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# Effect of Activation Temperature on The Strength and Distribution of Acid and Base Sites on Neodymium -Zirconium Mixed Oxides

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**Abstract**: Surface acidity/ basicity and of Neodymium - Zirconium mixed oxides at various compositions have been reported at three activation temperatures viz 300ºC, 500ºC & 800ºC. The strength and distribution of acid and base sites on the oxides were determined by titration method using Hammett indicators. . The mixed oxides with various compositions ,Viz 0, 20, 40, 60, 80, and 100% of the rare earth oxide were studied.

**Key words**, **Acid strength, Base strength, Acid amount , Base amount, $H_o$ value, $H_{o\ max}$**

## I. INTRODUCTION

The thermochemistry of rare earth metal doped Zirconia indicates that the addition of rare earth metal increases the thermal stability of the host oxide and stabilise it in a high surface area form [1]. The catalytic property of metal oxides depend on many factors. Attempts are now being done to establish valid correlations between the catalytic activity and other surface properties

A detailed review of the literature revealed that no attempts were made to study the surface acid- base properties of mixed oxides of zirconium with Neodymium . Zirconium is a transition element and zirconia is unique in exhibiting acid, base, oxidising and reducing properties. Further zirconia based materials are now attracting much attention because of their promising potential as catalysts for use in combustion and hydrogenation [2], Piezo electric ceramics and thermal barriers. Flourite structure is the structure of the high temperature form of $ZrO_2$ and of the so called stabilized Zirconias. At room temperature $ZrO_2$ has a deformed structure, derived from the fluorite structure. Pure $ZrO_2$ , when cooled from high temperatures, undergoes several phase transitions which are accompanied by relatively large volume changes. Due to the volume changes caused by the phase transitions, sintered compacts of pure $ZrO_2$ are pulverised on cooling. By doping $ZrO_2$ with lower valent ions the cubic structure is stabilized and remains viable down to room temperature, even though it is metastable at that temperature.

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 occcur at high dopant concentrations, depending on the ratio of the radii of the $Zr^{4+}$ to dopant ion. When an equimolar amount of trivalent ions has been added the formula of the mixed oxide is $A_2B_2O_7$ and, depending on the type of A and B ion an ordered super structure of the flourite structure, the pyrochlore structure is formed. Pyrochlore has a unit cell, consisting of 8 fluorite cells with an ordered arrangement of oxygen vacancies. Six of the remaining oxygen are of the same crystallographic type the seventh has a different crystallographic type. There is also cation ordering and the lattice is distorted in such a way that the smaller of the cations is surrounded by a distorted octahedron of oxygen, the larger by a distorted cube of oxygens.

When comparing the phase diagrams of the different $ZrO_2$ -$Ln_2O_3$ systems, it is clear that the pyrochlore structure becomes less stable as the radius ratio r $(Ln^{3+})/r(Zr^{4+})$ decreases. As a consequence of the lanthanide contraction, from Gadolinium onwards the pyrochlore structure is no longer formed. Around the corresponding composition the stable phase is then the cubic fluorite structure with a random distribution of the metal cations over the accessible sites in the structure [3].

In this paper we report the acid/base properties of Neodymium - Zirconium mixed oxides at various compositions. The surface acidity / basicity of the oxides were determined by titration method [4] using the following Hammett indicators; the pKa values of the indicators are given in brackets. :-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 only dimethyl yellow, methyl red and bromothymol blue responded to the acidity/ basicity of the oxides under study.

## II. EXPERIMENTAL

The mixed oxides were prepared through the hydroxide route. The mixed oxides with variouscompositions, Viz. 20, 40, 60 and 80 % (abbreviated as 20 Nd, 40 Nd, 60 Nd and 80 Nd) of therare earth oxide were prepared. Pure oxides were also prepared in the same fashion and

incorporated in the study for comparison. All the oxides were heat treated at a particular

temperature viz 300oC, 500oC &800oC, for two hours prior to each experiment. All the reagents were purified by standard methods before use.

Surface area of the oxides were determined by BET method using Carlo Erba Strumentazione Sorptomatic Series 1800. The surface acidity/ basicity of the oxides were determined by a procedure reported earlier [4].

## III, RESULTS AND DISCUSSION

The strength and distribution of acidic and basic sites on the oxide surface were studied using a series of Hammett indicators . They are given in Table 1.

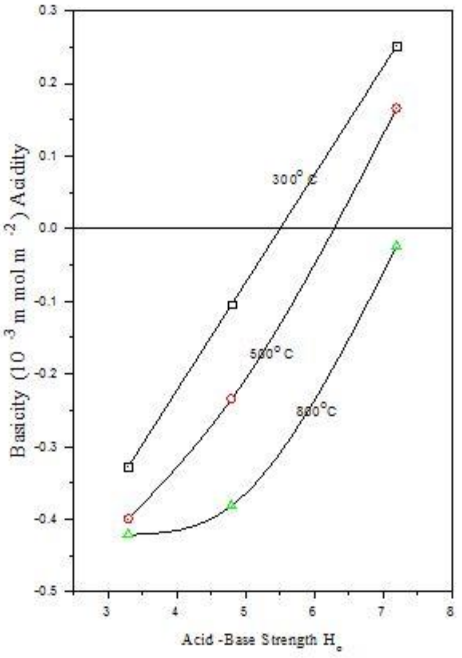
Table 1 Hammett Indicators Used

| Hammett Indicator | $pK_a$ | Acid Colour | Base Colour |
|---|---|---|---|
| Crystal violet | 0.8 | Yellow | Blue |
| Dimethyl Yellow | 3.3 | Red | Yellow |
| Methyl Red | 4.8 | Red | Yellow |
| Neutral red | 6.8 | Red | Yellow |
| Bromo Thymol Blue | 7.2 | Yellow | Blue |
| 4-Nitroaniline | 18.4 | Yellow | colourless |

The surface acidity/ basicity of the oxides were determined by titration method using the same set of Hammett indicators [4] ; given in chapter 3, table 2. Of these the oxides under study responded only to dimethyl yellow, methyl red and bromothymol blue the acidity/ basicity. The acid/ base strength distribution of the oxides were measured on a common $H_o$ scale [5] (Table 3 Fig. 1).

Acid -Base Strength distribution curves on $Nd_2O_3$ activated at different temperatures

**Figure 1**



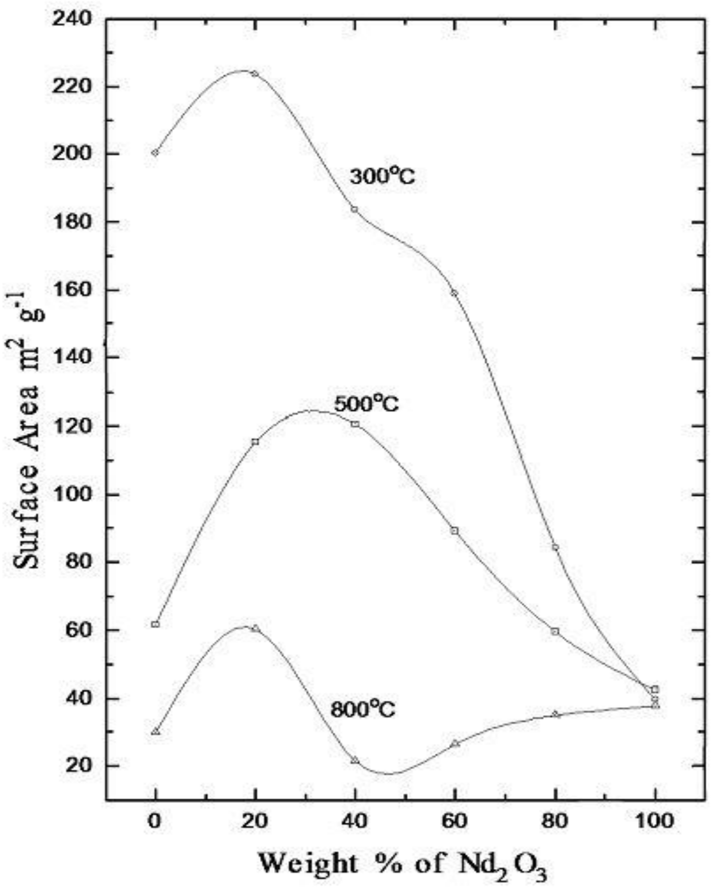


**Figure 2. Surface areas of Nd -Zr mixed oxides as a function of composition**

The oxides under study responded only to Dimethyl yellow, Methyl red and Bromothymol blue. Acidity at various acid strengths of the oxide was measured by titrating solid suspended in benzene with 0.1N n-butyl amine in benzene. Basicity was measured by titrating solid suspended in benzene with 0.1N trichloroacetic acid in benzene, using the same set of indicators as for acidity measurement. By this procedures we measured acid / base strength distribution on a common scale [6]. The acid-base strength distribution curves intersect at a point on the abscissa where acidity = basicity = 0 [7]. The point of intersection defined as $H_{o,max}$ value was determined for the oxides and are reported. $H_{o,max}$ value can be regarded as a practical parameter to represent the acid-base properties of solids. A solid with a large $H_{o,max}$ value has strong basic sites and weak acid sites. On the other hand, a solid with a small $H_{o,max}$ value has strong acid sites and weak basic sites.

Table . 2 Surface Areas of Neodymium-Zirconium Mixed Oxides Activated at Different Temperatures

| Weight % of Rare Earth Oxide | Surface areas m$^2$ g$^{-1}$ Nd-Zr Mixed Oxides Activated at | | |
|---|---|---|---|
| | 300$^o$C | 500$^o$C | 800$^o$C |
| 0 | 200.3 | 61.496 | 29.75 |
| 20 | 223.5519 | 115.2785 | 60.29195 |
| 40 | 183.7774 | 120.568 | 21.45165 |
| 60 | 158.8979 | 89.098 | 26.334 |
| 80 | 84.3458 | 59.594 | 34.884 |
| 100 | 39.7 | 42.4 | 37.9 |

$ZrO_2$ is having very high surface area when activated at 300$^o$C, surface area decreased with activation temperature, the decrease is steep (table.1). In the case of $Nd_2O_3$ the surface area is less compared to $ZrO_2$ . The surface area of $Nd_2O_3$ increases from 300$^o$C up to 500$^o$C and then decreases. At 300$^o$C and 500$^o$C, surface areas of all mixed oxides are greater than that of neodymia. At all activation temperature 20 Nd have larger surface areas than zirconia. At 800$^o$C surface areas of 60 Nd and 40 Nd were less than the component oxides. However, surface areas can be considered to be improved by the mixing of oxides especially at lower activation temperatures.

Pure zirconia is more acidic than neodymia.

The base amount of zirconia increases first with activation temperature up to 500°C and then decreases. For neodymia the base amount increases with activation temperature having its maximum at 800°C. At the acid strength of $H_o \geq 3.3$, base amount is less in the mixed oxides than the pure oxides. Acidity is being created on mixing the oxides. At activation temperature 500°C, the base amount of all the mixed oxides is greater than that activated at 300°C. For most of the mixed oxides the base amount for the samples activated at 800°C is less than that at 500°C. For most of the mixed oxides the maximum value of the base amounts are for samples activated at 500°C.

**Figure 3**

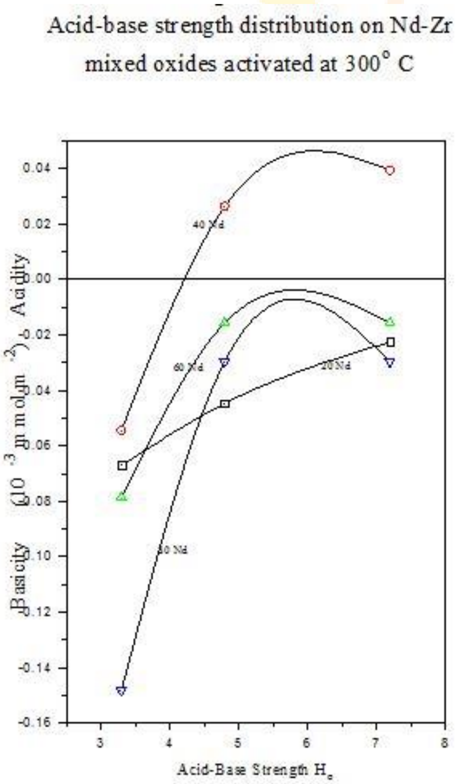
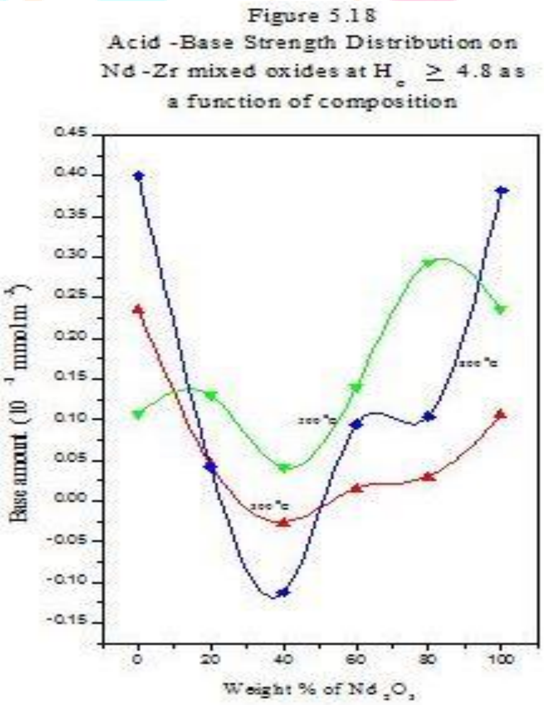


**Figure . 4**



At the acid strength of $H_o \geq 4.8$ the base amount of zirconia decreased first up to 500°C and then increased, the maximum exhibited at 800°C. For neodymia, the base amount increased with activation temperature, showing its maximum at 800°C. For all the mixed oxides activated at 300°C the base amount is less than the pure component oxide. For samples activated at 500°C except 40 Nd have base amounts greater than the pure component oxides. For samples activated at 800°C, all the mixed oxides have less basicity than the component oxides, 40 Nd being the lowest.

Table . 3
Acid-Base strength Distribution on Neodymium-Zirconium Mixed Oxides
Activated at different Temperatures

| Weight % of $Nd_2O_3$ | Activat. Temp. | Basicity $H_o \geq 3.3$ | Acidity $H_o \leq 3.3$ | Basicity $H_o \geq 4.8$ | Acidity $H_o \leq 4.8$ | Basicity $H_o \geq 7.2$ | Acidity $H_o \leq 7.2$ |
|---|---|---|---|---|---|---|---|
| | °C | $10^{-3}$ m mol m$^{-2}$ | | | | | |
| 0 | 300 | 0.9655 | - | 0.2361 | - | - | 0.1679 |
| 20 | 300 | 0.0671 | - | 0.0447 | - | 0.0224- | - |
| 40 | 300 | 0.0544 | - | - | 0.0263 | - | 0.0394 |
| 60 | 300 | 0.0786 | - | 0.0157 | - | 0.0157 | - |
| 80 | 300 | 0.1481 | - | 0.0296 | - | 0.0296 | - |
| 100 | 300 | 0.327 | - | 0.1051 | - | - | 0.251 |
| 0 | 500 | 2.738 | - | 0.1072 | - | - | 2.7448 |
| 20 | 500 | 0.1725 | - | 0.130 | - | 0.0217 | - |
| 40 | 500 | 0.1036 | - | 0.0414 | - | 0.0257 | - |
| 60 | 500 | 0.3646 | - | 0.1402 | - | 0.1122 | - |
| 80 | 500 | 4.193 | - | 0.2935 | - | 0.2516 | - |
| 100 | 500 | 0.4 | - | 0.235 | - | - | 0.165 |
| 0 | 800 | 2.45 | - | 0.4 | - | - | 3.0794 |
| 20 | 800 | 0.1659 | - | 0.0415 | - | - | 0.0401 |
| 40 | 800 | 0.1165 | - | - | 0.1125 | - | 0.2250 |
| 60 | 800 | 0.759 | - | 0.0949 | - | 0.0949 | - |
| 80 | 800 | 2.86 | - | 0.1043 | - | 0.0716 | - |
| 100 | 800 | 0.421 | - | 0.382 | - | 0.025 | - |

At the acid strength of $H_o \geq 7.2$ the pure oxides activated at 300°C and 500°C and $ZrO_2$ activated at 800°C are acidic. For samples activated at 300°C all the mixed oxides except 40 Nd show basicity. At 500°C all the mixed oxides exhibit basicity even though the pure oxides are acidic. For samples activated at 800°C all the zirconium rich samples are acidic and then neodymium rich samples are basic.

The coordination numbers of Nd is six and oxygen is four in pure $Nd_2O_3$. The coordination numbers of Zr is eight and oxygen is four in pure $ZrO_2$ . When the two oxides are mixed with $ZrO_2$ as the major component, coordination numbers of the cations will remain as such but that of the anion will be 4 as by postulate 1 & 2 As the covalency (charge to radius ratio ) of the oxide is greater, the oxide will be more acidic [8] . Ce is having +4 charge and the ionic radius will be less than the trivalent ions and so the covalency of the metal ion in the oxide will be higher and $CeO_2$ is found to be more acidic than the other two rare earth oxides.

According to Tanabe's hypothesis [9] , acidity generation is by an excess of a positive or negative charge in the model structure of a binary oxide. The model structure is pictured according to the following two postulates.

1. The coordination number of the positive element of a metal oxide, $C_1$, and that of the second metal oxide, $C_2$, are maintained even when mixed.

2. The coordination number of the negative element (oxygen) of the major component oxide is retained for all oxygens in the binary oxide.

In its structure the positive charge of the Nd (the added cation ) will be distributed along six bonds (+3/6 for each bond). The negative charge of the oxygen will be distributed along four bonds (-2/4 for each bond). The charge imbalance produced at one Nd-O bond is (+3/6 - 2/4 = 0) zero, and the total charge difference produced by one Nd cation is again zero. In this case no acidity is assumed to appear upon the mixing of two oxides.

When the two oxides are mixed with $Nd_2O_3$ as the major component, the coordination number of cation will remain as such and that of the anion will be four ( as in $Nd_2O_3$ ). In its structure the positive charge of the Zr (the added cation) will be distributed along eight bonds (+4/8 for each bond). The negative charge of the oxygen will be distributed along four bonds (-2/4 for each bond ). The charge imbalance produced at one Zr-O bond is (+4/8 - 2/4 = 0) zero, and the total charge difference produced by one Zr cation is again zero. In this case also no acidity is assumed to appear, because no charge imbalance is created on mixing the oxides. In any case of Nd - Zr mixed oxide acidity will not be generated according to Tanabe's [9] hypothesis and it agrees well with our studies.

## IV CONCLUSIONS

The surface acid and base properties changes on mixing Zirconium oxide with Neodymium oxide. The surface acid - base properties depend on composition of the oxide as well as on the activation temperature. No acidity is being generated on mixing the two oxides. The observation agrees very well with Tanabe's hypothesis.

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