

# Polymer-supported nitroxyl radical catalysts for the hypochlorite and aerobic oxidation of alcohols

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Available online 19 June 2006

## Abstract

PS-TEMPO, a polymer-supported 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) was successfully applied as a recyclable, active and selective catalyst for the oxidation of alcohols. Bleach, molecular oxygen and air were successfully used as terminal oxidant under conditions suitable for industrial applications. The intrinsic activity and selectivity of TEMPO for primary alcohols to aldehydes were retained while the heterogenisation of TEMPO allowed a much simpler purification of the oxidation products and gave the possibility to recover and reuse the catalyst thus reducing cost.

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*Keywords:* TEMPO; Alcohol; Oxidation; Immobilisation

## 1. Introduction

The oxidation of alcohols is one of the most important transformations in organic chemistry [1]. Early protocols for this transformation relied on the use of stoichiometric oxidants such as chromium(VI) reagents [2]. The development of new environmentally friendly methods for the selective catalytic oxidation of alcohol substrates to aldehydes and ketones is an important goal in the development of modern methods for chemical synthesis [3]. Many systems have been reported in the literature for the catalytic oxidation of alcohols, mainly involving the use of catalysts containing transition metals [4]. Of particular interest in the area of alcohol oxidation is the conversion of primary alcohols to aldehydes. This conversion is crucial for the synthesis of fine chemicals such as fragrances or food additives [3b,5]. Systems involving nitroxyl radicals such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) [6], have shown great efficiency for the selective oxidation of primary and secondary alcohols to the corresponding aldehydes and ketones with high yields and selectivities. TEMPO has been used in combination with a wide range of stoichiometric oxidants [7] with sodium hypochlorite [8] being arguably the

most widely used. In 1984 Semmelhack et al. [9] showed that TEMPO can be used in combination with molecular oxygen in conjunction with a transition metal. In the presence of a catalytic amount of copper salt and molecular oxygen, TEMPO could oxidise benzylic and allylic alcohols but failed to oxidise unactivated aliphatic alcohols. Since this first example, several TEMPO based systems have been developed that are capable of oxidising a wide range of benzylic, allylic and aliphatic alcohols [10].

The immobilisation of homogeneous catalysts onto solid supports provides potential for extending the benefits of heterogeneous catalysts to homogeneous systems [11]. These benefits may include, the ease of separation of catalyst and reaction products leading to improved efficiency and the potential for reuse of the supported catalyst leading to reduced cost. The immobilisation of TEMPO onto organic [12] and inorganic [13] supports is well documented in the literature, however, very few catalytic systems combine the advantages of using molecular oxygen as terminal oxidant with the possibility to recover and recycle the *N*-oxyl radical catalyst. We have recently reported [14] the synthesis of a polymer-supported TEMPO, and its application for the aerobic oxidation of primary alcohols. We report herein the immobilisation of TEMPO on various organic and inorganic supports and their application for the oxidation of alcohols using either sodium hypochlorite, molecular oxygen or air as terminal oxidant.

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## 2. Experimental

### 2.1. PS-TEMPO preparation

FibreCat<sup>TM</sup> (15 g) was suspended in anhydrous dichloromethane (150 ml) before addition of diisopropylcarbodiimide (32 ml, 204 mmol), dimethylaminopyridine (1.25 g, 10 mmol), 4-hydroxy-TEMPO (17.5 g, 102 mmol) and triethylamine (28.5 ml, 204 mmol). The reaction mixture was stirred overnight at room-temperature under an atmosphere of nitrogen. The solid material was collected by filtration and washed with dimethylformamide and dichloromethane. The solid was then extracted using dichloromethane and finally dried in vacuum. Yield on PS-TEMPO: 23 g, estimated TEMPO loading 2 mmol g<sup>-1</sup> (estimated by measuring the quantity of unreacted 4-hydroxy-TEMPO by GLC).

### 2.2. Catalyst testing

- **Hypochlorite oxidation.** Alcohol (0.8 M, 30 ml) in dichloromethane, KBr (0.5 M, 5 ml) in water, 4-methoxyacetophenone (500 mg, internal standard) and PS-TEMPO (200 mg) were added to a round-bottom flask. The reaction mixture was stirred at 0 °C before addition of NaOCl (0.35 M, pH 8.7, 90 ml). Sample aliquots were regularly taken and analysed by GLC.
- **Aerobic oxidation at atmospheric pressure.** Alcohol (20 mmol), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mmol, 116 mg), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mmol, 116 mg), PS-TEMPO (800 mg), 4-methoxyacetophenone (500 mg, internal standard) and glacial acetic acid (15 ml) were added to a round bottom flask equipped with a condenser and heated at 40 °C under an

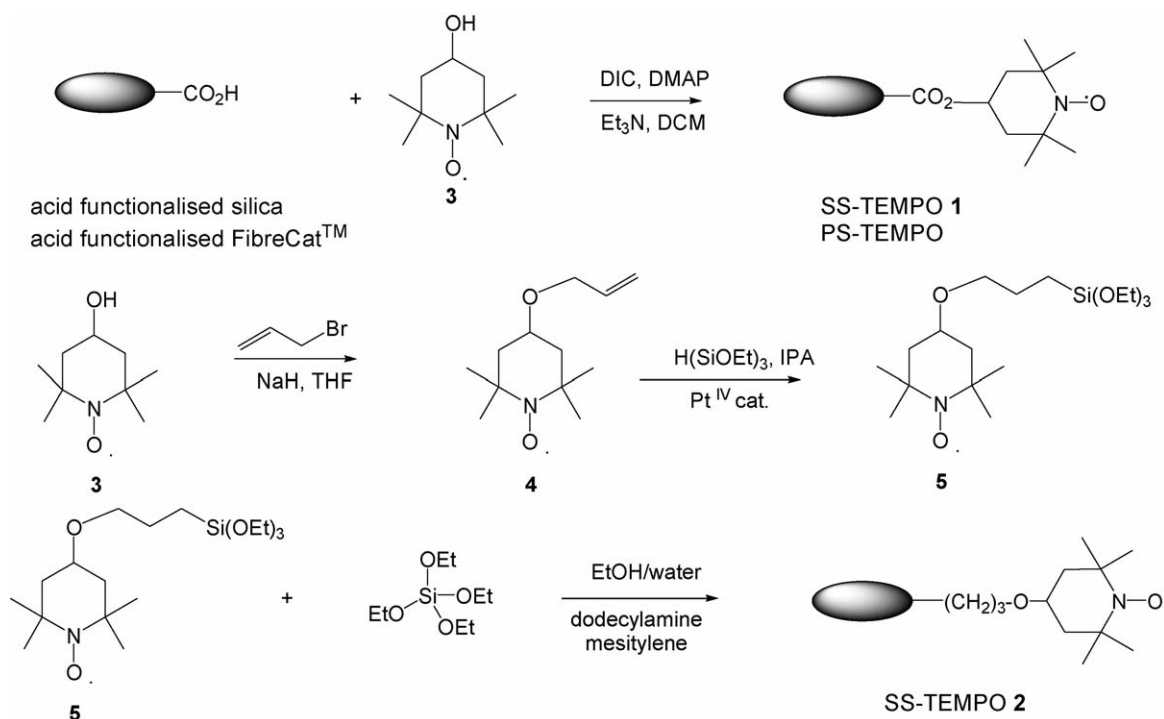
oxygen atmosphere. Sample aliquots were regularly taken and analysed by GLC.

- **Aerobic oxidation at high pressure.** Alcohol (20 mmol), Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mmol, 116 mg), Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.4 mmol, 116 mg), PS-TEMPO (800 mg), 4-methoxyacetophenone (500 mg, internal standard), in glacial acetic acid (15 ml) were added to a high pressure reactor and heated to 40 °C under a continuous stream (10 ml min<sup>-1</sup>) of an oxygen–nitrogen mixture (8:92, v/v). Sample aliquots were regularly taken and analysed by GLC.

## 3. Results and discussion

### 3.1. Catalyst synthesis

Three different immobilised TEMPO have been prepared: SS-TEMPO **1** and **2** are TEMPO supported on silica and PS-TEMPO is an organic polymer anchored TEMPO (Scheme 1). For SS-TEMPO **1** a carboxylic acid functionalised mesoporous silica was used. The acid functionalised silica was prepared by sol–gel process using tetraethylorthosilicate (TEOS) and 4-triethoxysilylbutyronitrile in the presence of dodecylamine and mesitylene as pore expander [15]. The cyano groups were hydrolysed in the presence of sulphuric acid. BET analysis of the acid functionalised silica showed a surface area of 442 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 4.4 nm. The coupling of 4-hydroxy-TEMPO **3** onto the support was performed in the presence of diisopropylcarbodiimide, dimethylaminopyridine and triethylamine in dry dichloromethane. SS-TEMPO **2** was prepared by co-hydrolysis of a silyl-functionalised TEMPO **5** [13c] with TEOS in the presence of dodecylamine and mesitylene as pore expander [15]. BET



Scheme 1. Preparations of immobilised TEMPO.

Table 1  
Bleach oxidation of 1-octanol<sup>a</sup>

Run	Material	Cycle	Conversion (%)	Selectivity (%)
1	SS-TEMPO 1	1	99	96
		2	77	91
2	SS-TEMPO 2	1	86	90
		2	84	92
3	PS-TEMPO	1	96	95
		2	95	>99

<sup>a</sup> 1-Octanol 0.8 M in dichloromethane (30 ml), PS-TEMPO (200 mg), KBr 0.5 M in water (5 ml), NaOCl 0.35 M, pH 8.7 (90 ml), 0 °C.

analysis of SS-TEMPO 2 showed a surface area of 469 m<sup>2</sup> g<sup>-1</sup> and an average pore diameter of 5.5 nm. Finally, PS-TEMPO was prepared following the same procedure as above using an acid functionalised FibreCat<sup>TM</sup> [16]. FibreCat<sup>TM</sup> consists of a polymer produced by graft co-polymerisation of polyolefin fibres with functionalised monomers. This process results in a high density of active functional sites being generated on the polymer (6.5 mmol g<sup>-1</sup>). Furthermore, the open structure of the polymer and its good functional group accessibility is the reason it achieves high catalyst loading (2 mmol g<sup>-1</sup> of nitroxyl radical).

### 3.2. Hypochlorite oxidation of alcohols

These three materials were tested for the bleach oxidation of 1-octanol to the corresponding aldehyde under the conditions developed by Anelli [8] (Table 1). SS-TEMPO 1 and PS-TEMPO proved to be the most active materials: over 95% conversion and selectivity were obtained after 15 min of reaction (runs 1 and 3). After reuse of the catalyst PS-TEMPO does not show any drop of activity (run 3) however upon recycling SS-TEMPO 1, the conversion dropped from 99 to 77% (run 1). We can reasonably explain these results by the leaching of *N*-oxyl radical from the support to the reaction mixture. Part of the initial activity of SS-TEMPO 1 may be in fact due to some homogeneous catalyst in the reaction mixture, upon recycling the catalyst, loading is reduced and the activity drops. SS-TEMPO 2 showed the lowest activity of the three materials but it proved to be recyclable without loss of activity (86 and 84% conversion, respectively, for the first two runs). Octanoic acid and octyl octanoate were the only two by-products that could be detected by GLC analysis.

Table 2  
Bleach oxidation of various alcohols using PS-TEMPO<sup>a</sup>

Run	Alcohol	Product	Time (min)	Conversion (%)	Selectivity (%)
1	1-Octanol	Octanal	10	99	99
2	Benzyl alcohol	Benzaldehyde	10	99	99
3	3-Phenyl-1-propanol	3-Phenylpropionaldehyde	15	96	97
4	Undecanol	Undecanal	10	94	80
5	1-Phenylethanol	Acetophenone	25	93	99
6	2-Octanol	2-Octanone	90	73	96

<sup>a</sup> Alcohol 0.8 M in dichloromethane (30 ml), PS-TEMPO (200 mg), KBr 0.5 M in water (5 ml) NaOCl 0.35 M pH 8.7 (90 ml), 0 °C.

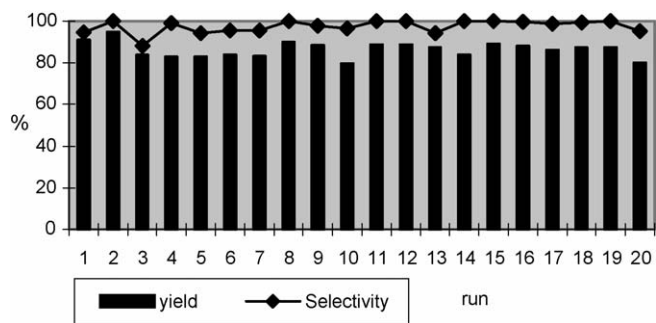


Fig. 1. Yields and selectivities obtained in the hypochlorite oxidation of 1-octanol to give octanal in the presence of PS-TEMPO after 15 min.

The synthesis of the silyl-functionalised compound 5 involves several steps and the sol-gel process to prepare SS-TEMPO 2 proved delicate to scale-up. The acid functionalised FibreCat<sup>TM</sup> is commercially available and the coupling with 4-hydroxy-TEMPO 3 is a straightforward process. This makes PS-TEMPO the easiest and cheapest material to make, so PS-TEMPO was the catalyst of choice for the bleach oxidation of alcohols.

PS-TEMPO was successfully applied for the oxidation of a range of alcohols using bleach (Table 2). Primary aliphatic and benzylic alcohols were readily converted into their corresponding aldehydes with high conversions and selectivities (runs 1–4). The oxidation of secondary alcohols proved more difficult: the oxidation of phenyl ethanol under the same conditions required 25 min to achieve 93% conversion with acetophenone produced with 99% selectivity (run 5). For the more challenging transformation of 2-octanol, 2-octanone was obtained with high selectivity (96%) but only 73% conversion after 90 min of reaction.

PS-TEMPO can easily be removed by filtration, therefore facilitating any purification of the carbonyl compound produced; it can also be reused very effectively (Fig. 1). The oxidation of 1-octanol was performed on a larger scale (48 mmol of alcohol, 400 mg of PS-TEMPO). The catalyst was recovered by filtration after 15 min of reaction, washed with dichloromethane and reused without any reactivation process. No addition of fresh catalyst to keep the amount of catalyst constant was performed. PS-TEMPO was used 20 times without significant loss of activity/selectivity.

In conclusion, PS-TEMPO is a very efficient and selective catalyst for the bleach oxidation of primary aliphatic and benzylic alcohols. In addition it is very easy to recycle by filtration without any loss of activity. However, bleach is not the

Table 3  
Aerobic oxidation of alcohols<sup>a</sup>

Run	Catalyst	Substrate	Time (h)	Conversion (%)	Selectivity (%)
1	PS-TEMPO	1-Octanol	2.5	99	99
2	PS-TEMPO	2-Octanol	24	99	95
3	SS-TEMPO 1	1-Octanol	4	67	94
4	SS-TEMPO 1	2-Octanol	24	29	98
5	SS-TEMPO 2	1-Octanol	4	95	97
6	SS-TEMPO 2	2-Octanol	24	63	94

<sup>a</sup> Substrate 5 mmol, PS-TEMPO 250 mg, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 29 mg, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 29 mg, AcOH 5 ml, 40 °C, O<sub>2</sub> 1 bar.

ideal oxidant [8]. With the growing pressure to develop greener, cleaner processes for the production of fine chemicals [5] we applied our catalyst in non-chlorinated solvents using molecular oxygen as terminal oxidant.

### 3.3. Aerobic oxidation of alcohols

The conditions developed by Minisci [10c] were particularly attractive. The oxidation of 1-octanol is performed under mild conditions: O<sub>2</sub> 1 bar, 40 °C using cheap simple co-catalysts, Mn(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> in the presence of 10 mol% of TEMPO (Table 3).

SS-TEMPO 1 and 2 and PS-TEMPO were tested under these conditions: while SS-TEMPO 2 performed very well (run 5), SS-TEMPO 1 proved to be less active as only 67% conversion was achieved after 4 h of reaction (run 3). The best results were obtained using PS-TEMPO: 1-octanol was completely consumed and octanal was obtained as the sole detectable product after 2.5 h of reaction (run 1). In order to confirm these results, the three materials were tested for the more demanding oxidation of 2-octanol. Good conversion and selectivity were observed for PS-TEMPO after an extended reaction time (24 h, run 2). Under the same conditions SS-TEMPO 1 and 2 were significantly less active: 29 and 63% conversion, respectively (run 4 and 6). These results confirm the superiority of PS-TEMPO over SS-TEMPO 1 and 2 as catalyst for alcohol oxidation already observed using bleach as terminal oxidant. Primary aliphatic and primary and secondary benzylic alcohols were readily oxidised in the presence of PS-TEMPO with complete conversion and high selectivity to the corresponding carbonyl compounds (Table 4, runs 1–5). The oxidation of secondary aliphatic alcohols proved more challenging for this

Table 4  
PS-TEMPO oxidation of alcohols<sup>a</sup>

Run	Substrate	Product	Time (h)	Conversion (%)	Selectivity (%)
1	1-Octanol	Octanal	2.5	99	98
2	1-Undecanol	Undecanal	3	>99	92
3	3-Phenyl-1-propanol	3-Phenylpropionaldehyde	2.5	95	94
4	Benzyl alcohol	Benzaldehyde	2	>99	>99
5	1-Phenylethanol	Acetophenone	1.5	>99	>99
6	2-Octanol	2-Octanone	24	99	95

<sup>a</sup> Substrate 10 mmol, PS-TEMPO 500 mg, AcOH 10 ml, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 58 mg, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 58 mg, 40 °C, O<sub>2</sub> 1 bar.

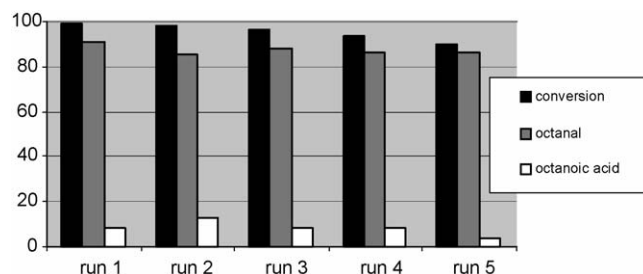


Fig. 2. Conversion and yield obtained in the oxidation of 1-octanol in the presence of PS-TEMPO, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (acetic acid, O<sub>2</sub> 1 bar, 40 °C).

system. A longer reaction time was required for the oxidation of 2-octanol (24 h, 99% conversion at 95% selectivity run 6).

We investigated the recyclability of the catalyst under these conditions (Fig. 3). PS-TEMPO was recovered by filtration after 3 h of reaction and reused, without any reactivation process, in a sequence of oxidations using 1-octanol as substrate. Fresh Mn(NO<sub>3</sub>)<sub>2</sub> and Co(NO<sub>3</sub>)<sub>2</sub> were added to each successive run. The results presented in Fig. 2 show that even after five subsequent runs the catalyst activity and selectivity remained high, proving the efficiency of the catalyst recovery. The slight decrease in the conversion of 1-octanol observed during the successive runs could be due to loss of some catalyst during filtration of the small amount of catalyst; no fresh PS-TEMPO catalyst to keep the amount of catalyst used constant was added.

The results were very promising but these conditions (i.e. pure molecular oxygen at 1 bar) are not applicable on industrial scale due to risk of fire and explosion. In order to work under safe conditions, the reaction has to be performed in diluted oxygen in nitrogen (typically 8/92, v/v) at higher pressure. Several parameters (pressure, temperature, catalyst loading) were screened in order to identify the optimum conditions for the oxidation of 1-octanol (Table 5).

In the first run (Table 5) 1-octanol was oxidised in the presence of PS-TEMPO (50 mg/mmol) at 40 °C and under 3 bar pressure, octanal was obtained with 94% selectivity at 81% conversion after 3 h of reaction. Increasing the pressure to 6 bar allowed the reaction to reach 92% conversion with 99% selectivity (run 2). The reaction was then performed with reduced catalyst loading, i.e. 40, 30 and 20 mg of PS-TEMPO per mmol of alcohol. Nearly full conversions were achieved in each case providing an increased reaction time was applied, however with the lowest loading, 20 mg/mmol, the selectivity

Table 5  
Oxidation of 1-octanol under pressure using PS-TEMPO<sup>a</sup>

Run	PS-TEMPO (mg/mmol)	T (°C)	Pressure (bar)	Time (h)	Conversion (%)	Selectivity (%)
1	50	40	3	3	81	94
2	50	40	6	3	92	99
3	40	40	6	5	98	99
4	30	40	6	7	98	99
5	20	40	6	9	99	86

<sup>a</sup> In an autoclave: 1-octanol 20 mmol, PS-TEMPO, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 116 mg, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 116 mg, AcOH 15 ml, continuous stream (10 ml min<sup>-1</sup>) of an O<sub>2</sub>/N<sub>2</sub> mixture (8/92, v/v).

Table 6  
PS-TEMPO oxidation of alcohols<sup>a</sup>

Run	Substrate	Product	Time (h)	Conversion (%)	Selectivity (%)
1	1-Octanol	Octanal	5	99	98
2	1-Undecanol	Undecanal	6	99	95
3	3-Phenyl-1-propanol	3-Phenylpropionaldehyde	5	93	81
4	Benzyl alcohol	Benzaldehyde	3	99	99
5	1-Phenylethanol	Acetophenone	3.5	93	96
6	2-Octanol	2-Octanone	22	96	90

<sup>a</sup> In an autoclave: substrate 20 mmol, PS-TEMPO 800 mg, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 116 mg, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O 116 mg, AcOH 15 ml, continuous stream (10 ml min<sup>-1</sup>) of an O<sub>2</sub>/N<sub>2</sub> mixture (8/92, v/v).

toward the formation of octanal was only 86% (run 5). High yield and selectivity could be achieved using 30 of PS-TEMPO per mmol of alcohol with the reaction performed at 40 °C under 6 bar pressure of 8% oxygen in nitrogen. The results obtained for the oxidation of 1-octanol using pure molecular oxygen (Table 4) could be reproduced under safe conditions suitable for industrial scale application (Table 5, runs 3 and 4).

Benzylic and primary aliphatic alcohols were readily oxidised with over 90% conversion and selectivities ranging from 81 to 99% in less than 6 h (Table 6, runs 1–5). Similar results could be obtained for the oxidation of 2-octanol providing a longer reaction time (run 6).

#### 4. Conclusion

In conclusion, TEMPO was successfully immobilised using a simple method and a commercially available support. The polymer-supported TEMPO proved efficient for the selective oxidation of alcohols using sodium hypochlorite, molecular oxygen and air as terminal oxidant under conditions suitable for industrial applications. The activity and selectivity of TEMPO were retained with the added advantages of a heterogeneous catalyst namely, ease of separation and purification, catalyst recovery and recycling. To our knowledge this represents the first example of a truly heterogeneous TEMPO catalyst, active and selective for the difficult conversion of unreactive aliphatic primary alcohols into aldehydes using molecular oxygen as terminal oxidant.

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