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Short Communication

Surface acidity/basicity of yttria and its mixed oxides with alumina catalysts

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Acid/base strength distribution of Y_2O_3 and its mixed oxides with alumina catalysts are measured on Hammett acidity function scale and expressed in terms of Ho_{max} value. Basicity of Y_2O_3 increases with increase in activation temperature and for mixed oxides the basicity increases with increase in concentration of Y_2O_3 in the catalyst.

Surface acidic and basic sites of metal oxides are involved in their catalytic activity for various reactions such as cracking, isomerization and polymerization[1]. Rare earth oxides have been classified as base catalysts on the basis of O_{1s} binding energy study of these oxides[2]. Acid-base nature of some of the rare earth oxides have been reported[3]. Yttrium oxide and its mixed oxides are widely used as catalysts, supports and promoters[4]. In this paper, the acidity and basicity of Y_2O_3 activated at various temperatures and its mixed oxide with alumina at different compositions have been reported.

Experimental procedure –Y_2O_3 (99.99% pure) obtained from Indian Rare Earths Ltd. Udyogamandal was regenerated by hydroxide method[5]. Mixed oxides of yttrium and aluminium (5, 10, 15 and 20% by weight) were prepared by co-precipitation from their sulphate solutions[6]. The oxides were activated at 300, 500 and 800°C for 2 h, ground and sieved to prepare powders of 100-200 mesh size. The specific surface area of the oxides were determined by the BET method using Carlo Erba Strumentazione Sorptomatic Series 1800.

Hammet indicators used for this study are shown in Table 1. Tanabe's method was used for acidity/basicity measurements[7]. The acidity at various acid strengths of the solid was measured by titrating 0.1 g of solid suspended in 5 mL of benzene with 0.1 *N* solution of *n*-butyl amine and basicity by titrating with a 0.1 *N* solution of trichloroacetic acid in benzene.

Table 1—Hammet indicators and their pK_a values

Indicator	pK_a
Crystal violet	0.8
Dimethyl yellow	3.3
Methyl red	4.8
Neutral red	6.8
Bromothymol blue	7.2
4-Nitro aniline	18.4

Visible colour change was obtained only for four indicators: dimethyl yellow, methyl red, neutral red and bromothymol blue. Tanabe's method makes it possible to determine acid-base strength distribution on a common scale and permits the determination of basicity at relatively weak basic strength. The acidity at any *Ho* value shows the number of acid sites whose acid strength is equal to or less than the *Ho* value and the basicity at an *Ho* value shows the number of basic sites whose basic strength is equal to or greater than the *Ho* value Fig. 1 shows the acidity and basicity of Y_2O_3 at various strengths at different activation temperatures. The acid-base strength distribution curves intersect at a point on the abscissa (Ho_{max}) where acidity = basicity = 0 (ref. 8). Hence, the strongest *Ho* value of acid sites is equal to the strongest *Ho* value of basic

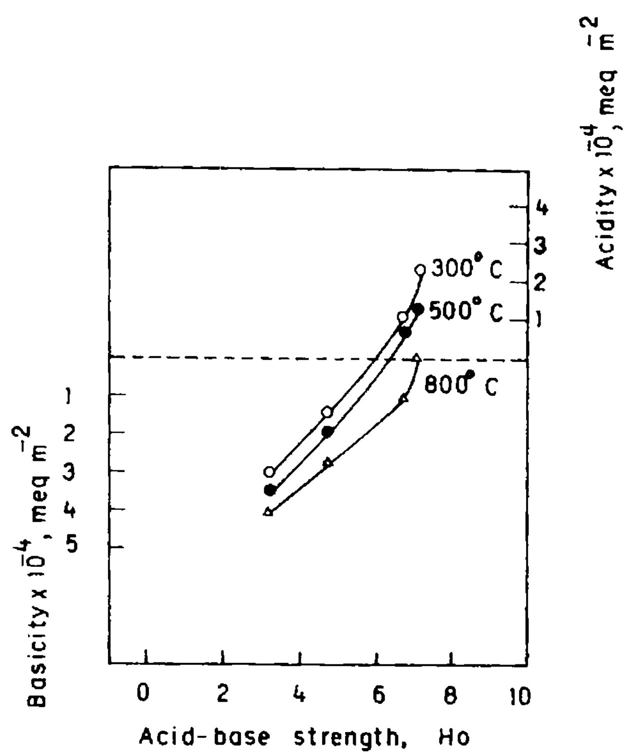

Fig. 1—Acid-base strength distribution of Y_2O_3

Table 2—Acidity and basicity of $Y_2O_3^*$ and its mixed oxides**

Oxide	Surface area $m^2\ g^{-1}$	Basicity × 10^{-4}, meq m^{-2}				Acidity × 10^{-4}, meq m^{-2}				Ho_{max}
		Ho ≥3.3	Ho ≥4.8	Ho ≥6.8	HO ≥7.2	Ho ≤3.3	Ho ≤4.8	Ho ≤6.8	Ho ≤7.2	
Y_2O_3 (300)	46.3	3.07	1.42	—	—	—	—	1.17	2.38	5.8
Y_2O_3(500)	81.5	3.43	2.04	--	—	—	—	0.71	1.32	6.3
Y_2O_3(800)	38.0	4.12	2.85	1.18	0.18	—		—	—	7.2
Al_2O_3 (500)	41.2	0.58	0.82	0.17	--	—	—	—	—	7.4
5% Y_2O_3	106.4	1.11	0.67	0.21	0.09	—		—	—	7.5
10% Y_2O_3	108.48	1.52	0.78	0.36	0.16	—	—	—	—	7.5
15% Y_2O_3	108.68	1.72	1.01	0.59	0.20	—		—	—	7.5
20% Y_2O_3	104.20	1.98	1.21	0.61	0.27	—	—	—	—	7.6

* activation temperature (°C) is given in brackets

** composition of the mixed oxide is expressed as % by weight of Y_2O_3 in alumina. The mixed oxides are activated at 500°C.

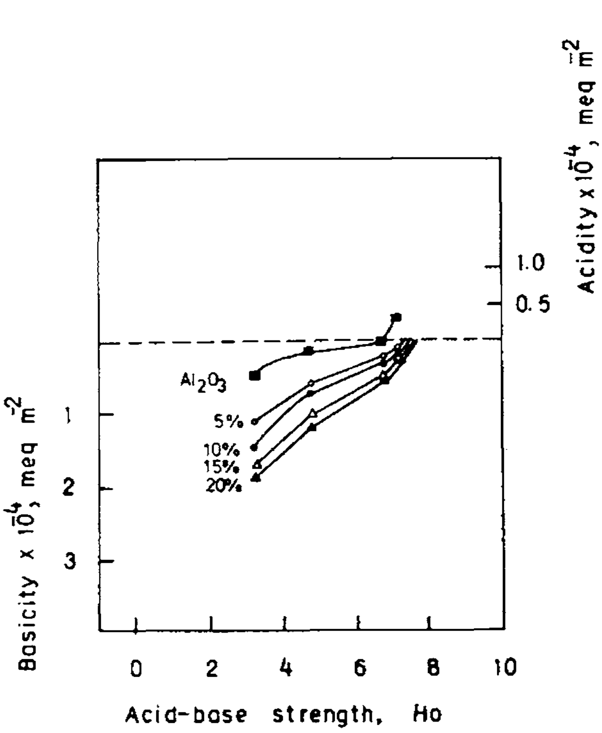

Fig. 2—Acid-base strength distribution of Y_2O_3-Al_2O_3

sites and Ho_{max} expresses the equal strongest Ho value for both acid and basic sites. For Y_2O_3 activated at 800°C only basic sites were present and Ho_{max} was determined by extrapolating the basicity curve to the abscissa. Ho_{max} can be regarded as a parameter to represent acid-base property on solids. A solid with a large positive Ho_{max} has strong basic sites and weak acid sites and a solid with a large negative Ho_{max} has strong acid sites and weak basic sites. Data show that for Y_2O_3 as the activation temperature increases Ho_{max} value increases which in turn shows the increase in basic sites on oxide. Two possible electron sources exist on oxide surface[9,10]. One of these has electrons trapped in intrinsic defects and the other has hydroxyl ions. The free electron defect site on the oxide surface is created at activation temperatures above 500°C where the presence of surface hydroxyl ions would be insignificant. The effect of the higher activation temperature is to increase the concentration of electrons trapped in intrinsic defects.

For mixed oxides activated at 500°C, only basic sites were present. Fig. 2 shows the acid-base strength distribution curves for mixed oxide Y_2O_3-Al_3O_3 for different compositions. Data are given in Table 2. Basicity increases with increase in concentration of Y_2O_3 in the mixed oxide. A similar variation of the ability of catalyst to form anion radicals was noted in our own studies on the adsorption of electron acceptors of various electron affinity such as TCNQ, Chloranil and *p*-dinitrobenzene[9,10].

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