

Surface acidity/basicity and catalytic activity of mixed oxides of Zr, La and Al

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The surface acidity/basicity of binary oxides of Zr and La and the ternary oxides of Zr, La and Al are reported. The data have been correlated with their catalytic activity towards liquid phase reduction of cyclohexanone.

Transition metal oxides are considered as impractical catalysts due to their low acid/base strength. Acid-base properties of some of the metal oxides have been studied extensively and correlated with their catalytic activities¹. Rare earth oxides are classified as basic oxides on the basis of O_{1s} binding energy study² and of the reaction characteristics³. Supported rare earth oxides are often used as catalysts for reactions such as polymerization⁴, carbon monoxide hydrogenation⁵ etc. The catalytic activity of hydrous zirconium oxide calcined at various temperatures have also been reported⁶. Mixed oxides often behave differently from their parent oxides. Catalytic activity and acid base properties of mixed oxides of Zr with La have not been reported so far. In this note we report the acid/base properties and catalytic activity of the binary oxides of Zr and La of various compositions and their ternary oxides with alumina for various compositions. The catalytic activity of oxides towards the liquid phase reduction of cyclohexanone has been studied. Since the properties depend upon the activation temperatures of the oxides, studies were carried out at different temperatures.

Experimental

All the solvents were purified by standard procedure before use. The oxides were prepared by the hydroxide method using 1:1 ammonia. The precipitate after coagulation and settling was filtered through a Whatman No. 1 filter paper, washed free of NO₃⁻ and dried at 120°C for two hours. The precipitate was dried and powdered and heated at 300°C in an electric furnace to get the oxide. It was then sieved to get powders of 100-200 mesh size.

The oxides were activated by heating in CO₂ free air for 2 h at 300°, 500° and 800°C. Binary oxides of zirconium and lanthanum and their ternary oxides with alumina of various compositions were prepared by co-precipitation method⁷ from their respective nitrate solutions. Elemental analysis of the samples done with a Perkin-Elmer 23-80 atomic absorption spectrometer gave results within 1% error.

The acid/base strength distribution on the oxides were evaluated by titration method using a series of Hammett indicators⁸. The acidity was determined by titration with *n*-butylamine and basicity with trichloroacetic acid. The indicators used were (*pK_a* values are given in brackets) crystal violet (0.8), dimethyl yellow (3.3), methyl red (4.8), neutral red (6.8), bromothymol blue (7.2) and 4-nitroaniline (18.4). Of these only three indicators, namely, dimethyl yellow, methyl red and bromothymol blue responded to the oxides under study. The oxides were activated for 2 h at the desired temperature before each experiment.

The catalytic activity was determined by a standard procedure reported earlier⁹. In a 25 ml round bottomed flask equipped with a reflux condenser 4 mmol of cyclohexanone (in 20 ml isopropanol) and 1 g activated catalyst was heated under gentle reflux. The reaction products were analyzed periodically. No by-products were detected. The activity was reported as the first order rate coefficient for conversion of cyclohexanone to cyclohexanol per minute per m² of the catalyst surface. The reaction was followed using Shimadzu UV-vis spectrophotometer by noting the change in absorbance of cyclohexanone in the reaction mixture at 283 nm. The surface area of the activated catalysts

were determined by BET method using Carlo-Erba Sorptomatic series 1800.

Results and discussion

The results on the surface acidity/basicity and catalytic activity of the oxides under study are given in Table 1. Both the acidity and basicity were determined by a common H_0 scale. $H_{0,max}$ values, obtained by plotting the acidity/basicity values against the H_0 of the indicator, intersect at a point on the abscissa defined as $H_{0,max}$ and it is very sensitive to surface structure. $H_{0,max}$ can be considered as a practical parameter to represent the acid/base properties of the solid¹⁰. Large $H_{0,max}$ values show

strong basic sites and weak acid sites whereas a low $H_{0,max}$ values show stronger acid sites and weak basic sites.

The acid base strength distribution of the binary oxides shows the same trend at all compositions with respect to activation temperatures. The basicity of the binary oxides increases as the activation temperature increases up to 500°C and then decreases at higher activation temperatures. Two types of electron sources are responsible for the basicity of metal oxides¹¹. One of these is surface hydroxyl ions and other is trapped electrons at intrinsic defect sites in the lattice. Since the concentration of the surface hydroxyl ions decreases

Table 1—Acidity, basicity and catalytic activity of the oxides

Act temp °C	Surf. area m ² g ⁻¹	Basicity (10 ⁻⁴ mol g ⁻¹) H ₀ (≥)			Acidity (10 ⁻⁴ mol g ⁻¹) H ₀ (≤)			H _{0,max}	Cat act 10 ⁻⁵	
		3.3	4.8	7.2	3.3	4.8	7.2			
		ZrO ₂								
300	200.3	0.1934	0.0473	-	-	-	0.3363	5.2	0.423	
500	-	0.1684	0.0659	-	-	-	0.1688	5.6	-	
800	-	0.0729	0.0119	-	-	-	0.1129	5.1	-	
		Binary oxide (80% Zr and 20% La)								
300	226.16	1.233	0.261	1.007	-	-	-	9.0	0.702	
500	150.11	0.967	0.315	0.120	-	-	-	9.5	1.104	
800	-	2.436	-	-	-	0.338	0.150	3.8	-	
		Binary oxide (60% Zr and 40% La)								
300	123.13	0.954	0.237	0.045	-	-	-	8.6	1.114	
500	109.79	1.006	0.264	0.068	-	-	-	9.4	0.874	
800	-	0.392	-	-	-	0.128	0.057	4.0	-	
		Binary oxide (40% Zr and 60% La)								
300	134.87	1.678	0.271	0.135	-	-	-	10.4	0.666	
500	90.84	1.198	0.401	0.135	-	-	-	11.8	0.985	
800	40.84	0.487	-	-	-	0.156	0.003	3.9	2.135	
		Binary oxide (20% Zr and 80% La)								
300	76.55	3.594	0.533	0.179	-	-	-	10.0	0.603	
500	87.12	3.650	0.673	0.111	-	-	-	8.0	2.332	
800	67.74	2.579	-	-	-	0.271	0.224	4.0	1.116	
		La ₂ O ₃								
300	86.4	7.290	0.475	0.244	-	-	-	11.0	0.405	
500	81.98	6.127	0.955	0.562	-	-	-	11.5	0.605	
800	45.88	1.496	1.127	0.676	-	-	-	11.8	1.758	
		Al ₂ O ₃								
500	193.5	2.668	1.642	0.511	-	-	-	8.7	-	
		Ternary oxide (75% Zr, 15% La and 10% Al)								
500	69.60	2.817	1.950	1.299	-	-	-	11.5	0.6	
		Ternary oxide (50% Zr, 30% La and 20% Al)								
500	133.12	0.866	0.433	-	-	-	0.738	5.8	1.2	
		Ternary oxide (25% Zr, 45% La and 30% Al)								
500	115.2	2.167	1.083	-	-	-	0.985	6.1	0.6	
		Binary oxide (60% Zr and 40% Al)								
500	144.5	2.90	2.00	0.50	-	-	-	7.8	1.37	

with rise in temperatures the trapped electrons must be responsible for the increase in basicity of the oxides with increase in temperature¹². Acid sites are found to occur especially at H_0 values of 4.8 and 7.2 at 800°C. No acid sites are reported at 300 and 500°C with change in composition of La. It has been reported that the generation of acid sites on mixed oxides is due to the charge imbalance localized on M_1 -O- M_2 bondings on the mixed oxides where M_1 and M_2 are the two metal ions¹³.

The data show that the activity depends upon acidity/basicity. But no correlation is obtained. The catalytic activities are markedly influenced by the activation temperatures. The inactivity of ZrO_2 at higher temperatures was accounted as due to the change in crystallinity from amorphous to monoclinic at about 500°C and was confirmed by DSC measurements¹⁴. For compositions with 80 and 60% by weight of Zr no activity is found at 800°C due to the generation of strong acid sites. For the remaining compositions acidity is negligible at about 800°C. At higher activation temperatures the Lewis acid sites are formed by the removal of water molecules from the two hydroxyl groups⁸. At much higher activation temperatures the lattice distortion also contributes to an increase in acid sites. Ternary oxides show the increase in activity with decrease in

percentage of Zr, but no linearity is observed. Activity of all oxides parallels the basicity.

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