Article

Catalytic Transfer Hydrogenation of Biobased HMF to 2,5-Bis-(Hydroxymethyl)Furan over Ru/Co$_3$O$_4$

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Abstract: 2,5-Bis-(hydroxymethyl)furan (BHMF) is an important biomass-based platform chemical that can be derived from the hydrogenation of biomass-based 5-hydroxymethylfurfural (HMF). In this paper, the formation of BHMF from HMF via the catalytic transfer hydrogenation (CTH) process, using isopropanol as the hydrogen source and Ru/Co$_3$O$_4$ as the catalyst, was studied. The results revealed that the Ru/Co$_3$O$_4$ catalyst displayed a high catalytic efficiency, and that a BHMF yield of up to 82% was obtained at 190 °C in 6 h. Moreover, it was found that the recovered Ru/Co$_3$O$_4$ exhibited a similar catalytic activity to the pristine Ru/Co$_3$O$_4$ catalyst. These results supported the conclusion that the present CTH process is an attractive green route for the synthesis of BHMF from biomass-based HMF.
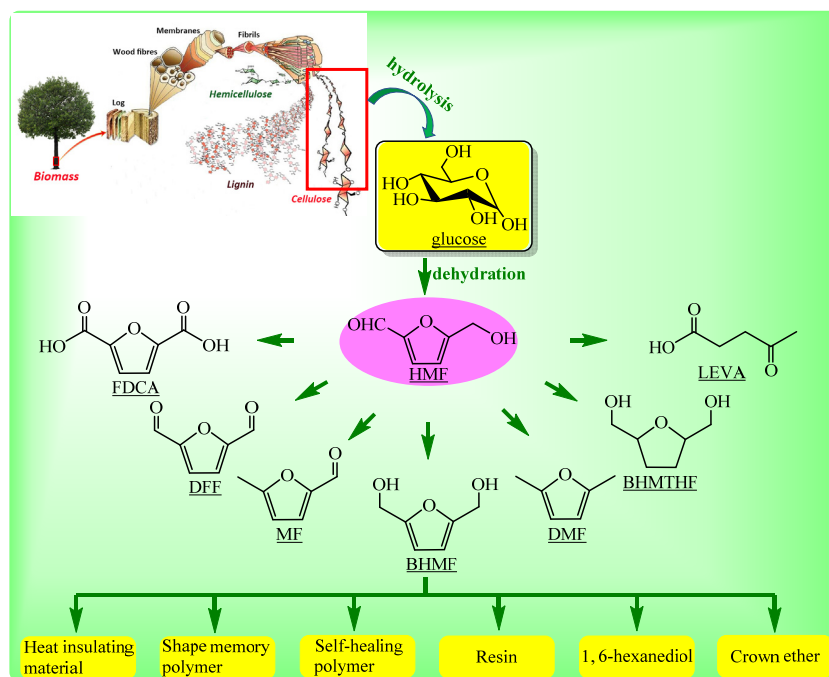
Keywords: biomass; 5-hydroxymethylfurfural; 2,5-bis-(hydroxymethyl)furan; catalytic transfer hydrogenation; ruthenium based catalyst

1. Introduction

The development of efficient production technologies for biomass-based fuels and chemicals has received much attention [1,2]. In this context, 5-hydroxymethylfurfural (HMF), which was identified as a key precursor and called a "sleeping giant" for the synthesis of biofuels and high value-added chemicals, has been widely studied. As shown in Figure 1, HMF possesses two functional groups: an aldehyde and an alcohol, so it can be easily converted into value-added compounds to be used in a wide variety of chemical manufacturing applications and industrial products [3]. Importantly, HMF can be hydrogenated to 2,5-bis-(hydroxymethyl)furan (BHMF), which is a monomer for the synthesis of heat insulating material [4], resins, and crown ethers [5]. Moreover, BHMF is a promising diol that can be used either directly for the synthesis of shape memory and self-healing polymers or for the synthesis of 1,6-hexanediol, which is also an important polymer precursor [6].

Several studies reported the conversion of HMF to BHMF. For example, Kang et al. [7] reported that HMF is converted to BHMF via a Cannizzaro reaction using ionic liquids as a recyclable solvent under water-free conditions, and an excellent yield was obtained when [EMIm]TFSI was used as the solvent. Subbiah et al. [8] reported that a 40% BHMF yield can be obtained through the Cannizzaro reaction of HMF using NaH in dry THF. Usually, 5-hydroxymethylfuranoic acid (HMFA) is also formed (in an equimolar amount) during the same course of Cannizzaro reactions, which results in

challenges in the subsequent separation processes. In addition to the Cannizzaro reaction, the catalytic hydrogenation of HMF can lead to the formation of BHMF. Zhu et al. [9] reported a 99.1% selectivity for the conversion of HMF to BHMF at 100 °C over 3 h of reaction in ethanol with Cu–ZnO as the catalyst. Chatterjee et al. [10] reported that Pt/MCM-41 could be used as an efficient catalyst for the hydrogenation of HMF to BHMF, and 98.9% selectivity of BHMF was obtained at 35 °C and 0.8 MPa H_2. In these studies, molecular hydrogen was used.

Figure 1. 2,5-Bis-(hydroxymethyl)furan (BHMF) is a biomass-based platform chemical, which can be made from 5-hydroxymethylfurfural (HMF).

The catalytic transfer hydrogenation (CTH) process has been reported as an efficient and simple method for the reduction of biomass-derived chemicals in the absence of molecular hydrogen [11]. The CTH process can also be used for the hydrogenation of HMF to other high value-added chemicals, such as 2,5-dimethylfuran (DMF) [12]. Therefore, the CTH process may be an alternative for the conversion of HMF to BHMF if a suitable catalyst can be identified.

Ruthenium is a cost-effective noble metal for the catalytic hydrogenation reaction [13,14]. In the present work, Ru/Co_3O_4 was prepared by a co-precipitation method and used as a catalyst for the CTH of HMF to BHMF, while isopropanol was used as the hydrogen donor. The study would be helpful in assessing the feasibility of CTH of HMF to BHMF in the presence of a Ru/Co_3O_4 catalyst, which will provide a potential route for the green synthesis of BHMF from biomass-based materials.

2. Results and Discussion

2.1. CTH of HMF to BHMF

The detailed results regarding the effect of the reaction temperature and time are shown in Table 1. It was found that the effect of the reaction temperature on the CTH of HMF to BHMF is significant (Table 1, Entries 1–5). At 130 °C, only 37.1% of HMF was consumed, and the BHMF yield was 24.4%. In contrast, the conversion reached 94.4% when the temperature was elevated to 170 °C, and the BHMF yield was 80.3%. When the temperature was further increased to 190 °C and 210 °C, no residual HMF was found; however, the BHMF yields were decreased to 79.3% and 67.7% due to the further hydrogenation of BHMF to 5-methyl furfuryl alcohol (MFA) (the MFA yield was 9.0% at 190 °C, and

17.2% at 210 °C). In addition to the reaction temperature, the effect of the reaction time is also shown in Table 1 (Entries 4 and 6–7). As shown, the maximum BHMF yield of 82.8% was obtained with an HMF conversion of 100% at 6 h, and no MFA was found. Upon further increasing the hydrogenation time, a small decrease in the BHMF yield was observed due to the further hydrogenation of BHMF to MFA, and a 7.7% and 9.0% MFA yield were found at 8 h and 10 h, respectively.

Furthermore, the catalyst recovery experiment was also performed. In a typical recycling test, the catalyst was separated from the reaction mixture by filtration after reaction and dried at 105 °C for 12 h, followed by $NaBH_4$ reduction. The result showed that the regenerated catalyst exhibited similar catalytic activity to that of the pristine catalyst, the BHMF yield reached 75.2% with an HMF conversion of 95.3% at 170 °C in 10 h, and a recovery efficiency of 94% (Table 1, Entry 8).

Table 1. Catalytic transfer hydrogenation (CTH) of HMF to BHMF in isopropanol using Ru/Co_3O_4 as the catalyst (0.5 wt % HMF, 0.25 wt % Ru/Co_3O_4 and 20 mL of isopropanol).

Entry	T (°C)	t (h)	Conv. (%)	Yield %	
				BHMF	MFA
1	130	10	37.1	24.4	-
2	150	10	66.7	51.7	-
3	170	10	94.4	80.3	-
4	190	10	100	79.3	9.0
5	210	10	100	67.7	17.2
6	190	6	100	82.8	-
7	190	8	100	79.9	7.7
8 *	170	10	95.3	75.2	-

* Recycled Ru/Co_3O_4.

2.2. H_2-TPR Profiles

The H_2-TPR profiles of the three Ru/Co_3O_4 catalysts (calcined, reduced and recycled Ru/Co_3O_4 samples) are shown in Figure 2. As can be observed, the three catalysts are all displaying a two-stage reduction mechanism, and the first peak of each H_2-TPR profile is due to the reduction of Co_3O_4 to CoO [15,16]. It was reported by Zu et al. that the typical H_2-TPR profile of Co_3O_4 has two reduction peaks: the main reduction peak at 330–450 °C with a shoulder peak at 323 °C [15]. The two reduction peaks of calcined Ru/Co_3O_4 are all shifted to a low temperature range, and the maximum reduction peak of calcined Ru/Co_3O_4 is at 250–400 °C with a shoulder peak at 245 °C (Figure 2). This may be due to the existence of Ru, which will promote the reduction of Co_3O_4 and CoO. Besides, a low temperature peak at around 140 °C can be ascribed to RuO_x because the catalyst did not undergo a reduction treatment.
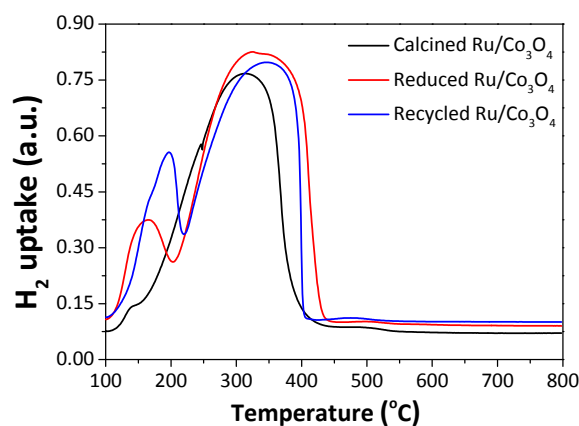
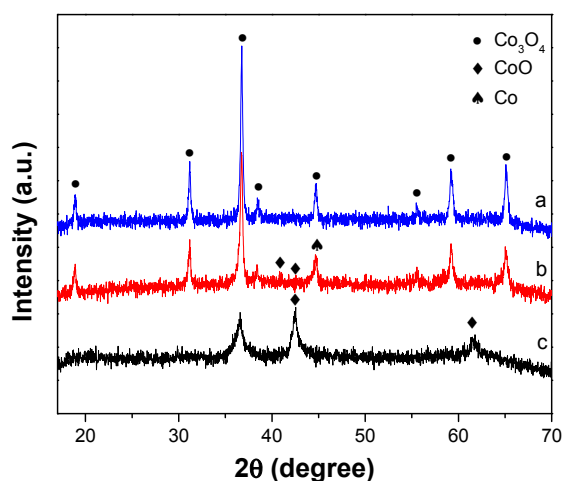**Figure 2.** H_2-TPR of the calcined, reduced, and recycled Ru/Co_3O_4 catalysts.

For the reduced Ru/Co_3O_4 catalyst, the reduction peaks of Co_3O_4 to CoO and CoO to Co have shifted to a low temperature range (165 °C and 200–435 °C, respectively), which is due to the presence of Ru [15]. The reduction peak at around 165 °C should be the overlapping peaks for the reduction of RuO_x to Ru and Co_3O_4 to CoO, indicating that the reduced Ru/Co_3O_4 catalyst has the highest catalytic activity at about 165 °C. These results are consistent with those in Table 1 (Entries 1–5) with respect to the effect of temperature, which showed that the highest BHMF yield was obtained at 170 °C. For the recycled Ru/Co_3O_4 catalyst, the first reduction peak shifts to a high temperature (197 °C) due to the loss of Ru. As a result, the catalytic activity of the recycled Ru/Co_3O_4 catalyst was slightly decreased at 170 °C (Table 1, Entry 8).

In addition, the reduction peak of RuO_x was absent in the reduced and the recycled Ru/Co_3O_4 catalysts, which may be due to a lower RuO_x amount in the reduced and recycled Ru/Co_3O_4 catalyst.

2.3. XRD Patterns

Figure 3 shows the XRD patterns of the calcined, reduced, and recycled Ru/Co_3O_4 catalysts. From Figure 3a, it can be observed that the reflections belong to the diffraction of Co_3O_4 [17]. After the reduction with $NaBH_4$, the intensity of the Co_3O_4 diffraction peaks is slightly lower than the calcined sample, due to the reduction of part of Co_3O_4 to CoO and Co, and their reflections were confirmed in the reduced Ru/Co_3O_4 sample (Figure 3b).

The XRD patterns (Figure 3c) of the recycled Ru/Co_3O_4 samples are different from those of the calcined and reduced catalysts. The characteristic peaks of Co_3O_4 at $2\theta = 18.9°$, $31.3°$, $38.4°$, $44.7°$, $55.6°$, $59.2°$, and $65.2°$, the peak of Co at $2\theta = 44.7°$ are absent, only that at $36.5°$ is identified (although a decrease in its intensity), indicating that Co_3O_4 have been largely reduced to CoO or Co. As a result, characteristic peaks of CoO at $2\theta = 42.3°$ and $61.5°$ were evident. For all of the three catalysts, the characteristic peak of RuO_x could not be found in the XRD patterns, which is possibly due to the high dispersion of RuO_x in minute quantities.


Figure 3. XRD patterns of the calcined (**a**), reduced (**b**), and recycled (**c**) Ru/Co_3O_4 samples.

2.4. TEM Images

The TEM images of the reduced and recycled Ru/Co_3O_4 are shown in Figure 4. The nano-platelets were formed in the reduced Ru/Co_3O_4 catalyst, and the diameters of the particles are all in the range of 20–40 nm (Figure 4a). For the recycled Ru/Co_3O_4 catalyst, the diameters of the particles are larger than the reduced ones, which are all in the range of 30–50 nm (Figure 4c). This may be due to the size aggregation in the recycling process, resulting in decreased catalytic activity (in agreement with a slightly lower BHMF yield in the presence of the recycled Ru/Co_3O_4 catalyst, Table 1, Entry 8), which is in accordance with the H_2-TPR observation.

In addition, although the RuO_x particles were not found in the TEM images, the EDX analyses display that the reduced (Figure 4b) and recycled (Figure 4d) Ru/Co_3O_4 catalysts do contain Ru (in addition to Co and O), indicating that there is a lower RuO_x amount in the reduced and recycled Ru/Co_3O_4 catalysts, which is in accordance with the H_2-TPR observation. In addition, the lower amount of RuO_x particles may be highly dispersed in the matrix, so we cannot find the RuO_x particles in the TEM images [15].
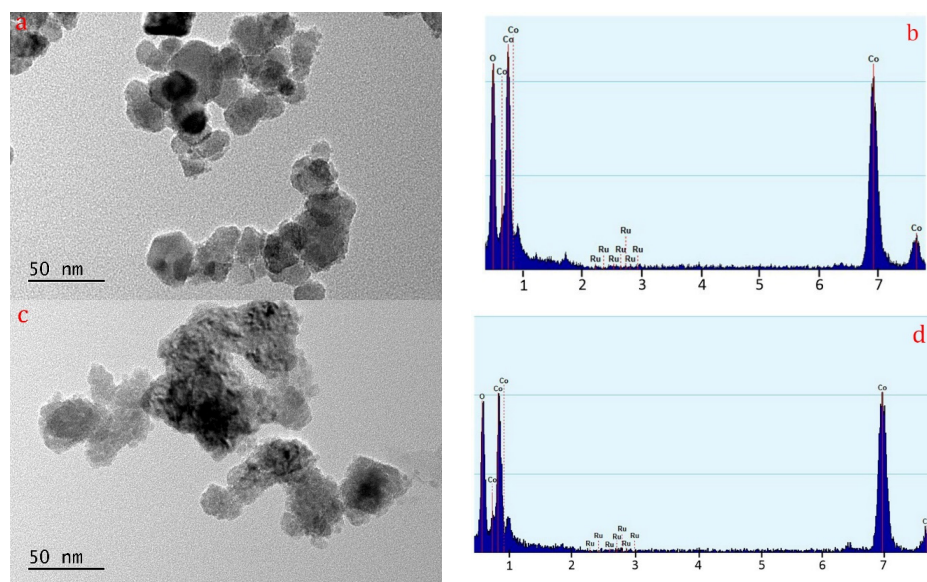

Figure 4. TEM images (**a**,**c**) and EDX (**b**,**d**) of the reduced and recycled Ru/Co_3O_4 samples.

3. Reaction Processes for the CTH of HMF to BHMF

The reaction pathways for the CTH of HMF under the conditions studied are proposed in Scheme 1 based on the published work [18]. The main steps are as follows: (1) the activation of a hydrogen donor (isopropanol) with ruthenium forms a ruthenium hydride (Reaction 1); (2) the generated ruthenium hydride will break to Ru–H and acetone (Reaction 2); (3) Ru–H will react with a carbonyl compound ($O=CR_2$) on HMF to yield Transition Complex I; (4) Generated Transition I will react with isopropanol through a five-membered transition state to attack the carbonyl carbon of HMF and lead to the formation of Transition Complex II; (5) the objective product, BHMF, will be generated with the elimination of ruthenium hydride, which will participate in a new catalytic cycle; (6) a small amount of BHMF can be further hydrogenated to MFA through a CTH route under very strong reaction conditions (Table 1, Entries 4–5 and 7), while no 2,5-dimethylfuran (DMF) was identified in the reaction system, indicating that the present catalytic system cannot lead to the reduction of both hydroxyl groups on BHMF under the conditions studied. This is the primary reason for the high yield of BHMF.

In addition, it was reported by Liu et al. that the etherification of the short chain alkyl alcohols would occur in the presence of Lewis acids [19]. In the present system, it is reasonable to assume that Ru/Co_3O_4 may act as a Lewis acid, and the etherification products of 5-[(1-methylethoxy) methyl] furfural (MMF), 5-hydroxymethyl-2-[(1-methylethoxy)methyl]furan (HMMF), and 2,5-[bis(1-methylethoxy)-methyl]furan (BMMF) may be formed (with isopropanol). 2-methyl-5-[(1-methyletyoxy)methyl]furan (MMMF) may be formed via the CTH of HMMF and isopropanol or the etherification of MFA and isopropanol. The formation of 5-methyl furfural (MFL) may also be possible via the CTH on the hydroxyl group of HMF, and the aldehyde group of MFL can then be further hydrogenated to a hydroxyl group to form MFA. Similarly, MMF can be hydrogenated to HMMF, and HMMF to MMMF, as suggested in the literature [13].
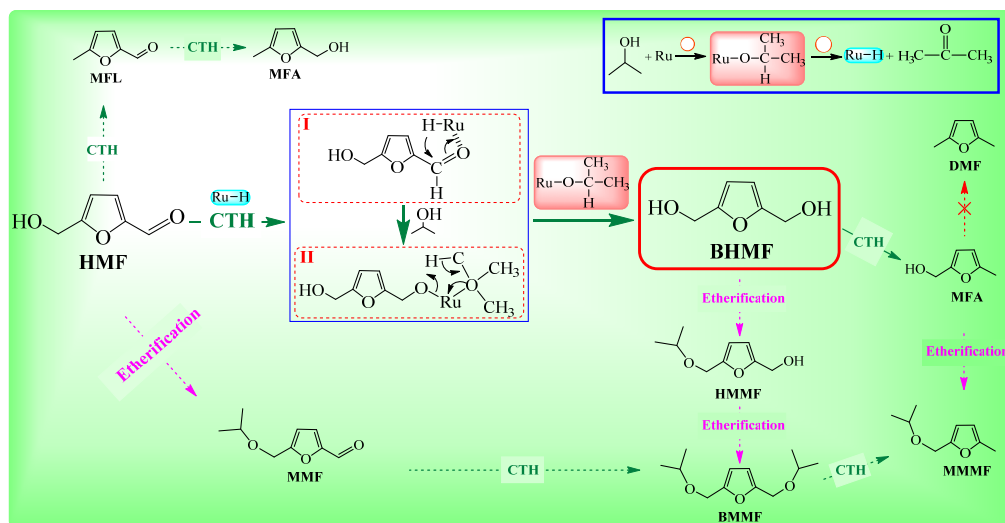
Scheme 1. Proposed reaction pathways of the CTH of HMF to BHMF using the isopropanol and Ru/Co$_3$O$_4$ reaction system.

4. Materials and Methods

4.1. Chemicals and Materials

HMF (80%) was purchased from Tengzhou Wutong Aromatizer Co., Ltd. (Shangdong, China), and RuCl$_3$·H$_2$O was from Aldrich. Other chemicals and solvents, including isopropanol, NH$_3$·H$_2$O, Co(NO$_3$)$_2$·6H$_2$O, Na$_2$CO$_3$, and NaBH$_4$ were bought from Mike Chemical Instruments Co., Ltd. (Hangzhou, China). All chemicals and solvents were used without further purification. Deionized water was used for all experiments.

4.2. Catalyst Preparation

The Ru/Co$_3$O$_4$ precursor was prepared by following a reported procedure in the literature [19]. The obtained mental oxide was reduced using NaBH$_4$ by following a reported procedure [20]. Then, the solution was filtrated and the filtrate was dried at 50 °C for 12 h to obtain a Ru/Co$_3$O$_4$ catalyst.

4.3. Catalytic Activity Tests

The CTH experiments were carried out in a 50 mL cylindrical stainless steel high-pressure reactor with temperature and stirring controllers. For a typical reaction, the reactor was charged with 0.5 wt % HMF, 0.25 wt % Ru/Co$_3$O$_4$ and 20 mL of isopropanol. The reactor was sealed, purged with nitrogen, and then heated to the prescribed temperature for a desired reaction time with stirring. At the completion of the reaction, the reactor was cooled to room temperature using cooling water. The solid catalyst was removed by filtration and recovered by calcining at 500 °C for 4 h and reduced by NaBH$_4$ then dried at 50 °C for 12 h to get the regenerated Ru/Co$_3$O$_4$ catalyst for the next use. Filtrate samples were taken for analysis on a Thermofisher Trace 1300 & ISQ LT GC-MS instrument with a TR-5 MS column (30.0 m × 250 μm × 0.25 μm).

4.4. Catalyst Characterization

The reduction properties of the calcined, reduced, and recycled Ru/Co$_3$O$_4$ were measured by means of temperature-programmed reduction (H$_2$-TPR) techniques, and the measurements were carried out in a gas mixture of 5 vol % hydrogen in nitrogen at a flow rate of 30 cm^3·min^{-1} and a heating rate of 10 °C·min^{-1} from 100 °C to 800 °C. The X-ray diffraction (XRD) patterns of the catalyst were recorded on a Panalytical X'pert Pro diffractometer using a Cu Kα radiation source

with the following parameters: 40 kV, 30 mA, 2θ from 20° to 70° at a scanning speed of $7° \cdot min^{-1}$. The morphology and elemental composition of the catalyst were investigated using a Tecnai G2 20 transmission electron microscope (TEM, Tecnai G2 20, FEI, Hillsboro, OR, USA) equipped with an energy dispersive X-ray spectroscopy (EDX) unit. The TEM was operated at an accelerating voltage of 200 kV and with a low beam current to minimize beam damage. Counting time for X-ray spectra was 15 live seconds.

5. Conclusions

The Ru/Co_3O_4 catalyst was synthesized via a co-precipitation method and used for the CTH of HMF to BHMF in the presence of isopropanol. It was found that such a system displayed a high selectivity of BHMF, and the highest BHMF yield of 82.8% was obtained at 190 °C in 6 h. The as-prepared catalyst exhibited good stability, and the recovery efficiency attained 94% at 170 °C in 10 h. Based on the observation of the catalysts and the analysis of the oxidation products, a plausible reaction pathway of HMF to BHMF via the CTH routes was proposed. Based on the high activity, recyclability, safety, and controllability, the CTH process of converting HMF to BHMF from the present study has the potential to produce BHMF from a biomass-based precursor of HMF, which fits well with the green conversion process.

Author Contributions: Ting Wang and Junhua Zhang conceived and designed the experiments; Ting Wang and Wenxing Xie performed the experiments; Ting Wang, Wenxing Xie, and Junhua Zhang analyzed the data; Yanjun Tang and Daliang Guo contributed reagents/materials/analysis tools; Ting Wang and Junhua Zhang wrote the paper; Yonghao Ni revised the paper.

Conflicts of Interest: The authors declare no competing financial interest.

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