

# High-speed experimentation techniques applied to the study of the synthesis of zeolites and silsesquioxanes

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## Abstract

High-speed experimentation (HSE) techniques are newly developed methods that, allowing the fast preparation and analysis of large numbers of parallel experiments, enable to screen an extensive parameter space. These techniques are particularly useful to investigate chemical systems for which a precise knowledge of the overall reaction or formation mechanism is not available. Here, we report the application of HSE techniques to the study of the synthesis of two families of siloxane compounds: zeolites and silsesquioxanes. Zeolites are well known crystalline microporous materials with broad applications as heterogeneous catalysts. Silsesquioxanes are small, discrete siloxane cages used both as homogeneous catalysts and as model compounds for silica surfaces and zeolites. With our HSE approach we were able to investigate the synthesis of aluminium-rich zeolite beta (Si/Al ratio from 2.5 to 5) and to identify a new and fast way to synthesise silsesquioxane precursors for Ti-catalysts active in the epoxidation of alkenes. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** High-speed experimentation techniques; Zeolites; Silsesquioxanes; Heterogeneous catalysts; Homogeneous catalysts

## 1. Introduction

High-speed experimentation (HSE) techniques [1] recently have found applications in the field of catalysis [2]. These techniques are based on the use of automated workstations allowing the preparation and the screening of large numbers of compounds. Synthesis and analysis are performed in parallel wells, i.e. each sample in a separate vessel. Typically, 100 samples can be prepared and screened in a working week with these parallel workstations. This is a large number compared to a standard experimental approach on a lab scale, but is still small if compared to a mix and split combina-

torial approach, in which thousands of compounds are synthesised in a single pot [1]. Nevertheless, the parallel approach used in HSE techniques allows correlating each sample with its properties (i.e. its activity as catalyst), while this is not possible using mix and split methods where the samples are screened as a whole. In this sense, HSE techniques are more suitable when the goal of identifying a new lead is coupled with that of a fundamental understanding of the system under study.

Here, we present the application of HSE techniques to the study of the synthesis of two families of siloxane compounds: zeolites and silsesquioxanes. Zeolites are well-known crystalline microporous materials with broad applications as heterogeneous catalysts. Silsesquioxanes are small, discrete siloxane

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cages of general formula  $(\text{RSiO}_{1.5})_a(\text{H}_2\text{O})_{0.5b}$  [R: organic group;  $a + b = 2n$ ;  $n = 1, 2, 3, \dots$ ;  $b \leq a + 2$ ]. Completely condensed silsesquioxanes ( $b = 0$ ) can be seen as model compounds for building blocks present in zeolite structures [3]. Incompletely condensed silsesquioxanes ( $b \neq 0$ ) can be used as model compounds for silica surfaces and as homogeneous catalysts after the insertion of a metal centre [4]. For both zeolites and silsesquioxanes, the synthesis consists of a multiple-step reaction for which an overall mechanism is not available; many parameters influence the syntheses determining which structures are formed and in which amounts. Therefore, an HSE approach allowing the fast screening of broad parameter spaces can be suitable to study and optimise the synthesis of both families of compounds.

## 2. Experimental

### 2.1. Synthesis of zeolite beta

Experiments were performed on an automated parallel synthesis workstation<sup>1</sup> coupled with a personal computer supplied with software enabling to program the workstation. Reactants: Ludox-HS 40 colloidal silica (40 wt.% suspension of  $\text{SiO}_2$  in water) as silica source; sodium aluminate (40–45 wt.%  $\text{Na}_2\text{O}$ , 50–56 wt.%  $\text{Al}_2\text{O}_3$ ) as alumina source; tetraethylammonium hydroxide (TEAOH) (35% solution in water) as template source; deionised water. Appropriate amounts of reactants for the zeolite synthesis were dispensed by the pipette arm of the workstation in a  $6 \times 4$  matrix of small 3 ml teflon-lined stainless steel autoclaves. An equal amount of alumina source was dispensed in each autoclave in order to set the pH of all the samples at  $\sim 14$ . In a typical experiment, after dispensing the alumina, the template and the silica sources, the autoclaves were filled up to 75% of their volume with water. Next, the obtained aluminosilicate gels were placed in an ultrasonic bath ( $T \cong 60^\circ\text{C}$ ) for 1 h. The autoclaves were then closed and heated statically at  $170^\circ\text{C}$ . After 48 h, heating was stopped and the autoclaves were cooled down to room temperature. Finally, the autoclaves with the formed solids were washed twice with deionised water, centrifuged

at 1500 rpm for 1 h and dried in a vacuum centrifuge (see Footnote 1). After the experiment, the teflon inserts were cleaned overnight with NaOH (4 M) at reaction temperature or with HF (10%) at room temperature.

Powder diffraction data were collected on a Philips PW1840 diffractometer generating Cu  $K\alpha$  radiation. Data were obtained from  $5$  to  $50^\circ 2\theta$  with a step of  $0.01^\circ$  and a counting time of 0.5 s per step. The receiving slit had a width of 0.3 mm. The tube voltage was 40 kV and the tube current was 50 mA. In order to reduce the analysis time, an automatic sampler was installed, thus allowing X-ray analysis of 24 samples in 15 h. Elemental analyses were performed on a Perkin-Elmer 3000 DV ICP-OES. After dissolving the zeolites in a 1% HF (40%)/1.3%  $\text{H}_2\text{SO}_4$  solution, the concentrations of silicon, aluminium and sodium were measured with induced coupled plasma optical emission spectroscopy (ICP-OES). The samples were analysed twice as independent duplicates to get an indication of the precision of the analysis. The accuracy in the analysis of Si and Al are estimated at about  $\pm 5\%$ , for Na at  $\pm 10\%$  (relative values). High-resolution solid-state  $^{27}\text{Al}$  MAS NMR spectra were recorded on a 400 MHz Varian Inova spectrometer.

### 2.2. Synthesis of incompletely condensed silsesquioxanes

Experiments were performed on the same automated workstation used for the synthesis of zeolite beta. Reagents: cyclohexyl, cyclopentyl, phenyl, methyl, ethyl, *tert*-butyl, normal-octyl, and allyl trichlorosilanes ( $\text{RSiCl}_3$ ); acetone, acetonitrile, methanol and tetrahydrofuran (THF) as solvents; deionised water. In a typical experiment, 2 ml aliquots of each of the four solvents were dispensed in a rack containing 4 ml glass tubes, followed by the addition of 340  $\mu\text{mol}$  of each of the organosilanes. The hydrolysis reaction was started by adding 0.5 ml of deionised water to each reaction tube and placing the rack on an orbital shaker (see Footnote 1) at  $50^\circ\text{C}$  for 18 h. By means of a vacuum centrifuge (see Footnote 1), the solvents and the excess water were removed from the samples, which were then stored under argon. Titanium insertion was performed by dissolving each crude silsesquioxane mixture in 2 ml of THF, followed by the addition of 54  $\mu\text{mol}$  of titanium isopropoxide,

<sup>1</sup> Kindly provided by Avantium Technologies.

Ti(OPr<sup>*i*</sup>)<sub>4</sub>. After 5 h at 60 °C, THF was removed with the help of the vacuum centrifuge and the samples were stored under argon.

The activity of the Ti–silsesquioxanes in the epoxidation of 1-octene with *tert*-butyl hydroperoxide (TBHP) was determined by adding to each dried sample ~0.36 mmol of TBHP in cyclohexane solution (TBHP: catalyst ratio = 7.5) and 0.0144 mol of 1-octene, that, therefore, acted both as reactant and solvent (1-octene: catalyst ratio = 300). The employed 1-octene contained 2% in volume of decane as an internal standard for the following GC analysis. Samples were taken after reacting for 5 h at 80 °C and analysed on a UNICAM Pro GC (see Footnote 1) using a CP-Sil-5B column. The epoxidation reaction did not proceed further at room temperature. The reported activities were obtained by normalising the 1,2-epoxyoctane GC peak area by means of the internal standard. Since 1-octene was used both as reactant and solvent, it has not been possible to realise a mass balance. The reaction is completely selective towards 1,2-epoxyoctane: no other products were detected. The conversion selectivity of TBHP towards 1,2-epoxyoctane is between 80 and 94%.

### 3. Results and discussion

#### 3.1. Synthesis of zeolite beta

The synthesis of zeolite beta has been studied by means of HSE techniques. Beta is a large pore zeolite characterised by three families of mutually perpendicular channels with 12-membered ring apertures [5], which make it suitable as heterogeneous catalyst for numerous organic reactions [6]. Zeolite beta has been prepared with a wide range of Si/Al ratios (from 5 to ∞) [7]. The control of the Si/Al ratio is particularly interesting since it allows tuning the number of acid sites and the hydrophobicity of the zeolite. In this work, we report the optimisation of the synthesis of aluminium-rich zeolite beta in order to reach the lowest possible Si/Al ratio. The synthesis of an aluminium-rich zeolite beta is particularly interesting also because Tschernichite, the natural form of beta, has Si/Al = 3 [8].

#### 3.1.1. The HSE approach

Various parameters influence the synthesis of zeolites: the nature of the silica and alumina sources and the ratio between the two, the nature and the concentration of the template, the presence, type and concentration of alkali cations, the water content, the pH, the temperature and the reaction time [9]. The HSE workstation employed in the project can only handle low-viscosity liquids: this influenced the choice of the silica and alumina sources used in the experiments. As silica source we chose the cheap, easy to handle Ludox-HS 40 colloidal silica and as alumina source an aqueous solution of sodium aluminate. Hydrothermal synthesis using tetraethylammonium ions (TEA<sup>+</sup>) as templates in an alkaline environment was chosen from among the methods commonly used for the preparation of aluminium-rich zeolite beta for its adaptability to the HSE workstation. The method we applied is similar to that described by Borade and Clearfield [10], with a different silica source and a higher water content in order to allow handling by the HSE workstation. Given these restrictions, we selected the Si/Al ratio and the TEA<sup>+</sup>/Al ratio in the starting reaction mixture as the most relevant parameters determining the formation of aluminium-rich zeolite beta. Therefore, we screened the parameter space defined by the combination of six Si/Al ratios and four TEA<sup>+</sup>/Al ratios as a function of the presence of zeolite beta. The range in which the two parameters were varied had been chosen in order to investigate the possibility of lowering the Si/Al in zeolite beta and the amount of the expensive TEA<sup>+</sup> employed with respect to the synthesis method proposed by Borade and Clearfield [10]. The screening was performed by means of an X-ray powder diffractometer supplied with an automated sampler. The intensity of the strongest peak in the diffractogram for each zeolite species present was taken as a measure of crystallinity.

#### 3.1.2. The HSE results

The products of the 24 syntheses mainly consist of a mixture of two zeolites: zeolite beta and zeolite NaP1 (Fig. 1).<sup>2</sup> NaP1 is a gismondine type of zeolite, with a Si/Al ratio of 1.5 and Na<sup>+</sup> ions as template ions. For this reason, NaP1 is found as a product at low

<sup>2</sup> All the reported results are averages of the values obtained in different sets of experiments.

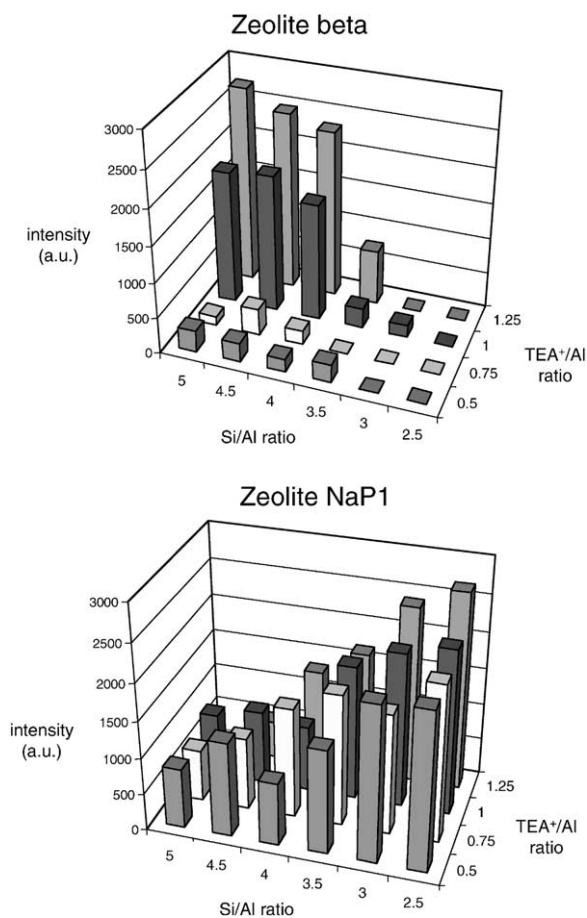


Fig. 1. Presence of zeolite beta and zeolite NaP1 in the screened parameter space.

values of Si/Al ratio in the starting reaction mixture, while beta is formed at higher values of Si/Al ratio. Pure zeolite beta is obtained at a Si/Al ratio of 5 and TEA<sup>+</sup>/Al ratio of 1.25 in the starting reaction mixture, while pure NaP1 is obtained at a Si/Al ratio of 2.5 for the entire screened TEA<sup>+</sup>/Al ratio. In between, mixtures of both zeolites were observed. Some samples also contain amorphous silica and small amounts of crystalline impurities (consistent with analcime). A higher value of TEA<sup>+</sup>/Al ratio causes a positive trend towards the formation of zeolite beta, as competition takes place between the two templates (Na<sup>+</sup> for NaP1 and TEA<sup>+</sup> for beta). This experiment suggests that a Si/Al ratio of 5 and a TEA<sup>+</sup>/Al ratio of 1.25 in the original reaction mixture are the limit values to obtain

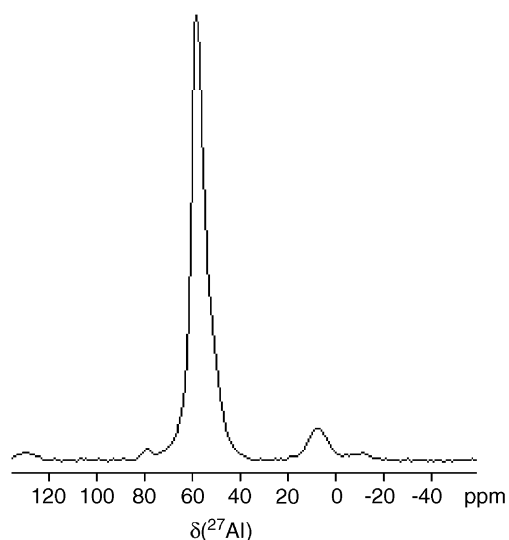


Fig. 2. <sup>27</sup>Al NMR of the pure zeolite beta obtained with Si/Al = 5 and TEA<sup>+</sup>/Al = 1.25 in the starting reaction mixture.

pure zeolite beta with this hydrothermal synthesis and using TEA<sup>+</sup> as template ion. The corresponding sample has been further characterised to determine the actual Si/Al in the zeolite framework. From ICP-OES analysis a Si/Al ratio of 4.7 and an Al/Na ratio of 0.8 were determined. To check if all the aluminium species in the sample are part of the zeolite framework, the sample was characterised by <sup>27</sup>Al NMR. The <sup>27</sup>Al NMR spectrum shows a high intensity peak at 59 ppm corresponding to tetrahedral aluminium species and a low intensity peak at 4 ppm corresponding to octahedral aluminium species (Fig. 2). Tetrahedral aluminium species are those present in the zeolite structure, while octahedral species are likely to be due to non-zeolitic aluminium phases. The ratios between the integrals of the two peaks is 92/8. Considering just the tetrahedral aluminium as part of the zeolite framework, the Si/Al ratio has then to be corrected to a value of 5.1. This value is slightly higher than the Si/Al ratio of 4.5 reported by Borade and Clearfield [10] and is obtained using a higher TEA<sup>+</sup>/Al ratio (1.25 against 0.8). The highest TEA<sup>+</sup>/Al ratio needed can be due to the higher water content used in our method. A relevant advantage of our synthesis method is the use of Ludox HS-40 as silica source instead of fumed silica, since the former is cheaper, easier and safer to handle and forms a less dense synthesis gel.

Scaling-up of the synthesis of zeolite beta with a Si/Al ratio of 5 and a TEA<sup>+</sup>/Al ratio of 1.25 in the original reaction mixture to a 50 ml autoclave lead to a similar result even if small amounts of NaP1 were present as byproducts. Differences in results using HSE 3 ml autoclaves and conventional larger volume autoclaves are probably due to the higher heating rate of the small autoclaves, which is mainly caused by their lower heat capacity, and to the higher surface/volume ratio of the small autoclaves, which favours heterogeneous nucleation and, therefore, speeds up the crystallisation process.

### 3.2. Synthesis of incompletely condensed silsesquioxanes

The synthesis of silsesquioxane precursors for Ti-catalysts has been optimised by means of HSE techniques. Incompletely condensed silsesquioxane **1**, R<sub>7</sub>Si<sub>7</sub>O<sub>12</sub>H<sub>3</sub> (*a* = 7, *b* = 3) is known to provide an active homogeneous catalyst for the epoxidation of alkenes after insertion of a titanium centre [11] (Fig. 3). Silsesquioxane **1** is obtained by the hydrolytic condensation of the corresponding organosilane RSiX<sub>3</sub> (X = Cl, OMe, OEt) [12]. The synthesis is rather time-consuming and can yield other silsesquioxane structures as byproducts. Among these compounds there might be incompletely silsesquioxanes other than **1** that, after insertion of a titanium centre, generate active epoxidation catalysts. On the basis of these considerations, we used HSE techniques to identify a new and efficient synthetic route towards silsesquioxane precursors for Ti-catalysts: the

synthesis of silsesquioxanes has been optimised as a function of the activity of the catalysts obtained after complexation of a titanium centre to the silsesquioxane structures. The epoxidation of 1-octene with TBHP as oxidant was chosen as test reaction (activity measured by means of an automated GC).

#### 3.2.1. The HSE approach

To decide which parameter space had to be screened to optimise the synthesis of silsesquioxanes, we considered all the parameters influencing the hydrolytic condensation: the nature of the organic group R and of the group X in the organosilane and its concentration in the reaction mixture, the solvent in which the synthesis is carried out, the rate of addition and quantity of H<sub>2</sub>O, the pH, the temperature and the reaction time [13]. Among these parameters, we selected the organic group R and the solvent as the most influential in determining which silsesquioxane structures are formed and in which quantities. Then, we defined a parameter space as a combination of eight organosilanes with different organic groups (cyclohexyl, cyclopentyl, phenyl, methyl, ethyl, *tert*-butyl, normal-octyl and allyl) and four water-miscible solvents (acetone, acetonitrile, methanol, THF) and we screened it as a function of the activity of the catalyst obtained by insertion of a titanium centre in the silsesquioxane structures. Since the goal is to identify a more efficient way to synthesise silsesquioxane precursors, the reaction time was set at 18 h, a much shorter time than that commonly required for the synthesis of silsesquioxane **1** [12].

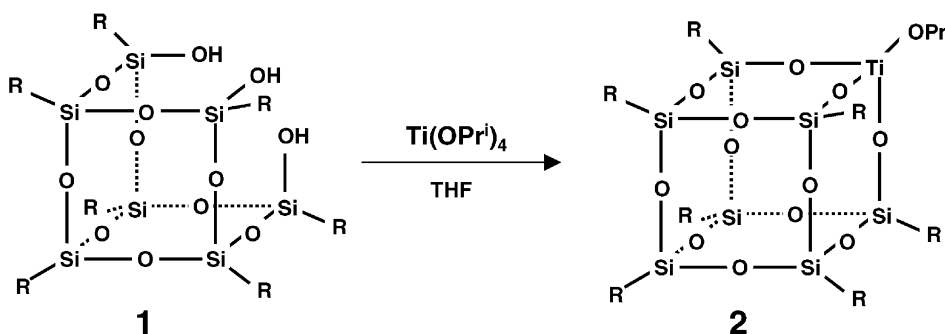


Fig. 3. Insertion of  $\text{Ti}(\text{OPr}^i)_4$  on the incompletely condensed silsesquioxane  $\text{R}_7\text{Si}_7\text{O}_{12}\text{H}_3$  (R: cyclohexyl, cyclopentyl).

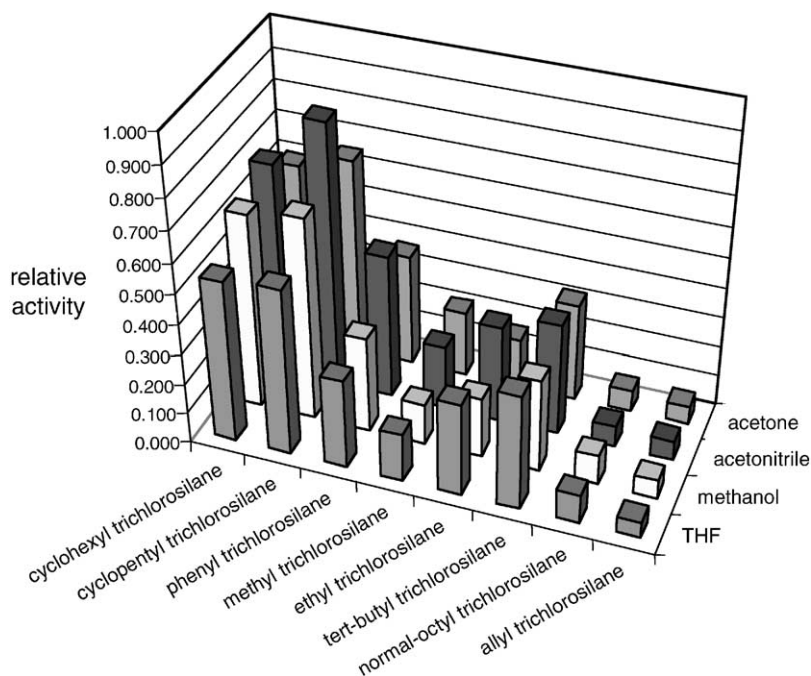


Fig. 4. Catalytic activity in the epoxidation of 1-octene of the Ti-silsesquioxanes in the screened parameter space.

### 3.2.2. The HSE results

The activity in the epoxidation of 1-octene of the Ti-catalysts as a function of the parameters varied in the synthesis of the silsesquioxanes precursors is reported in Fig. 4 (see Footnote 2). The values are normalised to the activity of the catalyst obtained by insertion of  $\text{Ti}(\text{OPr}^i)_4$  on the pure silsesquioxane **1** (the activity of which is set at 1). The results show some general trends:

Among the R-groups, the order of activity is cyclopentyl > cyclohexyl > phenyl > *tert*-butyl > ethyl > methyl > allyl ~ normal-octyl ~ 0, for all solvents apart from THF for which *tert*-butyl and ethyl organosilanes yield more active catalysts than phenyl organosilanes. This trend seems to be related to the size of the organic substituent: bulky groups probably hinder the formation of completely condensed silsesquioxanes, which are not able to complexate titanium centres and therefore to generate active catalysts.

Among the solvents, the order of activity is acetonitrile > acetone > methanol > THF, for any

of the R-group apart from ethyl and *tert*-butyl for which silsesquioxanes synthesised in THF generate more active catalysts than those synthesised in acetone and methanol. The fact that acetonitrile gives the best results can be explained on the basis of its high polarity: it has been proposed that the presence of a polar molecule reduces the activation barrier for the condensation reactions that lead to the formation of silsesquioxanes [14].

The Ti-silsesquioxane obtained by the hydrolytic condensation of cyclopentyltrichlorosilane in acetonitrile presents the highest catalytic activity in the screened parameter space (Fig. 4). This activity is 87% of that of the Ti-silsesquioxane obtained using pure silsesquioxane **1**, with the advantage that the synthesis of our catalyst does not require any purification process and is much less time-consuming than the synthesis of compound **1**. The experiment has been scaled-up from 2 to 100 ml scale yielding to a similar catalytic activity, thus proving that for this system the use of small-scale HSE equipment produces results comparable to those from conventional experiments.

#### 4. Conclusions

We showed that HSE techniques can be successfully applied to study the synthesis of both heterogeneous and homogeneous catalysts. In the case of the synthesis of zeolites, we have been able to identify a facile and cheap method to produce pure zeolite beta and pure zeolite NaP1. Moreover, we studied the effect of the Si/Al and TEA<sup>+</sup>/Al ratios on the formation of these two zeolites. In a similar way, we identified a fast and straightforward method to synthesise silsesquioxane precursors for Ti-catalysts. At the same time, we gained some knowledge on the effects of the solvent and of the organic group R on the synthesis of incompletely condensed silsesquioxanes.

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