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## Highly selective aerobic oxidation of alkyl arenes and alcohols: cobalt supported on natural hydroxyapatite nanocrystals<sup>+</sup>

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Cobalt was successfully immobilized on natural hydroxyapatite nanocrystals which were obtained from cow bones (Co–NHAp). The chemical, structural, and electronic properties of this nanobiocatalyst were investigated using flame atomic absorption spectroscopy (FAAS), Fourier transform infrared (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and energy dispersive spectroscopy (EDS) analysis. Natural hydroxyapatite (NHAp) as the support enhanced both catalytic activity and selectivity in the liquid phase aerobic oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds. The use of air as an inexpensive oxidant, the recyclability of the Co–NHAp nanobiocatalyst without significant decrease in its catalytic activity and easy workup are some advantages of this work.

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### 1. Introduction

The selective aerobic oxidation of organic compounds to their corresponding carbonyl compounds is one of the most important commercial processes for the production of aldehydes and ketones. In conventional oxidation of alcohols and arenes, the use of stoichiometric amounts of toxic oxidizing agents such as nitric acid, potassium dichromate, sodium hypochlorite, potassium permanganate or organic peroxides is required which generate large amounts of hazardous waste. From an environmental and economic viewpoint, there is an urgent need to develop environmentally benign oxidation procedures such as using green oxidants and heterogeneous recoverable catalysts under mild conditions, which is particularly suitable for industrial practices.<sup>1-3</sup>

Hydroxyapatite (HAp),  $Ca_{10}(PO_4)_6(OH)_2$ , as a calcium phosphate-based material is a main component of bones and hard tissues.<sup>4</sup> Due to its extensive properties such as good chemical and thermal stability, biocompatibility, noncarcinogenic and non-immunogenic, and high flexibility for a great variety of cationic and anionic species,<sup>5-7</sup> it was used as matrix for the purification,<sup>8</sup> bioceramics, excellent osteoconductive,<sup>5,9,10</sup> chemical sensors, retardant of cancer cells, drug delivery agent, ion conductors and catalysts support.<sup>11-16</sup> Because of its potential applications, various synthetic methods such as chemical precipitation, solid–state reaction, hydrothermal synthesis, sol–gel route and so on have been reported for the synthesis of HAp.<sup>8</sup> The tendency of cobalt complexes to bind with molecular oxygen<sup>17,18</sup> and the use of such dioxygen–cobalt complexes as catalysts in various oxidation reactions has received intensive attention in recent decades.<sup>1,19</sup> The dioxygen–cobalt complexes formed from cobalt complexes in the presence of oxygen catalyze a variety of organic reactions like oxidation of phenols,<sup>20,21</sup> thiols,<sup>22</sup> aldehydes<sup>23–25</sup> and hydrocarbons<sup>26,27</sup> involving hydrogen abstraction or one electron transfer. Cobalt as one of the most active transition metals is supported on (bio)polymers, cellulose, mesoporous materials (MCM-41), nanoshell carbon, silica and activated carbon for aerobic oxidation of organic compounds such as alkyl arenes, alcohols, olefins, terpenes,  $\alpha$ -hydroxy ketones, tertiary nitrogen compounds and sulfides and due to its activity, it was used as homogeneous and heterogeneous catalysts.<sup>28–40</sup>

Using air as a green and low-cost oxidant for oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds and using natural and biocompatible supports for heterogeneous catalysts are important in view of both ecofriendly and green chemistry approach. In a continuation of our efforts to synthesis of bio-supported heterogeneous catalytic systems<sup>40-43</sup> and aerobic oxidation of alkyl arenes and alcohols,<sup>40,44-46</sup> herein, we describe the selectively aerobic oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds using Co–NHAp under heterogeneous conditions without using any oxidizing reagents.

### 2. Experimental

#### 2.1 General

All reagents were obtained from Aldrich or Merck and used without further purification. Co determination was carried out on a flame atomic absorption spectroscopy (FAAS) (Shimadzu



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#### Paper

model AA-680 atomic absorption spectrometer) using an airacetylene flame. Thermogravimetric analysis (TGA) was carried out using STA 1500 instrument at a heating rate of 10 °C min<sup>-1</sup> in air. Products were analyzed using a Varian 3900 GC. The GC thermal program was: heating at 12 °C min<sup>-1</sup> from 50 °C to 250 °C. X-ray diffraction (XRD) pattern was recorded on a STOE STADI P with scintillation detector, secondary monochromator using Cu K $\alpha$  radiation ( $\lambda = 0.1540$  nm). Scanning electron microscopy (SEM) observations were carried out on an electron microscopy Philips XL-30 ESEM. All samples were sputtered with gold before observation. Melting points were measured on an Electrothermal 9200 apparatus. IR spectra were recorded on a Shimadzu IR-470 spectrometer (the number of scans = 25).

#### 2.2 Preparation of NHAp

Cow bones were boiled in water for 12 h to remove the traces of meat. Then, they were soaked in 5% (w/v) NaOH aqueous solution under reflux conditions for 5 h to remove protein, lipids, oils and other organic impurities.<sup>47</sup> Finally, they were washed with distilled water, dried and broken in smaller pieces and were ground with mill (Fig. 1).

#### 2.3 Preparation of Co-NHAp

Co-NHAp was prepared using a chemical immobilization method. To 100 mL of  $Co(OAc)_2$  (5% w/v) solution, 2 g NHAp was slowly added under vigorous stirring condition over 1 h at room temperature. Then, the mixture was irradiated with ultrasound for 20 minutes. After stirring at room temperature for 24 h, the resulting violet powders were filtered and washed three times with distilled water and ethanol, and dried overnight at 70 °C (Fig. 1c).

#### 2.4 General procedure for the oxidation of alkyl arenes

An alkyl arene (1.00 mmol), KOH (0.50 mmol), Co–NHAp (0.18 g, 6.00 mol%), and *p*-xylene (10 mL) as a solvent were added to a two-necked round-bottom flask. The mixture was heated under air blowing at 100  $^{\circ}$ C for the indicated times in Table 2. The thin layer chromatography (TLC) method was used to investigate the progress of the reaction. Upon completion of reaction, analysis of the crude product has been done by gas chromatography (GC) method.

#### 2.5 General procedure for the oxidation of alcohols

An alcohol (1.00 mmol) was added to a two-necked flask containing Co–NHAp (0.18 g, 6.00 mol%), KOH (0.50 mmol), and *p*xylene (10 mL) and stirred under air blowing at 80 °C for the indicated times in Table 4. The progress of the reaction was followed by TLC. Upon completion, the reaction mixture was filtered and the crude product analyzed by GC method. The yields were determined from the integrals of the GC analysis.

### 3. Results and discussion

Hydroxyapatite as the main component of bones is insoluble in aqueous solutions.<sup>48</sup> Preliminary experiments have shown that organic part of the system can be nearly totally removed from bones by treating them with hot sodium hydroxide solution.<sup>47</sup> So this biocompatible material can be used as a natural and reproducible solid support. The relatively high surface area provided on catalyst combined with its availability, biodegradability and renewability makes this material attractive as a solid support. The P–OH groups on the surface of NHAp acts as a sorption site for metals and also considerably decrease metal leaching. Co was immobilized on NHAp and the Co content of the Co–NHAp nanocatalyst was determined 2 wt% using FAAS method.

The TGA curves of NHAp and Co–NHAp were obtained under air atmosphere (Fig. 2). In the TGA curves of NHAp and Co– NHAp two stages could be observed. First stage occurred over 30-200 °C in which the mass slowly decreased by 6% and 9% for NHAp and Co–NHAp, respectively ascribing to removal of



Fig. 2 TGA curves of NHAp and Co–NHAp.



Fig. 1 Images of bone (a), NHAp (b) and Co-NHAp (c).

adsorbed water on the surface of catalyst and loss of lattice water. In second stage, between 200 and 500  $^\circ \rm C$  a large weight loss was observed which correspond to the disintegration of



Fig. 3 XRD patterns of NHAp and Co-NHAp.



Fig. 4 FT-IR analysis of NHAp and Co-NHAp.

macromolecules and other organic substances which are along with the NHAp. The introduction of Co on NHAp enhanced the thermal stability of support in Co–NHAp to some extent.

XRD pattern of NHAp and Co–NHAp was also employed to investigate the structure of the catalyst (Fig. 3). The crystallinity of the NHAp was confirmed by strong peaks at  $2\theta$  values of  $25.77^{\circ}$ ,  $31.88^{\circ}$ ,  $33.91^{\circ}$ ,  $46.72^{\circ}$ ,  $49.46^{\circ}$  and  $53.14^{\circ}$ . The pattern of Co–NHAp is similar to NHAp indicating that the NHAp remains intact at the end of the procedure without loss in the crystallinity.<sup>49</sup>

The FT-IR spectra of NHAp and Co-NHAp (Fig. 4) show the characteristic bands of absorbed water, hydroxyl and phosphate species corresponding to NHAp structure. As seen, the wave numbers for characteristic peaks of both spectra are approximately identical. The peaks corresponding to stretching and bending modes of PO<sub>4</sub><sup>3-</sup> ions were detected at around 960-1115, 467 and 559-602 cm<sup>-1</sup>, respectively. The broad band at 3518  $\text{cm}^{-1}$  and a small band at about 1666  $\text{cm}^{-1}$  are due to absorbed water. The shoulder at 3672 cm<sup>-1</sup> and the absorption band at 694 cm<sup>-1</sup> corresponds to the stretching vibration and vibrational mode of hydroxyl group. Existence of carbonate ion could be confirmed through spectra at 1658, 1747, 2063 and 2129 cm<sup>-1</sup>. FT-IR spectrum of Co-NHAp has well corresponding absorption band of NHAp as shown in Fig. 4. The broadening of carbonate absorption band and the slight shift to 1500 and 1658  $cm^{-1}$  may be due to the chelation of Co on the surface of NHAp.

As shown in Fig. 5a and b, the SEM analysis has been used to study the structure and morphology of the Co–NHAp. The SEM analysis of the catalyst showed the morphology of the Co–NHAp which is composed of particles with irregular shapes and



Fig. 5 SEM images (a and b) and EDS analysis (c) of Co-NHAp.

Table 1 Optimization of the reaction conditions for aerobic oxidation of arenes<sup>a</sup></sup>

Entry	Catalyst	Amount of catalyst (mol%)	Solvent	Base (mmol)	$\operatorname{Yield}^{b}(\%)$
1	$Co(OAc)_2$	0.004 g (6.00)	<i>p</i> -Xylene	KOH (0.50)	20
2	Co(II)-NHAp	0.18 g (6.00)	<i>p</i> -Xylene	KOH (0.50)	90
3	Co(II)-NHAp	0.18 g(6.00)	<i>p</i> -Xylene	_ ``	10
4	Co(II)-NHAp	0.18  g(6.00)	DMF	KOH (0.50)	5
5	Co(II)-NHAp	0.18 g(6.00)	<i>n</i> -Hexane <sup>c</sup>	KOH (0.50)	0
6	Co(II)-NHAp	0.18  g(6.00)	Toluene	KOH (0.50)	70
7	Co(II)-NHAp	0.18  g(6.00)	$H_2O$	KOH (0.50)	0
8	Co(II)-NHAp	0.18 g(6.00)	MeOH <sup>c</sup>	KOH (0.50)	0
9	Co(II)-NHAp	0.18  g(6.00)	$EtOH^{c}$	KOH (0.50)	0
10	Co(II)-NHAp	0.18 g(6.00)	EtOAc <sup>c</sup>	KOH (0.50)	0
11	Co(II)-NHAp	0.18  g(6.00)	$CH_3CN^c$	KOH (0.50)	5
12	NHAp	0.18 g	<i>p</i> -Xylene	KOH (0.50)	15

<sup>*a*</sup> Reaction conditions: indane (1.00 mmol), solvent (10 mL), KOH (0.50 mmol), air oxidant, 100 °C, 8 h. <sup>*b*</sup> Yield determined by GC analysis with internal standard. <sup>*c*</sup> Reaction conditions: indane (1.00 mmol), solvent (10 mL), KOH (0.50 mmol), air oxidant, reflux, 8 h.

 Table 2
 Aerobic oxidation of various alkyl arenes to corresponding ketones<sup>a</sup>

			Time (h)		Melting point (°C)	
Entry	Arene	Product		$\operatorname{Yield}^{b}(\%)$	Found	Reported
1			8	80	45-46	46-48 (ref. 50)
2		O C	6	75	_	_
3	$\bigcirc \frown \frown$		6	70	_	_
4	$\bigcirc \qquad \qquad$		12	60	_	_
5		O C	8	75	_	_
6			8	90	38-40	39-42 (ref. 51)
7			8	85	80-81	80-82 (ref. 52)
8			8	90	171-173	170-172 (ref. 53)
9	<b>O</b>	o	8	75	_	_
10		ОН	24	0	_	_

<sup>a</sup> Reaction conditions: alkyl arene (1.00 mmol), Co-NHAp (0.18 g), *p*-xylene (10 mL), KOH (0.50 mmol), air oxidant, 100 °C. <sup>b</sup> Yield determined by GC analysis.

different size. The chemical composition of the Co–NHAp was investigated using energy dispersive spectroscopy (EDS) analysis (Fig. 5c). The EDS spectra illustrated peaks for P, Ca, Co and O, which are the major constituents of Co–NHAp.

In the next step, the catalytic activity of Co-NHAp as a catalyst was investigated in aerobic oxidation of alkyl arenes and alcohols. Optimization studies of the effects of solvents, bases and the amount of catalyst were performed in order to find the best reaction conditions for the aerobic oxidation of alkyl arenes to their corresponding carbonyl compounds (Table 1). To evaluate the effect of solvents, the aerobic oxidation of indane was carried out using different solvents: p-xylene, DMF, n-hexane, toluene, H<sub>2</sub>O, MeOH, EtOH, EtOAc and CH<sub>3</sub>CN. As indicated in Table 1, p-xylene was found to be the most suitable solvent. No reaction took place in water due to insolubility of substrate. Moreover, the oxidation did not proceed in low boiling solvents such as *n*-hexane, MeOH, EtOH and EtOAc. The optimum conditions of reaction were obtained using 6 mol% of Co-NHAp in the presence of 0.50 mmol KOH as a base, p-xylene as a solvent and at 100 °C (Table 1) (Scheme 1). As indicated in Table 2 (entry 10), toluene due to the less reactivity of primary benzylic C-H bond could not be oxidized under the same reaction conditions and reaction did not proceed even after 24 h.

Although the oxidation of C–H groups is thermodynamically favorable, it also has large activation barriers that translate into their characteristic inert nature against most reagents. This lack of reactivity is because C–H bonds are strong, non-polarized, and localized, with a highly stabilized HOMO and a high lying



Table 3 Optimization of the reaction conditions for aerobic oxidation of alcohols<sup>a</sup>

Scheme 1 Oxidation of alkyl arenes using Co-NHAp

LUMO. Therefore highly reactive oxidizing reagents are required to overcome these barriers, and this most commonly compromises selectivity.<sup>54-56</sup> To test the site selectivity of this catalyst system, molecules with different secondary sites were oxidized (Table 2, entries 3, 4, 5). According to GC analysis the ketone product shown in Table 2 was the only product observed for these substrates and it is apparent that this catalyst system mediates the benzylic oxidation preferentially over other oxidized products *via* more reactive benzylic C–H abstraction.

In continue, optimization studies of the effects of solvents, bases and the amount of catalyst were performed in order to find the best reaction conditions for the aerobic oxidation of alcohols (Table 3). To evaluate the effect of solvents, the aerobic oxidation of diphenylmethanol was carried out using different solvents: p-xylene, DMF, n-hexane, toluene, H<sub>2</sub>O, MeOH, EtOH, EtOAc, THF, CH<sub>2</sub>Cl<sub>2</sub>, AcOH and CH<sub>3</sub>CN. As indicated in Table 3, *p*-xylene was found to be the most suitable solvent. Similar to arenes, no reaction took place in water due to insolubility of substrate. Moreover, the oxidation did not proceed in low boiling solvents such as n-hexane, MeOH, THF and CH<sub>2</sub>Cl<sub>2</sub>. In polar and protic solvents, hydrogen bond between NHAp and solvent can be formed and it leads to deactivation of the catalyst and difficult adsorption of substrate on the surface of the catalyst. No reaction was observed in these solvents which may be explained by this relatively weak interactions between catalyst and the substrate. The optimum conditions for aerobic



Scheme 2 Oxidation of alcohols using Co-NHAp.

Entry	Catalyst	Amount of catalyst (mol%)	Solvent	Base (mmol)	$\operatorname{Yield}^{b}(\%)$
1	Co(II)-NHAD	0.06 g (2.00)	<i>p</i> -Xvlene	KOH (0.50)	20
2	Co(II)-NHAD	0.12 g (4.00)	<i>p</i> -Xvlene	KOH (0.50)	50
3	$Co(\pi)$ -NHAp	0.18 g (6.00)	<i>p</i> -Xylene	KOH (0.50)	93
4	Co(II)-NHAp	0.18  g(6.00)	<i>p</i> -Xylene	$K_2CO_3(0.50)$	5
5	Co(II)-NHAp	0.18 g(6.00)	<i>n</i> -Hexane	KOH (0.50)	0
6	Co(II)-NHAp	0.18  g(6.00)	Toluene	KOH (0.50)	80
7	Co(II)-NHAp	0.18  g(6.00)	$H_2O$	KOH (0.50)	0
8	Co(II)-NHAp	0.18 g(6.00)	MeOH <sup>c</sup>	KOH (0.50)	0
9	Co(II)-NHAp	0.18  g(6.00)	EtOH <sup>c</sup>	KOH (0.50)	0
10	Co(II)-NHAp	0.18 g(6.00)	EtOAc <sup>c</sup>	KOH (0.50)	0
11	Co(II)-NHAp	0.18  g(6.00)	$CH_3CN^c$	KOH (0.50)	5
12	Co(II)–NHAp	0.18  g(6.00)	$CH_2Cl_2^{\ c}$	KOH (0.50)	0
13	Co(II)–NHAp	0.18  g (6.00)	$\mathrm{THF}^{c}$	KOH (0.50)	0
14	Co(II)–NHAp	0.18  g(6.00)	DMF	KOH (0.50)	15
15	Co(II)–NHAp	0.18  g (6.00)	AcOH	KOH (0.50)	25
16	Co(II)–NHAp	0.18  g (6.00)	<i>p</i> -Xylene	_	5
17	$Co(OAc)_2$	0.004 g (6.00)	<i>p</i> -Xylene	KOH (0.50)	55
18	NHAp	0.18 g	<i>p</i> -Xylene	KOH (0.50)	30

<sup>*a*</sup> Reaction conditions: diphenylmethanol (1.00 mmol), solvent (10 mL), air oxidant, 80 °C, 3 h. <sup>*b*</sup> Yield determined by GC analysis with internal standard. <sup>*c*</sup> Reaction conditions: diphenylmethanol (1.00 mmol), solvent (10 mL), air oxidant, reflux, 3 h.

#### Table 4 Aerobic oxidation of various alcohols to corresponding aldehydes and ketones<sup>a</sup>

					Melting poin	t (°C)
Entry	Alcohol	Product	Time (h)	Yield <sup><math>b</math></sup> (%)	Found	Reported
1	OH OH		4	85	_	_
2	ОН	O H	4	95	_	_
3	OH		5	85	79–81	80-82 (ref. 52)
4	OH O		3	95	93–95	93-95 (ref. 57)
5	OH		5	80	_	_
6	OH C		6	93	44-46	46-48 (ref. 50)
7	ОН		5	95	39-40	39-42 (ref. 51)
8	ОН		6	65	_	_
9	HO		6	70	_	_
10	Br	Br	6	80	55-57	58–60 (ref. 58)
11	СІ		6	75	43-46	45-47 (ref. 59)
12	O <sub>2</sub> N OH	0 <sub>2</sub> N	5	75	106-107	105–107 (ref. 60)
13	Ме	Me	5	70	_	_
14	МеО	MeO	5	65	_	_
15	Он		8	75	_	_
16	ОН	O O	8	75	_	_
17	он	o	8	70	40-42	40-42 (ref. 50)

					Melting point (°C)	
Entry	Alcohol	Product	Time (h)	Yield <sup><math>b</math></sup> (%)	Found	Reported
18	ОН		8	78	_	_

<sup>*a*</sup> Reaction conditions: alcohol (1.00 mmol), Co–NHAp (0.18 g), KOH (0.50 mmol), *p*-xylene (10 mL), air oxidant, 80 °C. <sup>*b*</sup> Yield determined by GC analysis with internal standard.

oxidation reaction of alcohols were obtained using 6 mol% of Co-NHAp in the presence of 0.50 mmol KOH in *p*-xylene at 80  $^{\circ}$ C (Table 3) (Scheme 2).

In order to investigate the scope and limitation of this catalysis system, various types of alkyl arenes, benzylic, allylic and aliphatic alcohols, both primary and secondary, have been successfully used (Tables 2 and 4). The oxidation reaction were proceeded to produce corresponding carbonyl compounds of alkyl arenes and alcohols at various times and in good yields with high selectivity using this catalytic system. It has to be noted that, the aerobic oxidation of various substituted benzyl

alcohols (containing both electron-withdrawing and electron-

releasing groups) was explored and as indicated in Table 4 (entries 9–14), in all cases almost same results were found.

The comparison of catalytic activity of Co–NHAp as a heterogeneous catalyst with previously reported cobalt containing catalytic systems which are used in oxidation reaction of alkyl arenes and alcohols is presented in Table 5. Using air as a green and inexpensive oxidant is the main advantage of this work.

Although the mechanism of this reaction has not been studied, it probably proceeds through the removal of a hydrogen atom from the carbon attached to the hydroxyl

Table 5 Comparison of literature catalysts and this work for oxidation of benzyl alcohol

Entry	Catalyst	Oxidant	Reagent/base	Solvent	Temperature (°C)	Molar ratio of substrate to cobalt	Time (h)	Yield (%)	Ref.
1	Co(II)complex-SiO <sub>2</sub>	$O_2$	NHPI	CH <sub>3</sub> CN	60	1:0.002	55	94	61
2	Co(II)-complex	TBHP	_	CH <sub>3</sub> CN	82	1:0.010	5	85	62
3	CoL <sub>1</sub>	NaOCl	_	[EMIM]Cl	25	1:0.200	0.25	94	63
4	Co(II)-SBC	_	Pyridine	H <sub>2</sub> O	80	1:0.005	4	88	64
5	[Co]	TBHP	_	CH <sub>3</sub> CN	82	1:0.010	48	93	65
6	Co-Si/SBA-15	TBHP	_	Hexane	70	1:0.001	6	87	66
7	Na-Co-POM	$H_2O_2$	_	$H_2O$	100	1:0.001	3	97	67
8	Со-МНАр	Air	КОН	<i>p</i> -Xylene	80	1:0.060	4	95	—



Scheme 3 Plausible mechanism of the aerobic oxidation.



Fig. 6 Reusability of the catalyst for oxidation of diphenylmethanol by Co–NHAp.

group of alcohols or from the benzylic position of alkyl arenes by superoxocobalt(m),<sup>44,68–70</sup> as shown in Scheme 3.

Finally, recyclability of catalyst was investigated. For this purpose, catalyst was separated after completion of oxidation reaction and was washed with ethanol, dried in oven and it was reused for five times without any significant decrease in its activity and selectivity (Fig. 6).

### 4. Conclusions

In conclusion, we have reported the application of Co–NHAp as an effective catalyst for selective aerobic oxidation of alkyl arenes and alcohols to their corresponding carbonyl compounds. It was found that this catalysis system is highly efficient and selective for the oxidation of various secondary benzylic C–H bond. It is worth mentioning that oxidation of toluene, a primary benzylic C–H bond, did not take place. Further, it is more efficient for the oxidation of secondary benzylic alcohols and less efficient for aliphatic primary and secondary alcohols. To the best of our knowledge, this novel heterogeneous catalyst has not been reported previously for aerobic catalytic oxidations of alkyl arenes and alcohols. Advantages of this heterogeneous catalyst are using NHAp as a natural support, air as a green oxidant, simple procedures, high efficiency and excellent reusability.

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