



Short communication

Effect of nitric acid modification of montmorillonite clay on synthesis of solketal from glycerol and acetone

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ABSTRACT

The effect of acid modification of a natural montmorillonite clay (MM) by HNO₃ on the catalytic properties of MM from Dash-Salakhinsk (Kazakhstan) has been investigated in the synthesis of solketal from glycerol and acetone in solvent free and acetonitrile media. HNO₃ concentration allowed to control the chemical composition, the surface acidity, the porous structure of the acid-activated MMs and their catalytic performance. The main reaction product was solketal with 86.6–98% selectivity. Conversion of glycerol depended on the Brønsted acidity. The most active sample, namely, MM activated with 0.5 mol/dm³ HNO₃, showed good reusability for 3 catalyst cycles.

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1. Introduction

Nowadays, great attention is focused on the environmentally friendly catalytic reactions in which wastes are converted into useful products. One of the trends is the comprehensive recycling of glycerol to compounds for new applications, because now glycerol is produced in large amounts as a by-product of biodiesel production, equivalent to approximately 10 wt% of the total biodiesel produced [1]. According to recent reviews [2,3], glycerol can be utilized for the synthesis of the biodiesel additives, for example solketal, which allows to improve the cold properties and lowering the viscosity of the biodiesel formulation. It is well-known that acid heterogeneous systems used as catalysts for this reaction lead to form five-membered solketal (2,2-dimethyl-1,3-dioxane-4-methanol, (II)) and six-membered acetal (2,2-dimethyl-dioxane-5-ol, (III)) (Scheme 1) [4,5]. Reaction between glycerol and acetone can be carried out over homogeneous catalysts, as H₂SO₄ and *p*-toluenesulfonic acids [3,6–8] and heterogeneous acid systems which include Amberlyst-15 and Amberlyst-36 [3,9], montmorillonite K-10

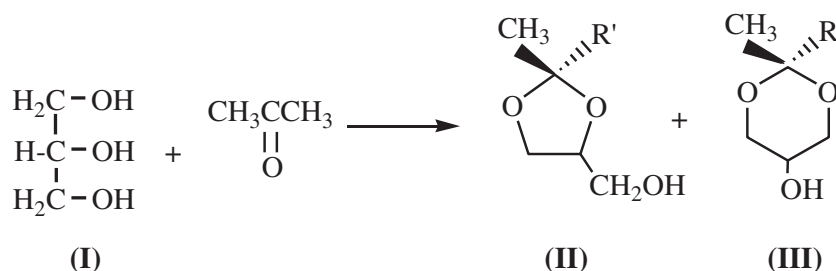
[9,10] and zeolites [11,12]. In general, the yield of (II) depends on the surface acidity [2,13]. Thus, yield of (II) was 74% in the presence of sulfonic mesostructured silicas SAC-13 with 0.12 meq/g acid strength, while in the presence of Amberlyst-15 with acidity of 4.8 meq/g yield of (II) was 85% [14]. The effect of acidity was also demonstrated by Nanda et al. [9], screening the catalytic properties of several acid systems in a continuous flow reactor pointed out that the catalytic behavior of some heterogeneous catalysts correlated with their acidity. Yield of (II) was higher in the presence of Amberlyst 36 with acidity of 5.4 meq/g (88%) than in the presence of K10 montmorillonite with acidity of 4.6 meq/g (68%). Unfortunately, the information on K10 montmorillonite is rather limited, which have encouraged us to investigate the effect of the surface acidity of montmorillonite on its activity in this reaction.

According to our previous investigations, catalytic properties of acid modified clays (montmorillonite, kaolin and metakaolin) can be adjusted by the variation of the acid concentration used for clay modification [15,16]. Thus, the activity of these systems rose with increasing Brønsted acidity in the Prins cyclization of isopulegol with vanillin to form octahydro-2*H*-chromen-4-ol. Reasonably, this factor should also be important for the reaction between glycerol and acetone. In the present work, a natural montmorillonite clay from the bed located in Dash-Salakhinsk (Kazakhstan) modified by HNO₃ was investigated as catalyst for the reaction between glycerol and acetone in solvent free and acetonitrile media. One of the purposes of this investigation was to

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Scheme 1. Main reaction products in the glycerol (I) acetalization with acetone.

demonstrate the potential application of acid-activated clays as heterogeneous catalysts in this reaction. Moreover, the effect of HNO_3 concentration on the surface acidity, the textural properties, and the catalytic behavior of 0.125–3.0 mol/dm³ montmorillonite samples was revealed. Acid-base properties were studied by FT-IR spectroscopy using pyridine as probe molecule. Combination of physicochemical and catalytic methods can allow to establish the main factors which affect the reaction rate and the isomer selectivity.

2. Experimental

2.1. Materials

Glycerol (99.5%) and acetone (99.5+% for analysis) were purchased from Acros Organic. Octadecane (99+%) and nitric acid (70%, ACS reagent) were purchased from Aldrich. The natural clay was a sodium-rich natural montmorillonite from the bed located in Dash-Salakhinsk (Kazakhstan), hereafter denoted as MM. Chemical composition of clay is shown in Table 1.

For the preparation of the acid activated clays, 5 g of MM was suspended in 150 cm³ of 0.125–3.0 mol/dm³ HNO_3 aqueous solutions and the mixture was stirred at room temperature for 7 days. Then, the solid was separated, washed with water and dried at room temperature. The designation of the samples and the conditions of their synthesis are presented in Table 1.

2.2. Instrumental measurements

The chemical analyses of the solids were carried out by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES).

The porous structure of the materials was studied from nitrogen (Praxair, 99.999%) adsorption at -196°C using a static volumetric apparatus (Micromeritics ASAP 2010 adsorption analyzer). The methods of measurement and calculation are described in [17].

The X-ray diffraction patterns from random samples were collected on a X-ray diffractometer (Ultima-IV, Rigaku), acquired as part of the Moscow State University Development Program, using Cu-K_α radiation

Table 1
Chemical composition of natural and acid-activated montmorillonites.

	Experimental conditions		Chemical composition (wt%)		Si/Al (mol/mol)
	HNO_3 (mol/dm ³)	HNO_3/clay (mmol/g)	Si	Al	
MM	–	–	28.5	7.25	3.78
0.125 M MM	0.125	3.75	27.0	6.35	4.08
0.25 M MM	0.25	7.5	26.5	6.24	4.08
0.5 M MM	0.50	15.0	27.8	6.54	4.08
1.0 M MM	1.0	30.0	28.7	6.21	4.43
3.0 M MM	3.0	90.0	27.7	6.12	4.35
0.25 M MM (HCl)	0.25	7.5	27.2	6.21	4.22

($\lambda = 1.54056 \text{ \AA}$), rapid detector D/Tex-Ultra, scan range $3.6\text{--}65^\circ 2\theta$, scan speed $5^\circ/\text{min}$, step $0.02^\circ 2\theta$, maximum intensity $\sim 25,000$ counts.

The analysis method of the Brønsted surface acidity, strength and amount of Brønsted acid sites (BAS), based on IR spectroscopy using pyridine as probe molecule is described in [15]. IR spectra were recorded on a Shimadzu FTIR-8300S spectrometer in the range between 400 and 6000 cm^{-1} with a resolution of 4 cm^{-1} .

2.3. Catalytic tests

The reaction of glycerol with acetone was carried out in a glass reactor (15 cm³) equipped with reflux condenser and a magnetic stirrer. Before the reaction, all the catalysts were dehydrated at 200°C for 3 h in air to remove the residual water in the solids.

2.3.1. Reaction in solvent free conditions at 50°C

The standard catalytic procedure was as follows: 11.5 mmol (1.06 g) of glycerol, 29 mmol (1.68 g) of acetone, 0.010 g of octadecane (as internal standard) and 0.030 g of catalyst (1.5 wt% of catalyst based on the total mass of the reaction mixture) were introduced into the reactor. At various time intervals, aliquots were taken from the reaction mixture and analyzed after separation of the catalysts by centrifugation. The products were analyzed using a gas chromatograph (Agilent 7820) equipped with a flame ionization detector and a capillary HP-5MS column (30 m \times 0.25 mm \times 0.25 mm). Injection port temperature was 270°C . Temperature program was the following: 40°C (2 min) – $10^\circ\text{C}/\text{min}$ – 170°C (10 min). For all analysis helium was used as carrier gas. The error of experimental measurements was always less than 10%.

2.3.2. Reaction in acetonitrile medium at 25°C

The standard procedure was as follows: 2.17 mmol (0.20 g) of glycerol, 10.19 mmol (0.59 g) of acetone in 5 cm³ of acetonitrile and 0.010 g of catalyst were introduced into the reactor. At various time intervals, aliquots were taken from the reaction mixture, catalyst was removed by centrifugation. Then, octadecane (as internal standard) was added to the mixture and the products were analyzed by chromatographic analysis. A mass spectrometer (Shimadzu GCMS QP-2010 Ultra with a GsBP1-MS column, 30 m \times 0.32 mm, thickness 0.25 μm) was used to identify the reaction products.

3. Results and discussion

3.1. Structural properties of HNO_3 activated montmorillonite catalysts

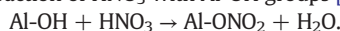
In general, the modification of natural montmorillonite by HNO_3 bears a strong resemblance to that of modification of this clay by HCl. The chemical composition of the samples obtained by acid-activation of MM with 0.125–3.0 mol/dm³ HNO_3 (Table 1) depends on the HNO_3 concentration. The Si/Al molar ratio slightly increases from the parent clay to the activated ones, being constant for 0.125–0.5 mol/dm³ solutions, and then again increases when HNO_3 concentration increases (Fig. S1, Supporting information). The increasing Si/Al molar ratio with the more diluted HNO_3 solutions, constant in all cases, suggests the

Table 2
Textural properties of natural and acid-activated montmorillonites.

	Textural properties					
	S_{BET} (m^2/g)	S_{ext} (m^2/g)	$S_{\text{ext}}/S_{\text{BET}}$ (%)	V_{Σ} (cm^3/g)	V_{μ}/V_{Σ} (%)	d_{001} (Å)
MM	105	97	92	0.224	1.3	12.6
0.125 M MM	102	55	54	0.161	13.6	13.2
0.25 M MM	112	56	50	0.164	15.9	12.9
0.5 M MM	114	56	49	0.164	13.4	13.0
1.0 M MM	130	57	44	0.175	20.6	12.7
3.0 M MM	141	69	49	0.187	19.3	12.8

cleaning of a soluble impurity, probably an amorphous solid not detected by XRD. The further increase of Si/Al ratio from 4.08 to 4.43 for the more concentrated solutions is explained by the leaching of Al^{3+} cations from the octahedral sheets.

The changes of chemical composition in the course of acid activation were also confirmed by IR spectroscopy (Fig. S2, Supporting information). According to IR spectroscopic data, the band attributed to $\nu_{\text{as}}(\text{Si}-\text{O}-\text{Si}(\text{Al}))$ shifts [18] from 1034 to 1042 cm^{-1} after acid activation of MM by HNO_3 , while the intensity of the band at 700 cm^{-1} , attributed to the $\text{Si}-\text{O}-\text{Al}$ vibrations (where Al is in octahedral positions), decreases. These changes can point to the leaching of Al from the clay. Moreover, the band in the region of 1420–1570 cm^{-1} (maximum 1489 cm^{-1}) disappears in the spectrum of 0.125 M MM after acid modification, and the intensity of the band at 880 cm^{-1} decreases, that can point out to the dissolution of calcite in acid medium. The band associated with the bending vibration mode of surface-adsorbed water, located at 1633 cm^{-1} in the spectrum of MM, shifts to 1625 cm^{-1} in the spectra of 0.125–3.0 M MM samples; this shift may be related to the interaction of HNO_3 with Al-OH groups [19]:



The band at 1386 cm^{-1} is the evidence of coordinated nitrate species on the surface of clay.

The phase changes were also confirmed by XRD method (Fig. S3, Supporting information). According to the XRD data, montmorillonite is the main component of the clay mineral and is characterized by strong basal (001) reflection at 12.5 Å and non-basal reflections at 4.47, 2.55 and 1.70 Å. Interestingly, the position of the (001) reflection, i.e. interlayer distance, depends on the HNO_3 concentration. Parent montmorillonite has a basal spacing of 12.6 Å, typical of a smectite with a monolayer of water molecules coordinated to the compensating cations. Acid activation with dilute solutions slightly increases the basal spacing, up to a value of 13.2 Å, slightly decreasing again for higher acid concentrations. The treatment provokes the “cleaning” of the solid due to the elimination of possible soluble impurities and the substitution of interlayer ions (Na^+ and Ca^{2+}) by H^+ , which are also accompanied in the interlayer space by a monolayer of water molecules, the small differences in spacing being due to the orientation of such molecules.

Table 3
Catalytic activity of MM modified by 0.125–3.0 mol/dm³ HNO_3 in reaction of glycerol with acetone.

		Solvent free conditions ^a			CH_3CN^b			
		Conversion of (I) (%)	Selectivity (%)		Conversion of (I) (%)	Consumption of (I) ^c ($\text{mmol}/((\text{m}^2/\text{g}) \cdot (\text{mmol}/\text{g}))$)	Selectivity (%)	
			(II)	(III)			(II)	(III)
1	0.125 M MM	39	97.6	2.4	62	$5.7 \cdot 10^{-3}$	86.6	13.4
2	0.25 M MM	47	97.7	2.3	82	$1.9 \cdot 10^{-3}$	90.6	9.4
3	0.5 M MM	54	97.7	2.3	94	$1.2 \cdot 10^{-3}$	95.4	4.6
4	1.0 M MM	57	97.4	2.6	92	$1.1 \cdot 10^{-3}$	97.3	2.7
5	3.0 M MM	57	98.0	2.0	94	$1.1 \cdot 10^{-3}$	96.9	3.1
6	0.25 M MM (HCl)	57	97.5	2.5	–	–	–	–

^a Experimental conditions: 11.5 mmol of glycerol, 29.0 mmol of acetone, 0.030 g of catalyst, 50 °C, 30 min.

^b Experimental conditions: 2.17 mmol of glycerol, 10.19 mmol of acetone in 5 cm^3 of acetonitrile, 10 mg of catalyst, 25 °C, 10 min.

^c Consumption of glycerol based on S_{BET} and amount of BAS.

The changes of chemical and phase compositions affect the textural properties of the activated samples. Specific surface area (S_{BET}) rises from 105 to 141 m^2/g with increasing HNO_3 concentration from 0 to 3.0 mol/dm³ (Table 2). The effect of HNO_3 concentration on the external surface area (S_{ext}) is negligible. At the same time the microporosity (V_{μ}/V_{Σ}) rises with increasing HNO_3 concentration due to the elimination of soluble impurities that favors the change in the crystallite size and the character of their interaction.

3.2. Catalytic properties of 0.125–3.0 M MM materials

Reaction between glycerol and acetone catalyzed by 0.125–3.0 M MM materials were investigated under two experimental conditions, namely under solvent free conditions and in acetonitrile medium. It may be underlined that both conditions used are rather different, avoiding direct comparison of the results because various experimental conditions (stirring speed, catalyst addition amount, pressure, temperature, moisture content and the feed composition) can affect the reaction rate [20]. The glycerol-acetone mixture has high viscosity at large amounts of glycerol, hampering the homogenization of the reaction medium, what recommends the use of a solvent. It is well-known that in oxygenation reactions the reaction rate and the distribution of products can be adjusted by the variation of nature of solvent [21]. Thus, in oxygenation of alkenes, reaction rate decreases with increasing the solvent polarity, which is related to the influence of solvent on the formation of intermediates, acetonitrile ($\mu = 9.0$) and methanol ($\mu = 9.5$) have been reported to be the most suitable solvents for such type of reactions [21], acetonitrile being chosen for the present reaction. Besides, the use of acetonitrile as reaction medium allowed to carry out the experiments of oxygenation of glycerol at room temperature [9,22]. In the experiments carried out in acetonitrile solution the acetone/glycerol molar ratio used was 4.7 and the temperature 25 °C, while under solvent free conditions the acetone/glycerol molar ratio was 2.5 and the temperature 50 °C. Both set of conditions chosen allowed to maintain the conversion in intermediate values. In the second case, the reaction mixture constitutes a two-phase system for the first 3–7 min due to the low intermiscibility of glycerol and acetone [23], becoming a single liquid phase system when enough amount of the products was formed.

In both reaction conditions, the main products were five-membered solketal (II) and six-membered acetal (III) (Scheme 1). The typical kinetic profiles in the presence of 0.125–1.0 M MM are shown in Fig. S4A and S5 (Supporting information). In the presence of 0.5–3.0 M MM samples, the conversion of glycerol and selectivity towards (II) were 94% and 95.4–97.3%, respectively, after 15 min of reaction at 25 °C in acetonitrile medium (Table 3). At the same time under solvent free conditions the conversion of glycerol and selectivity towards (II) were 47–57% and 97.4–98.0% after 30 min of reaction at 50 °C considering the same catalysts. In both cases, the conversion of glycerol depends on the amount of catalyst in the reaction mixture and acetone/glycerol

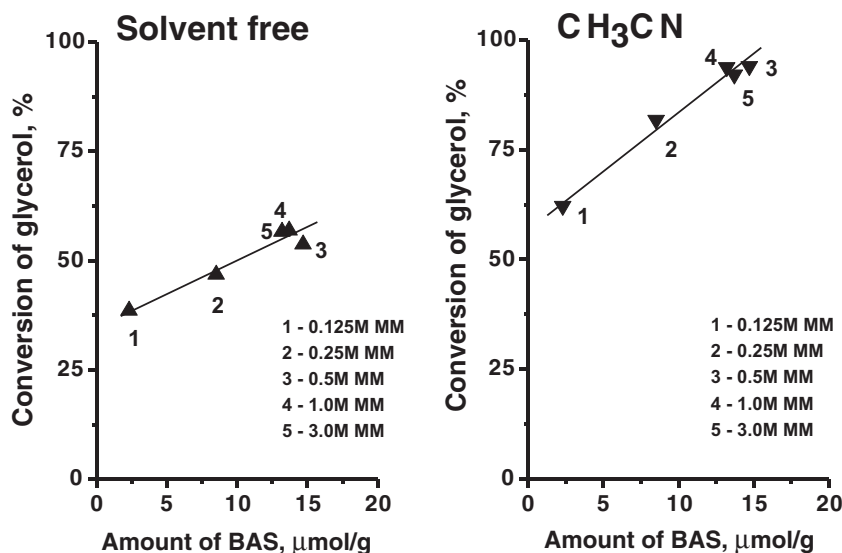


Fig. 1. Effect of the amount of Brønsted acid sites in MM modified by 0.125–3.0 mol/dm³ HNO₃ on conversion of glycerol and selectivity towards (II) in reaction of glycerol with acetone in different experimental conditions. (Experimental conditions: (solvent free) 11.5 mmol of glycerol, 29 mmol of acetone and 0.030 g of catalyst, 50 °C, 30 min); (acetonitrile) 2.17 mmol of glycerol, 10.19 mmol of acetone in 5 cm³ of acetonitrile and 0.010 g of catalyst, 25 °C, 15 min).

molar ratio (Fig. S4B–C, Supporting information). The conversion of glycerol rose with increasing acetone/glycerol molar ratio from 1 to 6 (Fig. S4C, Supporting information), but further increasing molar ratio did not cause further increase in the conversion.

The concentration of HNO₃ used for the acid activation of MM affects the conversion of glycerol (Table 3, Fig. S6, Supporting information). The conversion of glycerol and selectivity towards (II) increase with increasing the HNO₃ concentration up to 0.5 mol/dm³, and then do not change. This feature of catalytic behavior of MM modified by HNO₃ can be explained by two reasons. The first reason can be related to the variation in the surface acidities that follows from the investigation of Brønsted acidity by IR spectroscopy using pyridine as probe molecule, according to the increase of catalytic activity with the amount of BAS (Fig. 1). Dependence of the conversion of glycerol and the yield of (II) on the acidity of the catalysts in this reaction was also demonstrated by Nanda et al. [9]; in a flow continuous reactor the activity of the catalysts with stronger acidity correlated linearly with the amount of acid sites and decreased in the following order: Amberlyst 36 wet ~ Zeolite beta ~ Amberlyst 35 dry > Zirconium sulfate > K-10 Montmorillonite > Polymax 845.

The second reason can be related to the change of the facility of BAS access for the reactants. This supposition is in accord with the

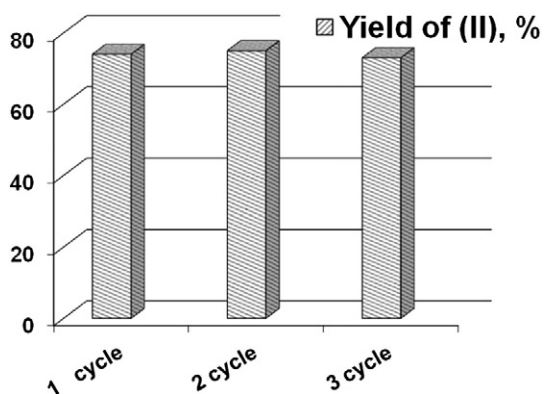


Fig. 2. 0.5 M MM recycling in reaction of glycerol with acetone. Experimental conditions: 0.7 wt% of catalyst (based on total mass of reaction mixture), acetone/glycerol = 4.1 mol/mol, 50 °C, 30 min. Amount of reactants was corrected based on reaction conditions.

decreasing microporosity (V_w/V_Σ) (Table 2) and the consumption of glycerol based on S_{BET} and amount of BAS (Table 3) when increasing the HNO₃ concentration.

It is well-known that the composition of acid modified clays depends on the type of acid used in the treatment [24,25]. For comparative purposes, MM was treated with HCl, using one of the concentrations employed when treating with HNO₃, namely 0.25 mol/dm³ (solid 0.25 M MM (HCl)). Comparing the catalytic properties of 0.25 M MM (HCl) and 0.25 M MM (HNO₃), in both cases the selectivity towards (II) was 97.5–97.7% (Table 3). At the same time, the conversion of glycerol was higher (57%) in the presence of 0.25 M MM (HCl) than in the presence of 0.25 M MM (HNO₃) (47%). Probably, the lower activity of 0.25 M MM (HNO₃) is related to the difference in the amount of BAS. Data of IR spectroscopy using pyridine as probe molecule confirm this assumption. 0.25 M MM (HCl) possesses larger amount of BAS (12.8 $\mu\text{mol/g}$) than 0.25 M MM (HNO₃) (8.3 $\mu\text{mol/g}$).

The stability of the most active sample, namely 0.5 M MM, was investigated by means of recycling tests under solvent free conditions at 4.1/1 acetone/glycerol molar ratio, 0.7 wt% of catalyst (based on total mass of reaction mixture), and 50 °C. After each catalytic test, the sample was separated from the reaction mixture by filtration, washed with acetone and used in a next cycle. The experimental data point out that this sample can be used repeatedly without significant loss of catalytic activity during at least 3 catalytic cycles (Fig. 2). The yield of (II) was 72–73% in each cycle. Nanda et al. [9] have investigated the catalytic behavior of K-10 montmorillonite in continuous-flow reactor at 40 °C, 600 psi and WHSV of 4 h⁻¹, finding yields of (II) of 60 and 68% at acetone/glycerol molar ratios of 2:1 and 6:1, respectively. These data point out that the acid concentration affects the catalytic behavior of acid activated clays.

4. Conclusions

The effect of acid activation of natural montmorillonite with HNO₃ on the physicochemical and catalytic properties of the resulting solids in the reaction between glycerol and acetone has been investigated. The increase in HNO₃ concentration led to the leaching of Al³⁺ cations from the octahedral sheets, and the increase in the specific surface area and microporosity of 0.125–3.0 M MM samples. A key factor for the adjustment of the reaction rate is Brønsted acidity. The increase in the amount of BAS leads to the rise of the reaction rate. Correlations

between the conversion of glycerol and the HNO_3 concentration used for clay modification, the amount of catalyst, the acetone/glycerol molar ratio, and the amount of BAS were the same both under free solvent experimental conditions and in acetonitrile medium. The most active 0.5 M MM solid was stable during at least 3 catalytic cycles under solvent free conditions at 4.1/1 acetone/glycerol molar ratio and 50 °C.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2016.11.020>.

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