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Micellar catalysis for partial oxidation of toluene to benzoic acid in supercritical CO_2: effects of fluorinated surfactants

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Abstract

One of the key hindrances on development of solid catalysts containing cobalt species for partial oxidation of organic molecules at mild conditions in conventional liquid phase is the severe metal leaching. The leached soluble Co species with a higher degree of freedom always out-performs those of solid supported Co species in oxidation catalysis. However, the homogeneous Co species concomitantly introduces separation problems. We have recently reported *for the first time*, a new oxidation catalyst system for the oxidation of organic molecules in supercritical CO_2 using the principle of micellar catalysis. $[CF_3(CF_2)_8COO]_2Co{\cdot}xH_2O$ (the fluorinated anionic moiety forms aqueous reverse micelles carrying water-soluble Co^{2+} cations in $scCO_2$) was previously shown to be extremely active for the oxidation of toluene in the presence of sodium bromide in water–CO_2 mixture, giving 98% conversion and 99% selectivity to benzoic acid at 120 °C. In this study, we show that the effects of varying the type of surfactant counterions and the length of the surfactant chains on catalysis. It is found that the use of $[CF_3(CF_2)_8COO]_2Mg{\cdot}yH_2O$/Co(II) acetate is as effective as the $[CF_3(CF_2)_8COO]_2Co{\cdot}xH_2O$ and the fluorinated chain length used has a subtle effect on the catalytic rate measured. It is also demonstrated that this new type of micellar catalyst in $scCO_2$ can be easily separated via CO_2 depressurisation and be reused without noticeable deactivation.

Keywords: Micellar catalysis; Partial oxidation; Toluene; Supercritical CO_2; Fluorinated surfactants; Cobalt; NaBr

1. Introduction

Partial oxidation of hydrocarbons with air or molecular oxygen is of a great industrial importance because relatively cheap petroleum hydrocarbon feedstocks, such as alkanes, olefins, and aromatics can be converted into more valuable oxygenated ‘building blocks’ for further chemical processing [1]. The primary industrial method employs pressurised air in *acetic acid* using simple Co^{2+} species in the presence of ionic promoter(s) (Mn ions and/or bromide) [1–3]. The use of acetic acid as a solvent is apparently crucial but its role is not well understood. It has been suggested that acetic acid provides a unique polar medium for the interactions of ionic cobalt salt/promoter with hydrocarbons in air, and it could facilitate electron transfer between Co(II) and Co(III) with acetate/acetic ligands during catalysis. However, with increasingly demanding environmental legislation, public and corporate pressure, and the disadvantages of this homogenous technology, the process is becoming less economically competitive [4]. Low energy efficiency due to decarboxylation of solvent and products, use of corrosive and toxic acetic acid, difficulty in solvent and catalyst recovery, and explosion hazards associated with organic solvent and dioxygen at high concentration (with reported explosions) are obvious [5]. There have been some recent developments with solid catalysts containing Co species for

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oxidation of organic molecules in solid–liquid interface without the use of acetic acid. It is however, found that there is always a severe metal leaching problem and the anchored Co species is not as active as the homogenous Co counterparts [6].

Supercritical carbon dioxide ($scCO_2$) is considered as an ecologically benign fluid [7] because of their non-toxic, chemically inert, and non-combustible nature. It has excellent mass transport properties and can facilitate product/catalyst separation by a simple depressurisation. The high expense and effort associated with the use high-pressure installations could be compensated by a closed loop system with simple recovery and separation [8]. It is particularly noted that $scCO_2$ recently is receiving considerable and even increasing interest as a versatile new medium for a variety of types of catalysis reactions, including free-radical polymerisation [9], hydroformylation [10], enzymatic processes [11], hydrogenation [12], Friedel–Crafts alkylations [13], and oxidations [14–16]. Thus, it would be very interesting to carry out partial aerial oxidation reactions over the Co^{2+} species in the $scCO_2$ as an alternative solvent medium.

Despite these encouraging results, its inability to disperse ionic/polar species (catalytically active Co^{2+} species and polar organic substrates/products commonly involved in oxidations) in the non-polar $scCO_2$ is the major problem regarding the catalytic oxidations. The poor interfacial contact between the substrates (dissolved in $scCO_2$) and catalytically active ionic species and mass transfer problems of polar oxidised products in the medium would have to be overcome.

On the other hand, the recent work on establishing aqueous microemulsion in $scCO_2$ may provide a solution to this problem. In 1994, Harrison et al. [17] showed that a bifurcated surfactant with fluorocarbon/hydrocarbon hybrid tails (F_7H_7) could form reverse micelles in CO_2 and the water-to-surfactant ratio (W) is as high as 32 at 25 °C and 231 bar. In 1996, a new fluoroether surfactant, ammonium carboxylic perfluoropolyether (PFPE) was demonstrated to form stable reverse aqueous micelles in $scCO_2$ [18]. The applications of water/$scCO_2$ microemulsion were also extensively investigated. Silver [19–21], copper [21] and silver halide [22] nanoparticles were successfully synthesised in line with this idea; however, no application in micellar oxidation catalysis in $scCO_2$ was yet disclosed before our preliminary study [23].

In fact, there are a lot of potential advantages of carrying out catalytic reactions in a micellar medium. Micelles can in principle: pre-concentrate the reactants (catalysts) within their small volumes; stabilise substrates, intermediates or products; and orient substrates so that ionisation potentials and oxidation–reduction properties, dissociation constants, physical properties, quantum efficiencies and reactivities could be altered or tuned [24]. With the unique properties of $scCO_2$, we have recently demonstrated that micellar catalysis can be carried out for air oxidation of toluene in the entirely organic-free environment (no organic catalyst ligand nor organic solvent used for any possible unselective C–H attacks) using fluorinated Co(II)/NaBr in water–$scCO_2$. Typically, for toluene oxidation, 98% conversion and 99% selectivity to benzoic acid with a high turnover frequency ($TOF = 6.19 \times 10^{-3}\ s^{-1}$) were achieved [23].

This current study is based upon the extension of our earlier work by focusing on the effects of varying the type of fluorinated surfactant ion pairs, the chain length of fluorinated anion and nature of cations used. A brief investigation on the recovery and reusability of this new catalyst has also been carried out.

2. Experimental

2.1. Synthesis of fluorinated surfactants

Bis(nonadecafluorodecanoate) cobalt(II) ($[CF_3(CF_2)_8COO]_2Co\cdot xH_2O$, designated as F-Co in this manuscript) was synthesised by addition of 2 mmol nonadecafluorodecanoic acid (NDFDA, 97%, Aldrich) to a 100 ml flask containing 25 ml pre-dried diethyl ether. Two millimoles pre-dried (in high vacuum) $CoCO_3$ was added into the solution under stirring. The mixture was allowed to reflux at 40 °C for 24 h under N_2. Product (soluble in diethyl ether) was separated by filtration and purified using a silica gel (Aldrich, 0.035–0.070 mm, pore diameter ca. 6 nm) packed column with diethyl ether as a mobile phase. The solvent was then removed at room temperature and a pink solid was obtained. Microanalysis and atomic absorption showed the material corresponded to $(CF_3(CF_2)_8CO)_{1.95}Co\cdot xH_2O$; IR (Nujol) showed a strong C=O stretch absorption at 1657 cm^{-1}. UV-Vis (diethyl ether as solvent) showed two maxima, λ_1 at 208 nm, $\varepsilon_1 = 5.35 \times 10^4\ dm^3\ mol^{-1}\ cm^{-1}$; λ_2 at 520 nm, $\varepsilon_2 = 1430\ dm^3\ mol^{-1}\ cm^{-1}$. Melting point was also measured (138–139 °C).

Bis(nonadecafluorodecanoate) magnesium ($[CF_3(CF_2)_8COO]_2Mg \cdot yH_2O$, designated as F-Mg) and Nonadecafluorodecanoate potassium ($CF_3(CF_2)_8COOK \cdot zH_2O$, designated as F-K) were also synthesised with $MgCO_3$ or K_2CO_3 as the starting materials in the similar method as described for the F-Co. IR showed a strong C=O stretch absorption at 1661 cm^{-1} for both of them. It is however, noted that the water of crystallisation of these three compounds was not determined. It was observed that F-Mg is highly soluble in diethyl ether with a melting range of 152–154 °C, but F-K is not soluble in diethyl ether but soluble in methanol with the highest melting range of 205–207 °C amongst three fluorinated ion pairs synthesised.

Nonadecafluorodecanoate ammonium ($CF_3(CF_2)_8COONH_4$, designated as F-NH_4) was synthesised by addition of 2 mmol nonadecafluorodecanoic acid into a 100 ml flask containing 25 ml methanol. Five millimoles of 2 M ammonia in methanol (Aldrich) was added into the solution under stirring. The mixture was allowed to reflux at 40 °C for 24 h. The product (soluble in methanol other than diethyl ether) was collected by removing solvent and excess ammonia at 60 °C. IR showed a strong C=O stretch absorption at 1670 cm^{-1}. The ammonium salt is highly soluble in methanol with a melting range of 173–174 °C. $CF_3(CF_2)_{12}COONH_4$ (designated as F_L-NH_4) and $CF_3(CF_2)_3COONH_4$ (designated as F_S-NH_4) were also synthesised in the same manner with $CF_3(CF_2)_{12}COOH$ (Aldrich) and $CF_3(CF_2)_3COOH$ (Aldrich) as the starting material, respectively. IR showed a strong C=O stretch absorption at 1685 cm^{-1} for F_S-NH4 and 1683 cm^{-1} for F_L-NH_4. Both of them are soluble in methanol with a melting range of 189–190 and 125–126 °C, respectively.

It is particularly noted that the IR (Nujol) characterisation of the samples is very important to confirm whether the conversions of molecular acid (NDFDA) to acid anions have readily been achieved or not. The acid showed a weak absorption at 1717 cm^{-1} (broad), however, a characteristic strong C=O absorption at 1657–1685 cm^{-1} (sharp) when it is in carboxylic anion form.

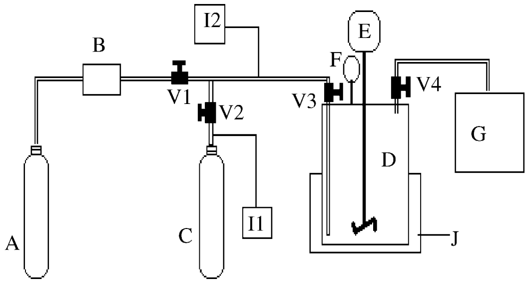

Fig. 1. Schematic apparatus design. A: carbon dioxide cylinder; B: gas booster compressor; C: oxygen cylinder; D: autoclave; E: overhead stirrer; F: pressure gauge, G: GC; I1: high-pressure indicator (0–350 bar); I2: low-pressure indicator (0–10 bar); V1, V2, V3 & V4: high-pressure valve; J: programmable heater.

2.2. Catalytic activity test

All the experiments were carried out in a 160 ml Parr autoclave with a Teflon cup insertion in a batch process shown as in Fig. 1. The valid volume of the reactor was ca. 111 ml. Fluorinated surfactants, cobalt (II) acetate tetrahydrate (Aldrich, +98%), NaBr (Aldrich, +99%) and toluene (Aldrich, 99.8%) were added into the autoclave directly, followed by adding a small amount of water and a trace of internal standard (benzene or methane). Ten bars dioxygen (BOC Gases) was charged from cylinder directly followed by charging carbon dioxide (BOC Gases) using a booster (Haskel) to 150 bar. The reaction was stirred at the set temperature for the desired reaction time. Stirring was achieved by means of an overhead magnetic stirrer; the motor was set at 1/2 maximum speed, giving approximately 360 rpm. Visual inspection through a sapphired windowed reactor to observe the physical properties of the mixture under the reaction conditions has been carried out. A clear disappearance of a phase boundary and the formation of completely transparent fluid clearly suggest that the mixture was in supercritical state at 120 °C at or above 120 bar. Quantities of toluene and the internal standard (20 μl benzene) were monitored intermittently at a regular interval (1 h) with an online GC (Perkin Elmer) by sampling a very small volume of supercritical fluid under the reaction conditions using a special high-pressure valve. Thus, it was anticipated that the lost of the small quantity of reaction mixture during the monitors would not critically affect the kinetic analysis. It was found that the amount of the hydrocarbon was readily soluble in the supercritical carbon dioxide mixture prior reaction. The GC analysis showed the disappearance of toluene in the supercritical fluid. After the experiment, all products were collected by releasing the supercritical fluid into a trap containing 50 ml CH_3CN at dry ice temperature. The products in autoclave were also extracted by another 50 ml CH_3CN. The two solutions were combined and analysed quantitatively using HPLC (Perkin Elmer) equipped with a UV-Vis detector. HPLC showed that the main product of the reaction was primarily, the benzoic acid (with only traces of benzaldehyde and benzyl-alcohol) with some remaining quantity of toluene. The conversion obtained from the HPLC matched with the GC data.

3. Results and discussion

3.1. Conversion and selectivity

It was shown from our previous results [23] that the traditional homogeneous catalyst system (cobalt acetate + sodium bromide) is not active (0.1% conversion at 12 h) due to the insolubility of these inorganic salts in $scCO_2$. An emulsion catalysis working state was introduced using F-Co in the presence of a small amount of water in $scCO_2$. Extremely high conversion and selectivity were achieved with an excellent turnover frequency [24]. The presence of water, supercritical CO_2 ($scCO_2$ vs. N_2) and the ionic bromide promoter (NaBr) appear to be crucial components for an optimum catalytic system. To extend this work, here, we have carried out a very brief study on the reusability of catalyst system and investigated whether catalyst deactivation occurred within the given period of time for the catalysis reaction. The entries 1 and 2 of Table 1 represent the 1st and 2nd subsequent test of the new catalyst system (the 1st test was analysed after 12 h, where the toluene conversion was virtually complete; the 2nd subsequent test was carried out by blending the product mixture left over from the 1st test (after the CO_2 depressurisation) with the same quantity of toluene followed by analysis after another 12 h). It should be borne in mind that this experiment does not yet demonstrate the potential separation advantage using the supercritical fluid (no attempt to separate the product from the catalyst). However, the preliminary results clearly show that the complete conversions were again achieved, which suggest the micellar catalyst system can be reconstructed in $scCO_2$ in the subsequent testing (detailed comparison of the rates of reaction at different times between 1st and 2nd subsequent test was also carried out indicating no sign of deactivation). Two new fluorinated surfactant ion pairs together with the simple $Co(OAc)_2$ salt were tested in order to verify whether the F-Co compound is pre-requisitely needed for the excellent catalysis. It was shown from Table 1 that high conversions (>91%) and selectivities (>95%) were also obtained at all other cases at prolonged period of time although some variations in the initial reaction rates were noted. Thus, the success in the replacement of F-Co with other fluorinated surfactant anions (F-Mg/Co(II) acetate) may markedly widen the application scope of this system since these results suggest that cationic species may

Table 1
Oxidation of toluene in water–$scCO_2$ with different fluorinated surfactants[a]

Entry	Toluene (mmol)	Surfactant (0.25 mmol)	Catalyst (Co^{2+}/Br^-) (0.25 mmol/0.2 mmol)	Water (μl)	Time (h)	Conversion (%)	Benzoic acid (S%[b])
1	18.8	F-Co	F-Co/NaBr	400	12	98.0	99.0
2	18.8	F-Co	F-Co/NaBr	400	12	99.1	99.1
3	18.8	F-Mg	$Co(OAc)_2$/NaBr	400	16.5	99.8	99.3
4	18.8	F-K	$Co(OAc)_2$/NaBr	400	73.3	98.1	99.3
5	14.1	F-NH_4	$Co(OAc)_2$/NaBr	500	10.5	94.2	97.8
6	14.1	F_S-NH_4	$Co(OAc)_2$/NaBr	500	9.7	95.1	98.2
7	14.1	F_L-NH_4	$Co(OAc)_2$/NaBr	500	12.3	91.3	95.5

[a] Typically reaction conditions (refer Section 2): 10 bar O_2; 150 bar total pressure balanced with CO_2 on 120 °C; 20 μl benzene used as internal standard.

[b] Selectivity/% to benzoic acid, other minor products such as benzaldehyde and benzyl-alcohol, were detected.

be exchangeable with some degree of mobility (within the droplet), despite their difference in binding with the fluorinated anion (mp). It is therefore unnecessary to directly fluorinate the Co species as the inexpensive cobalt acetate is equally effective when in combination with fluorinated anions. It is found that the highest conversion (99.8%) and selectivity (99.3%) were achieved with F-Mg in 16.5 h as similar to the F-Co, but in the case of F-K it took 77.3 h to obtain a comparable conversion of 98.1%. The distinctive slow rate associated with F-K/Co(II) acetate is a very interesting phenomenon since one would expect that exchange of cations by these hard ionic species should have readily occurred in water. We attribute this difference on the catalysis rate to their different behaviours in forming micelles (see discussion below). Three different lengths of fluorinated surfactant anionic moieties with ammonium counterion were synthesised. It is interesting to find that all of them gave nearly a complete conversion at a prolonged period of time (Table 1).

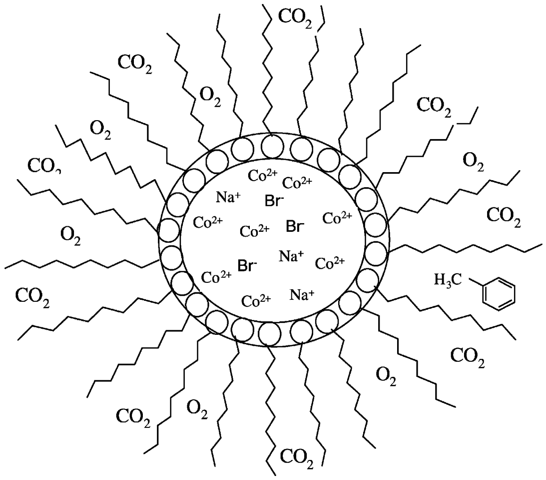

Fig. 3. Scheme of micellar catalysis.

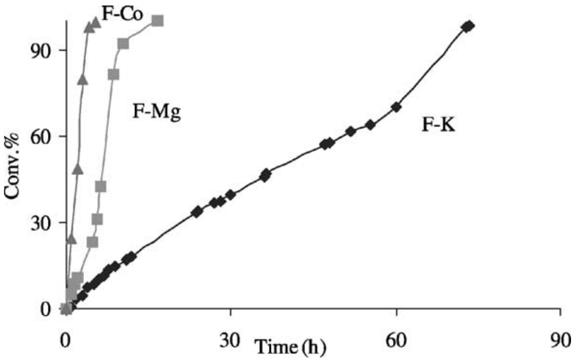

Fig. 2. The effects of counterion on conversion of toluene. Typically conditions: 0.25 mmol fluorinated surfactant; 0.25 mmol Co^{2+}; 0.2 mmol NaBr; 18.8 mmol toluene; 400 μl H_2O; 10 bar O_2 and 150 bar CO_2 @ 120 °C.

3.2. A kinetic study

3.2.1. Counterion effects on catalysis

For the detailed rate analysis, it is shown from Fig. 2 that the highest activity was observed when F-Co was used. A comparable activity was observed in the case of using F-Mg/Co(II) acetate. It is however found that the F-K/Co(II) acetate gave the poorest rate, which required the longest time for the complete conversion of toluene to benzoic acid. It is therefore believed that the exchange of cations within the micelle may not readily occur despite the fact that these ionic pairs should be completely dissociable in water. The structure of reversed ionic micelle in conventional solvent has been extensively studied in the past. It is generally accepted that an incomplete ionisation of the ion pairs is actually obtained (i.e. typically 30% ionised and 70% neutralised by the counterions) in the Stern layer in order to avoid the building up of a local Columbic/hydrophobic repulsions on the small micelle surface (extremely high surface charge density). The degree of counterion binding depends on several factors [26–28]. When the counterions (i.e. Na^+, $NH_4{}^+$, Mg^{2+}, K^+) of salts are added to the micelle, these will compete for the ionic head groups of micelles with the surfactant counterions (i.e. Co^{2+}) as shown in Fig. 3. Thus, displacements can occur depending on the nature of counterions and the head groups, i.e. on the relative affinities of counterions for the head groups [27,29,30]. From the present results, it is thought that the access of the catalytically active Co^{2+} species on the micelle surface by the substrate molecule in $scCO_2$ phase depends critically on the type and quantity of other cations added. High affinity of surfactant anions for K^+ cations (reflected from the high melting range of F-K) has apparently inhibited the Co^{2+} induced catalysis. It is noted that a similar cationic effect was previous observed influencing the solubility of fluorinated carboxylic anion surfactants in $scCO_2$ [25]. From this reference, it was found that

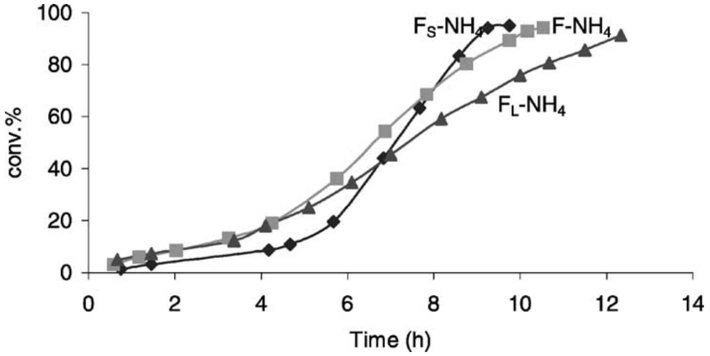

Fig. 4. The effects of surfactant structure on catalysis. Typically conditions: 0.2 mmol fluorinated surfactant; 0.2 mmol Co^{2+}; 0.2 mmol NaBr; 14.1 mmol toluene; 500 μl H_2O; trace methane as internal standard; 10 bar O_2 and 150 bar CO_2 @ 120 °C.

the K^+ salt is virtually insoluble in $scCO_2$ but the Na^+ is a fairly soluble salt. Thus, this clearly indicates the K^+-fluorinated carboxylic anion surfactant ion pair is indeed very strong and stable. However, a further investigation would be required to investigate the ionic interaction/exchange.

3.2.2. The effects of surfactant structure on catalysis

By following the conversion-time performances of the three different lengths of surfactants (F_S-NH_4=$CF_3(CF_2)_3COONH_4$; F-NH_4=$CF_3(CF_2)_8COONH_4$; F_L-NH_4=$CF_3(CF_2)_{12}COONH_4$), it is interesting to find that the surfactant with shortest chain gave the highest reaction rate after the induction period (Fig. 4). The surfactant with longest chain, on the other hand, gave the slowest reaction rate. Similar reaction profiles showing the same rate order (F_S-NH_4 > F-NH_4 > F_L-NH_4) upon the repeated measurements. At the present stage, it is not yet known how and why the use of shorter chain length sustains a faster rate. However, it is well known that fluorinated moiety of this type of surfactant is fluorophilic/CO_2-philic but hydrophobic/organophobic in nature. It is also well documented that a small change in surfactant structure can induce changes in the surface properties and the rigidity of the micelle, which markedly affect the reactivity of the substrates [31,32]. Thus, we postulate that the observation may be attributed to the poorer affinity of toluene to longer fluorinated chain; the richer fluorinated moiety possibly expels the toluene from access the surface of micelles accounting for a slower rate. Further work is in now progress to determine the rate differences over different lengths/structures of fluorinated chains.

4. Conclusions

The water–$scCO_2$ is shown to be an excellent alternative solvent to acetic acid for the important Co(II) air-oxidation reaction using micellar catalysis. The organic-free ligand/stabiliser and solvent system containing no C–H structure with an excellent dispersion of Co(II)/NaBr species are well suited for selective oxidation reactions. In addition, the concept of using the H_2O–$scCO_2$ emulsion to bring species of a very different polarity into contact with excellent mass and heat transfers in sustaining a fast catalytic reaction is also clearly demonstrated from this study. It is apparent from our study that H_2O–$scCO_2$ as a solvent will exhibit real advantages by providing a ‘green’ process with safer operation, easier separation and purification, high catalytic activity with selectivity and with no loss of solvent by oxidation. Because of the unique properties of $scCO_2$ as a solvent (pressure and temperature tunable solvency), the dispersed micelles containing Co^{2+} can catalyse a rapid hydrocarbon aerial oxidation (O_2 is completely miscible in $scCO_2$), which also facilitates separation/reuse of the catalytic micellar components in $scCO_2$. Here, we show that varying fluorinated chain length, nature of fluorinated surfactant ion pairs, salt addition, play a crucial role in affecting the rate of micellar oxidation catalysis in $scCO_2$.

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