

## Acidity/basicity, electron donor properties and catalytic activity of sulphate modified stannic oxide

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The surface electron donor properties of sulphate modified stannic oxide have been determined from the adsorption of electron acceptors of various electron affinities on the oxide surface. The acid base properties of stannic oxide have been determined by titration method using Hammett indicators. Catalytic activities of the oxide for esterification of acetic acid using *n*-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone have been studied. The data have been correlated with the surface electron donor properties of these oxides. The activity for reduction and oxidation decreases and that for esterification reaction increases on modification with sulphate ion. It has been found that electron donating capacity decreased when stannic oxide was modified with sulphate ion.

The recent breakthrough in the chemistry of catalysis by non-zeolitic solid superacids is related, in particular to the problem of activation and utilization of paraffins as well as to new applications of superacids for the production of fine chemicals. Solid superacids have been synthesized by the addition of sulphate ion to  $\text{Fe}_2\text{O}_3$  (ref.1),  $\text{TiO}_2$  (ref.2),  $\text{ZrO}_2$  (refs.3,4) and  $\text{HfO}_2$  (ref.5). The activity enhancement of metal oxides by sulphate addition was not observed for  $\text{MgO}$ ,  $\text{CaO}$ ,  $\text{CuO}$ ,  $\text{NiO}$ ,  $\text{ZnO}$ ,  $\text{CdO}$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{MnO}_2$ ,  $\text{ThO}_2$ ,  $\text{Bi}_2\text{O}_3$  and  $\text{CrO}_3$  (ref.6). For  $\text{SnO}_2$  acidity and activity are remarkably enhanced by sulphate addition, though its highest acid strength was not superacidic,  $H_0 = -8.2$  (ref.7). It was shown that for the surface of activated oxides modified by sulphate ion, the sulphate groups were described as covalently bonded to the metal oxide lattice<sup>8</sup>. Among the solid superacids studied so far sulphate supported zirconia is highest in acid strength ( $H_0 = -16.04$ ). Sulphated ternary oxide containing Fe, Mn and Zr has recently been developed, by Hsu *et al*<sup>9</sup>, and has shown higher superacidity than  $\text{SO}_4^{2-}/\text{ZrO}_2$ .

The purpose of this study is to find out whether the increase in acidity due to sulphate modification can be at the expense of basic sites already present on the surface, or it can be due to the generation of new acidic sites. For this purpose  $\text{SnO}_2$  is chosen as

a model oxide which possess both acidic and basic sites. We have investigated the changes in acid/base properties, electron donor properties and catalytic activity of tin oxide when it is modified with sulphate ion.

In order to correlate the acidity/basicity with catalytic activity, esterification of acetic acid using *n*-butanol, reduction of cyclohexanone in 2-propanol and oxidation of cyclohexanol with benzophenone are the selected reactions.

### Materials and Methods

Stannic chloride was prepared from stannous chloride by oxidation with aqua regia, which was then converted to stannic oxide by hydroxide method<sup>10</sup>. To the solution 1:1 ammonia solution was added to precipitate the hydroxide. The precipitate was washed free of  $\text{NO}_3^-$  ion and  $\text{Cl}^-$  ion. The sample was dried at  $110^\circ\text{C}$ . Then it was powdered and sieved to get samples below 75 micron mesh size. Sulphate modification was carried out by impregnation with 0.2 M ammonium sulphate solution. The precipitate was filtered without washing and dried and sieved as before. The samples activated by heating in  $\text{CO}_2$  free air for 2 hours at various activation temperatures viz 300, 500 and  $700^\circ\text{C}$  were studied.

The strength and distribution of electron donor sites on the oxide surface were determined by the adsorption of different electron acceptors (EA) from acetonitrile solution. The following EA were used for this purpose: (the electron affinity values are given in parenthesis) 7,7,8,8-tetracyanoquinodimethane [TCNQ (2.84eV)], 2,3,5,6-tetrachloro-1,4-benzoquinone [chloranil (2.40eV)], *p*-dinitrobenzene [PDNB (1.77eV)] and *m*-dinitrobenzene [MDNB (1.26eV)] in acetonitrile as a solvent which is a very weak base. The activated samples were placed in a 25ml test tube and outgassed at  $10^{-5}$  Torr for an hour. Subsequently 10ml of a solution of the electron acceptor of choice in the organic solvent was added. The solution was stirred for 4 h at 28°C, the oxide was collected by centrifuging the solution and dried at room temperature *in vacuo*. The amount of electron acceptor adsorbed was determined by means of UV-vis spectrophotometry by noting the absorbance of the solution of electron acceptor before and after adsorption at the  $\lambda_{\max}$  of electron acceptor in acetonitrile.

When electron acceptors were adsorbed on the surface of oxides, corresponding anion radicals were formed on the surface. The radical concentrations of EA adsorbed on these oxides were determined from the ESR spectra measured at room temperature using Varian E-112 X/Q band ESR spectrophotometer by comparison of the areas obtained by double integration of the first derivative curves for the sample and standard solutions of 2,2-diphenyl-1-picrylhydrazil in benzene. The reflectance spectra of adsorbed samples were measured using a Shimadzu (UV-160A) UV-visible spectrophotometer with a 200-0531 reflectance attachment.

The IR spectra of both modified and unmodified samples were measured using a Shimadzu IR-470 spectrophotometer. The surface area of the samples were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800.

The acidity/basicity was determined by the standard procedure by titrating the solid suspended in benzene against *n*-butyl amine/trichloroacetic acid for acidity and basicity<sup>11</sup> respectively using a set of Hammett indicators. Following indicators ( $pK_a$  values in brackets) were used: Crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), bromothymol

blue (7.2), neutral red (6.8) and 4-nitroaniline (18.4). The oxides under study responded only to methyl red, dimethyl yellow and bromothymol blue. The activity of both tin oxide and sulphate modified tin oxide were determined by the following procedure.

#### Esterification

In a round bottomed flask equipped with a reflux condenser were placed 1 g catalyst (below 75 micron mesh size), 2 mmol acetic acid and 32 mmol *n*-butanol and *n*-butane was used as the internal standard. The reaction temperature was maintained at 98°C and stirred continuously using a magnetic stirrer for 5 h.

#### Oxidation

In a round bottomed flask equipped with a reflux condenser were placed 0.5 g catalyst (below 75 micron mesh size), 10 ml of a toluene solution of cyclohexanol (0.25 mmol), benzophenone (14.6 mmol) and *n*-decane (0.20 mmol) as an internal standard. The contents were heated under gentle reflux.

#### Reduction

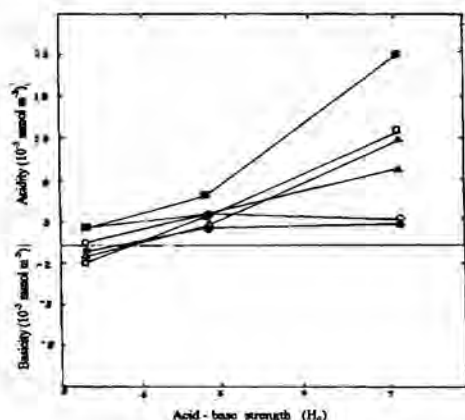
To 0.5g of the catalyst placed in a round bottomed flask equipped with a reflux condenser, 5 mmol of cyclohexanone, 10 ml 2-propanol and 0.5 mmol of xylene were added. The contents were heated under gentle reflux. The reaction products were analyzed by CHEMTO-8510 Gas Chromatograph using a calibration obtained with standard samples<sup>12</sup>. The reactions showed a first order dependence on the concentration of the reactants.

#### Results and Discussion

Acidity/basicity at different activation temperatures are given in Table.1. The acid base strength distribution curves are given in Fig.1. Both acidity and basicity were determined on a common  $H_0$  scale, where strength of the basic sites were expressed as  $H_0$  of the conjugate acids. The positive region shows acidity at various  $H_0$  values and negative region shows basicity at various  $H_0$  values. The acidity increases with increase in  $H_0$  values and basicity decreases with increase in  $H_0$  values. The acid base distribution curves intersect at a point on the abscissa where acidity = basicity = 0. The point of intersection is defined<sup>13</sup> as  $H_{0,\max}$ . It can be regarded as a practical parameter to represent the acid base properties of solids which is sensitive to surface structure. A solid

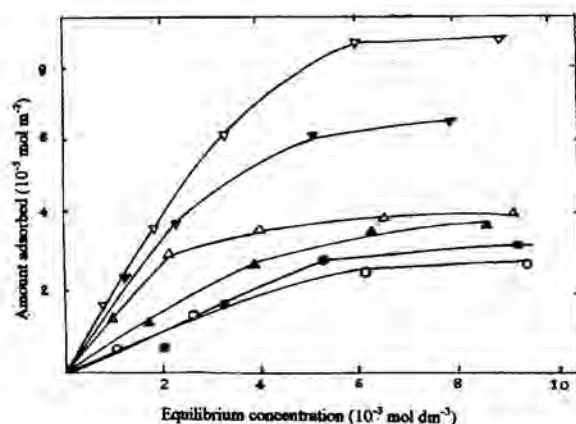
Table 1 - Acid base strength distribution of  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$  at different activation temperatures

| Catalyst                        | Activation temp.(°C) | Surface area ( $\text{m}^2 \text{g}^{-1}$ ) | Basicity ( $10^{-3} \text{mmol m}^{-2}$ )<br>$H_0 \geq 3.3$ | Acidity ( $10^{-3} \text{mmol m}^{-2}$ ) |                |                |                     |
|---------------------------------|----------------------|---------------------------------------------|-------------------------------------------------------------|------------------------------------------|----------------|----------------|---------------------|
|                                 |                      |                                             |                                                             | $H_0 \leq 3.3$                           | $H_0 \leq 4.8$ | $H_0 \leq 7.2$ | $H_{0, \text{max}}$ |
| $\text{SnO}_2$                  | 300                  | 122                                         | 0.66                                                        | ..                                       | 1.99           | 2.89           | 3.72                |
| $\text{SnO}_2$                  | 500                  | 31                                          | 0.85                                                        | ..                                       | 2.57           | 12.80          | 3.74                |
| $\text{SnO}_2$                  | 700                  | 13                                          | 1.97                                                        | ..                                       | 3.90           | 13.90          | 3.85                |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 300                  | 133                                         | ..                                                          | 0.61                                     | 2.43           | 3.34           | ..                  |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 500                  | 54                                          | ..                                                          | 2.50                                     | 4.00           | 9.01           | ..                  |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 700                  | 22                                          | ..                                                          | 2.45                                     | 6.11           | 23.23          | ..                  |

Fig. 1 - Acid base strength ( $H_0$ ) distribution of stannic oxide and sulphated stannic oxide activated at different temperatures of 300, 500 and 700°C (•  $\text{SnO}_2$  300°C; ○  $\text{SO}_4^{2-}/\text{SnO}_2$  300°C; △  $\text{SnO}_2$  500°C; ▲  $\text{SO}_4^{2-}/\text{SnO}_2$  500°C; ▽  $\text{SnO}_2$  700°C; and ■  $\text{SO}_4^{2-}/\text{SnO}_2$  700°C)

with a large positive  $H_{0, \text{max}}$  has strong basic sites and weak acidic sites and vice versa.

The adsorption of PDNB and MDNB from solutions on both stannic oxide and sulphate modified stannic oxide was so negligible that the amount could hardly be measured. TCNQ and chloranil gave adsorption with characteristic results. The amounts of electron acceptors adsorbed on these oxides were determined from the concentration difference of the electron acceptor before and after adsorption. On plotting the amount adsorbed ( $A_{\text{ads}}$ ) against the equilibrium concentration ( $C_{\text{eq}}$ ) of the electron acceptor, the isotherms obtained were of the Langmuir type. From such plots, the limiting amounts of EA adsorbed can be calculated. It was verified by the linear form of Langmuir isotherm, where  $A_{\text{ads}}/C_{\text{eq}}$  was plotted

Fig. 2 - Amount of chloranil in ( $10^{-5} \text{mol m}^{-2}$ ) vs. its equilibrium concentration in ( $10^{-3} \text{mol dm}^{-3}$ ) on  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$  activated at different temperatures of 300, 500 and 700°C (▼  $\text{SnO}_2$  300°C; ●  $\text{SO}_4^{2-}/\text{SnO}_2$  300°C; ▽  $\text{SnO}_2$  500°C; ▲  $\text{SO}_4^{2-}/\text{SnO}_2$  500°C; ▴  $\text{SnO}_2$  700°C; and ○  $\text{SO}_4^{2-}/\text{SnO}_2$  700°C)

against  $C_{\text{eq}}$ . The Langmuir adsorption isotherms obtained by the adsorption of chloranil and TCNQ are given in Figs 2 and 3 respectively.

When electron acceptors are adsorbed from the solution, the surface developed remarkable colouration characteristic of each EA adsorbed and the oxide surface<sup>14</sup>. Chloranil gave a light yellow colour and TCNQ gave an ash colour for both  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$ . The colouration indicates the formation of new adsorbed species on the surface. It was confirmed by the evidence that these samples showed ESR absorption indicating the formation of new free radical species. The plot of radical concentration against equilibrium concentration of electron acceptor in solution also corresponds to the Langmuir adsorption isotherms and are of the same shape as

Table 2 - Limiting amount of electron acceptor adsorbed and catalytic activity of  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$ 

| Catalyst                        | Activation temp. ( $^{\circ}\text{C}$ ) | Limiting amount of electron acceptor adsorbed ( $10^{-5} \text{ mol m}^{-2}$ ) |       | Catalytic activity                                         |                                                       |                                                       |
|---------------------------------|-----------------------------------------|--------------------------------------------------------------------------------|-------|------------------------------------------------------------|-------------------------------------------------------|-------------------------------------------------------|
|                                 |                                         | Chloranil                                                                      | TCNQ  | Esterification ( $10^{-7} \text{ m}^{-2} \text{ s}^{-1}$ ) | Reduction ( $10^{-7} \text{ m}^{-2} \text{ s}^{-1}$ ) | Oxidation ( $10^{-6} \text{ m}^{-2} \text{ s}^{-1}$ ) |
| $\text{SnO}_2$                  | 300                                     | 6.40                                                                           | 8.20  | 0.46                                                       | 0.82                                                  | 3.31                                                  |
| $\text{SnO}_2$                  | 500                                     | 8.76                                                                           | 11.27 | 0.58                                                       | 1.19                                                  | 9.21                                                  |
| $\text{SnO}_2$                  | 700                                     | 3.74                                                                           | 5.05  | 0.62                                                       | 0.43                                                  | 2.19                                                  |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 300                                     | 2.95                                                                           | 5.38  | 0.81                                                       | 0.73                                                  | 2.71                                                  |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 500                                     | 3.81                                                                           | 6.09  | 7.17                                                       | 1.02                                                  | 8.48                                                  |
| $\text{SO}_4^{2-}/\text{SnO}_2$ | 700                                     | 2.52                                                                           | 3.49  | 17.04                                                      | 0.30                                                  | 1.89                                                  |

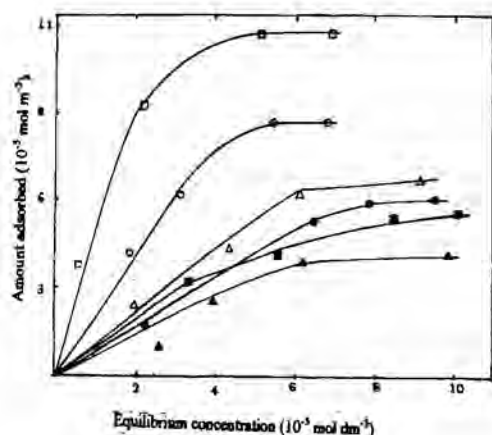


Fig. 3 - Amount of TCNQ in ( $10^{-5} \text{ mol m}^{-2}$ ) vs. its equilibrium concentration in ( $10^{-3} \text{ mol dm}^{-3}$ ) on  $\text{SnO}_2$  and  $\text{SO}_4^{2-}/\text{SnO}_2$  activated at different temperatures of 300, 500 and  $700^{\circ}\text{C}$  (○  $\text{SnO}_2$   $300^{\circ}\text{C}$ ; ●  $\text{SO}_4^{2-}/\text{SnO}_2$   $300^{\circ}\text{C}$ ; ■  $\text{SnO}_2$   $500^{\circ}\text{C}$ ; △  $\text{SO}_4^{2-}/\text{SnO}_2$   $500^{\circ}\text{C}$ ; ▲  $\text{SnO}_2$   $700^{\circ}\text{C}$ ; and ◆  $\text{SO}_4^{2-}/\text{SnO}_2$   $700^{\circ}\text{C}$ )

shown in Figs 2 and 3. From such plots the limiting radical concentrations of electron acceptor adsorbed can be estimated. The samples coloured by TCNQ adsorption gave an unresolved ESR spectra with a  $g$  value of 2.003, identified as being those of TCNQ anion radicals<sup>15</sup> and those samples after chloranil adsorption gave an unresolved ESR spectra having a  $g$  value of 2.011 (ref.16).

A strong electron acceptor (TCNQ) can accept electrons from both strong and weak donor sites whereas a weak electron acceptor like MDNB can accept electrons from stronger donor sites only. The difference in limiting amount of TCNQ and chloranil adsorbed on the oxide surface would be an estimate

of the number of stronger donor sites. It shows that the oxide surfaces have electron donor sites which can form anion radicals with acceptors having electron affinity greater than 2.40 but not less than 1.77. In other words the limit of electron transfer in terms of the electron affinity of the acceptors is between 1.77 and 2.40 eV for both oxides. The limiting amount of electron acceptor adsorbed on the oxides and the catalytic activity (expressed as the first order rate constant per  $\text{m}^2$  of the catalyst surface) are shown in Table 2. In order to study the nature of the interaction during adsorption, reflectance spectra of the adsorbed samples were measured. The spectrum gave bands appearing at 400 nm (corresponding to physically adsorbed state of neutral TCNQ which has an absorption band at 395 nm)<sup>17</sup> and near 600 nm (attributed to the dimeric TCNQ radical which absorb at 643 nm)<sup>18</sup>. In the case of chloranil, a broad band extending up to 700 nm was observed. It is in agreement with the reported results<sup>19</sup>.

From the data in Table 1 it is seen that unmodified  $\text{SnO}_2$  possess both weak acidic and weak basic sites on the surface. As the activation temperature increases acidity (number of acid sites) increases.

Regarding sulphate modified tin oxide acidity was generated at  $H_0$  value of 3.3, 4.8 and 7.2. This indicates that sulphate modified  $\text{SnO}_2$  is more acidic than unmodified ones.  $H_0$  values show that sulphate modified  $\text{SnO}_2$  does not have strong acid sites as other solid superacids. It may be due to the nature of  $\text{SnO}_2$  used for the study and also due to the concentration of sulphate ions present on it, which in turn depend on many of the preparative parameters<sup>20</sup>.

In general two types of sites are responsible for the electron donor properties of metal oxides. One

of these is electron trapped in intrinsic defect sites and the other is surface hydroxyl groups<sup>21</sup>. Surface  $O^{2-}$  can also act as electron donor sites at higher temperatures.

Surface hydroxyl ions are responsible for basicity at low temperature. As temperature increases the number of OH ions decreases and desorption of water molecules from adjacent sites occur. Basicity at higher temperature depends upon the availability of trapped electrons. From the data it is clear that as temperature increases, surface electron property increases up to 500°C for both  $SnO_2$  and  $SO_4^{2-}/SnO_2$ . The decrease in electron donor capacity after 500°C may be attributed to decrease in the number of surface hydroxyl groups. From the data it has been found that the electron donating capacity of  $SnO_2$  is decreased by modification with sulphate ion. The study of electron donor property revealed that, some of the basic sites are converted to acidic sites on modification with sulphate ion.

The nature of surface acidity in anion modified oxides remains controversial. Their catalytic property, however, clearly reveals the strong effect of surface modification of these metal oxides by electron rich anions. Superacidity is considered to be generated by the interaction between the oxide and sulphate ion. The strong acidity was attributed to the electron withdrawing anion groups, which lead to coordinatively unsaturated and electron deficient metal centers that behave as strong Lewis acid sites<sup>22</sup>.

Infrared spectra of  $SnO_2/SO_4^{2-}$  preheated at 500°C showed a strong absorption band at  $1400\text{ cm}^{-1}$ , which is attributed to an asymmetric vibrational mode of a S=O double bond<sup>23</sup>. The inductive effect of S=O double bonds of the complex formed by the interaction of oxides with the sulphate ion favours higher acidity. Both Lewis and Bronsted acid strengths increase due to the inductive effect of S=O double bond in the complex<sup>24</sup>.

The data in Table 2 indicate that sulphate modified tin oxide catalyzes the esterification reaction more effectively than the unmodified ones. On modification with sulphate ions both acidity and acid strength increases (Table 1) resulting in higher catalytic activity for esterification in agreement with the acid-base properties.

## References

1. Hino M & Arata K, *Chem Lett*, (1979) 1259
2. Hino M & Arata K, *J chem Soc Chem Commun*, (1979) 1148.
3. Hino M, Kobayashi S & Arata K, *J Am chem Soc*, 101 (1979) 6439.
4. Hino M & Arata K, *J chem Soc Chem Commun*, (1980) 85
5. Arata K & Hino M, *React Kinet Catal Lett*, 25 Nos (1-2) (1984) 143.
6. Hino M, Thesis Kokkaido University (1982).
7. Wang G, Hattori H & Tanabe K, *Chem Lett*, (1983) 277.
8. Jin T, Yamaguchi T & Tanabe K, *J phys Chem*, 90 (1986) 4794.
9. Hollestern E J, Wei J T & Hsu C V, U S Patents 4, 918, 041, 4, 956, 519 (1974).
10. Foster D S & Leslie S E in *Encyclopedia of industrial chemical analysis*, Vol 15 (Inter Science, New York), 1972, P 152.
11. Tanabe K, *Solid acids and bases*, (Academic Press, New York), 1990, P 136.
12. Shibagak M, Takahashi K, Kuno H & Matsushita H, *Bull chem Soc Japan*, 63 (1990) 258.
13. Yamanata T & Tanabe K, *J phys Chem*, 80 (1976) 1.
14. Che M, Naccache N & Imelic B, *J catal*, 24 (1970) 328.
15. Hosaka H, Fugiwara T & Meguro K, *Bull chem Soc Japan*, 44 (1971) 2676.
16. Esmi K & Meguro K, *J Japan Colour Mater*, 48 (1975) 539.
17. Acker D S & Hertler W R, *J Am chem Soc*, 84 (1862) 328.
18. Boyd R H & Phillips W D, *J chem phys*, 43 (1965) 2927.
19. Foster R & Thomson T J, *Trans Faraday Soc*, 58 (1962) 860.
20. Bolis V, Fubini B, Garrone E, Morterra C & Ugliengo P, *J chem Soc Faraday Trans*, 88 (1992) 391.
21. Meguro K & Esumi K, *J colloid inter Sci*, 59 (1973) 93.
22. Jin T, Yamaguchi T & Tanabe K, *J phys Chem*, 90 (1986) 4794.
23. Mahamed Waqif, Jean Bachelier, Odette Saur & Jean-Claude Lavalley, *J molec Catal*, 72 (1992) 127.
24. John J R & Kim H J, *J catal*, 101 (1986) 428.