CRYSTAL STRUCTURE, SURFACE ACIDITY, SURFACE AREA, CATALYTIC ACTIVITY AND ELECTRICAL CONDUCTIVITY BEHAVIOUR OF SiO$_2$–ZrO$_2$ SYSTEM

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SUMMARY

Crystal structure, surface acidity, surface area, catalytic activity and electrical conductivity behaviour of SiO$_2$–ZrO$_2$ system of various composition has been investigated. Samples with 50 % ZrO$_2$ calcined at 550, 650 and 750°C showed a high concentration of acidic sites and catalytic activity for the H$_2$O$_2$ decomposition. The electrical conductivity of SiO$_2$–ZrO$_2$ mixture calcined at 750°C showed a lower value than the pure ZrO$_2$. The results obtained have been discussed and correlated.

1– INTRODUCTION

The amorphous silica of commercial importance have a high surface area (100–500 m$^2$/g) and find industrial use as adsorbents, catalysts, supports, and filters for paints, toothpaste, etc. Intrusion of ZrO$_2$ in the mixed SiO$_2$.x H$_2$O–ZrO$_2$ systems forming crystal defects which causes a change in the physical and chemical characteristics, especially their acidity and their electrical conductivity (1–7).

Many types of defects can be present in the texture of the crystal lattice of solids. Surface defects have different energy and structure from that of the bulk of the solid. These effects indicate that the material gains certain physical properties such as catalytic activity due to these defects(8).

There are a number of reports concerning the acid properties of solid catalyst and the correlation between catalytic activity and surface acidity. ZnO–TiO$_2$ was most extensively studied(9) and recently some other mixed metal oxides were also studied Silica–zirconia(10) and Silica–Magnesia(11) were reported to be solid acid which can act a cracking catalysts. Kawaguchi and Haregawa studied(12) the surface acidity SiO$_2$–TiO$_2$ catalysts with various amounts of TiO$_2$ content. They found
that the highest acid amount and acid strength for a molar ratio of 1:1. The acid amount were 0.34, 0.57 and 0.65 mmol/g at Ho = −8.2, −5.6, −3.0 and +4.0 respectively. From the previous works, (13–15) decomposition of H2O2 and the acidic properties of some inorganic soilds showed a good correlation between the acidic and the catalytic properties.

The present work was designed to measure the acidity of the binary metal oxides. ZrO2–SiO2, with n-butylamine and benzoic acid respectively, using various indicator of pKₐ = −8.8 to −3.3. Effects of the chemical composition and the crystal structure on the acid properties were also studied. The electrical conductivity and the catalytic decomposition of H2O2 by these catalysts have been studied.

2– EXPERIMENTAL

The binary oxides SiO2, x H₂O – ZrO₂ were prepared in the composition 10:90, 20:80, 40:60, 50:50, 70:30 and 90:10 mole % of ZrO₂ – SiO₂, x H₂O respectively, from BDH quality chemicals by impregnation technique. The samples are designated as sample I, II, III, IV, IV, V and VI respectively. The impregnated oxides were dried at 115°C for 5 hours. The samples were then ground and only such samples collected between 100 and 200 mesh series were used. The powders, thus obtained were calcined at 550, 650 and 800°C for 5 hours at each of these temperature. The samples after calcination were cooled in a dessicator and kept in covered glass tubes under vacuum.

X-ray diffraction patterns of the samples investigated by the aid of Philips diffractometer, type Pw 2103/100 using Cu−target and Ni−filter.

IR absorption spectra on the samples were carried out with Beckman infrared spectrophotometric, unit, adopting KBr technique.

DTA and TGA experiments were carried out using a Shimadzu Thermal Analyzer (model 30) at heating rate 20°C min⁻¹ in air atmosphere using 20 mg Sample.

Surface area on the samples were carried out using the nitrogen adsorption technique. Adsorption–desorption isotherms were obtained for each sample from the adsorption of nitrogen gas at liquid nitrogen temperature (77.2 K). Each sample was outgassed for 5 hours at 110°C prior to any adsorption run.
The acidic sites for the pure and mixed oxides surface were determined by using the amine titration method developed by Johnson. (16) So 0.2g of the sample suspended in benzene was titrated with a solution of 0.1N n-butylamine in benzene using anthraquinone (pKa = -8.2), benzal acetophenone (pKa = -5.6), dicinimal acetone (pKa = -3.0), as indicators. The decomposition of H2O2 was selected for the study on catalytic reactivity of the catalysts (17) in a temperature range 30–50°C. The electrical conductivity has been measured by a method was reported elsewhere. (18)

3– RESULTS AND DISCUSSION

Figures (1, 2) represent the DTA and TG diagrams respectively for SiO2·xH2O, ZrO2 and SiO2·xH2O–ZrO2 mixtures. The TG diagrams of silica gel shows continuous decrease in weight at a temperature range of 30–1200°C whereas the DTA diagram shows two endothermic peaks at 70 and 600°C. The first small peak appearing at 70°C may be attributed to the desorption of H2O molecules from the surface of the oxide while the second peak appearing at 600°C is explained on the basis of the transformation of silica gel to SiO2. This transformation was also studied by other authors. (19–23)

The DTA–TG diagram of the impregnated ZrO2, Fig. (1) showed endothermic peak at 150°C with a decreasing in the weight (3.2 %) due to the elimination of lousy bonded water molecules and a broad exothermic peak around 480°C which attributed to the crystallization of zirconia.

Fig. 1. DTA Curves of (a) Zirconia, (b) Silica gel and (c) Silica gel–Zirconia Mixture.
Fig. 2. TGA Curves of (a) Zirconia, (b) Silica gel and (c) Silica gel-Zirconia Mixture.

The DTA–TG diagrams SiO$_2$.xH$_2$O – ZrO$_2$ mixture (1:1 molar ratio) showed only the same peaks characteristic for the pure oxides, which means that no chemical reaction occurs between the two oxides in the investigated temperature range.

Figure (3) shows the IR spectra of SiO$_2$.xH$_2$O and ZrO$_2$ and their mixtures with (1:1 molar ratio). The IR spectra for silica gel samples shows 4 bands at 800, 1100, 1650 and 3400 cm$^{-1}$. The first 2 bands are assigned to Si–O vibrations. (24, 25) The last two bands is assigned to Si...OH and H...O...H binding vibration. On the other hand, the IR spectra of ZrO$_2$ show two band at 740 and 3400 cm$^{-1}$ due to Zr–O and H...O...H binding vibration. The IR spectra of oxide mixtures show a modification in the bands of the SiO$_2$ catalyst by ZrO$_2$ lead to a significant change. The addition of 10, 20 and 40 mole % ZrO$_2$ to SiO$_2$ causes a change in the sharp absorption band at 800°C to a broad band and the appear of new band from 730 to 780 cm$^{-1}$. This modification in the vibration bands are increased by increasing the percentage of ZrO$_2$ in the oxide mixture. This shift can be attributed to the presence of Zr$^{+4}$ in sites near to the Si–O vibrating band.

Fig. (4) shows the X-ray diffraction patterns for calcined pure and mixed oxides (1:1 molar ratio of the products of thermal treatment of SiO$_2$.xH$_2$O and ZrO$_2$ at different calcination temperature. All calcined samples of ZrO$_2$ and its mixtures with silica gel showed the same diffraction lines, which are characteristic for monoclinic ZrO$_2$ structure. The absence of new X–ray diffraction lines for the investigated product
Fig. 3. IR Absorption Spectra of ZrO$_2$-SiO$_2$×H$_2$O Mixtures with Different Mole Ratios.
indicates that no reaction has occurred between ZrO$_2$ and SiO$_2$. $\times$ H$_2$O at the investigated calcination temperature (550, 650 and 800°C).

Fig. 4. X-ray Diffraction Patterns for (a) SiO$_2$ + ZrO$_2$ Calcined at 850°C, (b) SiO$_2$ Calcined at 850°C, (c) ZrO$_2$ Calcined at 850°C.
From Fig. 5a) non linear behaviour between the acidity and the composition of the oxides can be observed. Maximum acid amount at any acid strength and different calcination temperature were observed

![Graph showing the variation of acidity with composition of ZrO₂](image)

**Fig. 5.** The Variation of Acidity (Expressed as m. mol. of n. butylamine/g of Catalyst) With The Composition and Calcination Temp.
for sample with the molar ratio 1:1. Moreover, the number of acid sites was found to decrease with increasing calcination temperature for all samples investigated. Fig. (6) shows a linear correlation between the acidity and the calcination temperature for each investigated com-

![Graph showing the effect of calcination temperature on the acidity of SiO<sub>2</sub>-ZrO<sub>2</sub> at various compositions.]

Fig. 6. Effect of Calcination Temperature on The Acidity of SiO<sub>2</sub>-ZrO<sub>2</sub> at Various Compositions.
position. This indicates that the decrease in acidity of SiO$_2$–ZrO$_2$ with the heat treatment due to the decrease in the number of acid sites rather than to the change in their nature of the SiO$_2$–ZrO$_2$ system. The acidity at various strengths of the catalysts are shown in the Figure (5). The maximum acidities at pK$_a$ = −3.3, −5.6 and −8.3 observed for SiO$_2$–ZrO$_2$ of mole ratio 1:1 where higher than the acidity of SiO$_2$–TiO$_2$, SiO$_2$–ZnO and SiO$_2$–Al$_2$O$_3$. The all ratios for SiO$_2$–ZrO$_2$ changed even the basic colours of acid indicators. Specific surface areas of the catalysts calcined at 550 and 650°C were determined in Table (1). It shows that the specific surface areas for SiO$_2$–ZrO$_2$ system increases with increasing ZrO$_2$ ratio up to 50 % and then decreases again up to 100 % ZrO$_2$. This means that the change in acidic property by mixing each oxide is partly due to the change in surface area, but the acidities per unit surface area of SiO$_2$–ZrO$_2$ are much larger than those of single oxides.

Table 1. Specific surfaces area for calcined samples at different temperatures.

<table>
<thead>
<tr>
<th>Composition samples</th>
<th>$A_1$, m$^2$/g</th>
<th>$A_2$, m$^2$/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>160</td>
<td>152</td>
</tr>
<tr>
<td>I</td>
<td>190</td>
<td>184</td>
</tr>
<tr>
<td>II</td>
<td>220</td>
<td>185</td>
</tr>
<tr>
<td>III</td>
<td>245</td>
<td>215</td>
</tr>
<tr>
<td>IV</td>
<td>270</td>
<td>230</td>
</tr>
<tr>
<td>V</td>
<td>220</td>
<td>170</td>
</tr>
<tr>
<td>VI</td>
<td>185</td>
<td>165</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>62</td>
<td>46</td>
</tr>
</tbody>
</table>

$A_1$: For the samples were calcined at 550°C.  
$A_2$: For the samples were calcined at 650°C.

The specific rate constants, k, for the catalyzed decomposition of H$_2$O$_2$ on SiO$_2$–ZrO$_2$ system are shown in Table (2). From which it can be seen that the rate of the decomposition of H$_2$O$_2$ changes with the composition of oxides, a typical plot is given in Fig. (7). Similar behaviours were observed for each of the calcination temperatures. The k–values decrease with increasing calcination temperatures in the order $k_{500} > k_{600} > k_{800}$. The effect of calcination temperatures on the reactivity of the oxides follows the same trend observed for the acidity results, where the number of acidic sites on the oxides at 800°C are lower than those obtained at lower calcination temperatures. From Fig. (7) it can also be seen that the rate of H$_2$O$_2$ decomposition increases first with increasing the concentration of ZrO$_2$ to a maximum at 50 mole % ZrO$_2$, then decreases to a minimum at 100 mole % ZrO$_2$.  

Table 2. Kinetic Data (at 50 °C) of the catalytic decomposition of H₂O₂ over different composition of ZrO₂–SiO₂ System.

<table>
<thead>
<tr>
<th>Calcination Temperature (°C)</th>
<th>550 °C</th>
<th></th>
<th></th>
<th>650 °C</th>
<th></th>
<th></th>
<th>750 °C</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>kx 10⁻⁵</td>
<td>E</td>
<td>(S⁻¹)</td>
<td>(kjmol⁻¹)</td>
<td>r</td>
<td>kx 10⁻⁶</td>
<td>E</td>
<td>(S⁻¹)</td>
<td>(kjmol⁻¹)</td>
</tr>
<tr>
<td>n Samples</td>
<td>SiO₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>1.126</td>
<td>53.531</td>
<td>0.975</td>
<td></td>
<td>0.800</td>
<td>100.02</td>
<td>0.992</td>
<td></td>
<td>2.097</td>
</tr>
<tr>
<td>II</td>
<td>5.257</td>
<td>84.08</td>
<td>0.980</td>
<td></td>
<td>4.58</td>
<td>80.60</td>
<td>0.984</td>
<td></td>
<td>3.918</td>
</tr>
<tr>
<td>III</td>
<td>7.0928</td>
<td>68.035</td>
<td>0.905</td>
<td></td>
<td>7.656</td>
<td>52.340</td>
<td>0.981</td>
<td></td>
<td>5.89</td>
</tr>
<tr>
<td>IV</td>
<td>8.489</td>
<td>24.671</td>
<td>0.999</td>
<td></td>
<td>21.543</td>
<td>68.69</td>
<td>0.884</td>
<td></td>
<td>6.96</td>
</tr>
<tr>
<td>V</td>
<td>7.156</td>
<td>42.6455</td>
<td>0.991</td>
<td></td>
<td>5.242</td>
<td>24.360</td>
<td>0.998</td>
<td></td>
<td>3.651</td>
</tr>
<tr>
<td>VI</td>
<td>5.6015</td>
<td>36.820</td>
<td>0.994</td>
<td></td>
<td>2.215</td>
<td>36.441</td>
<td>0.999</td>
<td></td>
<td>2.15</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>7.610</td>
<td>32.707</td>
<td>0.999</td>
<td></td>
<td>0.5089</td>
<td>61.27</td>
<td>0.986</td>
<td></td>
<td>1.45</td>
</tr>
</tbody>
</table>

Fig. 7. Effect of Composition and Calcination Temperature on The Decomposition Rate of H₂O₂.
THE PROPERTIES OF SiO₂-ZrO₂ SYSTEM

By comparing the reactivity results with those obtained for acidity (maximum at 50 mole % ZrO₂), it can be seen that the decomposition of H₂O₂ over the oxides with different concentration is attributed to the acidic sites present on the surfaces. On the other hand, the reactivity of the oxides containing lower or higher concentration (less or higher than 50 mole % ZrO₂) can be attributed to the increase in their acidity and or to the increase in their surface area. The activation energies, Eₐ for the oxides investigated were calculated from the plots of log k against 1/T.

The Eₐ values obtained are given in table (2) from which it can be seen that the lowest activation energies is for the decomposition of 50 % ZrO₂. This indicates that the acidic sites present on the oxides surface accelerate the decomposition rate of H₂O₂ according to the following mechanism.

\[ \text{A}^+ + \text{H}_2\text{O}_2 \rightarrow \text{A}^+\text{HO}_2 + \text{H}^+ \]

\[ \text{A}^+ + \text{A}^+\text{HO}_2 + \text{H}_2\text{O}_2 \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{A}^+\text{OH} \]

Where A⁺ are the acidic sites present on the surface.

Electrical conductivity may give a schematic model for the mechanism of semiconductivity in solid, containing OH groups. The electrical conductivity, σ of calcined samples ZrO₂, SiO₂ and their mixture was measured as a function of temperature in the range 25–500°C. The results obtained are represented graphically by plotting in σ against 1/T; Fig. (8) and all conductivity data are summarized in Table (3). There are two distinct lines (I and II).

The first portion (I) may be represent the extrinsic conductivity and the second (II) portion represents the intrinsic domain of conductivity.

The conductivity values of ZrO₂ lie in the range of semiconductors. For pure ZrO₂ sample and for those with 90 mole % respectively, a thermoelectric effect investigated at room temperature was measured. It showed that the charge carriers are of electronic nature. The temperature T₀ at which the break in the distinct lines appear, shifts to a higher temperature with increasing ZrO₂ ratio. This can be attributed to the decrease in the concentration of impurities. Table (3) shows that the minimum conductivity attributed to the pure SiO₂.
Fig. 8. The Effect of Temperature on The Electrical Conductivity of The Mixed Oxides SiO$_2$. xH$_2$O – ZrO$_2$ Calcined at 750°C.
THE PROPERTIES OF SiO$_2$–ZrO$_2$ SYSTEM

Table 3. Electrical conductivity data of SiO$_2$–ZrO$_2$ system.

<table>
<thead>
<tr>
<th>Composition samples</th>
<th>Tb(°C)</th>
<th>$\sigma^*$</th>
<th>E$^*$ kJ mol$^{-1}$</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>I</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>200</td>
<td>4.598$^{-19}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>III</td>
<td>220</td>
<td>3.755$^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IV</td>
<td>250</td>
<td>1.526940$^{-9}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>270</td>
<td>4.12924$^{-7}$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VI</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\sigma^*$ = Electrical conductivity in ($\Omega^{-1}\text{cm}^{-1}$).
Tb = Temperature at which break in conductivity occurs.

REFERENCES