Vietnam Journal of Catalysis and Adsorption, 10 – issue 4 (2021) 43-49

Vietnam Journal of Catalysis and Adsorption
Tạp chí xúc tác và hấp phụ Việt Nam

https://chemeng.hust.edu.vn/jca/

Preparation of catalyst as Au doped $Mn_1Co_9O_x$/ceramic system for total oxidation of CO

Phuong Pham Thi Mai[1*], Hoan Nguyen Quoc[2], Quan Do Quoc[3], Hung Nguyen Thanh[3]

[1] Advanced Institue of Science and Technology, Hanoi University of Science and Technology
[2] Labour and Environmental Protection Center, Viet Nam National Institute of Occupational Safety and Health
[3] School of Chemical Engineering, Hanoi University of Science and Technology
**Email: phuong.phamthimai@hust.edu.vn*

ARTICLE INFO

Received: 09/8/2021
Accepted: 03/9/2021
Published: 12/9/2021

Keywords:

CO Oxidation, Au doped $MnCoO_x$, Sol-gel, Wet impregnation

ABSTRACT

In this paper, the Au doped $Mn_1Co_9O_x$ was investigated for total oxidation of CO. The sol-gel method was applied to prepare this catalyst and some modern analysis methods as XRD, EPR, TPx, SEM were utilized to characterize its properties. The XRD patterns showed only Co_3O_4 phase without any peaks belonging to Mn or Au. However, the presence of Au and Mn was confirmed by EPR and O_2-TPD results. With the aim to further apply catalyst in reality, the Au doped $Mn_1Co_9O_x$ was deposited on ceramic by sol-gel, wet impregnation. The SEM images displayed the successful coating of active phase on substrate. However, the complete catalyst system didn't have the high activity in total CO oxidation like the catalyst powder because of large agglomerations on coatings.

Introduction

CO oxidation has been researched for many years for the application in exhausted gas treatment, gas sensor and fuel technologies [1]. Recentlty, CO oxidation at low-temperature has been a hot issue because the high potential activity of catalysts may be a brige to solve this problem [2].

There are numerous of researches on catalysis materials for treatment of CO, such as noble metals (Pt, Pd, Rh, Au), perovskite, catalysts based on transition metals. Amongst the noble metals catalysts [3-5], nano gold has been well-known to have extraordinary performance, especially in excess O_2. T_{100} (temperature at which conversion reached 100%) of catalysts prepared by co-precipitation was -5°C, while that of catalysts prepared by sol-gel was 50°C [6]. However, the catalyst deactivate, and the deactivation has been proposed to be due to nanoparticles sintering, formation of carbonates absorbed onto reactive sites of catalysts, or change of oxidation gold state. Therefore, with the aim to overcome the deactivation process, the bimetallic catalyst is a promising solution.

In order to searching the second metal possessing higher affinity of O_2 than gold and synergy effects between gold and that metal (for instance, Ag, Cu, Ni ...), a plausible explanation for this promotional effect of Au-Ag catalyst has been given by Mou and co-workers: the Ag sites on the cluster surfaces could easily adsorb and activate oxygen, while the neighboring gold sites adsorb CO allowing O and CO to easily react together thus giving a high rate of reaction [7]. In case of Au-Cu catalyst, it has been found that the CuO* species were found to be very active, because of their excellent ability to transport the surface lattice oxygen [8]. Due to high oxygen mobility,

https://doi.org/10.51316/jca.2021.066

the single oxide as MnO_2, Co_3O_4 and CeO_2 were employed as support for nano Au catalyst in many reactions [9-11]. These single oxides not only played an excellent role of dispersing the active phase, but alo took part in the reactions, thus the catalytic activities of these catalysts were increased remarkably.

In these papers, the interactions of Au-MnO_2 [9], Au-Co_3O_4 [10] and Au-CeO_2 [11,12] were investigated, but there hasn't got any reports on catalyst Au on bimetallic catalysts which could oxidize CO completely at low temperature. Recently the mixed oxides Mn-Co-Ox have been reported for the oxidation of propane [13], CO [14]. The optimized synergistic effect of manganese and cobalt improves low temperature reducibility and produces rich surface active Co^{3+} species and surface-absorbed oxygen. Thus, based on the findings of remarkable properties of mixed oxides Mn-Co-Ox, it is possible to dope Au in this mixed oxide to increase the catalytic activity for the CO oxidation.

It is noticed that the deposition method has been one of the important factor to bring the success in the lab to the reality. Thus, many various coating methods have been extensively investigated and applied in manufacture. In our paper, for the purpose of scaling-up further, the sol-gel and wet impregnation were applied to deposit active phase Au doped Mn-Co-Ox on ceramic for the preparation of efficient catalyst system for total oxidation CO.

Experimental

Preparation catalysts

Au doped $Mn_1Co_9O_x$ catalyst

Au doped $Mn_1Co_9O_x$ catalyst powder was prepared by sol-gel method. Initiallly, the precusor as $Mn(NO_3)_2$ 50% ; $Co(NO_3)_2.6H_2O$ was dissolved into distilled water to make solution Mn and Co. Then, these two solutions was mixed to get the desired molar ratio of Mn/Co as 1/9 [14]. At this time, the solution $HAuCl_4$ ($5,04.10^{-3}$ M) was dropped into the solution MnCo up to the amount of Au was 0.1wt%, which was proved to be efficient to enhance the catalytic activity for CO oxidation [9,10]. After that, the citric acid was added to the metalic solution to make sol under stirring and heating at 60°C til the sticky gel was formed. This gel was dried at 120°C overnight to get dry xerogel. Finally, this dried gel was calcined at 500°C for 3 hour

Au doped $Mn_1Co_9O_x$ / ceramic

In this paper, the Au doped $Mn_1Co_9O_x$ was deposited on ceramic by two methods as wet-impregnation and sol-gel to evaluate which one would produce the efficient catalyst system as Au doped $Mn_1Co_9O_x$ / ceramic.

Similar to prepare Au doped $Mn_1Co_9O_x$ powder by sol-gel, the bare ceramic was put into the solution of Au-Mn-Co after adding citric acid. After 10 minutes, the coated ceramic was taken out and dried at 120°C for half an hour to finish the first coating. The second and third coatings were repeated subsequently. Then, the mixture of coated ceramic and remained solution Au-Mn-Co was followed the steps of heating at 60°C to get sticky gel, dried at 120°C overnight and calcined at 500°C. This catalyst was called SG- Au doped $Mn_1Co_9O_x$ / ceramic.

In case of wet impregnation, the original ceramic was impregnated for 10 minutes in solution of Au-Mn-Co having same molar ratios of metal like in the preparation of Au doped $Mn_1Co_9O_x$. in part a, then get out to dry at 120°C for 30 minutes. This coating was repeated three times before absolute drying at 120°C overnight and calcined at 500°C, 3 hour. This catalyst was called WI- Au doped $Mn_1Co_9O_x$ / ceramic.

Characterization of catalyst

The composition phase of synthesized catalysts was determined by X-ray Diffraction (XRD) . XRD patterns were recorded on D8 Advance Bruker in Faculty of Chemistry, Hanoi University of Science under the condition as CuKα radiation, wavelength λ = 0,15406 nm, angle $2\theta = 30 \div 80^{\circ}$. The surface area of catalysts was measured on The Micromeritics Gemini VII 2390 equipment in Advanced Institute of Science and Technology, Hanoi University of Science and Technology. The morphology of catalyst was captured by Scanning Electronic Spectrocopy (SEM) on Novanosem 450(FEI), Ametek equiment in Physis Department, Hanoi University of Science. In order to investigate the desorption properties of catalyst, the temperature propgrammed desorption was utilized (TPx) on Autochem II 2920, Micrometics in labroratory of Rohan project, Hanoi University of Science and Technology. In the same lab, the element state of catalysts was studied on Bruker EMX-Micro EPR spectrometer using Electron Paramagnetic Resonance method.

Catalytic measurement

Catalytic activity was determined on micro-reactor connected with GC online coupled with Thermo Conductivity Detector on TRACE GC ULTRA system. The feed gas contained 15% CO/N_2 and 20% O_2/N_2 with flow rate as 62 ml/min going through 0.1 g catalyst bed (1 cm height) in 0.5 diameter quart line. The reaction temperature ranged from 50°C to 300°C, each temperature was run for one day to eliminate the deviation due to temperature change.

The program of the analysis method of GC are shown in table 1:

Table 1: Specification of GC

Detector	TCD	Oven	
Block temperature (°C)	180	Oven run time (min)	8.5
Trans temperature (°C)	180	Initial Temperature (°C)	60
The flow rate of N_2 (ml/min)	35	Initial Time (min)	1
The flow rate of He (ml/min)	20	Ramp (°C/min)	60
		Final temperature ((°C))	210
		Final Time (min)	5

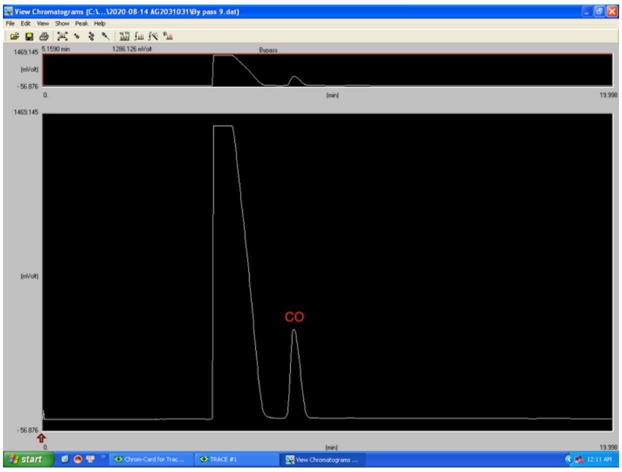


Figure 1: Chromatogram of reactant CO peak at t = 8.8 minute before reaction

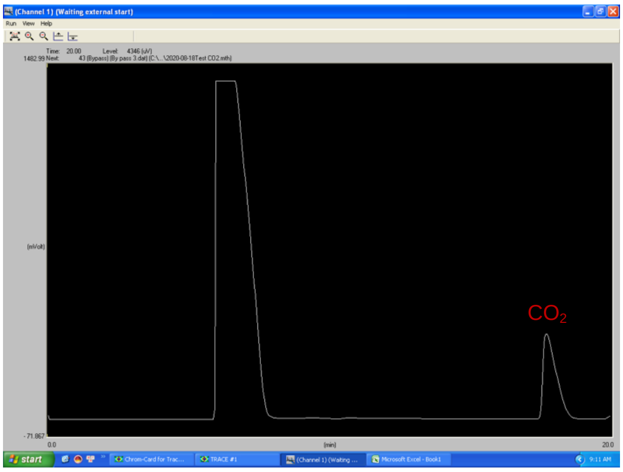


Figure 2: Chromatogram of product CO2 peak at t = 19.6 minute after reaction

Based on the change of peak areas, the conversion of CO was defined as:

$$\text{Conv (\%)} = \frac{A_{CO\ bypass} - A_{CO}}{A_{CO\ bypass}} \times 100\%$$

Where: Conv(%): Conversion of CO

$A_{CO\ bypass}$: Area of bypass CO peak

A_{CO} : Area of CO peak after reaction

Results and Discusions

Characterization of catalysts

Au doped $Mn_1Co_9O_x$ catalyst

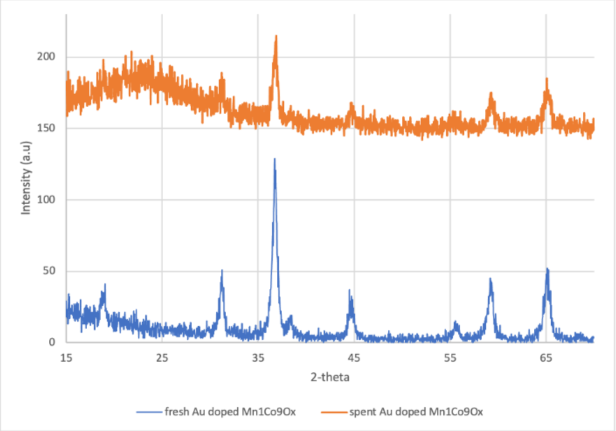


Figure 3: XRD patterns of fresh and spent Au doped $Mn_1Co_9O_x$ catalyst powder

The crystaline phase of catalyst were detected by XRD method, and the results were shown on figure 3. Before reaction, the typical peaks of Co_3O_4 appeared at angle 2-theta of 31.2°, 36.3°, 44.1°, 59.1°, 65.1° [2]. There wasn't any peaks proving the presense of Mn or Au, which may because the entering of these elements into the Co_3O_4 crystallite. Atfer reaction, the XRD patterns of spent catalyst was also exhibited only characteristic peaks of Co_3O_4 but with lower intensity. Likewise, the Mn and Au's peaks was still absent on the XRD patterns.

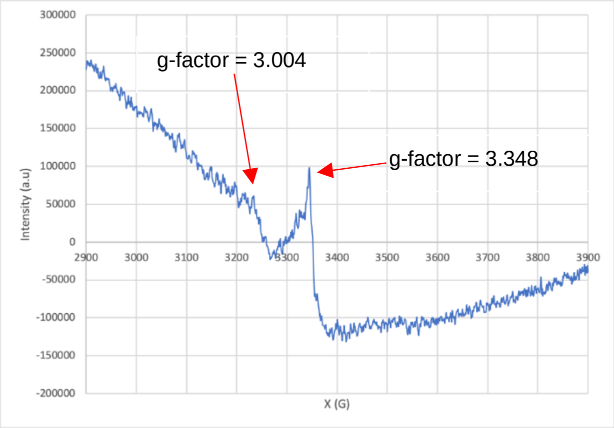


Figure 4: EPR spectra of Au doped $Mn_1Co_9O_x$ catalyst powder

The element states of catalyst would be informed by EPR spectra in figure 4. There were two peaks corresponded to g-factor as 3.004 and 3.348. According to research of R. Stoyanova*, M. Gorova, E. Zhecheva, g-factor of Mn^{4+} was 3.100 [15], additionally, the g-factor of element Au was about 3.480 [16]. So, the experimental numbers were quite consistent to the results of published paper which can elucidate for the presence of Mn and Au in the catalyst eventhough it was not seen their peaks on XRD patterns.

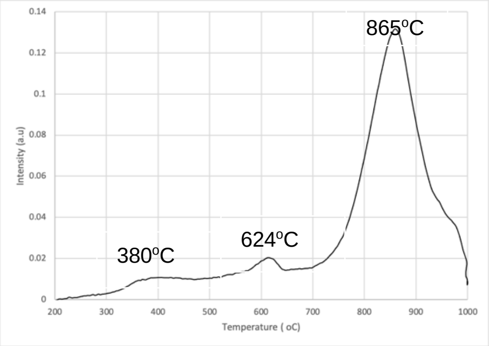


Figure 5: O_2- TPD profile of Au doped $Mn_1Co_9O_x$

For an improved understanding of the oxygen species involved in the catalytic process, the catalyst were subjected to O_2- temperature programmed desorption (O_2-TPD). On the firgure 5, there were three desorption peaks at 380°C, 624°C and 865°C . Generally, the peak at lowest temperature as 380°C can be assigned for surface absorded oxygen species, which is an factor accounting for low temperature catalytic activity. According to literature [13], the second peaks centered at 624°C may attributed to the latice oxygen of solid solution of Mn-Co- O, in addition, the biggest desorption peak at 865°C can be ascribed to the bulk latice oxygen of Co_3O_4.

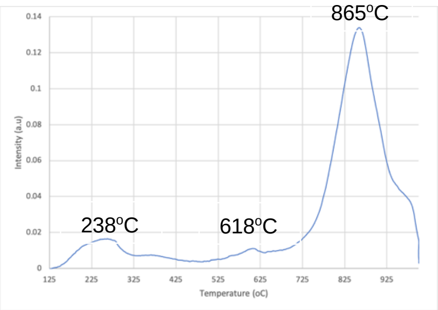


Figure 6: CO – TPD profile of Au doped MnCo catalyst

Futhermore, the catalysts was also investigated by CO-TPD to understand the adsorption of CO species in the catalysis process. Compared with O_2-TPD profile, the lowest desorption peak was at 238°C, and not the smallest peak. While the second and the third peaks in CO- TPD were at the same positions with two higher desorption peaks in O_2- TPD. This can be eluciated by the desorption peak of CO at 238°C assigning for molecular CO desorped from the surface, whereas the second and third peaks were accounted for desorption of CO after recombination of dissociated carbon and oxygen on the surface [17].

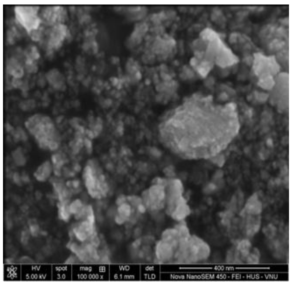


Figure 7: SEM image of Au doped $Mn_1Co_9O_x$ catalyst

The morphology of Au doped $Mn_1Co_9O_x$ catalyst was captured and illustrated on figure 7. It can be seen that many small particles from 10 to 50 nm were more popular than large particles having size of approximately 200 nm. As the small particles occupied largely, it would make the catalyst surface porous which would be beneficial for catalytic reaction.

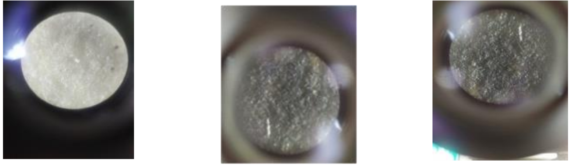
Au doped $Mn_1Co_9O_x$ / ceramic

All the pictures of ceramics before and after coating on figure 8 showed the changes of ceramic after depostion. It can be noticed that the bare ceramic was white with tough surface, and no cracks on it. Nonetheless, the white color of original ceramic turned to black after coating, which can be seen with both normal eye and under 40 times of magnitude. This results proved that both sol-gel and wet impregnation were successful in depositing Au doped $Mn_1Co_9O_x$ on the ceramics.

Observation with normal eye

Original ceramic | SG- Au doped $Mn_1Co_9O_x$ / ceramic | WI- Au doped $Mn_1Co_9O_x$ / ceramic

Observation under Micro Spectroscopy

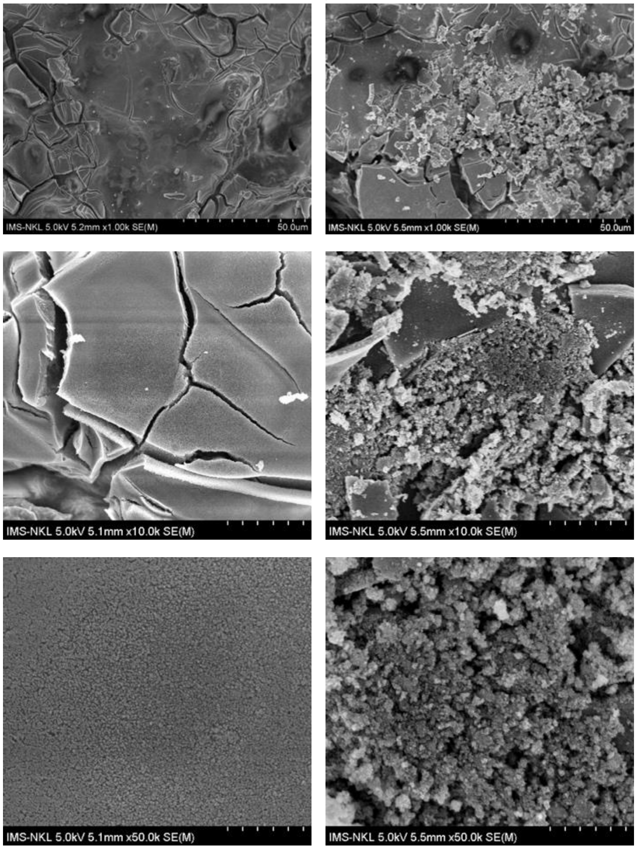


Original ceramic | SG- Au doped $Mn_1Co_9O_x$ / ceramic | WI- Au doped $Mn_1Co_9O_x$ / ceramic

Figure 8: Surface of original and coated ceramic

The BET surface area of coated ceramics by various methods were measured and listed on table 2. The values were quite the same at low value as 0.2 m^2/g. So the coating can be seen easily with normal eye, and the BET surface area were quite similar creating the difficulty in assessment which was the better deposition method. Therefore, it is necessary to utilize SEM to observe the differences of coating made by two methods. SEM images of coated ceramics by different methods at various magnification were displayed on figure 9. Under 5000 times of magnitude, there were both similarities and differences on the coatings from dissimilar methods. The similarities were the huge agglomerations and big cracks appearred on the coatings caused by the surface tension during calcination. Nevetheless, the porous structure observed on only SG- Au doped $Mn_1Co_9O_x$ / ceramic were the important factor to evaluate the efficiency of two methods. Indeed, at high magnification, the clearer observation can help study the porous coating of SG- Au doped $Mn_1Co_9O_x$ / ceramic owing to citric acid compared with absolutely smooth coating of WI- Au doped $Mn_1Co_9O_x$ / ceramic. Because the porous coating benefit for increasing the contact between active sites and reactants, the SG- Au doped $Mn_1Co_9O_x$/ceramic would be the better option than the remaining.

WI- Au doped $Mn_1Co_9O_x$ / ceramic | SG- Au doped $Mn_1Co_9O_x$ / ceramic



Firgure 9: SEM images of different coated ceramics

Table 2: BET surface area of different coated ceramics

Samples	BET surface area (m^2/g)
WI- Au doped $Mn_1Co_9O_x$ / ceramic	0.189
SG- Au doped $Mn_1Co_9O_x$ / ceramic	0.26

Catalytic activities

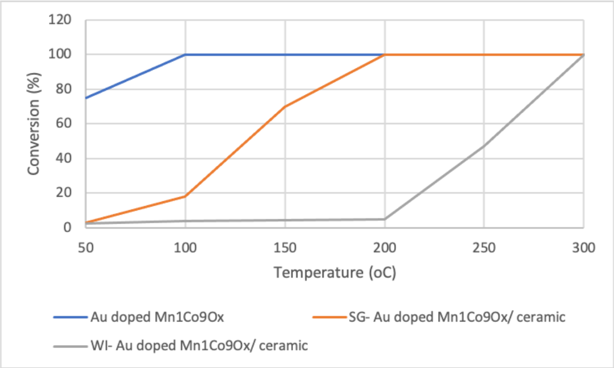


Figure 10: Catalytic activity of different catalysts

In order to determine the catalytic activities of catalyst powder and complete catalysts, they had the nearly same amount of catalyst as 0.1 g in the oxidation of CO, and the results were displayed on figure 10. The Au doped Mn_1Co_9Ox powder can oxidized CO completely at 100°C, while the SG- Au doped $Mn_1Co_9O_x$ / ceramic had T_{100} (temperature at which activity reached 100%) at 200°C, and the WI- Au doped $Mn_1Co_9O_x$ / ceramic was the worst with T_{100} at 300°C. From the characterization of catalys powder, the O_2-TPD and CO – TPD results proved that Au doped Mn_1Co_9Ox powder had both surface adsorpd oxygen species and adsorptive site for CO, combined with porous surface shown on SEM image to increase the contact possibility between active sites and reactants, the best activity of catalyst powder may be not difficult to eluciate. However, the large agglomerations on the coatings may be the reason to raise the T_{100} of coated catalysts higher three times than the catalyst powder. Furthemore, the other porous structure on coating of SG- Au doped $Mn_1Co_9O_x$ / ceramic would help its T_{100} lower 100°C than WI- Au doped $Mn_1Co_9O_x$ / ceramic.

Conclusions

The catalyst Au doped $Mn_1Co_9O_x$ powder and Au doped $Mn_1Co_9O_x$/ ceramic were prepared and characterized fully to explore their properties. Despite the fact that only typical peaks of Co_3O_4 on XRD patterns, the EPR spectra showed the presence of Au by the peak attributed at g-factor as 3.348, and the oxygen desorption peak at over 600°C in O_2-TPD profile may be a clue for the solid solution of Mn-Co-O in catalysts powder. Based on the adsorptive sited detected in CO-TPD, the catalyst Au doped $Mn_1Co_9O_x$ powder was able to oxidize CO totally at 100°C.

Both sol-gel and wet impregnation were capable to deposit Au doped $Mn_1Co_9O_x$ on ceramic. However, the SEM images of coated ceramics showd that sol-gel would be the more efficient method because of porous structure on coating. Indeed, the catalytic activity of SG - Au doped $Mn_1Co_9O_x$ / ceramic also showed the T_{100} at lower temperature than the SG - Au doped $Mn_1Co_9O_x$ / ceramic.

Acknowledgment

This investigation was supported by Vietnam General Confederation of Labour, funded by project 220/06/TLĐ implementing at Labour and Environmental Protection Center, Viet Nam National Institute of Occupational Safety and Health in corperation with E Hospital.

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