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## The influence of chemical and thermal treatment on the point of zero charge of hydrous zirconium oxide

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**Abstract:** Two zirconia samples were prepared by precipitation from aqueous zirconium oxychloride and zirconyl sulfate solutions with potassium hydroxide. The prepared zirconia samples were amorphous. The  $\text{pH}_{\text{pzc}}$  values of the zirconia samples, determined in NaCl and NaNO<sub>3</sub> solutions, were  $6.6 \pm 0.1$  and  $6.9 \pm 0.1$ , respectively. After prolonged hydration of zirconia in doubly distilled water, the  $\text{pH}_{\text{pzc}}$  decreased to  $4.7 \pm 0.3$ . Crystallization into tetragonal (metastable) + monoclinic zirconia appeared at 691 K. Above 873 K, the tetragonal metastable phase changes to a monoclinic phase. It was shown that crystallite sizes of zirconia treated at 673–1273 K increased from 9.5 to 40.5 nm, respectively. The increase in temperature from 385 to 1070 K increased the  $\text{pH}_{\text{pzc}}$  of zirconia samples from 6.6 to 9.0, respectively.

**Keywords:** zirconium oxide; point of zero charge; thermal analysis; surface properties.

### INTRODUCTION

Inorganic sorbents, especially metal oxides, can withstand high temperatures and high radiation doses. One of them is hydrous zirconium oxide used for the removal of corrosion products from nuclear reactor cooling systems, and as a catalyst support or membrane for various catalysts. Furthermore, zirconium oxide has been widely used, both pure and in mixtures with other oxides or compounds, for the preparation of both traditional and advanced ceramic materials. Finally, zirconium oxide has been used as a column packing material for gas chromatography and high-performance liquid chromatography.

In the last three decades, many experimental and theoretical attempts have been made to explain the chemical behavior of the oxide/aqueous interface. Solid oxides in aqueous suspensions are, in general, electrically charged. The main

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reasons for this are amphoteric association and dissociation of protons and hydroxyl groups existing on the oxide surface.<sup>1,2</sup> Therefore, the double layer at an oxide/aqueous interface can be investigated by studying the equilibrium distribution of these ions (called potential determining ions) between the surface and the bulk of the solution.

One of the main characteristics of aqueous metal oxide suspensions is the point of zero charge ( $\text{pH}_{\text{pzc}}$ ), which represents the suspension pH value at which an immersed oxide surface has zero net charge or the sum of surface positive and negative charges is zero (for hydrous zirconium oxide):

$$\sum [(= \text{ZrO}^-) + (= \text{ZrO}_2^+)] = 0 \quad (1)$$

Addition of hydrous zirconium oxide to the solution of higher pH than  $\text{pH}_{\text{pzc}}$  leads to a decrease in formed suspension pH. Similar, but opposite effect, will occur if the oxide is added to the solution of lower pH than  $\text{pH}_{\text{pzc}}$ . Such effects are the result of the charge formed on the oxide interface<sup>3,4</sup> accompanied by the sorption of ions from the solution. The sorption of cations occurs in the region of pH above  $\text{pH}_{\text{pzc}}$ , while that of anions in the region of pH below  $\text{pH}_{\text{pzc}}$ .

In the present study, a  $\text{ZrO}_2/\text{H}_2\text{O}$  system was investigated with the aim of determining the influence of different sample preparations and physicochemical treatments on the point of zero charge of hydrous zirconium oxide.

#### EXPERIMENTAL

Hydrous zirconium oxide samples were prepared by precipitation from aqueous zirconium oxychloride ( $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ) solution (sample 1) and zirconium sulfate ( $\text{Zr}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ ) solution (sample 2) (concentration  $0.71 \text{ mol dm}^{-3}$ ) with potassium hydroxide ( $3.0 \text{ mol dm}^{-3}$ ), similar to the procedure described previously.<sup>5,6</sup> All chemicals, obtained from various commercial sources, were of A. R. quality and used "as received".

The resultant precipitates were filtered and thoroughly washed with doubly distilled water until neutral reaction. Then, the precipitates were dried in air at 383 K for 72 h and lightly crushed.

Thermal analysis experiments (TGA and DTA) were performed in air (Dupont 1090 instrument) up to 875 K at a heating rate of  $10\text{--}20 \text{ K min}^{-1}$ . In addition, the obtained graphs were converted into digital form/format using the Graph digitizer program.

The calcinations of the samples was performed (in a Pt crucible) in a drying oven or in a Heraeus ceramic furnace (depending on the calcinations temperature) for 4 h.

Structural characterization of the dry and calcined samples was performed by X-ray diffraction (XRD) analysis (Siemens Kristalloflex 4 with a GM counter). The XRD patterns were transformed from graphical form into digital data using the Graph Digitizer program. The apparent crystallite sizes of the prepared zirconia powders were calculated from the full-width at half-maximum height of the (111) XRD peaks using the Scherrer formula<sup>7</sup> corrected for instrumental broadening, the method most frequently used in the literature:

$$D = 0.89\lambda / (\beta_{1/2} \cos \theta) \quad (2)$$

where  $D$  is the crystallite diameter, nm, 0.89 is a constant,  $\lambda$  is the wavelength for  $\text{CuK}\alpha$  (equal to 0.15405 nm),  $\beta_{1/2}$  is the half-width of the maximum intensity peak of the XRD pattern and  $\theta$  is the Bragg angle.

The point of zero charge ( $\text{pH}_{\text{pzc}}$ ) was determined by the batch equilibration technique.<sup>8,9</sup> The samples of hydrous zirconium oxide (0.500 g) with 50 cm<sup>3</sup> of NaCl or NaNO<sub>3</sub> solution were shaken in PVC vials for 4 h at 294 K. The initial pH values of the NaCl or NaNO<sub>3</sub> solution (in the pH range from 2.5 to 10.5) were adjusted by the addition of a small amount of HCl or NaOH (concentration of 0.1 mol dm<sup>-3</sup>) solution, keeping the ionic strength constant.

#### RESULTS AND DISCUSSION

The dependence of the  $\text{pH}_f$  of the filtered solutions, after equilibration with hydrous zirconium oxide, on the initial  $\text{pH}_i$  gives a smooth curve with a plateau at a pH that represents the  $\text{pH}_{\text{pzc}}$  (as was shown in previous papers<sup>6,8,9</sup>). The obtained  $\text{pH}_{\text{pzc}}$  value (sample 1) was  $6.6 \pm 0.1$  (obtained using NaCl solutions of three different ionic strengths).<sup>6</sup> In addition, the obtained value for sample 2 was also  $\text{pH}_{\text{pzc}} 6.6 \pm 0.1$ . The same  $\text{pH}_{\text{pzc}}$  value for both samples indicates that the prepared samples had the same surface stoichiometry. This  $\text{pH}_{\text{pzc}}$  value is in good agreement with the results of other authors<sup>10-13</sup> ( $\text{pH}_{\text{pzc}} 6.4-6.7$ ). The  $\text{pH}_{\text{pzc}}$  value of 4.0 reported by Milonjić *et al.*<sup>9</sup> refers to a hydrous zirconium oxide sample prepared by precipitation with ammonia. It is obvious that the surface stoichiometry of the oxide was changed by this synthesis procedure.

Most likely, the nature of the cations of the precipitating reagent could cause a change in the surface stoichiometry, and even in the surface purity and water content of the zirconia sample.

In the next experiment, a NaNO<sub>3</sub> electrolyte was used instead of a NaCl one. The dependence  $\text{pH}_f$  vs.  $\text{pH}_i$  (0.001, 0.01, and 0.1 mol dm<sup>-3</sup> NaNO<sub>3</sub>) for sample 1 is shown in Fig. 1 ( $\text{pH}_{\text{pzc}} 6.9 \pm 0.1$ ). Good agreement between the obtained  $\text{pH}_{\text{pzc}}$  values (determined using 0.1 mol dm<sup>-3</sup> NaCl and NaNO<sub>3</sub> solutions) denotes that there was no specific sorption of Na<sup>+</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup> on hydrous zirconium oxide.

The hydrous zirconium oxide already used in determination of the  $\text{pH}_{\text{pzc}}$  (sample 1) was collected, thoroughly washed with distilled water until neutral, dried at 385 K for 24 h (sample denoted as sample 1-U), and reused in  $\text{pH}_{\text{pzc}}$  determination experiments (from now on, all experimental data were obtained using 0.1 mol dm<sup>-3</sup> NaCl solution). A decrease in the  $\text{pH}_{\text{pzc}}$  was found ( $\text{pH}_{\text{pzc}} 4.6 \pm 0.3$ ).

To determine the effect of sorbed ions (possibly present on the oxide surface) on  $\text{pH}_{\text{pzc}}$ , a desorption experiment was performed using sample 1-U. The experiment was performed with dilute HNO<sub>3</sub> (0.1 mol dm<sup>-3</sup>) at a solid/liquid ratio of 5 g:100 cm<sup>3</sup> and an equilibration time of 2 h. The desorption procedure was performed three times. Finally, after filtration, the zirconium sample 1-U was thoroughly washed with distilled water until neutral and dried at 385 K for

24 h. The  $\text{pH}_{\text{pzc}}$  of so-treated sample was  $4.7 \pm 0.3$ . The obtained  $\text{pH}_{\text{pzc}}$  value is in good agreement with the  $\text{pH}_{\text{pzc}}$  value of the same sample 1-U determined before desorption. This means that the eventually sorbed ions ( $\text{Na}^+$  or  $\text{NO}_3^-$ ) have no influence on the  $\text{pH}_{\text{pzc}}$  value of the  $\text{ZrO}_2$  sample.

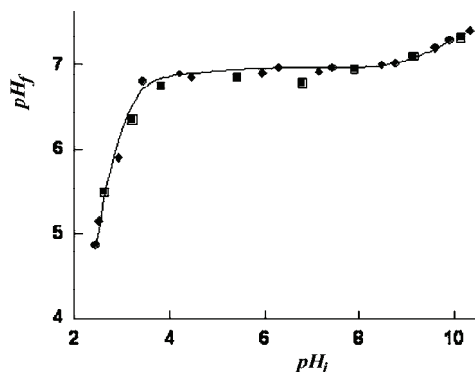


Fig. 1.  $\text{pH}_f$  vs.  $\text{pH}_i$  of zirconia (sample 1) suspensions. • – 0.001, □ – 0.01, ◆ – 0.10  $\text{mol dm}^{-3}$   $\text{NaNO}_3$ .

To explain the obtained  $\text{pH}_{\text{pzc}}$  value, the zirconia powder was further investigated. Fresh samples (sample 1) were placed in PVC bottles filled with doubly distilled water and equilibrated for various times (from 50 to 400 h). Then, the samples were filtrated, thoroughly washed with distilled water until neutral, dried at 383 K for 24 h, and used for  $\text{pH}_{\text{pzc}}$  determination.

The obtained  $\text{pH}_{\text{pzc}}$  values are shown in Fig. 2. A decrease in the  $\text{pH}_{\text{pzc}}$  of the zirconia samples with increasing hydration time is evident. A smooth curve with a plateau at  $\text{pH}_{\text{pzc}} 4.7 \pm 0.3$  indicates the influence of the hydrolysis/hydration time on the  $\text{pH}_{\text{pzc}}$  of the hydrous zirconium oxide. Most likely, the differences in  $\text{pH}_{\text{pzc}}$  in the present experiments were caused by the sorption or formation of simple zirconium hydrolytic complexes on the surface, which changed the surface stoichiometry. This is in accordance with the results of other authors for several oxides. Kanungo and Parida<sup>14</sup> showed that the  $\text{pH}_{\text{pzc}}$  of  $\text{MnO}_2$  increases with decreasing water content in the oxide. In the case of  $\text{MnO}_2$ <sup>15</sup> and  $\text{RuO}_2$ ,<sup>16</sup> the  $\text{pH}_{\text{pzc}}$  values underwent significant changes in the acid direction on passing from “dry” crystalline forms to hydrous oxides. Moreover, hydroxides were reported to present  $\text{pH}_{\text{pzc}}$  values more acidic than the corresponding “dry” oxides ( $\text{CuO}$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ ).<sup>17</sup>

Parks<sup>18</sup> indicated that one of the mechanisms of the formation of charges on oxide surfaces in aqueous solutions is the sorption of metal hydroxocomplexes derived from hydrolysis of the solid material, as might have been the case in the present investigations.

When used as a sorbent, hydrous zirconium oxide exposed to high temperatures undergoes some kind of thermal decomposition and transformation. The thermogravimetric (TG) and differential thermogravimetric (DTG) results for

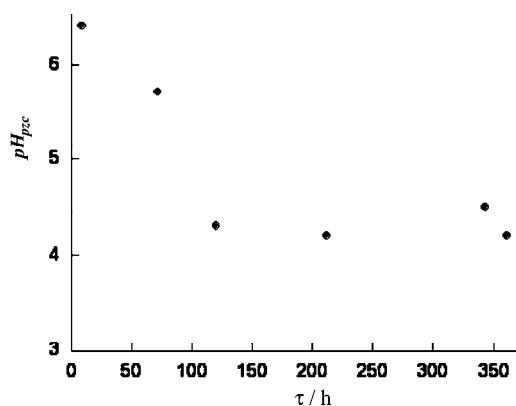


Fig. 2. The dependence of the  $\text{pH}_{\text{pzc}}$  of zirconia (sample 1) on the time of equilibration with deionized water.

fresh sample 1 are illustrated in Fig. 3. The sample lost about 20 % of structure water ( $\text{ZrO}_2 \cdot n\text{H}_2\text{O}$ ,  $n$  between 1 and 2), which corresponds to the loss of 1.5–1.6 molecules of  $\text{H}_2\text{O}$ . The  $\text{ZrO}_2$  sample contained adsorbed water, which was totally removed at around 500 °C. This is in good agreement with the result of Ardizzone *et al.*<sup>19</sup> The total mass loss between 100 and 500 °C was 14.4 mass %. This corresponds to the synthesized  $\text{ZrO}_2$  having the composition ( $\text{ZrO}_2 \cdot 1.2\text{H}_2\text{O}$ ) after drying in air at 110 °C for 72 h. The mass loss is considered to be the result of the removal of water (both physisorbed and chemisorbed at the surface of the particles). On the DTG curve presented in Fig. 3, three peaks are evident, *i.e.*, one large peak centered at 110 °C and two small ones centered at 207 and 461 °C. A differential thermal analysis (DTA) curve of zirconia sample 1 is given in Fig. 4. The first broad endothermic peak observed on the DTA curve at about 130 °C could be attributed to desorption of water molecules adsorbed on the zirconia surface. The subsequent sharp exothermic peak observed at about 410 °C was due to phase transformation (*i.e.*, crystallization) of the zirconia.

The XRD data for untreated zirconium particles and samples thermally treated at different temperatures are shown in Fig. 5. The X-ray diffraction pat-

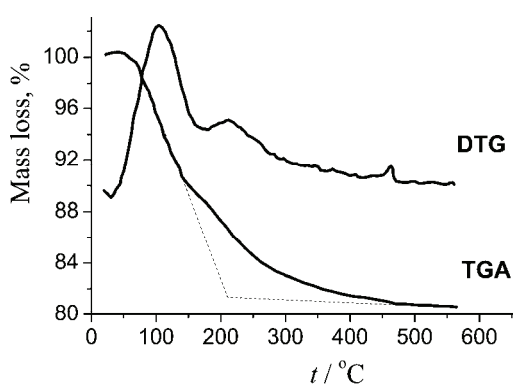


Fig. 3. The TG and DTG curves for zirconia (sample 1).

tern of the prepared, thermally untreated (385 K), sample shows no peaks except a broad, weak one at  $2\theta$  25–35°. This indicates that the prepared zirconium particles were amorphous. Amorphous precipitates usually transform into the metastable tetragonal phase upon thermal treatment, then into a mixture of tetragonal and monoclinic phases and finally into the monoclinic phase.

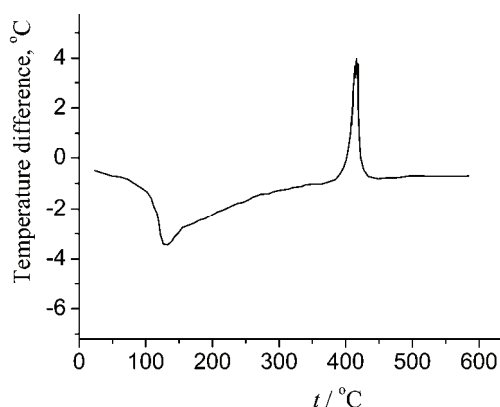


Fig. 4. The differential thermal analysis curves for zirconia (sample 1).

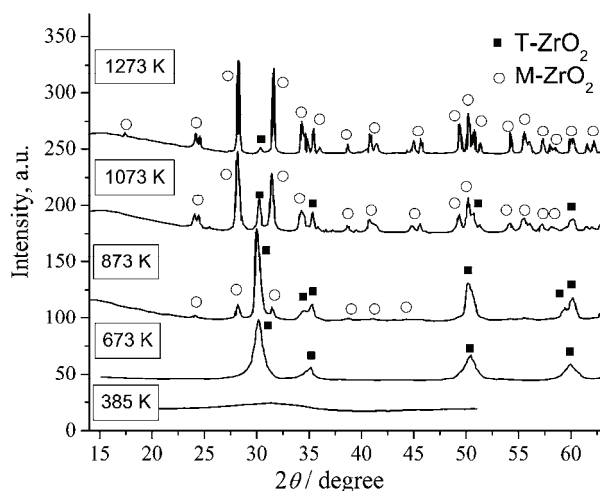


Fig. 5. XRD Patterns of zirconia (sample 1) treated at various temperatures.

Crystallization into tetragonal (metastable)  $ZrO_2$  appeared at 691 K (Figs. 4 and 5). Samples calcinated at 873 and 1073 K were a mixture of monoclinic and metastable tetragonal phases. The sample calcinated at 1273 K (or above) was monoclinic. This is in good agreement with the recently published result of Bortun *et al.*<sup>20</sup> The broad peak<sup>21</sup> at  $2\theta$  30° (Fig. 5) consists of two peaks, one for the monoclinic and one for the tetragonal phase (at a temperature above 720 to 870 K

these peaks are distinguishable).<sup>21,22</sup> Above 873 K, the tetragonal metastable phase changes to the monoclinic one.<sup>22</sup>

The calculated crystallite diameters of the  $ZrO_2$  samples (treated at 673, 873, 1073 and 1273 K) are plotted against calcination temperatures in Fig. 6. The crystallite size of the tetragonal phase (samples thermally treated at 673 and 873 K) was calculated from the characteristic peak  $2\theta$  30.5° (for the (111) reflection, data PDF 14-534), whereas the crystallite size of the monoclinic phase (samples thermally treated at 1073 and 1273 K) was calculated from the characteristic peak  $2\theta$  28.4° (for the (-111) reflection, data PDF 36-420). It is evident that the size of crystallites ( $D$ ) in the  $ZrO_2$  samples increases from about 9 nm after thermal treatment at 673 K to about 40 nm after calcinations at 1273 K. The obtained results are in good agreement with those previously reported by other authors.<sup>19,21,24,28</sup>

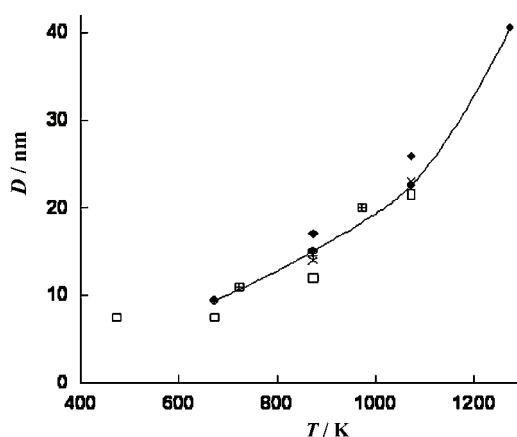


Fig. 6. Effects of treatment temperature on the crystallite size of zirconia (sample 1): ● – present results, □ – [17], ◆ – [20], × – [21], + – [22].

The increase in thermal treatment temperature from 385 to about 1070 K increased the  $pH_{pzc}$  of sample 1 from  $6.6 \pm 0.1$  to  $9.0 \pm 0.3$ . The  $pH_{pzc}$   $9.0 \pm 0.3$  corresponds to crystalline, totally dehydrated, zirconium oxide. According to the data presented, the point of zero charge of hydrous zirconium oxide depended far more on the degree of hydration than on the crystal structure of the oxide. The obtained results are in accordance with the literature data reviewed by Ardizzone and Trasatti.<sup>29</sup> They observed a shift of  $pH_{pzc}/pH_{iep}$  in the alkaline direction when going from the hydroxide to the crystalline oxide. The  $pH_{pzc}$  values of  $RuO_2$  obtained by calcination of different precursors in the presence of oxygen, at various temperatures, were between 4 (calcined at 300 °C) and 6 (calcined at 500–700 °C).<sup>29</sup> However, Kosmulski,<sup>30</sup> analyzing some literature data, concluded that the (hydro)oxides of some metals at certain degrees of oxidation show consistent  $pH_{pzc}$  values that are rather insensitive to the degree of their hydration and crystallographic forms.

## CONCLUSIONS

Two zirconia samples were prepared by precipitation from aqueous zirconium oxychloride and zirconyl sulfate solutions with potassium hydroxide (sample 1 and 2, respectively). The  $\text{pH}_{\text{pzc}}$  values of the zirconia samples, determined from NaCl and  $\text{NaNO}_3$  solutions, were  $6.6 \pm 0.1$  and  $6.9 \pm 0.1$ , respectively. This implies that there is no difference in surface properties of prepared zirconia samples and no specific sorption of  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{NO}_3^-$  on hydrous zirconium oxide. After prolonged (100 h) hydration of zirconia in doubly distilled water, the  $\text{pH}_{\text{pzc}}$  decreased to  $4.7 \pm 0.3$ . The prepared zirconia samples were amorphous. Crystallization into tetragonal (metastable) + monoclinic zirconia appeared at 691 K. Above 873 K, the tetragonal phase changed to a monoclinic one. It was shown that crystallite sizes of zirconia treated at 673–1273 K increased from 9.5 to 40.5 nm, respectively. The increase in temperature from 385 to 1070 K increased the  $\text{pH}_{\text{pzc}}$  of zirconia samples from 6.6 to 9.0, respectively. The  $\text{pH}_{\text{pzc}}$  value of 9.0 corresponds to totally dehydrated crystalline zirconia.

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## ИЗВОД

УТИЦАЈ ХЕМИЈСКОГ И ТЕРМИЧКОГ ТРЕТМАНА НА ТАЧКУ НУЛТОГ  
НАЕЛЕКТРИСАЊА ХИДРАТИСАНОГ ЦИРКОНИЈУМ(IV)-ОКСИДА

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Таложеем из воденог раствора цирконијум-оксихлорида или цирконил-сулфата са калијум-хидроксидом припремљена су два узорка цирконијум(IV)-оксида. Припремљени узорци цирконијум(IV)-оксида су аморфни. Тачке нултог наелектрисања,  $\text{pH}_{\text{tnn}}$ , припремљених узорака цирконијум(IV)-оксида, одређене из раствора натријум-хлорида и натријум-нитрата, износиле су  $6,6 \pm 0,1$  и  $6,9 \pm 0,1$ , редом. После дуже хидратације цирконијум(IV)-оксида у дестилованој води,  $\text{pH}_{\text{tnn}}$  опада до вредности  $4,7 \pm 0,3$ . Кристализација цирконијум(IV)-оксида у тетрагоналну (метастабилну) + моноклиничну фазу дешава се при 691 К. Изнад 873 К, тетрагонална метастабилна фаза прелази у моноклиничну. Показано је да величина кристалита цирконијум(IV)-оксида, третираног при 673–1273 К, расте од 9,5 до 40,5 nm, редом. Повишење температуре од 385 до 1070 К води до померања  $\text{pH}_{\text{tnn}}$  од 6,6 до 9,9, редом.

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