

Research Article

Spectroscopic Characterization of Stability and Interaction of Pd-Ag Complexes

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Colloidal metal nanoparticles are of great interest because of their use as catalysts, photocatalysts, adsorbents, and sensors as well as their application in optical, electronic, and magnetic devices. Supported bimetallic systems represent a large part of heterogeneous catalysts which have been used in various reactions important in the chemical, petrochemical, and oil industry. Pd-Ag bimetallic nanocatalysts have become vitally important in some of the petrochemical industry's processes like hydrogenation of C_2-C_5 olefins. A heat-treatment method for the preparation of well-stable Pd-Ag complexes is demonstrated using water, concentrated HCl and concentrated nitric acid as media. The stability and interaction of Pd-Ag complexes were characterized by UV-vis absorption spectroscopy. Pd-Ag bimetallic nanoparticles of spherical cubic and octahedral shape in the range of average particle size of 20–60 nm have been prepared and characterized by transmission electron microscopy (TEM).

1. Introduction

The selective hydrogenation of acetylene/ C_3 in raw stream from a steam cracker is an important industrial process for the purification of ethylene/propylene. Ethylene/propylene selectivity is a key objective in this process. Even a small increase in selectivity can represent sizable savings. Characteristics of catalysts directly affect the quality and yield of the goal product, ethylene/propylene. Many researchers [1–5] have published papers about the selective hydrogenation of acetylene. It is well known that, among the metals of VIII B group, palladium dispersed on a support is the best catalyst, with good activity and selectivity for this reaction. But oligomers (“green oil”) are also formed during acetylene hydrogenation on supported Pd catalyst, which shorten the recycle time and life of the industrial catalyst. In addition, Pd catalyst has poor selectivity at high levels of acetylene conversion. In industrial application, the hydrogenation catalyst must have good selectivity and proper activity. The traditional Pd catalysts are not preferred, if the higher selectivities are to be achieved. Hence the promoters are used to improve the selectivity of the catalyst. Experimental results [6, 7] indicated that Pd catalyst with addition of a group I B metal like Cu,

Ag, and Au can increase the selectivity towards alkene, reduce the yield of “green oil,” and improve the properties of the traditional catalyst. Recently, Ag has received considerable attention as a selectivity promoter in the literature and in industry [8, 9]. These bimetallic [10, 11] catalysts have generally shown enhanced catalytic stability and higher selectivity to the desired products compared to monometallic catalysts. The nature of supported bimetallic environment depends on the preparation methods including the sequence of metal loading, metal precursors, capping agent solvents used, and the composition of two metals. The main theories put forward to account for the improved properties of Pd-Ag bimetallic catalysts tend to involve either geometric and/or electronic effects. An electronic modification of active metal like Pd may be introduced by an interaction with a promoter or by Pd-Ag alloy formation. Thus, electron transfer from silver to palladium leads to the weakening of the bond strength between palladium and alkyne, reduces the rate of coke formation, and affects thereby the selectivity and catalyst stability. Pd-Ag alloy formation is exothermic and takes place with low heat of formation, which means that both components influence each other weakly. This influence can lead to the reorganization in the population of Pd-orbitals.

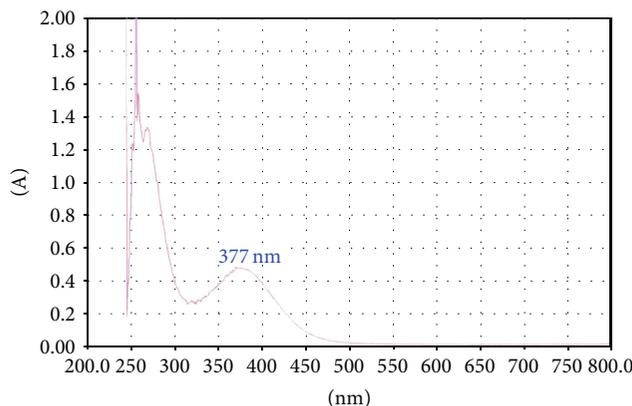


FIGURE 1: UV spectrum of palladium nitrate.

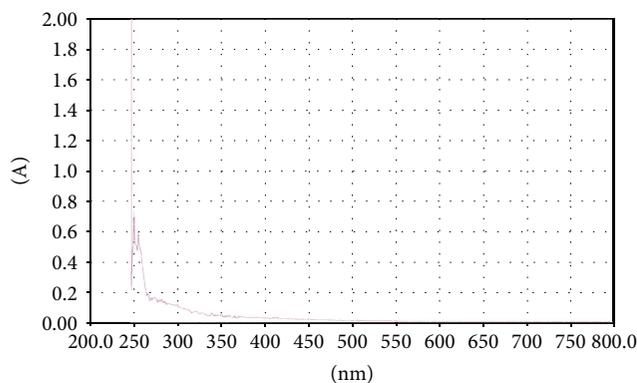


FIGURE 2: UV spectrum of silver nitrate.

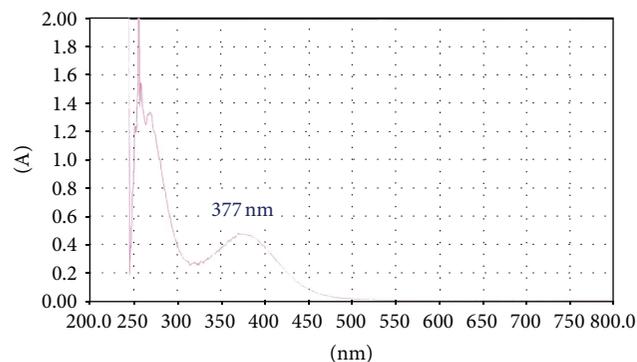


FIGURE 3: UV spectrum of Pd-Ag complexes with water.

Sheth et al. found that alloying Pd with Ag can suppress the rate of bond-breaking reaction (decomposition) and enhance the rate of bond-forming reaction (hydrogenation) [11]. The decrease in the number of active ensemble sites, responsible for high activity for coke formation or undesired reactions, was observed by addition of silver to palladium catalysts in selective hydrogenation reaction. In order to develop Pd-Ag bimetallic supported catalyst, it is important to understand the interaction and complex formation between Pd and Ag.

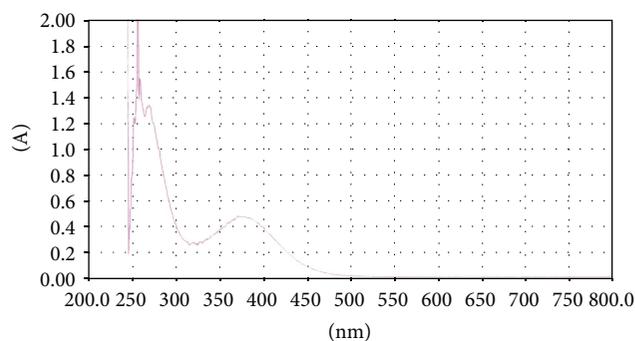
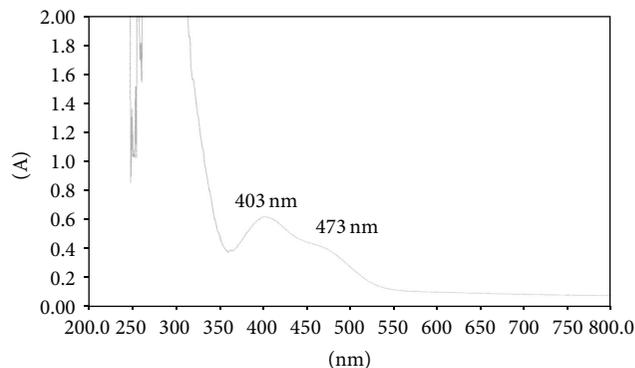
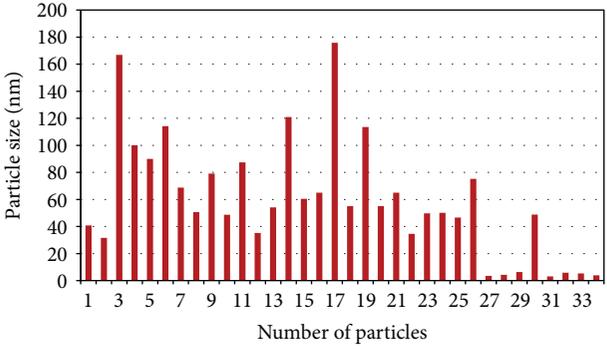
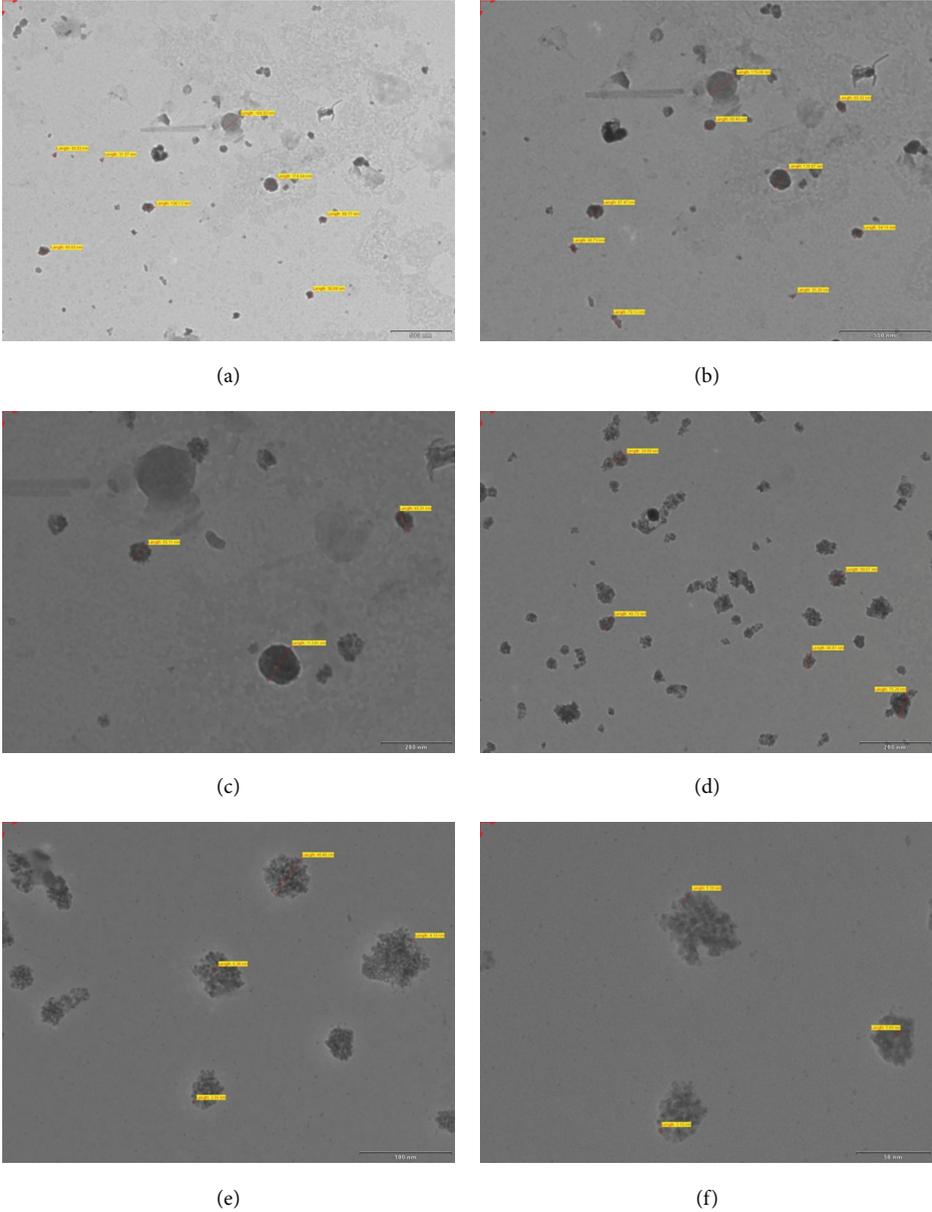
FIGURE 4: UV spectrum of Pd-Ag complexes with dilute HNO_3 .

FIGURE 5: UV spectrum of Pd-Ag complexes in conc. HCl medium.

The present study gives detailed account of experiments carried out to study the stability and formation of Pd-Ag complexes as well as the synthesis of Pd-Ag bimetallic nanoparticle characterized by transmission electron microscopy (TEM) analysis.

2. Experimental Section

2.1. Chemicals and Analysis. Palladium nitrate and silver nitrate were procured from Parekh Platinum Pvt. Ltd. Mumbai, India. Concentrated HCl and HNO_3 were procured



Particle size histogram: average particle size: 60 nm

FIGURE 6: TEM images ((a)–(f)) of Pd-Ag nanoparticles and particle size histogram.

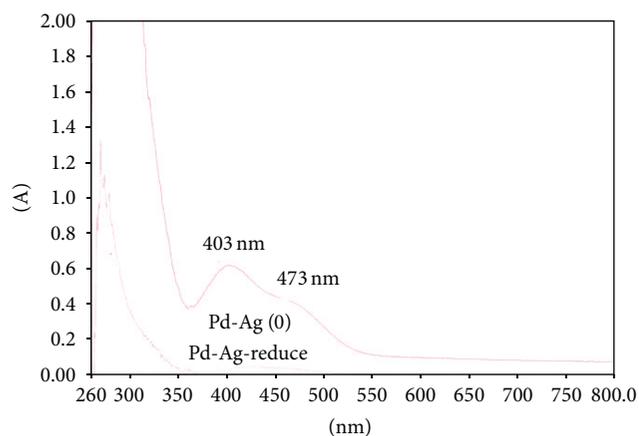


FIGURE 7: UV spectra of Pd-Ag complexes reduced with H₂ gas.

from Merck India Pvt. Ltd., India. All the chemicals used are of analytical grade and were used without any further purification. The stability of Pd-Ag complexes with various competitive ions like HCl and HNO₃ is studied in detail by using Ultra-Violet spectroscopy. Transmission electron microscope (CM 260-FEG-Philips) was also used to examine the particle size of Pd-Ag particles.

2.2. Preparation of Pd-Ag Complexes

2.2.1. Preparation of Pd-Ag Complexes in Water. Keeping in mind the 0.2 wt% Pd and 0.1 wt% Ag catalyst composition, the Pd and Ag solution was prepared in the following manner to study the complex formation. A 0.15 gm of palladium nitrate and 0.0047 gm of silver nitrate were dissolved together in 10 mL of distilled water and made up to 60 mL with distilled water. The above mixed solution was heated for 15 mins. at 60–70°C. The Pd-Ag complexes obtained were characterized by light absorption spectra using Perkin-Elmer Lambda 35 UV/Vis spectrometer. Water was used as the reference solution.

2.2.2. Preparation of Pd-Ag Complexes with Dilute HNO₃. Again, 0.15 gm of palladium nitrate and 0.0047 gm of silver nitrate were dissolved individually in 10 mL of water and 5 mL of the dilute HNO₃ was added to each solution. The above solution was then mixed and made up to 60 mL with 5 mL of dilute HNO₃ and finally heated for 15 mins. at 60–70°C. The complex solution was then cooled and directly used for UV analysis to measure absorbance.

2.2.3. Preparation of Pd-Ag Complexes with Concentrated HCl. Now again, 0.15 gm of palladium nitrate, 0.0047 gm of silver nitrate dissolved in 10 mL of water, and 5 mL of concentrated HCl was added to the mixed solution. The above solutions make up to 60 mL with 5 mL of concentrated HCl and heated for 15 mins. at 60–70°C. There is slight silver chloride precipitation formation observed. The dark red color Pd-Ag complex is formed. The complex was solution cooled and directly used for UV analysis to measure absorbance.

3. Results and Discussion

3.1. UV-Vis Analysis of Palladium Nitrate. 0.15 gm of palladium nitrate is dissolved in 60 mL distilled water and directly used for UV analysis. From Figure 1, it can be seen that there is a prominent absorption peak at around 377 nm for palladium nitrate. Khairulin et al. also reported the similar type of UV spectra for palladium nitrate [12].

3.2. UV-Vis Analysis of Silver Nitrate. 0.0047 gm is dissolved in 60 mL distilled water and directly used for UV analysis. From Figure 2, it can be seen that absorption spectrum has a peak observed at around 250 nm, which is due to silver ion. Mallik and Mandal also reported the similar observation for UV analysis of silver nitrate [13].

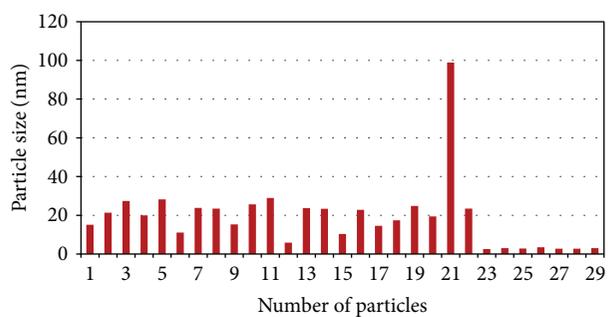
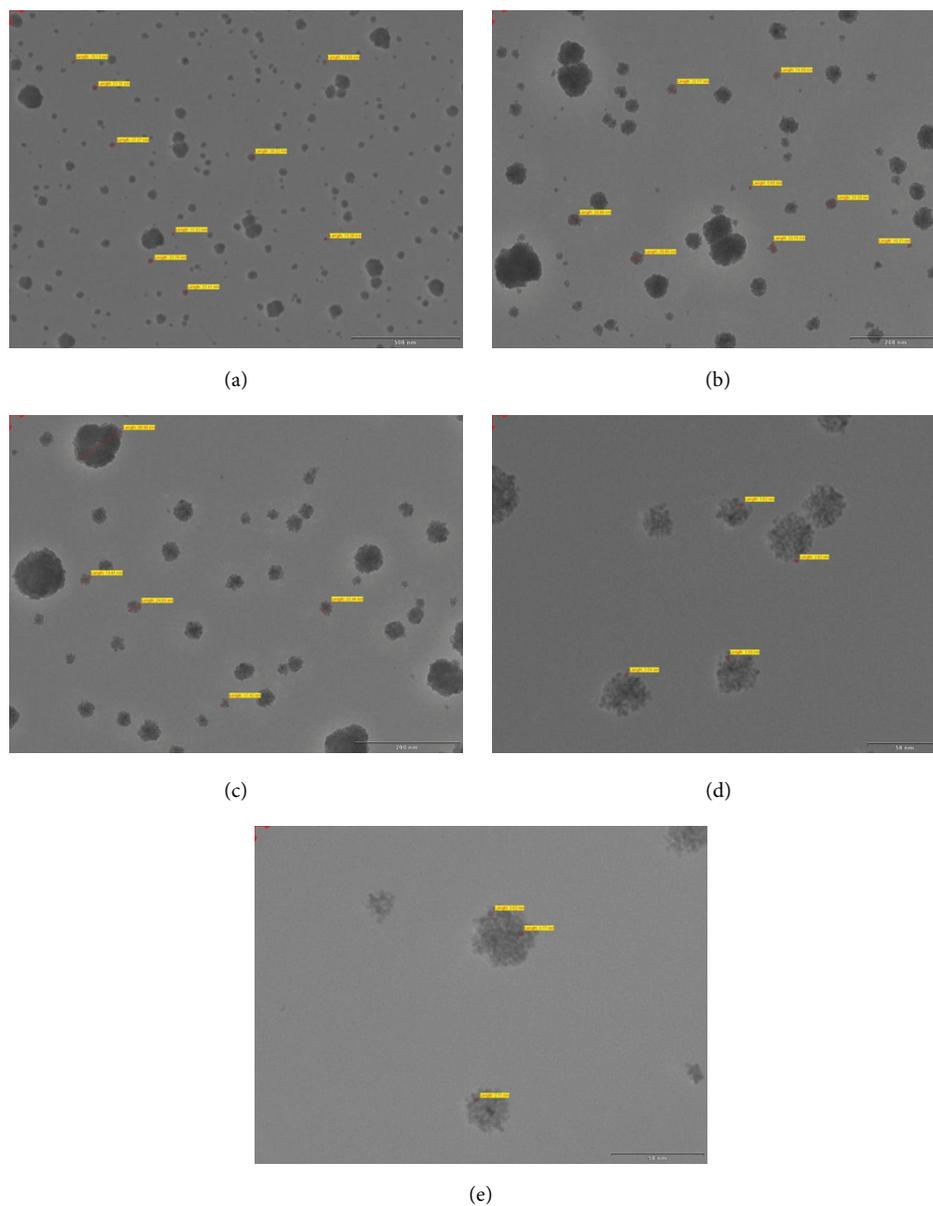
3.3. UV-Vis Analysis of Pd-Ag Complexes with Water. Pd-Ag complex is formed by mixing palladium nitrate and silver nitrate in distilled water as mentioned in Section 2.2.1. Figure 3 showed that Pd-Ag with water shows similar absorption spectrum like that of palladium nitrate, indicating that no charge transfer has taken place in presence of water and this observation which did not support the formation of Pd-Ag complex. It also indicates that water media are not suitable for metal-metal complex formation.

3.4. UV-Vis Analysis of Pd-Ag Complexes with Dilute HNO₃. Pd-Ag complex is prepared by mixing palladium nitrate and silver nitrate in distilled water and dilute HNO₃ as mentioned in Section 2.2.1. Figure 4 shows that Pd-Ag with dilute HNO₃ gives similar absorption spectrum as that of palladium nitrate in the UV spectrum. It indicates that no charge transfer takes place between Pd and Ag ion in presence of dilute HNO₃ and this observation did not support the formation of Pd-Ag complex.

3.5. UV-Vis Analysis of Pd-Ag Complexes in HCl Medium. Pd-Ag complex was prepared by dissolving palladium nitrate and silver nitrate in distilled water using dilute HCl as mentioned in Section 2.2.1. From Figure 5, it is observed that the UV spectrum of Pd-Ag with hydrochloric acid shows two absorption peaks at 403 and 473 nm, which correspond to charge transfer and d-d transition [14]. The HCl media accelerates the metal-metal complex formation under optimum conditions.

3.6. TEM Analysis of Pd-Ag Complexes in HCl Medium. Transmission electron micrograph (TEM) is used to study the Pd-Ag particle size, shape, and morphology. TEM images for Pd-Ag complex prepared in HCl medium were shown in Figures 6(a)–6(d). From TEM analysis and particle size histogram, it is observed that the Pd-Ag particles are in different shapes as spherical, cubic, and octahedral with average particle size 60 nm. Figure 6 also showed that some of the particles are in the bundles form and agglomerated also.

3.7. UV-Vis Analysis of Pd-Ag Complexes Reduced with Hydrogen Gas. The Pd-Ag complex solution prepared in



Particle size histogram: average particle size: 18 nm

FIGURE 8: TEM images ((a)–(e)) of Pd-Ag nanoparticles and particle size histogram.

HCl medium bubbled with hydrogen gas for 2 hrs at room temperature. The Pd-Ag complex ions were reduced and all the absorption peaks at 403 and 473 nm disappeared as shown in Figure 7. The color of the complex solution gradually changed from dark red to black indicating that the zero oxidation states for Pd-Ag metal particles.

3.8. TEM Analysis of Pd-Ag Complex Reduced with Hydrogen Gas. The TEM images for Pd-Ag complex prepared in HCl medium and reduced under H₂ gas are shown in Figures 8(a)–8(d). From TEM images and particle size histogram, it is observed that the average particle size for Pd-Ag bimetallic particles is 18 nm. Figures 8(a) and 8(b) show that after reduction the Pd-Ag particles are slightly well dispersed and not agglomerated. From Figures 8(d) and 8(e) it is observed that after reduction also some of the particles are in bundles form. After reduction of metal ions the bimetallic nanoparticle size of Pd-Ag particles reduced from 60 nm to 18 nm.

4. Conclusions

Based on the present study undertaken for Pd-Ag complex formation and stability the conclusion is made as follows.

- (i) Pd-Ag complexes have been prepared by using different media like water, nitric acid, and hydrochloric acid. The Pd-Ag complexes are formed in HCl medium as observed by UV spectroscopy study.
- (ii) TEM analysis showed the Pd-Ag bimetallic nanoparticles of average particle size from 20 to 60 nm with different shapes of spherical, cubic, and octahedral as prepared in HCl medium.
- (iii) TEM analysis also showed that after reduction the average particle size for Pd-Ag bimetallic particles is 18 nm. The Pd-Ag particles are well dispersed and not agglomerated.
- (iv) The concept of Pd-Ag complex formation and stability can be used in the preparation of supported bimetallic catalyst for hydrogenation reactions to increase the metal dispersion as well as stability and life of the catalyst.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

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