 10²⁰</td>
</tr>
<tr>
<td>Nd₂O₅</td>
<td>42.4</td>
<td>TCNQ light blue</td>
<td></td>
<td>7.36 × 10⁻³</td>
<td>4.01 × 10¹⁸</td>
<td>5.40 × 10²²</td>
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<tr>
<td>Pr₆O₁₁</td>
<td>11.4</td>
<td>Chloranil</td>
<td></td>
<td>3.39 × 10⁻⁵</td>
<td>1.99 × 10¹⁸</td>
<td>5.52 × 10²²</td>
</tr>
<tr>
<td>Pr₆O₁₃</td>
<td>11.4</td>
<td>TCNQ</td>
<td></td>
<td>7.44 × 10⁻⁵</td>
<td>4.03 × 10¹⁸</td>
<td>5.46 × 10²²</td>
</tr>
</tbody>
</table>

Results and discussion

The adsorption of three electron acceptors viz. TCNQ (7,7,8,8-tetracyano-quinodimethane), chloranil (2,3,5,6-tetrachloro-p-benzoquinone) and PDNB (p-dinitrobenzene) were studied on Y₂O₃, Nd₂O₃ and Pr₆O₁₁ activated at 500°C. The electron affinities were 2.84, 2.40 and 1.77 eV respectively. The adsorption of PDNB was negligible on all the systems studied. In the case of TCNQ and chloranil, the adsorption isotherms obtained were of Langmuir type and the limiting amount of electron acceptors adsorbed were determined from the Langmuir plot (Fig. 1).

When the electron acceptors were adsorbed on the oxides, their surfaces acquired characteristic colouration (Table 1) owing to interaction between electron acceptor and oxide surface. In the case of Pr₆O₁₁, the colourations acquired after the adsorption of TCNQ and chloranil could not be distinguished from the black colour of the oxide. The reflectance spectra of coloured samples indicated bands near 400, 600 and 700 nm corresponding to physically adsorbed state of neutral TCNQ, dimeric TCNQ radical and chloranil anion radical respectively. The electronic state of adsorbed species was studied by ESR spectroscopy which indicated the presence of radical species. The samples coloured by TCNQ and chloranil gave unresolved spectral line with a gvalue of 2.003 and 2.001 respectively with a width of approximately 30G indicating the presence of anion radicals on the surface. A representative plot (Fig. 2) shows the radical concentration of TCNQ adsorbed against the equilibrium concentration of electron acceptor in solution. The isotherm obtained is of the same shape as in Fig. 1. The limiting radical concentrations have also been calculated from the Langmuir plot and are given in Table 1.

It is observed that limiting amount of electron acceptor adsorbed and limiting radical concentration of electron acceptor increase with increase in electron affinity of electron acceptor and decrease with increase in basicity of solvent. A strong electron acceptor like TCNQ is capable of forming anion radicals even from weak donor sites whereas weak acceptor like PDNB is capable of forming anion radicals only at strong donor sites. Hence the limiting radical concentration of a weak acceptor is a measure of the number of strong donor sites on the surface and that for a strong acceptor is the total of all weak and strong donor sites on the surface. It is found that the limiting radical concentration and also the limiting amount of electron acceptor adsorbed decrease with decrease in electron affinity of electron acceptor.
the case of the oxides studied, the limiting amount decreased steeply between chloranil and PDNB. Hence the limit of electron transfer (in electron affinity) from Y$_2$O$_3$, Nd$_2$O$_3$ and Pr$_6$O$_{11}$ activated at 500°C was located between 2.40 and 1.77 eV.

It has been proposed that two types of electron donor sites are responsible for electron transfer from oxide surfaces. The electron donor sites of oxides are associated with surface hydroxyl ions at lower activation temperature and with electron defect sites at higher activation temperature. It has been observed by IR spectroscopy that the surfaces of Y$_2$O$_3$, Nd$_2$O$_3$ and Pr$_6$O$_{11}$ activated at 500°C contain hydroxyl groups (peak near 3400 cm$^{-1}$).

The electron donor strength can be expressed as the conversion ratio of an electron acceptor adsorbed on the surface to its anion radical. This ratio can be estimated by dividing TCNQ radical concentration by the corresponding half value of the limiting amount of TCNQ. The values obtained for the three oxides are given in Table 1. The larger the value of this ratio, the stronger the electron donor site. This ratio is almost constant for the three rare earth oxides studied implying a constant electron donor strength of the weak and strong donor sites.

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References