Short Communication

Acid base characteristics of binary oxides of Zr with Ce and La

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The surface acidity and basicity of binary oxides of Zr with Ce and La are determined using a series of Hammett indicators and $H_{o,max}$ values are reported. The generation of new acid sites have been ascribed to the charge imbalance of $M_1 - O - M_2$ bonds, where M_1 and M_2 are metal atoms. Both Bronsted and Lewis acid sites contribute to the acidity of the oxides.

The generation of new acid sites during the formation of binary oxides has already been reported in literature[1-3]. Based on the studies of dopant cations on several metal oxides, it was proposed that the generation of new acid sites was caused by the existence of coordinatively unsaturated cations[4,5]. It was proposed[6,7] that the generation of new acid sites could be ascribed to the charge imbalance at locally formed $M_1 - O - M_2$ bonding where M_1 is the host metal ion and M_2 is the doped metal ion. The charge imbalance might emerge even on single metal oxides due to the surface imperfections in small crystallites. The surface properties of zirconia have been extensively studied[6,7]. Hydrous zirconium oxide is used as an effective catalyst in the reduction of aldehydes and ketones with 2-propanol[8]. Rare earth oxides are classified as basic catalysts[9]. CeO_2 shows the lowest activity and selectivity in base catalysed reactions and La_2O_3 shows highest surface basicity among rare earth oxides[10]. Though a number of mixed oxide systems have been studied the binary oxide system of Zr with Ce and La have not so far been reported. In this paper, the surface acidity and basicity of mixed oxides of Zr with Ce and La for 0, 20, 40, 60, 80 and 100% ZrO_2 have been reported.

Experimental procedure- The mixed oxides were prepared by coprecipitation method from the nitrate solutions by hydroxide method[11]. The single oxides were also prepared by the same method for comparison. All the solvents were used after purification by standard methods. The oxide was ground and sieved to get powders of 100-200 mesh size. It was then activated in a furnace at the specified temperature for two hours. The acidity at various acid strength was deter-

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mined by titrating about 0.1 g of the activated solid suspended in 5 mL benzene against 0.1 N solution of n-butyl amine in benzene using the Hammett indicators[3]. The basicity was determined by the same procedure by titration against 0.1 N trichloroacetic acid[12].

Results and discussion—The results on the surface acidity and basicity of the oxides are given in Table 1. The $H_{o,max}$ value of the oxide was determined by plotting the acidity and basicity of the H_0 of the indicator[13]. $H_{o,max}$ value is the strongest H_0 value of the acid sites as well as the equal strongest H_0 value of the basic sites. $H_{o,max}$ value can be regarded as a practical parameter to represent an acid base property on solids. A solid with a large $H_{o,max}$ value has strong basic sites and weak acidic sites and vice versa. As the activation temperature is increased $H_{o,max}$ value passes through a maximum depending on the composition of the oxide (Fig. 1 for ZrO_2). Two types of electron sources are responsible for the basicity of metal oxides[14]. One of these is surface hydroxyl ions and the other is trapped electrons at intrinsic defect sites in the lattice. Since the concentration of surface hydroxyl ions decreases with increase in temperature the trapped electron centres must be responsible for the increase in basicity of the oxides with increase in temperature[15]. The decrease in basicity after a particular temperature must be understood as a consequence of the phase transition[16].
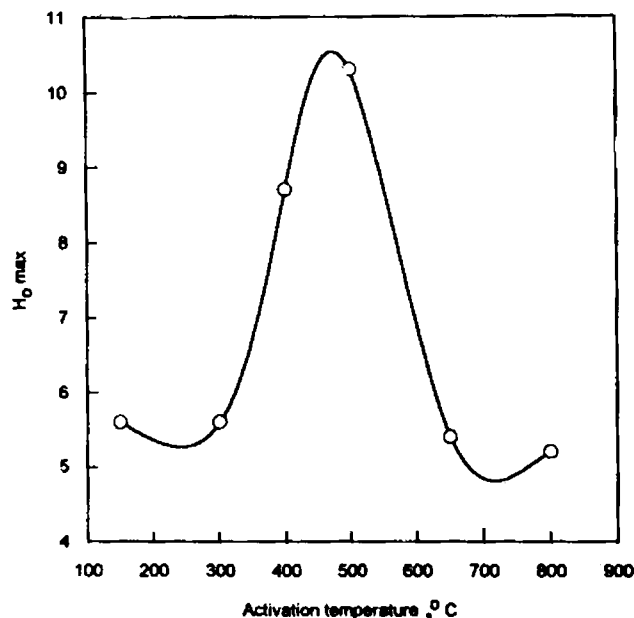

Fig. 1—$H_{o,max}$ as function of activation temperature of ZrO_2.

Table 1—Acidity and basicity of the oxides activated at various temperatures

Act. temp. °C	Basicity, mmol g^{-1}			Acidity, mmol g^{-1}			$H_{o,max}$
	H_o 3.3	H_o 4.8	H_o 7.2	H_o 3.3	H_o 4.8	$H2o$ 7.8	
ZrO$_2$							
150	0.305	0.102	—	—	—	0.225	5.6
300	0.198	0.058	—	—	—	0.119	5.6
400	0.158	0.021	0.007	—	—	—	8.7
500	0.192	0.095	0.050	—	—	—	10.3
650	0.131	0.033	—	—	—	0.060	5.4
800	0.055	0.011	—	—	—	0.081	5.2
ZrO$_2$.CeO$_2$ (80:20% by weight)							
300	0.068	—	—	—	0.059	0.104	3.9
400	0.037	—		—	0.096	0.334	3.7
500	0.043	—	—	—	0.138	0.307	3.7
650	0.035	—	—	—	0.048	0.048	3.8
800	—	—	—	0.111	0.350	0.430	3.2
ZrO$_2$.CeO$_2$ (60:40% by weight)							
300	—	—	—	0.124	0.240	0.520	1.6
400	—	—	—	0.032	0.144	0.176	3.2
500	0.024	—	—	—	0.095	0.160	3.6
650	—	—	—	0.049	0.350	0.420	3.2
800	—	—	—	0.250	0.760	0.790	3.2
ZrO$_2$.CeO$_2$ (40:60% by weight)							
300	0.013	—	—	—	0.012	0.016	3.8
400	0.018	0.006	—	—	—	0.017	4.2
500	0.034	—	—	—	0.085	0.240	3.6
650	—	—	—	0.030	0.075	0.090	2.4
800	—	—	—	0.024	0.068	0.085	2.6
ZrO$_2$.CeO$_2$ (20:80% by weight)							
300	0.019	0.006	—	—	—	0.002	6.5
400	0.023	0.006	—	—	—	0.011	5.5
500	0.023	—	—	—	0.006	0.017	4.3
650	0.017	—	—	—	0.015	0.090	4.2
800	0.064	—	—	—	—	0.022	4.8
CeO$_2$							
150	0.120	0.043	0.043	—	—	—	—
300	0.110	0.025	—	—	—	0.075	5.3
400	0.085	0.014	—	—	—	0.032	5.3
500	0.037	0.018	—	—	—	0.066	5.8
650	0.085	0.007	—	—	—	0.033	5.1
800	0.057	0.017	—	—	—	0.060	5.3
ZrO$_2$.La$_2$O$_3$ (80:20% by weight)							
300	0.122	0.026	0.101	—	—	—	9.0
500	0.097	0.032	0.012	—	—	—	9.5
800	0.244	—	—	—	0.034	0.015	3.8
ZrO$_2$.La$_2$O$_3$ (60:40% by weight)							
300	0.095	0.024	0.005	—	—	—	8.6
500	0.101	0.026	0.007	—	—	—	9.4
800	0.039	—	—	—	0.013	0.006	4.0
ZrO$_2$.La$_2$O$_3$ (40:60% by weight)							
300	0.168	0.027	0.014	—	—	—	10.4
500	0.119	0.040	0.014	—	—	—	11.8

(contd)

Table 1—Acidity and basicity of the oxides activated at various temperatures—Contd.

Act. temp. °C H_o	Basicity, mmol g⁻¹			Acidity, mmol g⁻¹			$H_{o,max}$
	H_0 3.3	H_0 4.8	H_o 7.2	H_o 3.3	H_o 4.8	H_o 7.2	H_o
800	0.049	—	—	—	0.016	0.001	3.9
ZrO₂.La₂O₃ (20:80% by weight)							
300	0.359	0.053	0.0179	—	—	—	10.0
500	3.650	0.673	0.018	—	—	—	8.0
800	0.258	—	—	—	0.027	0.022	4.0
La₂O₃							
300	0.729	0.048	0.024	—	—	—	11.0
500	0.613	0.096	0.056	—	—	—	11.5
800	0.150	0.113	0.068	—	—	—	11.8

The acidity of a solid is determined by the electronegativity of the compound and the coordination of the ions. Lower cation and anion coordination generally leads to stronger acid sites[4,5]. The Lewis acid site on an oxide surface can be considered as incompletely coordinated metal atom formed by dehydration of a weak Bronsted site. The basic site is considered to be a negatively charged oxygen[3].

Among the three single oxides the basic strength of CeO_2 is much less compared to the other two oxides. In the case of ZrO_2 as the activation temperature increases the number of basic sites first decreases then goes to a maximum (at about 500°C) and again decreases. Acidity is negligible and the values are given in Table 1. It is reported that for ZrO_2 a phase transition from amorphous to monoclinic occurs at about 500°C which is also confirmed by DSC analysis[15]. In the case of CeO_2 the surface acidity as well as basicity is found to be very small and almost independent of the activation temperature. But La_2O_3 shows the highest to basicity and the base strength increases with increase in activation temperature.

Incorporation of CeO_2 into ZrO_2 increases the acidity and decreases the basicity. The strength of the acid sites are also increased as evidenced by low $H_{o,max}$ values. But incorporation of lanthana into zirconia increases the basicity upto 500°C and then it decreases at higher activation temperatures. The same trend is observed at all compositions of lanthana. Generation of acid sites occur at $H_o = 4.8$ at 800°C. The plot of acidity versus temperature shows a maximum and minimum at temperatures depending on the composition of the oxide. These plots are comparable to those of alumina reported earlier[3]. In the case of zirconia-ceria as the activation temperature increases moderately strong acid sites appear which may be due to the conversion of weak acid sites to stronger Lewis site caused by loss of water molecules[17]. The generation of new acid sites can be ascribed to the charge imbala-

nce at locally formed $Zr-O-Ce$ bonding[6,7]. The existence of coordinatively unsaturated cations were proposed to be responsible for Lewis acidity[3]. It can chemisorb a water molecule giving rise to Bronsted acid site[3]. At lower temperatures Bronsted acid sites and at high temperatures Lewis sites are probable forms of acidity. $Zr-O-Zr$ and $Ce-O-Ce$ bonds are weakly basic while $Zr-O-Ce$ bonds are more acidic because of the charge imbalance. The maximum acidity will be shown by the oxide system which has maximum number of $Zr-O-Ce$ bonds on the surface. Further increase in ceria content increases $Ce-O-Ce$ bonds lowering surface acidity.

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