

Notes

Acid base and catalytic properties of ZrO₂ - Y₂O₃ systems

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The surface acidity and basicity of mixed oxides of Zr and Y and their mixed oxides have been determined by titration method using Hammett indicators. The acid base properties are evaluated on a common scale of acid strength. Liquid phase reduction of cyclohexanone has been selected as a model reaction to correlate catalytic activity.

The surface acidity of solid catalysts has been subject of considerable study to investigate the acid - base strength distribution among acid base centers and how the distribution varies with the type of the catalyst. Some of the mixed oxides were reported to show surface acidic properties¹. The acid strength and acidity on a solid surface were determined by Benesi method² based on Johnsons experiment³. In this note we report the acid base strength distribution of mixed oxides of Zr and rare earth metal Y by titration method using a series of Hammett indicators. Acidity and basicity were expressed on a common H₀ scale of acid strength. Acid strength (H₀) is expressed by the pK_a value of the conjugate acids of the basic indicators, while the basic strength is expressed by the H₀ value of the conjugate acid sites generated on the basic sites. Acid base properties of ZrO₂ have been already reported⁴ and it was found that ZrO₂ possess both weak acidic and basic sites. This was confirmed by activity towards particular reactions⁵. Rare earth oxides have been recognized as solid base catalysts⁶. Y₂O₃ is found to be a basic oxide. Acid base properties of mixed oxides of ZrO₂ with SiO₂^(ref.7), SnO₂^(ref.8), and TiO₂^(ref.9), etc have been reported. But no attempt has been made with mixed oxides of Zr and Y. Therefore, ZrO₂ - Y₂O₃ mixed oxides with different compositions have been prepared and acid base properties of these oxides activated at different temperatures were charac-

terized by titration method using Hammett indicators. The mixed oxides showed both acidic and basic sites with various strengths and the amount varies with activation temperatures. It enabled to quantify the differentiation between different acid base strengths of mixed oxides in terms of pK_a values of the used indicators. The data have been correlated with the activity towards the liquid phase reduction of cyclohexanone, which is analogous to Meerwin-Pondorf-Verley (MPV) reduction in which the carbonyl compound are generally reduced with 2-propanol in the presence of aluminium isopropoxide. The disadvantages of the above conventional reaction are overcome by use of our heterogeneous catalysts.

Experimental

All the solvents were purified before use. The oxides were prepared by the hydroxide method using a standard procedure¹⁰. Mixed oxides of the following compositions with 20, 40-60 and 80 % by weight of Y were prepared by co-precipitation of the hydroxides from solution containing calculated amounts of nitrate salts of Zr and Y. The precipitate after coagulation and settling was filtered, washed free of NO₃⁻ ions and dried at 120°C for 2h. The dried samples were calcined in an electric furnace at 300°C for 2h to get oxides. It was then sieved to get granules of 100-200 mesh size. Sieved samples activated at 300, 500 and 800°C were used.

The acidity/basicity were determined by a standard procedure¹¹. The acidity of the solid was determined by titrating the solid (preheated at particular temperature) suspended in benzene with a solution of *n*-butylamine in benzene using the indicators listed in Table 1. The basicity of the solid was measured by titrating the solid suspended in benzene with a solution of trichloroacetic acid in benzene using the same set of indicators as those used for the acidity measurements. The colour of the indicators on the surface at the end points of the titrations were the same as the colours which appeared by the adsorption of the respective indicators on the acid sites. The colour of

the benzene solution was the basic colour of the indicator at the end point. As the results for a titration lasting 2 h were the same as those for a titration lasting 24 h, 2 h was taken for titration.

Table 1—Hammett indicators used

Indicator	pK_a	Color change	
		Base form	Acid form
Crystal violet	0.8	blue	yellow
<i>p</i> -Dimethylamino-azo benzene	3.3	yellow	red
Methyl red	4.8	yellow	red
Bromothymol blue	7.2	blue	yellow
4-Nitroaniline	18.4	orange	yellow

The catalytic activity was determined by a standard procedure reported earlier¹². The activity was 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 using a Shimadzu UV- visible spectrophotometer by noting the change in absorbance of the cyclohexanone in the reaction mixture at 283 nm. The specific surface area of the catalysts were determined by BET method using Carlo Erba Sorptomatic series 1800.

Results and discussion

The data of surface acidity/basicity at various acid base strength distributions are given in Table 2. Mixed oxides behave differently from the single oxides. It is well known that two component metal oxide

Table 2—Acidity, basicity and catalytic activity of the oxides

Act temp °C	Surf area (m ² g ⁻¹)	Basicity (mmol g ⁻¹)			Acidity (mmol g ⁻¹)			H _{0,max}	Cat act 10 ⁵ K
		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	61.4	0.1684	0.0659	-	-	-	0.1688	5.6	-
800	25.8	0.0729	0.0119	-	-	-	0.1129	5.1	-
Binary oxide (80 % Zr and 20 % Y)									
300	210.7	0.1251	0.0503	-	-	-	0.0243	6.4	6.919
500	122.3	0.2126	0.0625	-	-	-	0.0365	6.3	2.785
800	56.9	0.0500	-	-	-	0.1095	0.1339	3.7	0.513
Binary oxide (60 % Zr and 40 % Y)									
300	187.8	0.1876	0.0750	0.0250	-	-	-	8.6	4.289
500	118.4	0.1376	0.0876	0.0250	-	-	-	8.3	2.630
800	44.7	0.0625	-	-	-	0.0365	0.730	4.2	0.267
Binary oxide (40 % Zr and 60 % Y)									
300	214.8	0.2001	0.0876	0.0625	-	-	-	12.0	1.821
500	123.1	0.1625	0.0875	0.0250	-	-	-	8.3	2.080
800	47.9	0.1251	0.0250	-	-	-	0.0243	6.0	1.221
Binary oxide (20 % Zr and 80 % Y)									
300	131.6	0.2251	0.0750	-	-	-	0.0608	6.1	0.586
500	108.4	0.2002	-	0.0625	-	0.0365	-	5.7	0.634
800	61.7	0.2502	0.0500	-	-	0.2710	0.0243	6.6	0.749
Y ₂ O ₃									
300	24.3	0.1500	-	-	-	0.0500	0.1400	4.5	0.554
500	24.4	0.2500	0.1500	-	-	-	0.0200	6.2	1.940
800	29.5	0.4000	0.0240	0.0500	-	-	-	7.9	7.530

systems exhibit characteristic properties which are not quantitatively predictable from consideration of independent properties of the parent oxides. Surface area of the oxides changes progressively with change in temperature. Surface area decreases with increase in temperature. The mixed oxides have different surface areas than the single oxides when compared at the same activation temperature.

By doping ZrO_2 with lower valent ions such as Y and Ca etc., the cubic phase is stabilized. In the stabilized zirconias the oxygen vacancies, which are present as the ionic majority defects, are randomly distributed over the crystallographic oxygen positions. In particular, ordering effects may occur at higher dopant concentrations, depending on the ratio of the radii of Zr^{4+} to dopant ion. As the radius ratio ($r_{Ln^{3+}}/r_{Zr^{4+}}$) decreases, pyrochlore structure becomes less stable. At 60 % of Y, the mixed oxide attains an ordered super structure of fluorite structure; the pyrochlore structure is formed. Then with the increase in dopant ion (Y) concentration, the stable phase is cubic fluorite structure with random distribution of metal cations over the accessible sites in the structure. The oxygen diffusion is strongly affected by dopant Y ions. When dopant concentration is relatively small, Y ions promote the migration of O ions. However, as dopant ion concentration increases, tetrahedra having the Y-Y edge increase and the diffusion path of O ions comes to be restricted by neighboring Y ions, causing the diffusion constant to decrease¹³. The maximum in surface area at 60 % Y can thus be understood.

Both acidity and basicity were determined on common H_0 scale. The strongest H_0 value of the acidic sites was equal to the strongest H_0 value of the basic sites and this strongest H_0 was termed $H_{0,max}$. $H_{0,max}$ is obtained from the point of intersection of acid-base strength distribution curves at a point on the abscissa where acidity = basicity = 0. $H_{0,max}$ expresses the equal strongest H_0 value of both acidic and basic sites, which can be regarded as a practical parameter to represent the surface properties of the solids and is sensitive to surface structure. A unique $H_{0,max}$ is found for every solid. $H_{0,max}$ values change with activation temperature.

ZrO_2 shows bifunctional behaviour with acidic and basic sites. The highest acid strength is at $H_0 = 7.2$ and highest basic strength is at $H_0 = 3.3$. This implies the weak acidic and basic character of ZrO_2 . The acid site is mainly Lewis acid and partly Bron-

sted sites¹⁴. It was already reported that ZrO_2 possess a low, but definite basicity¹⁵ and confirmed by the adsorption of CO. Basicity of rare earth oxides increases with increase in temperature. This indicates the decrease in number of acid sites whose strength is equal to or less than the pK_a value of the indicators used. This is because acidity at a definite H_0 value gives the number of acidic sites whose strength is equal to or less than the H_0 value and basicity at a given H_0 value gives the number of basic sites whose strength is equal to or greater than the H_0 scale. No acidic and basic sites of equal strength are found on the same solid surface, which shows the presence of significant acid base strength distribution.

Regarding the binary oxides, all compositions show independent behaviour compared to that of component oxides. The maximum basicity is found at 300°C. Basicity at $H_0 = 3.3$ and $H_0 = 4.8$ gave distinguishable basic sites with varying base amounts. Basicities of mixed oxides were higher than those of single oxides.

Acid base properties depend up on the activation temperature. Except in rare earth oxides, the basicity decreases with increase in activation temperature. For rare earth oxides the basicity increases with rise in temperature. Pre-activation temperature is crucial for acid site generation. The change in acid-base property of ZrO_2 at about 550°C was considered as due to the change in crystallinity from amorphous to the monoclinic and it was confirmed by DSC measurements¹⁶. The basicity of oxides were found to decrease from 300 to 800°C. As the % by character of Zr decreases, the monoclinic character decreases and C-type (cubic body centered) character increases and the basicity increases. Heat treatment at higher temperature facilitates the crystallization, resulting in stabilization of surface state and decrease in surface area. Therefore the acid sites decrease in number and strength.

The variation of acid-base property in terms of $H_{0,max}$ with composition of mixed oxides is shown in Fig. 1. For a certain composition of metal oxide, the number of acid and base sites generated usually depends on the composition of the binary oxide. Composition with 40% by weight of Zr exhibits high activity especially at 300°C, and then activity decreases. This parallels the change in basicity of oxides. There are two sources for basicity on mixed oxides, surface hydroxyl ions and the trapped electrons at intrinsic defects in the lattice^{1,13}. The basicity

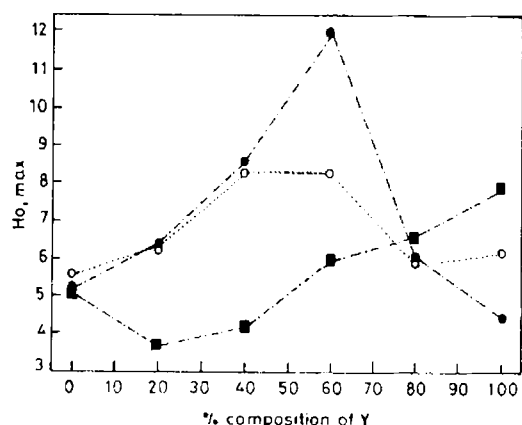


Fig. 1—Variation of $H_{0,max}$ with composition of mixed oxides at different solvation temperatures ($H_{0,max}$) (1) at 300°C; (2) at 500°C; and (3) at 800°C

at low temperature is due to the presence of surface hydroxyl ions and as the temperature increases the number of OH^- ions are reduced, due to the dehydroxylation and desorption of water molecules from adjacent sites. Therefore the trapped electrons are responsible for the basicity at high temperature. IR studies have revealed the presence of OH^- groups on $ZrO_{217,18}$.

All mixed oxides, irrespective of compositions, show acidity at high temperatures, especially at $H_0=7.2$. The generation of new acid sites on mixed has been ascribed to a charge imbalance localized on M_1-O-M_2 bonds formed in the mixed oxides, where M_1 and M_2 are two metal ions^{19,20}. The acid base property also depends on the method of preparation. It is found that even traces of impurities can alter the acid strength of the oxides, the extent of increase depending on the nature and amount of impurity.

The surface acidity and basicity studies reveal the presence of groups of sites of different energies. It has been suggested that the acid and base sites are metal ions and O_2^- in different coordinations, the lower coordinated ion sites being responsible for strong acid/base sites²¹. It was suggested that there are more than one kind of acid base sites which differ in strength of acidic and basic properties¹⁴.

Thus, the surface of mixed oxides of Zr is associated with acid- base sites of different strengths amounts and energy distributions, which can be used for selective reactions. The catalytic activities for ZrO_2 have been reported⁵. The activity toward the liquid phase reduction of cyclohexanone shows no linearity with $H_{0,max}$. It infers that the reaction is not

only catalyzed by basic sites, but acid sites are also involved in the reaction. The activity decreases with % by wt of Zr at low temperature, but it increases at high temperature. It is considered that the active sites for reduction at higher temperature are generated by the removal of surface carbonate groups from rare earth oxides. For each composition of mixed oxides the activity decreases from 300 to 800°C. Compared to all other compositions, mixed oxide with 20% Zr and 80% Y shows low activity at 500°C. This is due to the generation of comparatively strong acid sites at $H_0=4.8$ on this composition at 500°C and no acid sites at $H_0=7.2$. But for this composition there is an increase in activity at 500°C from 300°C. From data, it was found that acid sites generated at $H_0=7.2$ are unfavourable for catalytic activity. The activity decrease with increase in activation temperature indicates that the reaction is catalyzed by Bronsted sites at low temperatures whose amount decreases with the increase in activation temperature.

The decrease of surface area due to phase transformation at around 500°C might prevent the regeneration of Bronsted acid sites on the surface.

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