

## Surface acidity/basicity and catalytic activity of Zr-Sm mixed oxide systems

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Received 6 May 1994; revised 4 July 1994;  
accepted 3 August 1994

The surface acidity and basicity of oxides of Sm and Zr and their mixed oxides 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 cyclo-hexanone in 2-propanol.

Acid base properties of several solid catalysts have been studied and correlated with their catalytic activities<sup>1</sup>. Rare earth oxides have been recognized as solid base catalysts<sup>2</sup>. The catalytic activity of hydrous ZrO<sub>2</sub> calcined at various temperatures have been reported<sup>3</sup>. Mixed oxides often behave differently from the single oxide components. Catalytic activity and surface properties of mixed oxides of Zr and rare earth metals have not been reported so far. In this note we report the acidity/basicity of Zr-Sm mixed oxide systems and their catalytic activity towards the reduction of cyclohexanone in isopropanol. This reaction is analogous to the well known Meerwin-Ponndorf-Verley (MPV) reduction in which aldehydes and ketones are reduced with 2-propanol in the presence of aluminium isopropoxide. But the MPV reduction needs a strong acid treatment to neutralise the alkoxide salt and the isolation of products involve tedious procedures. These disadvantages are overcome in the use of heterogeneous catalysts.

### Experimental

All the solvents were purified before use. The oxides were prepared by the hydroxide method using a standard procedure<sup>4</sup>. 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 NO<sub>3</sub><sup>-</sup> and dried at 120°C. The dried precipitate was 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. Mixed oxides of the following compositions (15.0, 32.0, 51.5 and 73.9% by weight of

Sm) were prepared by coprecipitation of the hydroxides from solutions containing calculated amounts of nitrate salts of Zr and Sm.

The acidity/basicity was determined by a standard procedure by titrating the solid suspended in benzene against *n*-butylamine/trichloroacetic acid for acidity and basicity respectively<sup>2</sup> using a set of Hammett indicators. The oxides responded to the following indicators: (the *pK<sub>a</sub>* values are given in brackets) methyl red (4.8), dimethyl yellow (3.3) and bromothymol blue (7.2). Sieved samples activated at different temperatures (300, 500 and 800°C) were used in each case.

The catalytic activity was determined using a procedure reported earlier<sup>5</sup>. 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 m<sup>2</sup> of the catalyst surface. The reaction was followed using a Shimadzu UV-visible spectrophotometer by noting the change in absorbance of 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.

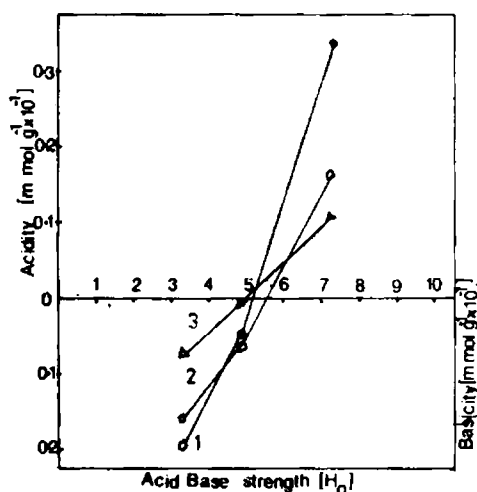
### Results and discussion

The results on surface acidity/basicity and catalytic activity are given in Table 1. Both acidity and basicity were determined on a common H<sub>0</sub> scale where strength of the basic sites were expressed by the H<sub>0</sub> of the conjugate acids. The acid-base distribution curves intersect at a point on the abscissa where acidity-basicity = 0 (Fig. 1). The point of intersection was defined as H<sub>0, max</sub><sup>6</sup>. H<sub>0, max</sub> can be regarded as a practical parameter to represent acid base properties on solids which is sensitive to surface structure. A solid with a large positive H<sub>0, max</sub> has strong basic sites and weak acid sites whereas a solid with large negative H<sub>0, max</sub> has strong acid sites and weak basic sites.

It is evident from the H<sub>0, max</sub> values that both ZrO<sub>2</sub> and Sm<sub>2</sub>O<sub>3</sub> are basic oxides, the latter being more basic. The basicity of mixed oxides is between those of their component oxides. The acidities/basicities at H<sub>0</sub> = 4.8 and 7.2 indicate the formation of acid sites in the mixed oxide. At activation temperatures of 300 and 800°C the composition with 32% of Sm contains the

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

Act. Temp. °C	Surf. Area m <sup>2</sup> g <sup>-1</sup>	Basicity (m mol g <sup>-1</sup> )			Acidity (m mol g <sup>-1</sup> )			H <sub>0</sub> , max	Cat. Act. 10 <sup>5</sup> k <sub>1</sub>
		H <sub>0</sub>			H <sub>0</sub>				
		≥3.3	≥4.8	≥7.2	≤3.3	≤4.8	≤7.2		
(a) ZrO <sub>2</sub>									
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	—
(b) Mixed oxide (15.0% Sm)									
300	218.9	0.1672	0.0390	—	—	—	0.1028	5.4	0.877
500	120.9	0.1009	0.0390	—	—	—	0.0489	5.7	1.090
800	56.9	0.0487	0.0263	—	—	—	0.0359	6.0	1.241
(c) Mixed oxide (32.0% Sm)									
300	204.9	0.1272	—	—	—	0.1007	0.2019	3.9	0.494
500	116.7	0.1005	0.0135	—	—	—	0.0251	5.3	0.817
800	54.9	0.0262	—	—	—	0.0644	0.1034	3.6	0.290
(d) Mixed oxide (51.5% Sm)									
300	113.8	0.0975	0.0135	0.0098	—	—	—	—	0.800
500	86.0	0.1131	0.0405	0.0148	—	—	—	9.0	1.627
800	32.3	0.0974	0.0119	0.0074	—	—	—	—	2.557
(e) Mixed oxide (73.9% Sm)									
300	85.3	0.1678	0.0670	0.0369	—	—	—	11.2	1.362
500	79.0	0.1508	0.0944	0.0272	—	—	—	8.8	2.099
800	39.9	0.0486	0.0327	0.0124	—	—	—	10.1	3.122
(f) Sm <sub>2</sub> O <sub>3</sub>									
300	47.6	0.2002	0.1501	0.0247	—	—	—	8.1	1.400
500	42.9	0.1885	0.0713	0.0346	—	—	—	11.5	1.989
800	33.2	0.0976	0.0596	0.0296	—	—	—	12.5	5.553

Fig. 1—Acidity/basicity versus H<sub>0</sub> for ZrO<sub>2</sub> at activation temperatures, 1; 300° (○), 2; 500° (□) and 3; 800° (Δ)

maximum number of acid sites while at 500°C this corresponds to the composition with 15.0% Sm. The generation of new and strong acid sites on mixed oxides has been ascribed to a charge imbalance localized on M<sub>1</sub>—O—M<sub>2</sub> bonds formed in the mixed

oxide where M<sub>1</sub> and M<sub>2</sub> are metal ions<sup>7</sup>. The data show that the number of basic sites increases with increase in activation temperature, reaches a maximum and then decreases with further increase in temperature. Two types of electron sources are responsible for the basicity of metal oxides: surface hydroxyl ions and trapped electrons at intrinsic defects in the lattice<sup>2</sup>. Since the concentration of the former decreases with increase in temperature the trapped electron centres must be responsible for the increase in basicity of the oxides with increase in temperature. The number of acid sites at activation temperature of 800°C is greater than that at 300°C. At high activation temperatures Lewis acid sites are formed by removal of water molecules from two hydroxyl groups<sup>2</sup>. At much higher activation temperatures the lattice distortions also contribute to an increase in acid sites.

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 ion and O<sup>2-</sup> on the surface and the site energy distribution is attributed to the presence of metal ion and O<sup>2-</sup> in different coordinations, the lower

coordinated ion sites being responsible for strong acid/base sites<sup>8</sup>. The data show that activity depends on both acidity and basicity, however, the relationship is not straightforward. The larger  $H_0, \max$  values for higher samaria content agree well with their higher activities than for  $ZrO_2$ . This suggests that basic sites play an important role in the reaction. But the lack of linear correlation between activity and basicity implies that basic sites do not control the catalytic activity. The data show that basic sites with strength greater than  $H_0=4.8$  may be the catalytically active sites. The catalytic activity is markedly influenced by the activation temperature. The fact that  $ZrO_2$  is active only at lower activation temperatures is in agreement with the results on the catalytic activity of hydrous  $ZrO_2$  in which the oxide calcined at  $300^\circ C$  was the most effective<sup>3</sup>. The lowering of catalytic activity at higher temperatures was accounted as due to the change in crystallinity of  $ZrO_2$ . The phase transition for  $ZrO_2$  from amorphous to monoclinic at  $500^\circ C$  was confirmed by DSC measurements<sup>9</sup>. For composition with 32.0% of Sm the activity increases with increase in activation temperature from 300 to  $500^\circ C$  and then decreases at  $800^\circ C$  due to the formation of acid sites. For rest of the

composition the activity increases steadily with increase in activation temperature. The data show that increase in activity with increase in activation temperature to  $800^\circ C$  becomes more prominent with increase in Sm content.

#### Acknowledgement

The authors wish to acknowledge their sincere gratitude to the State Committee on Science, Technology & Environment, Thiruvananthapuram for their financial assistance.

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