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ACIDITY, BASICITY AND CATALYTIC ACTIVITY OF La - Zn MIXED OXIDES

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Abstract

Surface acidity/basicity of mixed oxides of La and Zn activated at three different temperatures were determined. The data have been correlated with the catalytic activity for liquid phase reduction of cyclohexanone in isopropanol.

Keywords: Acidity, basicity, catalytic activity, rare earth oxides, mixed oxides

INTRODUCTION

The surface acid-base properties of many metal oxides have been studied and correlated with their catalytic activity for many reactions [1]. The surface acid-base properties and catalytic activity of La_2O_3 and ZnO have been reported earlier [2]. Mixed oxides of La_2O_3 and ZnO with many metal oxides have also been investigated [3]. Some of them were found to exhibit remarkable acidic properties and catalytic activity [4]. Surface properties of binary mixtures of La_2O_3 and ZnO have not been reported so far. Here, we report the surface acid-base properties and catalytic activity of binary oxides of La and Zn with various compositions. The data have been correlated with their catalytic activity. The model reaction chosen is the liquid phase reduction of cyclohexanone in isopropanol. The reaction is analogous to the Meerwein-Ponndorf-Verley (MPV) reduction, where the oxides under investigation act as a better substitute for aluminium isopropoxide due to the ease of product isolation.

EXPERIMENTAL

The mixed oxides were prepared by the decomposition of their mixed oxalates. To the boiling solution containing calculated quantities of nitrates of La^{3+} and Zn^{2+} , saturated solution of oxalic acid was added slowly with constant stirring and allowed to stand overnight. The precipitate was filtered through a Whatman No. 42 filter paper and washed with 2 % oxalic acid solution. It was dried at 100°C overnight and ignited at 900°C for 3 hours. The oxide was then sieved to get 100-200 mesh size. Mixed oxides of the following compositions were prepared (20, 40, 60 and 80 mole % of La_2O_3). Samples activated at 300, 600 or 900°C were studied together with pure oxides prepared under identical conditions. All solvents were purified by standard procedures.

The strength and distribution of acidic and basic sites on the oxide surface were characterized by titrating the solid suspended in dry benzene against benzene solutions of *n*-butylamine or trichloroacetic acid for acidity/ basicity measurements, respectively, using a set of Hammett indicators. The oxides responded only to the following indicators (pK_a values are given in brackets): Methyl red (4.8) and Bromothymol blue (7.2) for acidity, and Dimethyl yellow (3.3) and Methyl red (4.8) for basicity.

The catalytic activity was determined by a procedure reported earlier [5]. 5 mmol cyclohexanone and 20 mL isopropanol with 0.5 g of the oxide was taken in a 50 mL round-bottomed flask. It was heated under gentle reflux. The progress of the reaction was followed by noting the change in absorbance at 283 nm, using a UV-Vis spectrophotometer. The absorbance measurements gave the concentrations of cyclohexanone, the rate constant was calculated using a first order rate equation. The specific surface areas of the oxides were determined by the BET method using Carlo Erba Strumentazione Sorptomatic series 1800. The reaction shows a first order dependence on cyclohexanone concentration under our experimental conditions [5]. Catalytic activity is reported as first-order rate constant per unit surface area of the catalyst.

RESULTS AND DISCUSSION

The results of the measurements are given in Table I. Both acidity and basicity were determined on a common H_0 scale, where the strength of the basic sites were expressed by the H_0 of their conjugate acids. The acid-base strength distribution curves intersect at a point on the abscissa where acidity = basicity = 0. The point of intersection is defined as $H_{0,\text{max}}$, which can be regarded as a practical parameter to represent the acid-base properties of solids sensitive towards surface structure. A solid with large positive $H_{0,\text{max}}$ has strong basic

sites and weak acid sites and a solid with a large negative $H_{o,max}$ value has strong acid sites and weak basic sites [6].

Table 1
Catalytic activity, surface area and acid-base strength distribution of the oxides

| Lanthana (mole%) | Act. temp.(°C) | Surface area (m ² g ⁻¹) | Catalytic activity (10 ⁻⁶ s ⁻¹ m ⁻²) | Basicity (10 ⁻² m mol g ⁻¹) | | Acidity (10 ⁻² m mol g ⁻¹) | | $H_{o,max}$ |
|---------------------|-------------------|--|--|---|----------------|--|----------------|-------------|
| | | | | $H_b \geq 3.3$ | $H_b \geq 4.8$ | $H_a \leq 4.8$ | $H_a \leq 7.2$ | |
| 0 | 300 | -- | 0 | 5.255 | 0.26 | -- | 9.989 | 4.85 |
| 0 | 600 | -- | 0 | 5.255 | 0.26 | -- | 9.989 | 4.85 |
| 0 | 900 | -- | 0 | 5.255 | -- | 2.497 | 7.491 | 4.10 |
| 20 | 300 | 3.70 | 5.03 | 5.255 | 0.52 | -- | 2.497 | 4.95 |
| 20 | 600 | 8.18 | 1.38 | 2.627 | 0.52 | -- | 2.497 | 5.15 |
| 20 | 900 | -- | 0 | 2.627 | -- | 2.497 | 4.994 | 3.90 |
| 40 | 300 | 6.48 | 1.64 | 2.627 | 0.26 | -- | 2.497 | 4.95 |
| 40 | 600 | -- | 0 | 2.627 | 0.26 | -- | 4.994 | 5.0 |
| 40 | 900 | -- | 0 | 5.255 | 0.26 | -- | 2.497 | 4.95 |
| 60 | 300 | 6.39 | 1.29 | 2.627 | 0.26 | -- | 2.497 | 4.95 |
| 60 | 600 | 4.57 | 0.81 | 2.627 | 0.26 | -- | 4.994 | 5.0 |
| 60 | 900 | -- | 0 | 2.627 | -- | 2.497 | 4.994 | 3.90 |
| 80 | 300 | 10.47 | 1.77 | 2.627 | 0.26 | -- | 2.497 | 4.95 |
| 80 | 600 | 8.22 | 1.85 | 2.627 | 0.52 | -- | 2.497 | 5.95 |
| 80 | 900 | -- | 0 | 5.255 | 0.26 | -- | 2.497 | 4.95 |
| 100 | 300 | 10.78 | 1.19 | 5.255 | 0.52 | -- | 2.497 | 5.25 |
| 100 | 600 | 11.21 | 6.03 | 10.51 | 1.04 | -- | 2.497 | 5.30 |
| 100 | 900 | -- | 0 | 5.255 | 0.26 | -- | 2.497 | 4.95 |

The surface acidity-basicity data revealed the presence of sites of different energies. It has been suggested that the acid-base sites on oxide surfaces are metal ions and O²⁻ ions on the surface and the site energy distribution is due to their presence in different coordinations. The lower coordinated ions are responsible for stronger acid/base sites [7]. Zinc oxide is an acidic oxide with intermediate acidity and lanthanum oxide is a basic oxide. La₂O₃ prepared by decomposition of oxalate is found to be more acidic than that prepared from hydroxide precursor [8]. The acidity and basicity of the mixed oxides are between those of their component oxides. Acidity measurements show the formation and annihilation of new acid-base sites on mixing oxides. This is attributed to the charge imbalance localized on M₁-O-M₂ bonds formed in the mixed oxides, where M₁ is the host metal ion and M₂ is the added metal ion [9]. The acidity and basicity do not show a regular gradation with activation temperature.

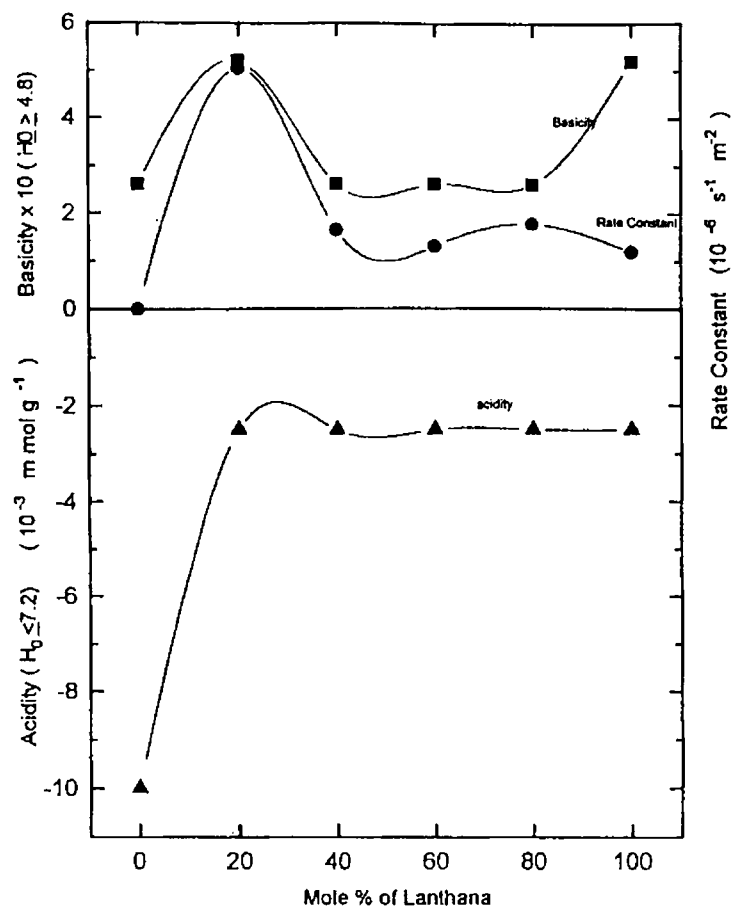


Fig. 1. Acidity, basicity and catalytic activity as a function of composition at activation temperature 300°C

The catalytic activity depends both on the acidity and basicity of the oxide surface. The catalytic activity for the reduction of cyclohexanone parallels basicity values at $H_0 \geq 4.8$. Figures 1 and 2 show the change in acidity and basicity and catalytic activity as a function of composition of the oxides activated at 300 and 600°C , respectively. This shows that basic sites having $H_0 \geq 4.8$ play an important role in the reaction and may be the catalytically active sites. Acidity at $H_0 \leq 7.2$ does have an inverse parallel relationship to the activity. The strong acid sites generated by activation at 900°C inhibit the reaction. It is a

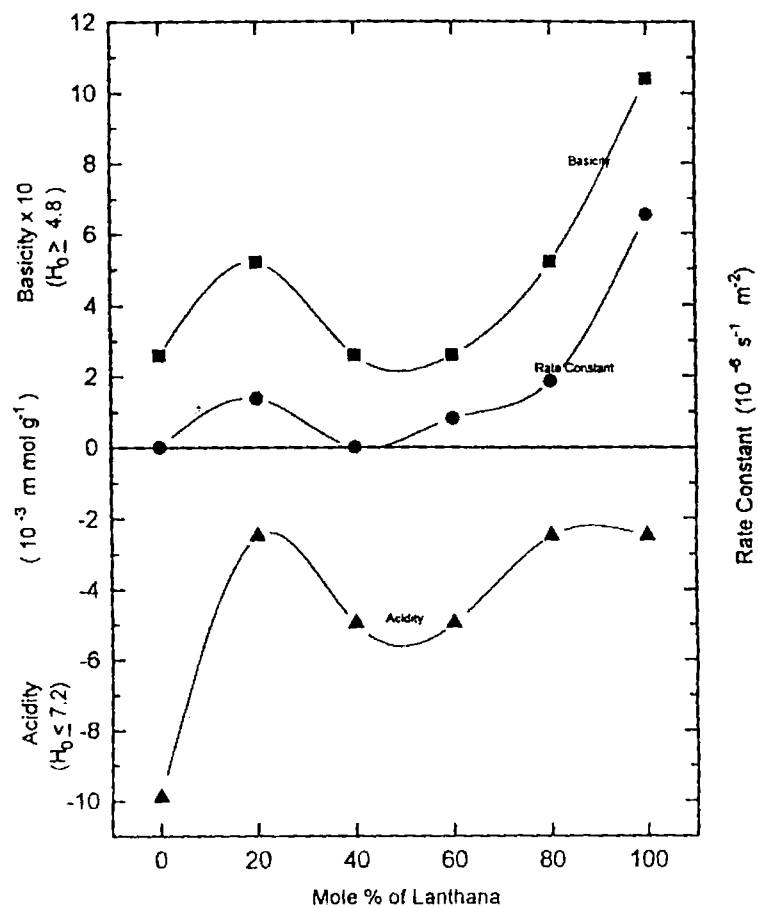


Fig. 2. Acidity, basicity and catalytic activity as a function of composition of the oxides at activation temperature 600°C

general observation that high temperature treatment destroys the catalytically active sites for many surfaces. Acid sites at high activation temperatures are created mostly by lattice distortions. It can be seen from the data that higher acidity is obtained for zinc oxide by incorporating 20 mole % of La_2O_3 in it. For an activation temperature of 300°C, it shows higher activity than pure lanthana. As the number of strong acid sites increases, the reaction is slowed down. Mixed oxides containing 20 and 80 mole% of lanthana have rather good activity.

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