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Support effect with rhenium sulfide catalysts

D. Laurenti [a,*], K.T. Ninh Thi [a], N. Escalona [b], L. Massin [a],
M. Vrinat [a], F.J. Gil Llambías [c]

[a] *IRCELYON, UMR 5256, CNRS, Université Lyon 1, 2 av. Einstein, F-69626 Villeurbanne Cedex, France*
[b] *Universidad de Concepción, Facultad de Ciencias Químicas, Casilla160c, Concepción, Chile*
[c] *Universidad de Santiago de Chile, Química y Biología, Cas. 40, Santiago, Chile*

Abstract

The well known support effect observed for molybdenum sulfide has been studied with rhenium sulfide, which was reported to be a very active hydrotreating catalyst. Solids containing from 0.8 to 4 rhenium atoms per nm^2 have been prepared on titania, zirconia and γ-alumina supports and sulfided using N_2-H_2S (15%) or H_2-H_2S (15%) mixtures. The catalytic activity in thiophene hydrodesulfurization (HDS) has been evaluated and additional information about the structure over the different supports has been obtained by XPS and HRTEM.

Keywords: Rhenium sulfide; Hydrotreating; Thiophene HDS; Support effect

1. Introduction

Support effect has been the object of a lot of studies in the hydrotreating area and it has been well demonstrated that the support was not only a carrier dispersing the active phase but it could introduce very interesting properties concerning the structure of the active phase or the bi-functionality which could improve the catalytic activity drastically.

The support effect with molybdenum sulfide has been frequently reported in the literature but the exact nature of the parameters responsible for the differences observed for various supports is still subject of debates. Two reviews, summarizing the support effect in hydrotreating catalysts have been published by Breysse et al. [1,2]. The examination of various support–sulfide interactions (mostly molybdenum sulfide catalysts) provided valuable information but it appeared that conclusions are sometimes contradictory. The difficult point is to distinguish between electronic and geometrical effect and to establish the relationship with the catalytic activity. Nevertheless, for hydrodesulfurization, promising new sulfide catalysts were MoS_2 supported on TiO_2 and ZrO_2 (despite the low surface area of titania and the instability of zirconia). The sulfidation has been demonstrated to be easier on TiO_2 than on γ-Al_2O_3 but the differences observed in the structure of the catalysts are much smaller in sulfided form than in oxidic state. This fact has been illustrated by XPS studies where no variations of Mo 3d binding energies over sulfided Mo/TiO_2 and Mo/γ-Al_2O_3 were observed [3]. The catalytic activity depends strongly of the morphology and orientation of MoS_2 on supports. On titania supports, multi-layered MoS_2 clusters with higher intrinsic activity due to smaller interaction with the support have been detected [4]. Furthermore, it has been demonstrated that the support itself could play a significant role accelerating or slowing down the sulfidation process [5]. The kinetic of sulfidation [6] and also the shape and the orientation of the nanoparticles of MoS_2 may be affected by the nature of the support. Different size and stacking of MoS_2 slabs on various supports were proposed to be responsible of the better activity on TiO_2 and ZrO_2 [7,8]. Concerning the promoting effect, the synergism observed with Co or Ni on γ-alumina was lower with other oxidic supports and several authors [9–11] suggested that this was due to a weaker Mo-support interaction which allowed formation of $CoMoO_4$ precursor of Co_9S_8 poorly active species. The decoration of MoS_2 by Ti^{3+} when TiO_2 was employed as support has been also evocated more recently [12,13]. Concerning ZrO_2, the rapidity of the sulfidation of the promoting agent has been found to be responsible of the low synergetic effect [14].

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[*] Corresponding author.
E-mail address: dorothee.laurenti@ircelyon.univ-lyon1.fr (D. Laurenti).

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Despite its high recognized activity, rhenium sulfide has not been extensively studied in HDS because of its cost [15] and because of its scarcity. This transition metal sulfide is interesting for two reasons. Firstly, ReS_2 was found one of the most active sulfides in hydrotreating and especially in HDS of DBT [16], and secondly, its structure has been reported to be lamellar and this morphology could induce support effect similar to that observed with MoS_2. The reported thiophene HDS activities for unsupported [16,17] or supported ReS_2 on carbon, alumina, or silica [18–22] were (on molar basis) 3–10 times higher than their MoS_2 counterparts and $ReS_2/\gamma\text{-}Al_2O_3$ has been found 1.6 times more active for thiophene HDS than a commercial $NiMo/\gamma\text{-}Al_2O_3$ [23]. After a study on the reducibility of rhenium oxide over several supports (C, $\gamma\text{-}Al_2O_3$ and SiO_2) which was found to depend mainly on the Re content and the nature of the support, and more precisely on the Re^{7+}-support interaction [24]. Arnoldy et al. proposed a detailed scheme for the sulfidation of oxidic Re^{7+} species on alumina [25] under H_2-H_2S mixture, which involved oxy-rhenium-sulfide species. Then, the same authors have compared the thiophene HDS activities of rhenium sulfides supported on carbon, silica and alumina. An inductive support effect coming from the polarization of metal–sulfur bond by polar support bonds has been postulated to explain the slight decrease of activity in the order: $C > \gamma\text{-}Al_2O_3 > SiO_2$ [22]. The activities in HDN and HDS of gasoil over supported rhenium sulfide on carbon and alumina have been also reported and the influence of Re loading has been discussed [26,27]. A maximum in activity has been found for a loading of 0.5 Re atoms per nm^2. The preparation, the structure and the catalytic activities published for rhenium sulfides in literature have been very recently reviewed [28]. Some disagreements about the structure of ReS_2 have been reported. Some authors have found spherical particles instead of slabs and this point has to be clarified. Furthermore, as far as we know, only alumina, silica and carbon have been used to prepare supported ReS_2 catalysts: ZrO_2 and TiO_2, which have been found to enhance supported MoS_2 activity, have not been explored as carriers for this sulfide. If we consider that the Re-O-support interaction is less strong for ZrO_2 and TiO_2 than for alumina [29], and that a weak interaction with the support make it possible to get higher catalytic activity [30], then these supports are worth being examined with ReS_2.

The objective of this work was to clarify the structure of rhenium sulfides over $\gamma\text{-}Al_2O_3$, TiO_2 and ZrO_2 and to evaluate the support effect on the catalytic activity of these solids in HDS of thiophene. Supported ReS_2 have been prepared, characterized and then tested in a continuous catalytic test. The sulfidation procedure and the presence of H_2 in the mixture could affect drastically the HDS activity as it was already mentioned on alumina [23]. Then, the effect of the nature of the mixture for the sulfidation step on the activity has been examined (N_2-H_2S (15%) or H_2-H_2S (15%) at 673 K). XPS and HRTEM studies have been carried out to get more information on the surface species.

2. Experimental

2.1. Catalysts preparation and reaction conditions

A series of differently loaded catalysts has been prepared by a classical pore volume incipient wetness impregnation of crushed and sieved (80–120 μm) supports ($\gamma\text{-}Al_2O_3$: GD532, ZrO_2: Norpro, TiO_2: Norpro) with the appropriate quantity of an aqueous solution of NH_4ReO_4 (Aldrich). The impregnation step has been carried out using an aqueous solution of NH_4ReO_4 kept at 323 K (in a water bath) because of the low solubility of this salt in water. After drying for one night at 383 K, the solids were calcined for 0.5 h at 573 K under flowing air (5 L/h). The weight percentage of Re (%Re) has been obtained by ICP analysis and was in agreement with the quantities of NH_4ReO_4 used for the impregnation. The sulfidation has been carried out with N_2-H_2S (15%) or H_2-H_2S (15%) stream (4 L/h) at 673 K for 4 h.

Freshly sulfided catalysts have been tested in thiophene HDS in vapour phase in a continuous fixed bed microreactor at atmospheric pressure of H_2. The partial pressure used for thiophene was 21.4 Torr.

Specific activities were determined after 15 h on stream in the pseudo-stationary state.

2.2. Catalysts characterization

Re contents were analyzed by plasma coupled atomic emission spectroscopy (AES-ICP). Textural properties were determined after degassing the samples at 573 K during 2 h. The surface area was determined by nitrogen adsorption at 77 K using BET equation and pore size distribution by using BJH method in the desorption isotherm.

High-resolution transmission electronic microscopy (HRTEM) measurements were performed with a JEOL JEM 2010 instrument (point to point resolution of 0.19 nm) equipped with an EDX microanalysis system which allow to estimate composition of particles. The solids were ultrasonically dispersed in ethanol and the suspension was collected on carbon-coated copper grids. The samples were kept under inert atmosphere until this last process.

The X-ray Photoelectron Spectroscopy (XPS) experiments were carried out in a KRATOS AXIS Ultra DLD spectrometer using a hemispherical analyzer and working at a vacuum higher than 10^{-9} mbar. All the data were acquired using monochromated Al Kα X-rays (1486.6 eV, 150 W), a pass energy of 5 eV, and a hybrid lens mode. The area analysed was 700 μm × 300 μm. Charge neutralization was required for all samples. Depending of the support and because of a very low carbon signal, the peaks were referenced to the Al 2p at 74.5 eV, Zr 3d at 182.2 eV or Ti 2p at 459 eV. The chemical state has been evaluated by curve fitting the Re 4f region using a minimum number of doublets.

The freshly sulfided samples were transferred under inert atmosphere into XPS chambers.

3. Results and discussion

3.1. Catalytic activity

In order to study the support effect with rhenium sulfides, several catalysts were prepared on γ-Al_2O_3, TiO_2 and ZrO_2 with loading from 1 to 4 Re atoms per nm^2 (Table 1). The exact Re surface loading was calculated using the surface area of the samples after impregnation. It can be seen that the surface areas of the Re supported catalysts decreased with increasing the Re content, suggesting a high dispersion of the active phase in all the catalysts. The average pore size in supported Re solids did not change significantly with the loading and the values obtained are similar for each support (around 8 nm).

Under the same condition of sulfidation (N_2/H_2S (15%), 673 K, 4 h), the catalysts have been tested in HDS of thiophene at atmospheric pressure. Specific (per gram of catalyst) and intrinsic (by metal atom) catalytic activities for this reaction are given at 613 K, as the function of Re content (wt.%) and Re atoms surface loading (atoms per nm^2), respectively (Figs. 1 and 2). At low Re content, the sulfided Re/γ-Al_2O_3 and Re/ZrO_2 have comparable specific activities as the function of Re wt.%. It appeared that for γ-alumina supported catalysts, the specific catalytic activity increases until high rhenium content whereas for titania and zirconia catalysts a plateau was rapidly reached (from 7% of Re). Regarding the activity by rhenium atom, ZrO_2-supported catalysts are the more active catalysts of the three series, titania-supported catalysts being less active. The slight decrease of the intrinsic activity when the Re content by surface unit is increased seems clearly due to the multilayer formation and the decrease of the dispersion. Similar behaviour has been observed on SiO_2 and γ-Al_2O_3 by Arnoldy et al. [22].

So, we can confirm, that with the supported rhenium sulfides catalysts, the support effect exists but it is weaker compared to the molybdenum sulfides analogs. Furthermore the positive effect found for TiO_2 supported MoS_2 catalysts has not been observed with Re sulfides.

3.2. Effect of the nature of the sulfidation mixture

Previous published results have shown that the ex situ sulfidation under H_2/H_2S had a negative effect on the catalytic activity compared to the sulfidation under N_2-H_2S [23] for ReS_2 supported on γ-alumina. Rhenium oxide sulfidation under N_2-H_2S mixture makes it possible to obtain a thiophene HDS activity 1.6 times higher than the one obtained with the same precursor sulfided under H_2-H_2S. Results given in Fig. 3 indicate that this sulfidation effect was similar for ReS_2 supported on TiO_2 and ZrO_2, even if, on the latter, this effect was weaker (only a gain of 1.2). This effect could be related to the high reducibility of Re species under H_2, which competes with the sulfidation process [25].

Table 1
Composition and surface areas of the supported ReS_2 catalysts

Catalysts	Support	Re (wt.%)	S (BET) ($m^2\ g^{-1}$)	At Re (nm^{-2})
1	γ-Al_2O_3	6.5	224	0.9
2	γ-Al_2O_3	10.1	212	1.6
3	γ-Al_2O_3	15.1	201	2.5
4	γ-Al_2O_3	19.7	181	3.4
5	ZrO_2	3.4	111	0.95
6	ZrO_2	5.4	94	1.6
7	ZrO_2	9.4	77	2.8
8	TiO_2	3.0	137	0.7
9	TiO_2	5.1	134	1.2
10	TiO_2	6.3	130	1.5
11	TiO_2	10.4	111	2.6

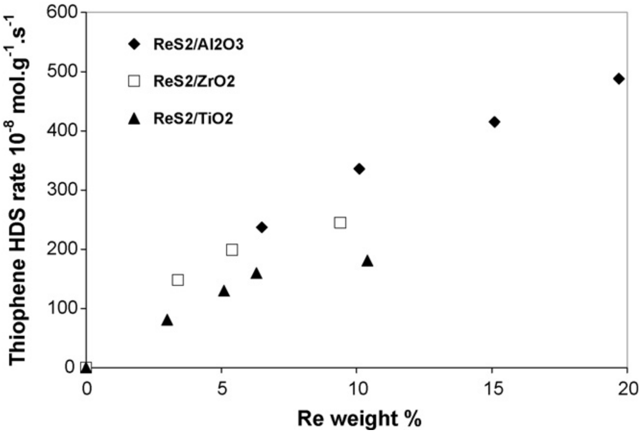

Fig. 1. Catalytic activities per gram in thiophene HDS at 613 K.

3.3. Structure of rhenium sulfides, HRTEM and XPS experiments

Even if ReS_3, Re_2S_4 have been studied or mentioned by several authors [31,32], the stable forms of rhenium sulfide are Re_2S_7 and ReS_2. Re_2S_7 is less stable and never detected in supported form, as it is readily transformed into ReS_2 especially under H_2 [33,34]. ReS_2 is known to have a lamellar structure despite some contradictory reports which described spherical structure for ReS_2 [35,36]. By using HRTEM, we found that for the three studied supports and when using either N_2 or H_2 in the sulfidation step, Re sulfide consisted exclusively of slabs but those decomposed into spherical particles under the electron

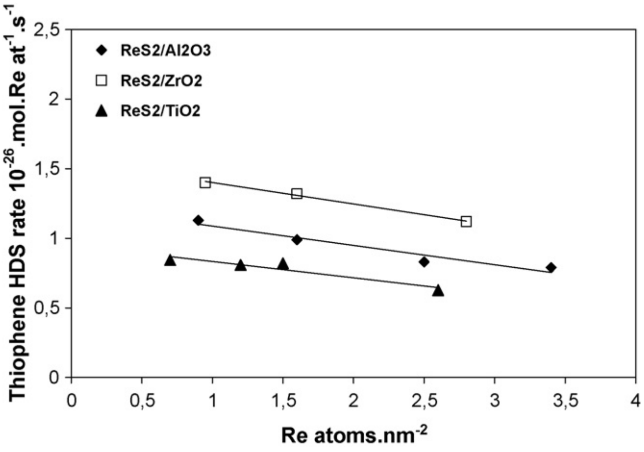

Fig. 2. Catalytic activities per Re atom in thiophene HDS at 613 K.

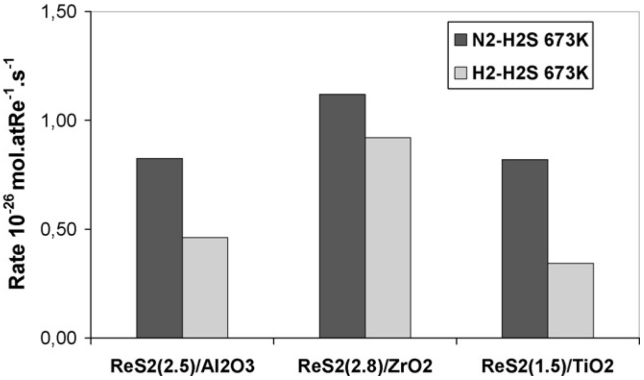

Fig. 3. Effect of the nature of the sulfidation mixture on the catalytic activity for supported ReS_2 (Re at nm^{-2}) at 613 K.

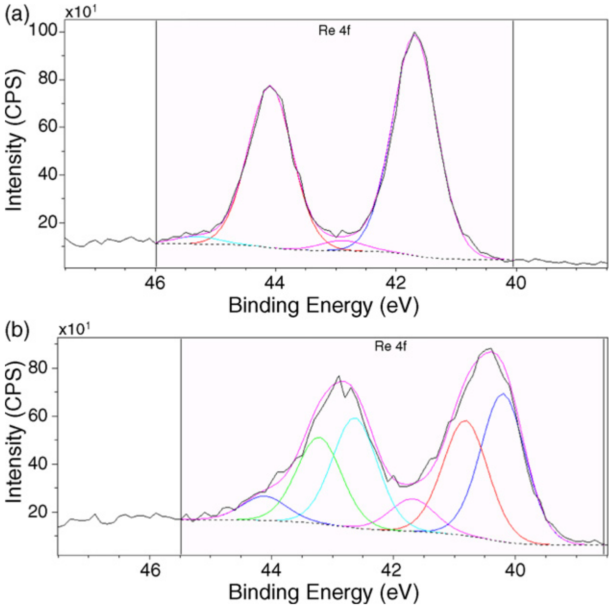

Fig. 5. XPS spectrum of Re 4f: (a) $ReS_2/\gamma\text{-}Al_2O_3$; (b) the same sample after reduction under H_2 at 823 K.

beam in less than 20 min (Fig. 4). After 15 min, EDX analyses gave a ratio S/Re close to 0.3 which means that ReS_2 is completely desulfurized to metallic Re under the beam. So the spherical particles which have been sometimes attributed to ReS_2 are in fact metallic rhenium.

Concerning the degree of sulfidation of the samples, according to XPS and HRTEM experiments, the S/Re ratios determined with freshly sulfided samples, were higher than the expected stoichiometric value for ReS_2. In the past, the same observation has been made for RuS_2 [37]. The excess of sulfur detected by the two techniques could be related to the nature of the sulfiding mixture. Effectively, when the sulfidation was made in a mixture H_2-H_2S instead of N_2-H_2S, the S/Re ratio decreased from 3.8 to 3.0 for zirconia supported catalysts and from 2.7 to 2.0 with γ-alumina. This has been previously explained by a deposition of sulfur on the carrier due to significant H_2S dissociation which easily takes place under low hydrogen partial pressure. Despite this high S/Re ratio we do believe that the major sulfided species present on the different supports is ReS_2. XPS results obtained for the different solids are summarized in Table 2. According to spectra, we propose two doublet contributions for Re 4f with γ-alumina and zirconia supported catalysts and only one doublet for titania solids. The major contribution attributed to ReS_2 has a binding energy of 41.5–41.7 eV, which is in agreement with the previous published value [19]. A second contribution has been found for Re 4f on $\gamma\text{-}Al_2O_3$ and ZrO_2 at 42.9 eV. This minor specie could be an oxy-rhenium-sulfide by analogy with molybdenum catalysts or may be some Re_2S_7, i.e. the other known sulfide species. However, this second possibility does not seem realistic if we consider that a sulfidation under H_2-H_2S which should transform any formed Re_2S_7 into ReS_2 gave the same minor doublet for $ReS_2/\gamma\text{-}Al_2O_3$. Such a contribution has been observed previously by Escalona et al. with a supported rhenium sulfide (H_2-H_2S, 623 K) and was related to an incomplete sulfidation [26].

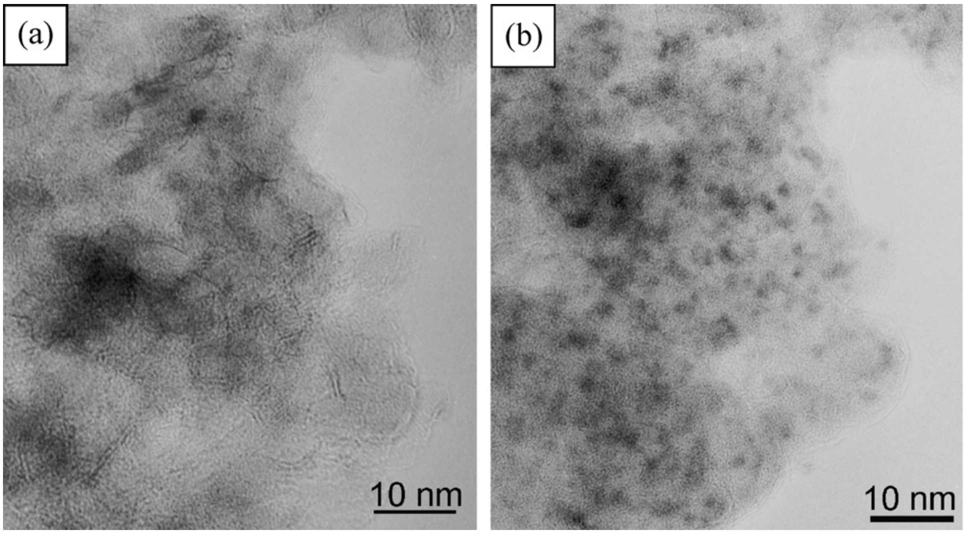

Fig. 4. HRTEM pictures of the degradation of $ReS_2/\gamma\text{-}Al_2O_3$ (sulfided under H_2-H_2S) under electron beam: (a) slabs, S/Re = 2; (b) the same region after 15 min: spherical particles, S/Re = 0.6.

Table 2
XPS binding energies (eV) of Al 2p, Zr 3d, Ti 2p and Re $4f_{7/2}$ peaks, relative proportion (in parenthesis) and surface atomic ratios for ReS_2/support catalysts

Catalysts (Re at nm^{-2})	Reference	Re $4f_{7/2}$	Atomic ratio Re/support	Atomic ratio S/Re
ReS_2 (3.4)/γ-Al_2O_3	Al 2p = 74.5	41.7 (95%); 42.9 (5%)	Re/Al = 0.14	2.7
ReS_2/γ-Al_2O_3 reduced under H_2 at 823 K	Al 2p = 74.5	40.2 (50%); 40.8 (39%); 41.7 (11%)	Re/Al = 0.09	0.7
ReS_2 (2.8)/ZrO_2	Zr 3d = 182.2	41.5 (92%); 42.6 (8%)	Re/Zr = 0.09	3.8
ReS_2 (3.9)/TiO_2	Ti 2p = 459	41.5 (100%)	Re/Ti = 0.19	3.7

Furthermore, the reduction of ReS_2/γ-Al_2O_3 under H_2 at 823 K gave interestingly three doublets for Re 4f (Table 2 and Fig. 5). After this treatment, only 11% of non-reduced ReS_2 was found on the surface. Two major contributions were found at 40.2 eV (50%) and 40.8 eV (39%). The lower one (40.2 eV) should correspond to the metallic Re as expected. The other one must be an intermediate species presenting an oxidation state between 0 and 4, with a lower S stoichiometry than ReS_2 such as for example $ReS_{(2-x)}$. Similar species with a S/Re ratio of 1.3 has been mentioned by Clark et al. previously [38], but the binding energy found was around 42.1 eV (comparatively Re^{4+} was given at 43.4 eV instead of 41.7 eV in this study). In addition, the S/Re ratio decreased from 2.7 to 0.7 during the reduction under H_2 at 823 K and the sulfur binding energy shifted from 162.2 to 161.8 eV.

Some more XPS experiments are needed to find the exact nature of the different surface species detected by the deconvolution of the Re 4f spectrum. If we consider that the lowest catalytic activity found for TiO_2 supported rhenium sulfides is due to the lack of this second contribution detected by XPS, it should be very interesting to describe this species more precisely.

4. Conclusion

In summary, at same Re molar content, the catalytic activity of supported rhenium sulfides in thiophene HDS was found to increase depending of the support in order: $TiO_2 <$ γ-$Al_2O_3 < ZrO_2$. For these supports, the presence of H_2 in the sulfidation mixture has a negative effect on the catalytic activity. The catalysts with the highest activity have been obtained by a sulfidation under N_2-H_2S (15%) at 673 K. By using HRTEM, we clearly detected a lamellar structure and its decomposition into spherical particles of metallic rhenium under the electron beam has been observed. By using XPS, one major contribution attributed to ReS_2 with the same binding energy was found for all the supported catalysts. However, an additional minor doublet was found for γ-alumina and zirconia-supported rhenium sulfides and its origin still has to be clarified. Finally, the correlation between the catalytic activity and the structure of the supported rhenium sulfides on γ-Al_2O_3, ZrO_2 and TiO_2 is not very pronounced.

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