

The surface acidity/basicity and catalytic activity of ternary oxides of La, Ce and Al

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The surface acidity and basicity of ternary oxides of La, Ce and Al have been determined using a set of Hammett indicators. The data have been correlated with the catalytic activity of these oxides towards the liquid phase reduction of cyclohexanone in 2-propanol.

The generation of acid sites on mixed oxides was first proposed by Thomas¹ and further developed by Tanabe and Thakisheta². The catalytic activity of Al₂O₃ in a range of reactions such as isomerization of hydrocarbons and polymerization of olefines has been attributed to acidic properties of the surface^{3,4} and the better catalytic activity of mixed oxides showed that catalytic activity depends on both surface acidity and basicity⁵. The acid and base strength distribution and catalytic activity/selectivity of various rare earth oxides viz. La₂O₃ and CeO₂ have been compared in the case of oxidative coupling of methane to C₂ hydrocarbons⁶. The catalytic activity and surface acidity/basicity of binary oxides of some of the rare earths with Al have also been reported⁷⁻¹¹. Though the catalytic activity of a number of ternary oxide systems have been studied¹²⁻¹⁵, the surface acidity/basicity and catalytic activity of ternary oxides of La, Ce and Al have not been investigated so far. In this note we attempt to establish the correlation between the surface acid/base properties and catalytic activity of ternary oxides of La, Ce and Al as a function of composition of the oxide. The reduction of cyclohexanone to cyclohexanol was chosen as the model reaction in this study.

Experimental

All the solvents were purified before use. The oxides were prepared by the hydroxide method using a standard procedure¹⁶. To the boiling solution of nitrate salt (4%), 1:1 ammonia solution was added to precipitate the corresponding hydroxide.

The precipitate after coagulation and settling was filtered through a Whatman No. 1 filter paper, washed free of NO₃⁻ and dried at 120°C. The dried precipitate was powdered and heated at 300°C in an electric furnace to form the oxide. It was then shifted to get samples of 100-200 mesh size. Ternary oxides of the various compositions (Table 1) were prepared by coprecipitation of the hydroxides from solutions containing calculated amounts of nitrate salts of Ce, La and Al.

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 respectively¹⁷ using a set of Hammett indicators. The oxides responded to the following indicators: (the *pK_a* values are given in brackets) methyl red (3.3), dimethyl yellow (3.3), methyl red (4.8), dimethyl yellow (4.8) and bromothymol blue (7.2). Sieved samples activated at 500°C were used in each case.

The catalytic activity was determined using the procedure reported earlier¹⁸. In a 25 ml round bottomed flask equipped with a reflux condenser 4 mmoles of cyclohexanone (in 20 ml isopropanol) and 1 g of the catalyst was heated under gentle reflux. The reaction products were analysed periodically. The activity is reported as the first order rate constant for the conversion of cyclohexanone per minute per m² of the catalyst surface. The reaction was followed by means of a Shimadzu UV-visible spectrophotometer by noting the change in absorbance of cyclohexanone in the reaction mixture at 283 nm. The specific surface areas of the 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 oxides are reported in Table 1. Both acidity and basicity were determined on a common H₀ scale where strength of the basic sites were expressed by H₀ of conjugate acids. The acid base distribution curves intersect at a point on the abscissa where acidity = basicity = 0. The point of intersection was defined as H_{0,max}¹⁹. It can be regarded as a practical parameter to represent the acid base properties on solids which is sensitive to surface structure. A solid

Table 1—Acid base properties and catalytic activity of oxides
 (activation temperature 500°C)

Metal oxide	Surface area (m ² g ⁻¹)	Basicity			Acidity			H _{0,max}	Catalytic activity (10 ³ Å ₁)
		H ₀	H ₁	H ₂	H ₀	H ₁	H ₂		
		(3.3)	(4.8)	(7.2)	(3.3)	(4.8)	(7.2)		
La ₂ O ₃	81.98	0.6269	0.0428	0.0215	—	—	—	11.0	0.605
Al ₂ O ₃	193.91	0.0400	0.0300	0.0100	—	—	—	7.5	2.085
CeO ₂	200.35	0.1876	0.0697	—	—	—	0.0938	6.2	0.197
20% CeO ₂ /Al ₂ O ₃	216.85	0.2128	0.475	0.0238	—	—	—	9.2	3.70
40% CeO ₂ /Al ₂ O ₃	160.14	0.1271	0.0508	0.0252	—	—	—	9.5	5.53
60% CeO ₂ /Al ₂ O ₃	143.70	0.1011	0.0453	0.0234	—	—	—	9.3	7.73
80% CeO ₂ /Al ₂ O ₃	125.24	0.1274	0.0253	—	—	—	0.0474	5.6	5.33
60% La ₂ O ₃ /20% CeO ₂ /20% Al ₂ O ₃	35.40	0.1204	0.0440	—	—	—	0.0575	5.4	0.79
40% La ₂ O ₃ /40% CeO ₂ /20% Al ₂ O ₃	42.89	0.0968	0.0396	—	—	—	0.0559	5.4	2.09
20% La ₂ O ₃ /60% CeO ₂ /20% Al ₂ O ₃	73.79	0.0698	0.0177	—	—	—	0.0476	5.2	0.99
50% La ₂ O ₃ /20% CeO ₂ /30% Al ₂ O ₃	86.98	0.1046	0.0212	—	—	—	0.0415	5.9	0.49
35% La ₂ O ₃ /35% CeO ₂ /30% Al ₂ O ₃	67.38	0.0978	0.0219	—	—	—	0.0480	5.8	0.48
20% La ₂ O ₃ /50% CeO ₂ /30% Al ₂ O ₃	33.18	0.1486	0.0178	—	—	—	0.0516	5.3	1.19
40% La ₂ O ₃ /10% CeO ₂ /50% Al ₂ O ₃	—	0.1390	0.0409	0.0203	—	—	—	9.2	—
30% La ₂ O ₃ /20% CeO ₂ /50% Al ₂ O ₃	4.82	0.1002	0.0604	0.0204	—	—	—	8.5	1.31
20% La ₂ O ₃ /30% CeO ₂ /50% Al ₂ O ₃	116.85	0.1019	0.0407	0.0169	—	—	—	8.2	0.29
10% La ₂ O ₃ /40% CeO ₂ /50% Al ₂ O ₃	135.57	0.1123	0.0614	0.0403	—	—	—	11.2	0.43

with a large positive H_{0,max} has strong basic sites and weak acid sites and vice versa.

The oxides La₂O₃, Al₂O₃ and CeO₂ are found to be basic and their basicity is in the order La₂O₃ > Al₂O₃ > CeO₂. CeO₂ is acidic at H₀ = 7.2 whereas acidic sites could not be detected in La₂O₃ and Al₂O₃ at the activation temperature of 500°C. The ternary oxide system is acidic for lower alumina content especially at H₀ = 7.2. It has been reported that generation of new acidic sites on mixed oxides is due to the charge imbalance localized on metal oxygen bonds^{20,21}. The basic sites arise due to weakly basic surface OH groups and strongly basic O²⁻ centers¹³. The characteristic basic sites estimated by titration method are contributed by Lewis and Bronsted sites.

Surface hydroxyls on metal oxides are shown to differ in chemical properties and the difference in acidity among the hydroxyl groups of several oxide surfaces have been reported⁶. This can be explained as due to different electron donor properties of the surface hydroxyl ions on metal oxide. The decrease in basicity with decrease in alumina content can be attributed to the difference in percentage of Al—O—La, Al—O—Ce and La—O—Ce bonds. The generation of new acidic sites on metal oxides differ from those of component single oxides²². In the case of binary oxides of Ce and Al basicity decreases with increase in ceria content. Up to 60% ceria no acidic sites are reported but in the binary oxide with 80% ceria

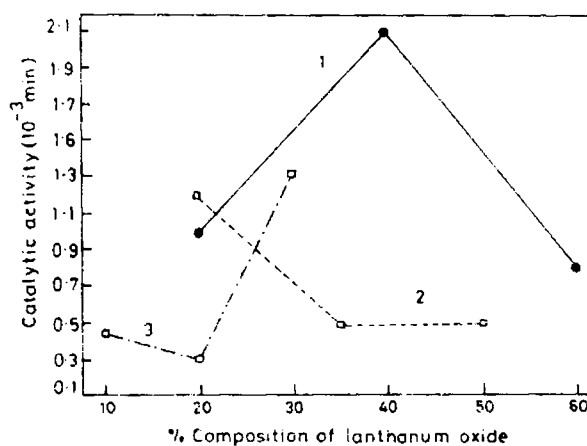


Fig. 1—Catalytic activity as a function of % composition of lanthanum (keeping alumina content constant, 1, 20% alumina; 2, 30% alumina and 3, 50% alumina)

generation acid sites are found to occur. This can be attributed to the lower electron donating property of ceria compared to alumina.

The basicity of ternary oxide is closely associated with the amount of alumina in the mixed oxide showing a tendency to decrease with decrease in alumina or lanthana content. The activity of ternary oxides towards liquid phase reduction of cyclohexanone depends on the composition of the oxide. The activity as a function of composition is shown in Fig. 1. For convenience, catalytic activity versus % La₂O₃ at constant Al₂O₃ content is plotted in the figure. It is already reported that lan-

thana, ceria and alumina are moderately active for this reaction²³. Binary oxides of Al and Ce are also found to be active for this reaction and the activity is maximum at 40% by weight of ceria²³. In the ternary oxide system low activity is observed at 50% by weight of alumina and it increases with decrease in alumina content. The activity is maximum for a composition of 40-40-20% by weight of ceria, lanthana and alumina. Involvement of an acid base pair is probable.

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