

## Surface acidity and catalytic activity of sulphated samaria

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We have investigated the changes in surface acidity/basicity and catalytic properties of samarium oxide due to surface modification by  $\text{SO}_4^{2-}$  ion. The acidity/basicity of the catalysts is determined by titration method using Hammett indicators. Esterification of acetic acid by *n*-butanol is chosen as a test reaction.  $\text{Sm}_2\text{O}_3$ , owing to its high basicity and low acidity, does not catalyze the reaction. But sulphated  $\text{Sm}_2\text{O}_3$  catalyzes the esterification reaction effectively. Activation temperature does not have much effect on the acidity of sulphated samaria.

It is well-known that sulphation of some metal oxides leads to superacid materials with much larger surface acidity and surface areas. The high acidity and surface area make many of these superacid compounds very active as catalysts when used in reactions that are generally catalyzed by strong acids<sup>1</sup>. Today it is well-known that the acidity plays an important role in virtually all organic reactions occurring over solid catalysts. Many solids which possess acidic sites on their surface are used either as catalysts or catalyst carriers. The sites of the carrier may influence the catalytic properties of a catalyst by (i) interaction with the active components (support effect) or by (ii) providing acidic sites which may make the catalyst bifunctional.

It was reported that the surface properties of titania strongly depend on the presence of impurities<sup>2</sup>. A Lewis type acidity is characteristic of pure anatase. Sulphated anatase has strong Brönsted acid sites and belongs to the small number of known superacids<sup>2</sup>.  $\text{Fe}_2\text{O}_3$ ,  $\text{TiO}_2$  and  $\text{ZrO}_2$  doped with sulphate ions have been described as superacidic solids. Sulphation enhances the strength of the weakest Lewis acid sites but poisons the strongest<sup>2</sup>. It also creates Brönsted acidity in the case of highly loaded samples<sup>3</sup>.

Crystallinity and morphological features of the sulphated  $\text{ZrO}_2$  systems are found to vary with preparative and activation conditions. The nature and relative concentrations of surface acidic sites (both Brönsted and Lewis centers) turn out to depend primarily on type and relative concentration of surface  $\text{SO}_4^{2-}$  which in turn depend on many of the preparative parameters<sup>4</sup>.

It is known that the activity of a catalyst is greatly influenced by the method of catalyst preparation and the conditions of pretreatment<sup>5</sup>. In 1979 Arata and co-workers<sup>6</sup> reported that zirconia, upon proper treatment with  $\text{H}_2\text{SO}_4$  or  $(\text{NH}_4)_2\text{SO}_4$  exhibits extremely strong acidity and is capable of catalyzing the isomerization of *n*-butane to isobutane at room temperature. The strength of an acid can be characterized by the so-called Hammett acidity function,  $H_0$ . Lower the value of the function the stronger is the acid. Though a number of studies have so far been reported about sulphate modified metal oxides, no studies have been made to understand the acidic and catalytic properties of sulphate modified rare earth oxides. In this paper we report the influence of sulphate ion on the acidity/basicity of samarium oxide activated at different temperatures of 300, 500 and 700°C. Esterification of acetic acid using *n*-butanol is chosen as a test reaction.

### Experimental

Samarium oxide was prepared by the hydroxide method using a standard procedure<sup>7</sup>. To the boiling solution of samarium nitrate, 1:1 ammonia solution was added to precipitate the hydroxide. The precipitate was filtered and washed free of nitrate ion and dried at 110°C. The dried sample was powdered and heated at 300°C for 2 hr in an electric furnace. It was then sieved to get samples below 75 micron mesh size. Sulphation of  $\text{Sm}_2\text{O}_3$  was carried out by impregnation of the oxide with 0.2*N* ammonium sulphate. The precipitate was filtered without washing and dried and sieved as before.

The acidity/basicity was determined by the standard procedure by titrating the solid suspended in

Table 1 - Acidity/basicity and catalytic properties of sulphated samaria

Catalyst	Act. temp. (°C)	Surf. area (m <sup>2</sup> g <sup>-1</sup> )	Basicity (mmol g <sup>-1</sup> )			Acidity (mmol g <sup>-1</sup> )		H <sub>0,max</sub>	Cat. activity (10 <sup>-5</sup> s <sup>-1</sup> m <sup>-2</sup> )
			H <sub>0</sub> (≥ 3.3)	H <sub>0</sub> (≥ 4.8)	H <sub>0</sub> (≥ 7.2)	H <sub>0</sub> (≤ 4.8)	H <sub>0</sub> (≤ 7.2)		
Sm <sub>2</sub> O <sub>3</sub>	300	30.40	0.141	0.015	-	-	0.027	5.85	-
Sm <sub>2</sub> O <sub>3</sub>	500	29.13	0.271	0.061	-	-	0.014	6.95	-
Sm <sub>2</sub> O <sub>3</sub>	700	26.16	0.022	0.092	0.077	-	-	-	-
SO <sub>4</sub> <sup>2-</sup> /Sm <sub>2</sub> O <sub>3</sub>	300	28.43	0.081	-	-	0.034	0.109	4.38	1.94
SO <sub>4</sub> <sup>2-</sup> /Sm <sub>2</sub> O <sub>3</sub>	500	27.45	0.135	-	-	0.014	0.095	4.65	1.55
SO <sub>4</sub> <sup>2-</sup> /Sm <sub>2</sub> O <sub>3</sub>	700	25.91	0.243	-	-	0.014	0.082	4.75	1.39

Catalytic activity is expressed in terms of rate constant per m<sup>2</sup> of the catalyst surface; none of the oxides responded to dimethyl yellow ( $pK_a = 3.3$ ) for acidity determination.

benzene against *n*-butyl amine/trichloroacetic acid for acidity/basicity<sup>8</sup> respectively using a set of Hammett indicators. Following indicators were used ( $pK_a$  values of the indicators are given in brackets): 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). Among them both modified and unmodified oxides responded only to methyl red, dimethyl yellow and bromothymol blue. Oxides activated at different temperatures (300, 500 and 700°C) were used.

The catalytic efficiency was determined using the procedure reported earlier<sup>9</sup>. The esterification was carried out in a 25 ml round bottomed flask equipped with a reflux condenser in which the catalyst (1g), acetic acid (2 mmol), *n*-butanol (32 mmol) were taken and *n*-decane was used as the internal standard. The reaction temperature was maintained at 98°C and stirred continuously using a magnetic stirrer for 5 hr. The reaction was followed by product analysis by means of a CHEMITO- 8510 gas chromatograph, by comparison of its retention time with that of the standard samples. From the peak areas of the product the concentration of the product formed was calculated with reference to that of the internal standard. The specific surface areas of catalysts were determined by BET method using Carlo Erba Sorptomatic series 1800.

## Results and discussion

The data on the surface acidity/basicity and catalytic activity of the surface modified and unmodified samarium oxide are reported in Table 1. Both acidity

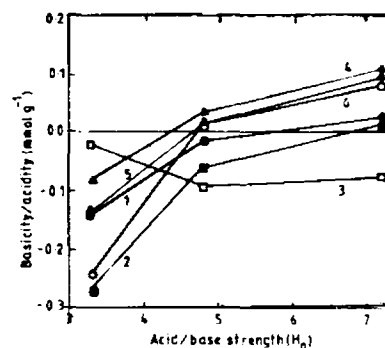


Fig. 1 — Plot for acidity/basicity against acid/base strength ( $H_0$ ) [curve 1, Sm<sub>2</sub>O<sub>3</sub> (300°C); curve 2, Sm<sub>2</sub>O<sub>3</sub> (500°C); curve 3, Sm<sub>2</sub>O<sub>3</sub> (700°C); curve 4, SO<sub>4</sub><sup>2-</sup>/Sm<sub>2</sub>O<sub>3</sub> (300°C); curve 5, SO<sub>4</sub><sup>2-</sup>/Sm<sub>2</sub>O<sub>3</sub> (500°C); curve 6, SO<sub>4</sub><sup>2-</sup>/Sm<sub>2</sub>O<sub>3</sub> (700°C)]

and basicity were determined on a common  $H_0$  scale, where strengths of the basic sites were expressed as  $H_0$  of the conjugate acids. The acid-base distribution curves intersect at a point on the abscissa where acidity = basicity = 0. The point of intersection is defined as  $H_{0,max}$  (ref.10) (Fig.1). It can be regarded as a practical parameter, representing the acid base properties on solids, which is sensitive to surface structure. A solid with a large positive  $H_{0,max}$  has strong basic sites and weak acidic sites and vice-versa.

Pure samarium oxide is more basic in nature, whereas sulphate modified samarium oxide is more acidic in nature. Esterification is an acid catalyzed reaction. The reaction follows first order kinetics. The rate determining step is the step subsequent to the adsorption of carboxylic acid and alcohol on the catalyst<sup>9</sup>.

The nature of the surface acidity in anion modified oxides remains controversial. Their catalytic properties, however, clearly reveal the strong effect of surface modification of these metal oxides by electron rich anions. The superacidity is considered to be generated by the interaction between the oxide and sulphate ion. Infrared spectra of  $ZrO_2-SO_4^{2-}$  preheated at  $500^\circ C$  showed a strong absorption band at  $1380\text{ cm}^{-1}$ , which is attributed to an asymmetric vibrational mode of  $S=O$  double bond. It has been shown that  $NiO-ZrO_2$  and  $ZrO_2$  modified with sulphate ion are very active for acid catalyzed reactions, even at room temperature.

The high catalytic activity of samaria can be attributed to the enhanced acidic properties, which originate from the inductive effect of  $S=O$  double bonds of the complex formed by the interaction of oxides with the sulphate ion. Both Lewis and Brønsted acid strengths increase due to the inductive effect of  $S=O$  double bond in the complex<sup>11</sup>. The surface species,  $SO_4^{2-}$  in the highest oxidation state is responsible for the superacidic property of sulphated oxide as evidenced by IR and X-ray photoelectron spectra<sup>12</sup>. Bensitel *et al.* observed that  $ZrO_2$  is less acidic than alumina or anatase. However, sulphation generates more acidic sites, the Lewis acidity of which is close to that observed on anatase<sup>13</sup>. The strong acidity was attributed to the presence of electron withdrawing anion groups, which leads to co-ordinatively unsaturated and electron-deficient metal centers that behave as strong Lewis acid sites. The  $H_{o,max}$  values show that sulphated samaria does not have as strong acid sites as other solid acid catalysts. Data in Table 1 indicate that unmodified samples did not have enough acid strength to catalyze the reaction. When samarium oxide was modified with sulphate ion, both acidity and acid strength increased resulting in higher

catalytic activities. Sulphated samaria show maximum acidity at activation temperature of  $300^\circ C$ . On increasing temperature, the increase in basicity is quite negligible, which shows that eventhough the acidity of unmodified samaria depends on activation temperature, the acidity and acid strength ( $H_{o,max}$  value) of sulphated samaria are independent of activation temperature. The catalytic activity data are also in agreement with the observations. samarium oxide due to its low acidity does not catalyze the reaction at all. But sulphated samaria catalyzes the esterification reaction effectively.

### References

- 1 Kaidong Chen, Yining Fan., Zheng Hu & Qijie Yan, *Catal Lett*, 36(1996) 139.
- 2 Al-Mashta F, Sheppard N & Devanzu U, *Mater Chem Phys*, 13 (1985) 315.
- 3 Waqif Mohamed, Bachelier Jean, Saur Odette & Lavalley Jean- Claude, *J mol Catal*, 72 (1992) 127.
- 4 Bolis V, Fubini B, Garrone E, Moreterra C & Ugliengo P, *J chem Soc Faraday Trans*, 88 (1992) 391.
- 5 Kayo A, Yamaguchi T & Tanabe K, *J Catal*, 83 (1983) 99.
- 6 Hino M & Arata K, *Chem Soc Chem Commun*, (1980) 851.
- 7 Foster D S & Laelie S E, *Encyclopedia of industrial chemical analysis*, (Interscience, New York) 15 (1972) 152.
- 8 Tanabe K, *Solid acids and bases* (Academic Press, New York) 1990, 136.
- 9 Kyoko Takahashi, Makoto Shibagaki & Hajime Matsushita, *Bull chem Soc Jpn*, 62 (1989) 2353.
- 10 Yamanata T & Tanabe K, *J phys Chem*, 80(1976) 1.
- 11 John J R & Kim H J, *J Catal*, 101 (1986) 428.
- 12 Jong Rack John & Hae Won Kim, *J mol Catal*, 52 (1982) 361.
- 13 Bensitel M, Saur O, Lavalley J C & Morrow B A, *Mater Chem Phys*, 19(1988) 147.