

Surface electron properties of yttrium oxide supported on alumina

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The absorption of electron acceptors on rare-earth oxides has been investigated to study and characterize the electronic properties of some rare-earth oxides [1, 2]. Since supported rare-earth oxides are used as catalysts for polymerization, carbon monoxide hydrogenation, etc. [3], we studied the surface electron properties of yttrium oxide supported on alumina. The amount of electron acceptor adsorbed was determined for different weight percentages of the catalyst at the same activation temperature. The electron acceptors used were 7,7,8,8-tetracyanoquinodimethane (TCNQ), 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil), *p*-dinitrobenzene (PDNB) and *m*-dinitrobenzene (MDNB). Acetonitrile and 1,4-dioxan were used as the solvents for the study.

Yttrium oxide was obtained from Indian Rare Earths Ltd, Udyogamandal, and aluminium sul-

phate from BDH Laboratories. Yttrium oxide was supported on alumina at different weight percentages by the coprecipitation method [4]. Aqueous NH_3 was added to a mixed aqueous solution of yttrium sulphate and aluminium sulphate until the pH of the solution was 9.5. The precipitate was filtered and washed until no SO_4^{2-} ions were detected. The precipitate was calcined at 500 °C. Similarly, catalyst was prepared for 5, 10, 15 and 20 wt % yttrium oxide. Aluminium hydroxide was precipitated from aluminium sulphate at pH 9.5 and calcined to obtain Al_2O_3 , which was also used for the study of adsorption of electron acceptors. Each catalyst was activated by heating in air at 500 °C for 3 h before each experiment. The specific surface areas of samples were determined by the Brunauer-Emmett-Teller (BET) method and are given in Table I.

Materials and methods used in the experimental technique were reported in [1]. The values of limiting amounts of the electron acceptors adsorbed on the catalysts are given in Table II.

It was found that the isotherms obtained were of Langmuir type. In the case of PDNB and MDNB the adsorption was so negligible that the amount was hard to estimate. The limiting amounts of electron acceptors adsorbed on the surface decreased with decreasing electron affinity of the electron acceptor

TABLE I Surface areas of oxides

| Catalyst | Surface area ($\text{m}^2 \text{g}^{-1}$) |
|--|---|
| Al_2O_3 | 41.2 |
| Y_2O_3 | 81.5 |
| $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ (5%) | 106.40 |
| $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ (10%) | 108.48 |
| $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ (15%) | 108.68 |
| $\text{Y}_2\text{O}_3/\text{Al}_2\text{O}_3$ (20%) | 104.20 |

TABLE II Limiting amounts of electron acceptors adsorbed

| Catalyst | Solvent | Electron acceptor | Limiting amount adsorbed (mol m^{-2}) |
|--|--------------|-------------------|--|
| Y_2O_3 | Acetonitrile | Chloranil | 2.462×10^{-5} |
| | Acetonitrile | TCNQ | 7.218×10^{-5} |
| | Dioxan | Chloranil | 1.260×10^{-5} |
| | Dioxan | TCNQ | 2.460×10^{-5} |
| $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ (5%) | Acetonitrile | Chloranil | 1.588×10^{-6} |
| | Acetonitrile | TCNQ | 1.984×10^{-6} |
| | Dioxan | Chloranil | 8.846×10^{-7} |
| | Dioxan | TCNQ | 1.512×10^{-6} |
| $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ (10%) | Acetonitrile | Chloranil | 1.652×10^{-6} |
| | Acetonitrile | TCNQ | 4.171×10^{-6} |
| | Dioxan | Chloranil | 1.498×10^{-6} |
| | Dioxan | TCNQ | 4.021×10^{-6} |
| $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ (15%) | Acetonitrile | Chloranil | 1.807×10^{-6} |
| | Acetonitrile | TCNQ | 4.589×10^{-6} |
| | Dioxan | Chloranil | 1.655×10^{-6} |
| | Dioxan | TCNQ | 4.197×10^{-6} |
| $\text{Y}_2\text{O}_3-\text{Al}_2\text{O}_3$ (20%) | Acetonitrile | Chloranil | 2.437×10^{-6} |
| | Acetonitrile | TCNQ | 5.540×10^{-6} |
| | Dioxan | Chloranil | 2.155×10^{-6} |
| | Dioxan | TCNQ | 4.997×10^{-6} |
| Al_2O_3 | Acetonitrile | Chloranil | 9.857×10^{-8} |
| | Acetonitrile | TCNQ | 1.527×10^{-7} |
| | Dioxan | Chloranil | 9.2009×10^{-8} |
| | Dioxan | TCNQ | 1.274×10^{-7} |

and with increasing basicity of the solvent, in agreement with earlier work.

When TCNQ and chloranil were adsorbed on the surface of these oxides the surface showed remarkable coloration owing to the interaction between the adsorbed acceptor and the oxide surface [5]. This is shown in Table III.

It was found that the electron donor centres formed on supported oxides were fewer than on the single oxide. It was reported that the $\text{TiO}_2\text{-SiO}_2$ and $\text{TiO}_2\text{-Al}_2\text{O}_3$ systems showed less activity than TiO_2 when the adsorbed state of TCNQ on these oxides was studied [6]. Two possible electron sources are responsible for electron transfer. One of these has electrons trapped in intrinsic defects and the other hydroxyl ions [7]. Since it was reported that free-electron defect sites on the metal oxide surface were created at the activation temperature of above 500°C [8], it might be expected that free hydroxyl ions present on the surface are responsible for the electron-donor properties of these oxides. This was confirmed from infrared spectral data. When Al_2O_3 prepared from aluminium sulphate by the same method was studied, it was found that the amount of electron acceptor adsorbed was less than that of yttrium oxide. It was also found that as the weight percentage of yttrium oxide in the supported catalyst increased, the limiting amount of electron acceptor adsorbed also increased. Fig. 1 shows the increase in the limiting amounts of electron acceptor adsorbed as a function of the composition of the catalyst. Also, the limit of electron transfer from the electron-donor sites of these oxides is located between 2.40 and 1.77 eV in both acetonitrile and 1,4-dioxan, as is the case for pure yttrium oxide [2]. It must be inferred that the surface electron properties of yttrium oxide are reduced by supporting the catalyst on alumina without changing the limit of electron transfer.

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TABLE III The coloration of oxide surfaces

| Catalyst | Electron acceptor | Colour of the oxide after absorption |
|--|-------------------|--------------------------------------|
| Y_2O_3 | TCNQ | Green |
| | Chloranil | Light pink |
| $\text{Y}_2\text{O}_3\text{-Al}_2\text{O}_3$ | TCNQ | Blue |
| | Chloranil | Pink |
| Al_2O_3 | TCNQ | Bluish green |
| | Chloranil | Yellow |

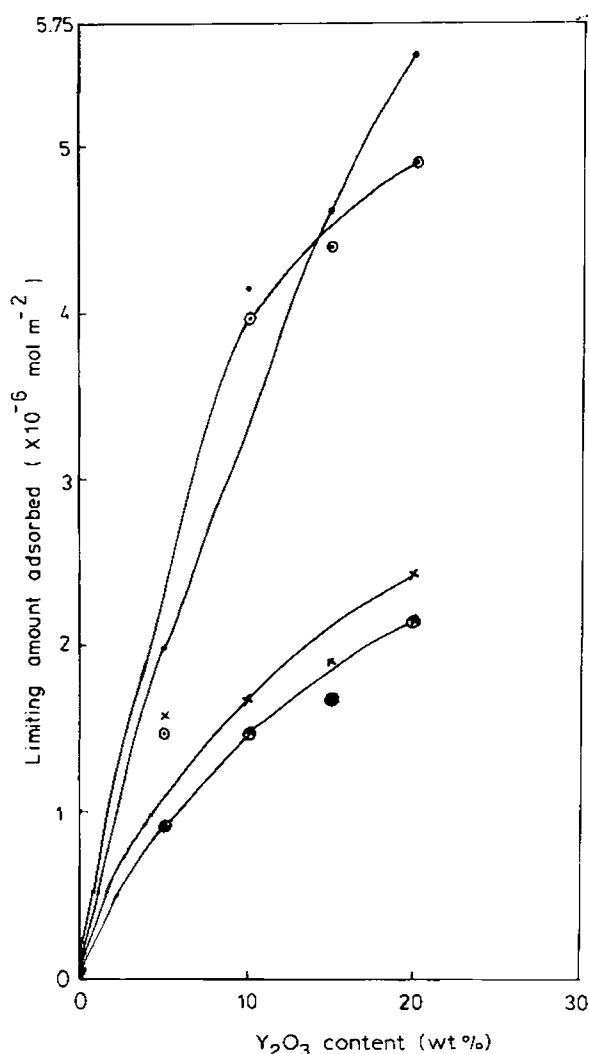


Figure 1 Limiting amounts of electron acceptors adsorbed as a function of the composition of the catalyst. (●) TCNQ in acetonitrile. (○) TCNQ in dioxan. (X) chloranil in acetonitrile and (⊗) chloranil in dioxan.

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