

Note

Surface acidity/basicity and catalytic activity of ternary oxides of Al, Ce and Dy

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The surface acidity and basicity of ternary oxides of Al, Ce and Dy 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 reaction is favoured by the higher basicity of the ternary oxide.

The acidic or basic properties of solid surfaces are interesting aspects of solid state chemistry and important in the fields of heterogeneous catalysts and ion exchange. Fundamental catalytic and surface properties of alkali, alkaline earth and other basic oxides have been extensively studied and documented. Empirical studies have demonstrated that following appropriate pretreatment, rare earth sesquioxides are active catalysts for a variety of reactions, including ortho/para hydrogen conversion¹, deuterium exchange reactions of hydrocarbons², H₂-D₂ equilibration³, alcohol dehydration⁴, oxidation reactions of hydrogen⁵, carbon monoxide⁶, and hydrocarbons^{7,8}. The acidic and basic properties seem to be responsible for the catalytic activities in many reactions. The acid and base strength distribution and catalytic activity and selectivity of various rare earth oxides have been reported. Though the catalytic activity of a number of ternary oxide systems have been studied, the surface acidity/basicity and catalytic activity of ternary oxides involving rare earths have not been investigated so far. The present work is aimed at an investigation of the acidic/basic properties and catalytic activities of Al₂O₃-CeO₂-Dy₂O₃ ternary oxide systems of different compositions. The model reaction chosen for the study of catalytic activity is the reduction of cyclohexanone to cyclohexanol.

Experimental Procedure--Both the binary oxides of Al₂O₃ and CeO₂ and ternary oxides of Al₂O₃-

CeO₂-Dy₂O₃ of different compositions were prepared by the coprecipitation method, using a standard procedure⁹. The coprecipitation is done by adding 1:1 ammonia solution to the boiling solutions containing calculated amounts of corresponding nitrate salts. The precipitates after coagulation and proper settling was filtered through Whatman No. 1 filter paper, washed free of nitrate ions and dried at 120°C. The dried precipitate was powdered and regenerated by heat treatment at 500°C in an electric furnace to get the oxide. The catalyst samples were then sieved to get powders of 100-200 mesh size. The surface acidity/basicity of the oxides were determined by a titration method¹⁰ using the following Hammett indicators (pK_a of indicators are given in parenthesis): 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, the oxides responded only to dimethyl yellow, methyl red and bromothymol blue.

Determination of acidity and basicity--The catalyst of desired mesh size (100-200) was activated at 500°C for two hours prior to the experiment. The acidity at various acid strengths of the solid was estimated by titrating 0.1 g of solid suspended in 5 mL of benzene with *n*-butylamine solution in benzene (0.01, 0.05 or 0.1 N) using Hammett indicators. At the end point, the basic colour of the indicator appeared¹⁵. Similarly, the basicity was measured by titrating 0.1 g of solid suspended in 5 mL of benzene with trichloroacetic acid solution in benzene, using Hammett indicators. At the end point, the basic indicator changes to the colour of the conjugate acid.

The catalytic activity towards reduction of cyclohexanone was studied as follows. In a 25 cm³ round bottomed flask equipped with a reflux condenser, 4 mmol of cyclohexanone in 20 cm³ of isopropanol, with 1 g of catalyst, was heated at 80°C for a period of 17 h. The reaction product was analysed by means of a UV-visible spectrophotometer (Shimadzu-160A). The percentage conversion was calculated from the change in the absorbance of cyclohexanone in the reaction mixture at 283 nm before and after the reaction. For absorbance measurements the reaction mixture was diluted to 50 times in isopropanol.

The catalytic activity is expressed in terms of the first order rate coefficient per m² of catalyst.

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Table 1—Surface area, $H_{0,max}$ and catalytic activity distribution of the mixed oxides (activation temp. 500°C)

Metal oxide	Surf. area m^2g^{-1}	$H_{0,max}$	Catal activity $10^5 k_1$
Dy ₂ O ₃	—	6.5	0
Al ₂ O ₃	193.91	7.5	2.09
CeO ₂	200.35	6.2	0.20
20% CeO ₂ /Al ₂ O ₃	216.85	9.2	2.70
40% CeO ₂ /Al ₂ O ₃	160.14	9.5	5.53
60% CeO ₂ /Al ₂ O ₃	143.70	9.3	7.73
80% CeO ₂ /Al ₂ O ₃	125.24	5.6	5.33
40% Dy ₂ O ₃ /10% CeO ₂ / 50% Al ₂ O ₃	—	—	0.00
30% Dy ₂ O ₃ /20% CeO ₂ / 50% Al ₂ O ₃	145.18	—	0.37
20% Dy ₂ O ₃ /30% CeO ₂ / 50% Al ₂ O ₃	121.75	—	0.35
10% Dy ₂ O ₃ /40% CeO ₂ / 50% Al ₂ O ₃	—	—	—
50% Dy ₂ O ₃ /20% CeO ₂ / 30% Al ₂ O ₃	159.43	5.1	0.31
30% Dy ₂ O ₃ /40% CeO ₂ / 30% Al ₂ O ₃	101.63	6.2	0.84
20% Dy ₂ O ₃ /50% CeO ₂ / 30% Al ₂ O ₃	121.71	6.0	0.56
60% Dy ₂ O ₃ /20% CeO ₂ / 20% Al ₂ O ₃	87.12	5.4	0.70
40% Dy ₂ O ₃ /40% CeO ₂ / 20% Al ₂ O ₃	93.02	6.25	1.24
20% Dy ₂ O ₃ /60% CeO ₂ / 20% Al ₂ O ₃	94.47	6.0	0.70

Surface area of the catalysts were determined by the BET method using Carlo Erba strumantazionesorptiomatic series 1800.

Results and discussion—The acidic and basic properties were estimated by titration method. The $H_{0,max}$ value of the oxides were determined by plotting the acidity and basicity of the oxides against H_0 of the indicator. The $H_{0,max}$ value of a solid is the strongest H_0 value of the acid sites as well as the equal strongest H_0 value of the basic sites¹². A solid with a large $H_{0,max}$ value has strong basic sites and weak acid sites. A solid with a small $H_{0,max}$ value has strong acid sites and weak basic sites. The oxides, Al₂O₃, Dy₂O₃ and CeO₂ are found to be basic but the basic strength of CeO₂ is much less compared to that of Dy₂O₃. CeO₂ is acidic at $H_0 = 7.2$.

In a binary oxide, to have Lewis acidity one must have coordinatively unsaturated cation on the surface. Moreover, the host oxide must be acidic or atleast should not be strongly basic¹³. The basic sites arise due to weakly basic surface

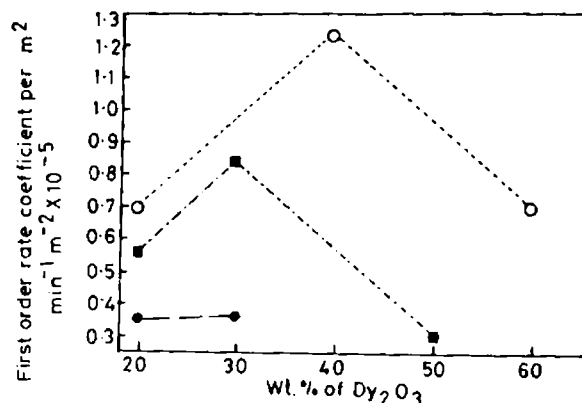


Fig. 1—First order rate coefficient per m^2 versus wt% of Dy₂O₃ at various compositions of the ternary oxide (Al₂O₃:CeO₂:Dy₂O₃).

● Al₂O₃:CeO₂:Dy₂O₃
50:20:30
50:30:20

○ Al₂O₃:CeO₂:Dy₂O₃
20:20:60
20:40:40
20:60:20

■ Al₂O₃:CeO₂:Dy₂O₃
30:20:50
30:40:30
30:50:20

OH groups and strongly basic O²⁻ centres¹⁴. The initial increase in basic centres with increase in activation temperature may be due to the removal of surface OH groups and the exposure of O²⁻ centres. It has been widely accepted that the generation of new and strong acid sites on mixing oxides is ascribed to a charge imbalance localized on M₁-O-M₂ bonds formed in the mixed oxide, where M₁ and M₂ are the mixed metal ions¹⁵.

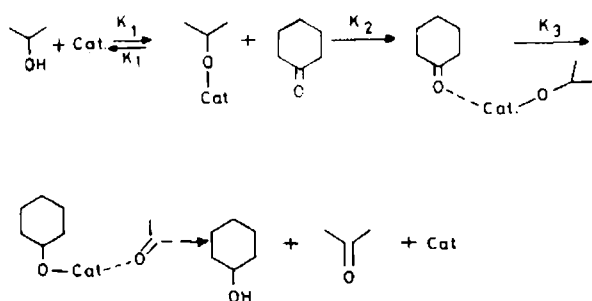
The data on surface acidity/basicity and catalytic activity of the oxides are reported in Tables 1 and 2. The highest $H_{0,max}$ value is for Al:Ce (40:60) composition for binary system. It can be seen that mixed oxide with 20 mol % Al, 40 mol% Ce and 40 mol% Dy is the catalyst with maximum acid strength.

Fig. 1 projects the variation of activity with the change in catalyst composition. The activity is maximum for the composition Al:Ce:Dy of (20:40:40). It may be noticed that the same composition has the highest $H_{0,max}$ value. It can be concluded that there should be a direct correlation between the $H_{0,max}$ values and catalytic activity.

The catalytic activity of these oxides can be rationalized in terms of the mechanism (Scheme 1) proposed by Shibagaki *et al.*¹⁶ for oxidation and reduction using ZrO₂ catalyst. It has already been established from kinetic isotope effect studies that k_3 is the rate determining step. The mechanism involves hydride transfer from alcohol to the carbonyl carbon.

Table 2—Acid-base strength distribution of the mixed oxides (Activation temp. 500°C)

Metal oxide	Basicity 10^{-2} mmol g^{-1}			Acidity $H_{0 < 7.2}$
	$H_{0 > 3.3}$	$H_{0 > 4.8}$	$H_{0 > 7.2}$	
Dy ₂ O ₃	0.250	0.150	—	—
Al ₂ O ₃	0.040	0.030	0.010	—
CeO ₂	0.187	0.069	—	0.093
20% CeO ₂ /Al ₂ O ₃	0.212	0.475	0.023	—
40% CeO ₂ /Al ₂ O ₃	0.127	0.050	0.025	—
60% CeO ₂ /Al ₂ O ₃	0.101	0.045	0.023	—
80% CeO ₂ /Al ₂ O ₃	0.127	0.025	—	0.047
40% Dy ₂ O ₃ /10% CeO ₂ / 50% Al ₂ O ₃	0.125	0.042	0.063	—
30% Dy ₂ O ₃ /20% CeO ₂ / 50% Al ₂ O ₃	0.167	0.042	0.105	—
20% Dy ₂ O ₃ /30% CeO ₂ / 50% Al ₂ O ₃	0.084	0.042	0.172	—
10% Dy ₂ O ₃ /40% CeO ₂ / 50% Al ₂ O ₃	0.084	0.021	0.088	—
50% Dy ₂ O ₃ /20% CeO ₂ / 30% Al ₂ O ₃	0.076	0.022	—	0.168
30% Dy ₂ O ₃ /40% CeO ₂ / 30% Al ₂ O ₃	0.289	0.186	—	0.142
20% Dy ₂ O ₃ /50% CeO ₂ / 30% Al ₂ O ₃	0.065	0.182	—	0.200
60% Dy ₂ O ₃ /20% CeO ₂ / 20% Al ₂ O ₃	0.051	0.048	—	0.135
40% Dy ₂ O ₃ /40% CeO ₂ / 20% Al ₂ O ₃	0.092	0.067	—	0.041
20% Dy ₂ O ₃ /60% CeO ₂ / 20% Al ₂ O ₃	0.088	0.080	—	0.084



Scheme 1

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