Characterization of combustion synthesized zirconia powder by UV-vis, IR and other techniques

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Abstract. Fine powders of zirconia were prepared by employing combustion method with varying fuel to precursor molar ratios. The zirconia powders contained more amount of monoclinic phase as the fuel content was increased. This aspect was studied using XRD, IR and UV-vis diffuse reflectance techniques. The surface acid-base properties of these samples were also investigated by indicator titration method. The catalytic activity was probed with transfer hydrogenation reaction in liquid phase. It was found that combustion synthesized zirconia did not provide required active sites for transfer hydrogenation reactions in liquid phase unlike hydrous zirconia.

Keywords. Combustion synthesis; ZrO_2; UV-vis; XRD; catalysis.

1. Introduction

Application of zirconium dioxide has been quite promising in catalysis and many other areas due to its versatile structural and surface chemical properties as well as good thermal stability (Mercera *et al* 1990; Yamaguchi 1994; Hattori 1995; Scheithauer *et al* 1998; Somiya and Akiba 1999). It has been reported as a better catalyst and catalyst support compared to classical materials such as Al_2O_3, SiO_2 and TiO_2 (Mercera *et al* 1990; Yamaguchi 1994; Hattori 1995; Song and Sayari 1996; Scheithauer *et al* 1998). The modified versions of zirconium dioxide, viz. the sulfated ZrO_2, zirconia substituted mixed oxides such as $Ce_xZr_{1-x}O_2$ solid solutions ($0 \leq x \leq 1$), various transition metal stabilized zirconia and hydrous zirconium oxide have been reported to be effective for several organic reactions, combustion and gas phase reactions (Choudhary *et al* 1996; Song and Sayari 1996; Aramendia *et al* 1997; Upadhya *et al* 1997; Fornasiero *et al* 1998; Kaspar *et al* 1999; Ranga Rao 1999). The partial substitution of ZrO_2 into CeO_2 improves the thermal stability, oxygen storage capacity and redox properties of ceria considerably. This is considered as a significant contribution to three-way catalyst (TWC) technology (Ranga Rao *et al* 1995; Fornasiero *et al* 1998; Kaspar *et al* 1999). However, the role of ZrO_2 in CeO_2–ZrO_2 mixed oxide catalysts seems to be elusive. The catalytic activity of ZrO_2 as a single oxide is attributed to the bi-functional acid-base properties, the oxidizing and reducing properties and the terminal and bridged surface OH groups. The catalytic performance of zirconium dioxide depends also on the structural, textural properties, surface area, synthesis method adopted and calcination temperatures (Yamaguchi 1994; Aramendia *et al* 1997).

Several procedures have been developed using number of precursor salts to prepare pure zirconia of desired phase formations and strong acid-base sites and surface areas (Srinivasan and Davis 1992; Arul Dhas and Patil 1994; Keshavaraja and Ramaswamy 1994; Nakabayashi 1996; Aramendia *et al* 1997; Calafat 1998; Rossignol *et al* 1999). Recently, the surface areas of zirconia and sulfated zirconia have been expanded employing surfactant template methods (Sudhakar Reddy and Sayari 1996; Kim *et al* 1997). The present study describes synthesis of nanocrystalline zirconia using combustion method and its bulk and surface characterization employing various techniques. The combustion approach is quite simple and quick to obtain fine particles of mono and multicomponent oxides that can be used as supports as well as catalyst materials (Aruna and Patil 1998; Terribile *et al* 1998). It is also a versatile method to synthesize fine support oxide with dispersed catalyst precursor in a single step. The method has been employed recently to synthesize homogeneous, and fine crystalline Cu/CeO_2 and Pd/alumina catalysts (Bera *et al* 1999; Greca *et al* 1999). There is a wide scope of using this method to produce other oxide materials with required properties for catalysis.

2. Experimental

2.1 *ZrO₂ preparation*

The fine zirconium dioxide powder material is synthesized using zirconyl nitrate, $ZrO(NO_3)_2 \cdot 2H_2O$, as precursor salt and carbohydrazide, $N_2H_3CON_2H_3$, as fuel

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(Arul Dhas and Patil 1994). Water of hydration of the precursor salt is determined using TG/DT analysis. Carbohydrazide is prepared by hydrazinolysis of diethylcarbonate as reported in the literature (Mohr *et al* 1953). In a typical batch preparation, 5·0 g of zirconyl nitrate and 1·75 g of carbohydrazide are dissolved in minimum amount of water and the mixture is kept in a furnace preheated to 350°C. The mixture instantaneously gets ignited producing a foamy material of homogeneous zirconium oxide, simultaneously releasing gaseous products. Several zirconium oxide samples are prepared by changing the molar ratio of zirconyl nitrate and carbohydrazide. The samples are coded according to the precursor to fuel molar ratio 1 : 1·00, 1 : 1·25, 1 : 1·75 and 1 : 2·25 as Zr-100, Zr-125, Zr-175 and Zr-225, respectively. Hydrous zirconium oxide is also prepared for comparison following the method (Aramendia *et al* 1997) and coded as HZr-500.

2.2 *Characterization*

The zirconia samples have been characterized using powder XRD (Philips PW 1710 using MoK$_\alpha$ radiation), UV-Diffuse reflectance (Varian 5E UV-vis-NIR spectrophotometer with BaSO$_4$ coated integration sphere) and IR (Shimadzu IR-470). We have calculated the crystallite size using the classical Scherrer formula

$$D = \frac{Kl}{b \cos q},$$

where D is the average crystallite size, $K = 1$, $l = 0\cdot7093$ Å for MoK$_a$, b the peak width and q the peak angle. The Scherrer formula indicates that MoK$_a$ radiation is useful in obtaining diffraction pattern from smaller crystallites because of smaller wavelength and the diffraction occurring at lower angles. The line broadening is effectively reduced. For UV-vis measurements, a pellet of 0·1 g of zirconia is used to record UV-vis diffuse reflectance spectra in the wavelength region 200–2000 nm. PTFE has been used as reference material. The Schuster–Kubelka–Munk (SKM) function for scattering is expressed as

$$F(R_\infty) = (1 - R_\infty)^2/2R_\infty = K/S,$$

where R_∞ is the reflectance of the infinitely thick solid sample, K and S are the absorption and scattering coefficients. The optical diffuse reflection spectra are presented here as $F(R_\infty)$ vs wavelength of the light in the UV-vis region (Schoonheydt 1984). The IR spectra of zirconia are recorded using KBr pellets. Surface areas of powder samples have been measured using CE instruments Sorptomatic model 1990.

2.3 *Surface acidity and basicity determination*

The total surface acidity and basicity of all the zirconia samples have been determined by simple back-titration methods (Karuppannasamy 1980; Sugunan and Varghese 1998). A 0·025 M solution of trichloroacetic acid in dry benzene is used for estimation. The catalyst weighing 0·5 g is suspended in the acid solution for 24 h and the excess acid is titrated against *n*-butylamine using neutral red as an indicator. This gives the total surface acidity of the zirconia sample. Similarly, the catalyst sample is suspended in *n*-butylamine for 24 h and the excess base is estimated by titrating it against trichloroacetic acid to obtain the total surface basicity.
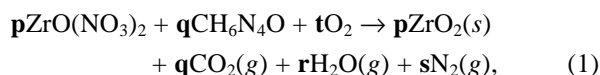
2.4 *Catalytic activity test*

Transfer hydrogenation of cyclohexanone with isopropyl alcohol as the hydrogen donor is carried out to test the catalytic activity of the zirconia samples. This reaction is reported to be efficiently catalyzed by hydrous zirconium oxide (Shibagaki *et al* 1988). The solution containing 1·0 ml of cyclohexanone and 20 ml of isopropyl alcohol is refluxed at 80°C for 24 h after adding 0·10 g of zirconium oxide catalyst. The catalyst is separated and the product conversion is obtained by gas chromatographic analysis (NUCON 5890) employing 10% carbowax column.

3. Results

3.1 *XRD*

The combustion reaction between the redox mixture of carbohydrazide and zirconyl nitrate giving zirconium oxide can be written as follows:

$$\mathbf{p}ZrO(NO_3)_2 + \mathbf{q}CH_6N_4O + \mathbf{t}O_2 \rightarrow \mathbf{p}ZrO_2(s)$$
$$+ \mathbf{q}CO_2(g) + \mathbf{r}H_2O(g) + \mathbf{s}N_2(g), \qquad (1)$$

where $\mathbf{p}$ through $\mathbf{t}$ represents the stoichiometric numbers of reactants and products involved for each C/Z molar ratio (table 1). Figure 1 shows the powder X-ray diffraction pattern of zirconium oxide samples prepared by varying the fuel to precursor molar ratios as presented in table 1. When equimolar amounts are used, XRD result shows only the characteristic reflections for metastable tetragonal zirconia phase (figure 1a). As the amount of fuel is increased from Zr-100 to Zr-225, there is a gradual change in crystal structures from the metastable tetragonal ZrO$_2$ (mt) to the stable monoclinic (m) phase (figure 1). The corresponding percentage increase in monoclinic phase is summarized in table 1. The amount of monoclinic phase present in the zirconia is estimated following the method using the expression (Calafat 1998),

$$\% M_{\text{monoclinic}} = \frac{\sum M_{\text{monoclinic}} \times 100}{T_{\text{tetragonal}} + \sum M_{\text{monoclinic}}},$$
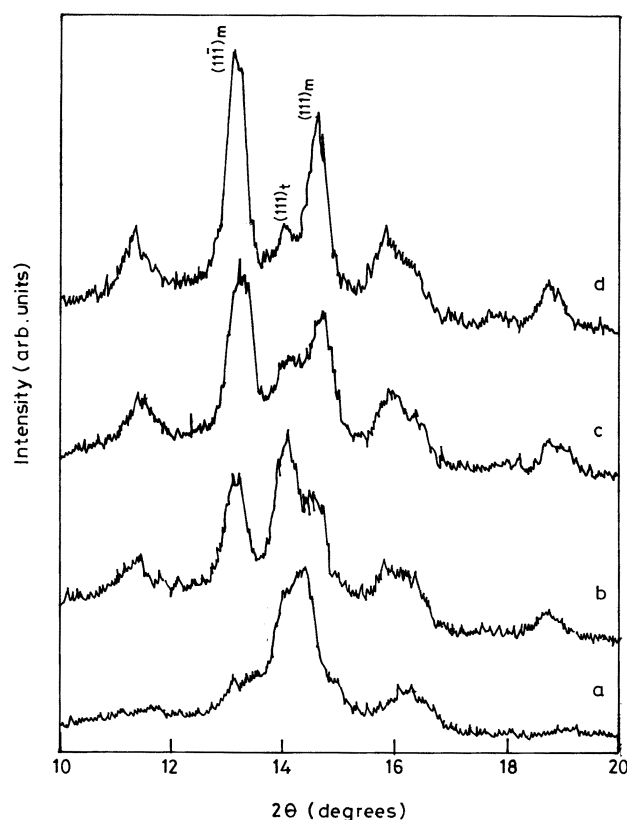
Table 1. Reaction parameters and phases formed in the combustion synthesis of zirconia.

| Sample | C/Z[§] | Reaction stoichiometry | | | | | ΔH_r^0 (STP) (Kcal/mol) | T_{ad} (°C) | | Phase | % Monoclinic |
		p	q	r	s	t		Experimental[†]	Calculated		
Zr-100	1·00	4	4	20	12	2*	− 789·5	−	1072·6	mt	0
Zr-125	1·25	4	5	23	14	0	− 1064·5	1100 ± 100	1316·9	mt + m	58
Zr-175	1·75	4	7	29	18	4	− 1614·6	−	1612·5	mt + m	76
Zr-225	2·25	4	9	35	22	8	− 2164·7	1400 ± 100	1807·0	mt + m	85

*Oxygen released during combustion; [†]From Arul Dhas and Patil (1994);
m = monoclinic; mt = metastable tetragonal;
[§]C/Z = carbohydrazide/zirconyl nitrate mole ratio.

Figure 1. X-ray diffraction pattern for combustion synthesized zirconium oxides using various precursor to fuel mole ratios: a. 1 : 1·00, b. 1 : 1·25, c. 1 : 1·75 and d. 1 : 2·25.

Table 2. Surface area and crystallite size data for combustion synthesized zirconia powders.

| Sample | C/Z[§] | Surface area (m²/g) | Crystallite size (Å) | |
			$(111)_{tetragonal}$	$(11\bar{1})_{monoclinic}$
Zr-100	1	15	54·18	−
Zr-125	1·25	11	149·00	80·99
Zr-175	1·75	23	76·02	88·34
Zr-225	2·25	22	62·71	105·98

[§]C/Z = carbohydrazide/zirconyl nitrate mole ratio.

gonal crystallites as a function of fuel ratio. It is also observed that the overall surface area of the powder samples increased moderately with fuel content.

3.2 *IR and UV-vis diffuse reflectance*

The IR spectra of all zirconia samples prepared by the combustion method are presented in figure 2. The IR spectra of zirconia samples essentially show the various stretching frequencies at 445 cm^{-1} and 410 cm^{-1} (doublet), 500 cm^{-1}, 572 cm^{-1}, 740 cm^{-1}, 1104 cm^{-1} and 1187 cm^{-1} respectively as reported earlier (Powers and Gray 1973). The features particularly at 740 cm^{-1} and 500 cm^{-1}, due to Zr–O$_2$–Zr asymmetric and Zr–O stretching modes respectively, confirm the formation of ZrO$_2$ phases. There is a strong additional feature observed around 1380 cm^{-1} when the fuel content is relatively less. This feature almost disappears as the fuel content is increased. This may be due to carbonate related signature (Trovarelli 1996). The broad feature around 1632 cm^{-1} seems to occur due to adsorbed water deformation mode.

Zirconium oxide is a direct band gap insulator with two direct band–to–band transitions at 5·2 and 5·79 eV (238 and 214 nm respectively) (Emeline *et al* 1998; Scheithauer *et al* 1998). The onset of the linear increase in the diffuse reflectance spectrum is taken as a measure of the forbidden gap that occurs at around 240 nm (5·17 eV). This is a characteristic of the edge position of the bulk tetragonal zirconia phase (Scheithauer *et al* 1998). The

where $\Sigma M_{monoclinic}$ is the sum of the areas under the diffraction peaks from the $(11\bar{1})$ and (111) planes of the monoclinic phase and $T_{tetragonal}$ stands for the area under (111) plane of tetragonal phase. These areas have been obtained using Gaussian curve fitting.

The surface areas and crystallite sizes of zirconia powders prepared using combustion synthesis are summarized in table 2. The powders contain nanostructured crystallites of size in the range 5–15 nm. The crystallite size of monoclinic phase increases while that of the tetragonal phase decreases when fuel ratio is increased. This indicates that the monoclinic crystallites grow at the expense of tetra-

typical diffuse reflectance spectrum for one of the catalysts (Zr-225) is shown in figure 3. A broad reflectance maximum $F(R_\infty)_{max}$ seems to occur around 214 nm which can be recognized as the interband transition in the monoclinic zirconium oxide (Aita and Kin 1990). The variation in the $F(R_\infty)_{max}$ at this position against the percentage composition of the monoclinic phase in various samples is given in table 3. It shows an interesting correlation that the $F(R_\infty)_{max}$ decreases as the percentage composition of the monoclinic phase increases.

3.3 *Indicator titration for surface acidity–basicity*

The results of the indicator acid/base titration are compiled in table 4. We have also included the results of hydrous zirconia (HZr-500) in the table. The data shows that the hydrous zirconia has maximum number of acidic as well as basic sites as compared to the combustion synthesized zirconia samples. By and large, the zirconia samples show higher number of acidic sites than the basic sites.

3.4 *Catalytic activity*

The catalytic activity of all catalysts towards transfer hydrogenation of ketone revealed that only hydrous zirconia (HZr-500) is active enough to carry out a total conver-

sion of the cyclohexanone to cyclohexanol where zirconia prepared by combustion method showed no activity. The reason why hydrous zirconia is catalytically active is still not clear (Hattori 1995). The present study indicates that the presence of relatively large number of acid sites could be responsible for hydrous zirconia to be active over combustion synthesized zirconia. There is also a clear indication that combustion synthesis destroys the active sites rendering it to be inactive for transfer hydrogenation reactions in liquid phase.

4. Discussion

Zirconia exists in tetragonal (*b*-ZrO$_2$), monoclinic (*a*-ZrO$_2$) and cubic (*g*-ZrO$_2$) phases. Among all these phases, monoclinic is more stable at ambient temperatures whereas tetragonal and cubic phases are stable at much

Table 4.   Total acidity and basicity parameters estimated from titration method for zirconia sample.

Sample	Acidity (mmol/g) n-butylamine titration	Basicity (mmol/g) Trichloroacetic acid titration
HZr-500	1·160	0·3560
Zr-100	0·410	0·1375
Zr-125	0·470	0·2625
Zr-175	0·110	0·0125
Zr-225	0·446	0·0750

Table 3.   Correlation between the $F(R_\infty)_{max}$ and percentage monoclinic phase of various zirconia samples.

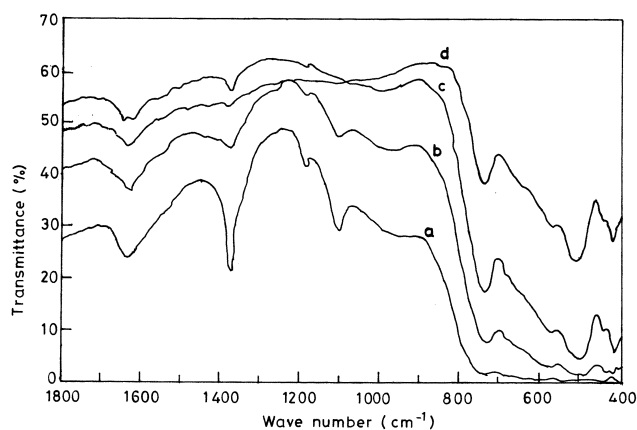| Sample	$F(R_\infty)_{max}$	Phase	% Monoclinic
HZr-500	0·5	Amorphous	–
Zr-100	3·5	mt	0
Zr-125	2·5	mt + m	58
Zr-175	1·5	mt + m	76
Zr-225	1·5	mt + m	86

m = monoclinic; mt = metastable tetragonal

Figure 2.   IR spectra of combustion synthesized zirconium oxides as mentioned in figure 1.
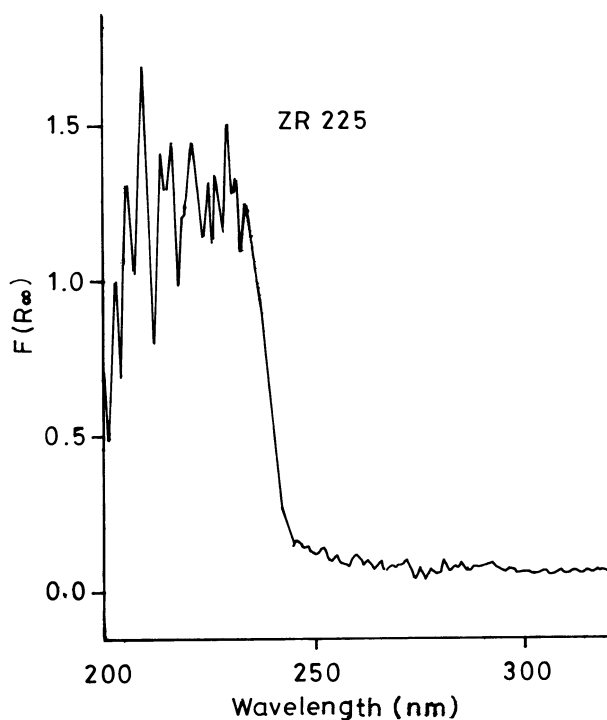

Figure 3.   Typical UV-vis diffuse reflectance spectrum for Zr-225 sample.

higher temperatures (Yamaguchi 1994; Emeline *et al* 1998). It also exists in metastable tetragonal phase up to about 650°C. It is believed that the metastable tetragonal phase is stabilized due to impurities and crystallite size. However, the gradual phase change from metastable tetragonal to monoclinic (mt → m) has been observed in this study as well as previously by Arul Dhas and Patil (1994). This transition has been ascribed to higher flame temperatures resulting from the presence of excess of fuel in the reaction mixture. High temperatures are usually generated during the decomposition of CH_6N_4O fuel which is an exothermic process ($\Delta H_f = + 31·79$ kJ/mol). Flame temperature of the order of $1400 ± 100°C$ has been measured by radiation pyrometer and this temperature seems to be sufficiently high to influence the above phase transition in zirconia. Since these combustion reactions occur in shorter duration at higher temperatures, the dissipation of heat produced during combustion process would be negligible. In such a thermally isolated system, the temperature to which the product is raised can be considered as an adiabatic temperature, T_{ad} (Holt and Munir 1986). The enthalpy of the reaction can be expressed as

$$\Delta H_{298}^0 = \int\limits_{298}^{T_{ad}} C_p \, (\text{product}) \, dT, \qquad (2)$$

where ΔH_{298}^0 is the enthalpy of reaction at 298 K, C_p (product) the heat capacity of the product and T_{ad} the adiabatic temperature to which the reaction is raised. The calculated enthalpies for combustion reactions of various stoichiometries producing different phases of zirconia are summarized in table 1. The adiabatic temperatures (T_{ad}) are calculated using (2) by substituting appropriate enthalpies of reactions and heat capacities of products (West and Astle 1980). The variation of heat capacity with temperature is also considered in the calculation and the results are given in table 1 in comparison with experimental values. They are in good agreement with each other.

It is clear from the data in table 1 that the reaction enthalpies increase rapidly with fuel content in the mixture and the excess heat generated raises the adiabatic temperature as high as 1500°C. At higher temperatures, the formation of homogeneous monoclinic phase is more favoured. Also the intensity of the vibrational feature at 740 cm^{-1} ($Zr–O_2–Zr$ asymmetric mode) appears to become more prominent as the monoclinic content increases in the combustion product. However there has been no direct correlation of this mode to the monoclinic zirconia phase (Powers and Gray 1973). It is evident from UV-vis and XRD data in table 3 that there is an inverse correlation between $F(R_\infty)_{max}$ at 214 nm and the percentage monoclinic phase in the final product. The crystallite size analysis in table 2 is also quite interesting. The average sizes of the crystallites reported here are significantly less than the values reported earlier on relatively low surface area samples (Arul Dhas and Patil 1994). The comparison of crystallite size values of monoclinic and tetragonal phases also indicates that there is a gradual growth of monoclinic phase. These observations once again corroborate the formation of monoclinic phase in fuel rich combustion environment.

The surface acid-base properties are inherent and characteristic of many oxide materials that are important in adsorption and surface catalytic reactions. A large body of information exists in the literature concerning the surface acidity and basicity of various oxides and their quantitative determination using titration and adsorption methods. Zirconia is a unique case exhibiting both acidic and basic sites on the surface. Previous studies show that these sites on micro-crystalline zirconia prepared by wet methods are affected by the surface area and calcination temperatures (Nakabayashi 1996; Aramendia *et al* 1997). We have estimated the acid-base site distribution of our samples employing indicator titration method. The results in table 4 show that the hydrous zirconia (HZr-500) sample has the same order of acid-base site distribution as reported elsewhere (Nakabayashi 1996). However, combustion synthesized samples show quite low acid-base site distributions. This is understandable from the fact that the nano-crystals of zirconia formed at high temperatures tend to be highly crystalline in nature and defect free. The defects and lattice imperfection sites on the crystallite surface are known to contribute to acid-base and redox properties of oxides (Ranga Rao 1999). This is also a plausible reason for the inactivity of zirconia samples towards conversion of the cyclohexanone to cyclohexanol as mentioned above. Therefore the zirconia samples prepared by combustion method can be used as good inert supports. However, if they were to be used as catalyst materials in the liquid phase reactions, the activity of the zirconia fine powders needs to be regenerated suitably using acid-base treatments. Work in this direction is in progress. However, preliminary results indicate that combustion synthesized zirconia powder as such shows significant activity for cyclohexanone to cyclohexanol conversions under vapour phase conditions at 300°C.

5. Conclusions

The following conclusions can be drawn from this study. Zirconia phase change can be achieved by changing the fuel content in the combustion mixture. Monoclinic phase formation is highly favoured at higher fuel content. A combined use of XRD, IR and UV-vis diffuse reflectance techniques conforms the formation of monoclinic phases. The surface acid-base sites are found to be an order of magnitude less compared to hydrous zirconia rendering combustion synthesized zirconia to be inactive for transfer hydrogenation reactions in liquid phase. However, this material seems to show catalytic activity for the same reaction under vapour phase conditions.

Acknowledgements

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