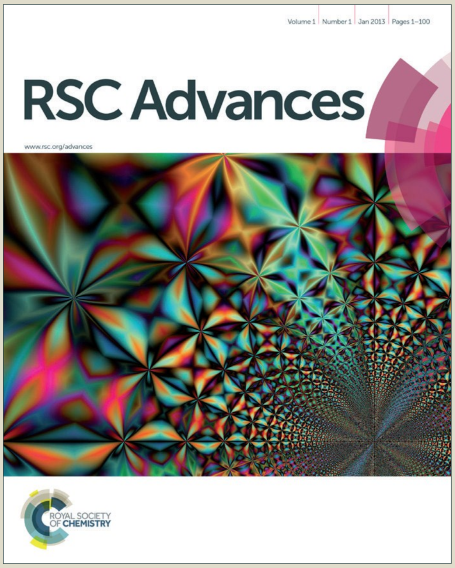
RSC Advances



Efficient Au^0/C catalyst synthesized by a new method for acetylene hydrochlorination reaction

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ABSTRACT

A new impregnation method involving mixture solvents and vacuum drying process was used to prepare gold catalyst (MIV-1Au/C1) for acetylene hydrochlorination reaction, which brought about twice higher catalytic activity than the traditional method (PI-1Au/C1). The method was green, mild and simple. Besides, it appeared to be controllable by solvents and temperatures. Excellent Au dispersion in MIV-1Au/C1 was revealed by transmission electron microscopy (TEM). Additionally, X-ray photoelectron spectroscopy (XPS) profiles proved that Au^0 was the only active species of MIV-1Au/C1 at the initial/highest point of the testing. Further XPS results showed that Au^0 could be oxidized to Au^{3+} during the reaction along with the deactivation of MIV-1Au/C1. Thus, Au^0 appeared to be preferred for the catalysis route. Our findings demonstrated the potentiality of the new method for catalysts investigation in acetylene hydrochlorination reaction. Moreover, this work highlighted the importance of Au^0 in this field.

Key words: Gold catalysts; Synthesis method; Dispersion of gold; Acetylene hydrochlorination;

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1 Introduction

Since 1980s, gold has become one of the most popular investigation topics in catalysis [1-7]. As one of the two typical catalytic systems unveiling the mystery of gold catalysis firstly [1,2], acetylene hydrochlorination reaction (C_2H_2+HCl→C_2H_3Cl), which accounts for nearly 40% of the global polyvinyl chloride (PVC) production ability, has drawn more and more attention in recent years. Along with the extensive environmental concerns, gold catalysts, especially $AuCl_3$, tend to be the most promising substitutes of commercial mercury-based catalysts for acetylene hydrochlorination reaction [8-16.]

Although nearly all of the past investigations in this field focused on Au^{3+}, the activity of Au^0 should not be completely ignored. For example, Nkosi and Huthcings [17] have prepared Au^0/C catalysts by thermal decomposition of immobilized AuCN in activated carbon. Performance tests showed that the resulting activity was competitive with Au^{3+} catalyst whilst being more stable. Besides, Wittanadecha and coworkers [14], using microwave assisted impregnation method, prepared Au^0/C catalysts that were quite active for this reaction. Regretfully, the synthesis procedures proposed by Nkosi and Huthcings was hazardous and expensive since toxic AuCN was used as precursor. Therefore, their Au^0 featuring catalyst failed to draw broad attentions. Besides, the method proposed by Wittanadecha still required the hazardous aqua regia as solvent to improve the distribution of Au during the impregnation step. In spite of the complexity in operation, aqua regia will inevitably influence the surface properties of carbon materials [18,19], which are entangled with the final catalytic performance [20-22]. According to the investigations of Conte and Hutchings [12], such situation was unfavored because it complicated further in-depth investigations on active sites. By these shortcomings, Wittanadecha's method was not appropriate for investigations of Au^0. Thereafter, a simpler and effective method to synthesize Au^0 based catalysts for acetylene hydrochlorination is imperative.

As is known to all, the catalytic efficiency of Au^0 catalysts is closely related with the dispersion degree of Au nanoparticles (Au NPs). In addition, traditional pore-volume impregnation (PI) method is extensively used to prepare gold catalysts for acetylene hydrochlorination reaction. However, without the help of aqua regia, the PI method is inefficient in gaining small AuNPs [6]. To solve this contradiction, an impregnation method using green mixture solvents, as well as vacuum drying process is introduced to synthesize Au^0/C catalyst for acetylene hydrochlorination. This technique, referred to as MIV ("M" for mixture solvents; "I" for impregnation; "V" for vacuum drying) process, has been used by our group to synthesize composite support [23]. To the best of our knowledge, it has not been used to prepare gold catalysts for acetylene hydrochlorination. We adopt this method because it is simpler than other methods designed to prepare Au^0 catalysts, such as the coprecipitation and sol gel method. Moreover, our method is much greener since it involved only green agents and mild drying conditions. Experiments testify that the MIV method is much more efficient than the PI method.

2 Experimental

2.1 Catalyst preparation

Impurities at carbon surface were removed by acid washing according to our previous report on this field [23]. Morphology and textural properties of the pretreated carbon (C1) were given in Fig. S1 and Table. S1 in the supporting information (SI).

Nominal content of Au was 1.0 wt% in the catalysts of this article, while inductively coupled plasma atomic emission spectroscopy (ICP-AES) determined Au content was used for detailed discussions.

Our MIV process involved addition of ethanol to $HAuCl_4 \cdot 4H_2O$ aqueous solution, impregnation and subsequent vacuum drying steps (Scheme 1). Since we found that the strong reducing ability of activated carbon [24,25] could help realize the fully reduction of $HAuCl_4$, no reducing agent was needed during the MIV process. The MIV method was as follows: $HAuCl_4 \cdot 4H_2O$ was dissolved in mixture of water and ethanol, wherein the solution volume was 3.2 times of the total pore volume of C1. In addition, the volume of ethanol was 2.25 times of the volume of water. The $HAuCl_4 \cdot 4H_2O$ solution was then added dropwise to the acid-washed carbon under shaking. Resulting wet sample was then dried under 60℃ for 6 h in a vacuum of −95 kPa to vaporize the solvents. Finally, the product was dried in air under 140℃ for 12 h to get rid of trace moisture in carbon before being collected for use. The final catalyst was denoted as MIV-1Au/C1 for distinction.

For comparison, gold catalyst prepared according with the pore-volume impregnation (PI) technique was denoted as PI-1Au/C1. Contrasting to other reports, we used H_2O to replace aqua regia to solve $HAuCl_4 \cdot 4H_2O$. In this case, Au^0 could be got by the reducing ability of carbon surface. Proper amount of $HAuCl_4$ aqueous solution (1.2 times of the pore volume of carbon) was added dropwise to the activated carbon support under shaking. After that, the wet product was kept at room temperature for 2 hours to gain a better impregnation. The sample was then dried at 140℃ for 12 h before being collected for use.

ICP-AES revealed that the Au content in PI-1Au/C1 and MIV-1Au/C1 was 0.983

and 0.924 wt% respectively.

2.2 Catalyst testing

The hydrochlorination of acetylene was carried out in a fixed bed laboratory microreactor. Catalysts were tested using a stainless steel reactor tube (inner diameter of 8 mm). 0.5 g of the synthesized catalyst was sandwiched between glass pearls inside the reactor for each run. N_2 was used as purging gas and the reactor was operated at atmospheric pressure at 180℃, in down-flow mode. After being heated to 180℃, hydrogen chloride was regulated by mass flow controllers and fed into the reactor alone for 10 min to remove the N_2 adsorbed in the catalysts. After that, acetylene was introduced into concentrated sulfuric acid to remove trace poisonous impurities such as acetone, moisture, S, P and As, and subsequently fed into the reactor to start the reaction. Pressure of the reactants, namely HCl and C_2H_2, was chosen for safety and in accordance with industrial condition.

A total GHSV (gas hourly space velocity) of 9800 h^{-1}, which gave a total MHSV (mass hourly space velocity) of 27.7 h^{-1}, was chosen for catalyst testing. Conversion of acetylene was not too high in this situation, thus all results obtained were in kinetic regime [26]. A reactor loaded with 0.5 g bare activated carbon presented only slight reactivity for hydrochlorination of acetylene (< 0.5% conversion of acetylene). The gas product was passed through a vessel filled with 15% sodium hydroxide solution and a drying tube in sequence to remove the remaining hydrogen chloride and moisture. The composition of the effluent was determined immediately using a gas chromatography equipped with a flame ionization detector. Catalytic performance was evaluated by conversion of acetylene (X_A), selectivity of VCM (S_{VCM}) and the deactivation rate (DR):

$$X_A=\varphi_{VCM}\times 100\% \qquad \text{(Eqn.1)}$$

$$S_{VCM}=\varphi_{VCM}/(1-\varphi_A)\times 100\% \qquad \text{(Eqn.2)}$$

$$DR=-(X_A^L-X_A^H)/t\times 100\% \qquad \text{(Eqn.3)}$$

Where φ_A and φ_{VCM} are the volume fraction of remaining acetylene and VCM in gas product separately, X_A^H and X_A^L refer to the highest and the last X_A obtained respectively during the experiment. Time span from X_A^H and X_A^L is denoted as t, in units of hours.

The specific rate of a catalyst was calculated based on the ICP-AES determined mass loading of Au in a catalyst [2]:

$$\text{specific rate}=\frac{\text{mol of acetylene converted}}{\text{mass of gold used }(g)\times\text{time }(h)} \qquad \text{(Eqn.4)}$$

2.3 Catalyst characterization

The X-ray photoelectron spectroscopy (XPS) analysis were performed by an ESCALAB 250 Xi XPS system of Thermo Fisher Scientific, England and excited by monochromatic Al Kα radiation (1486.6 eV). All binding energies were calibrated using the C(1s) carbon peak (284.6 eV).

X-ray powder diffraction spectra (XRD) were acquired with a Philips PW3050/60 vertical goniometer using Ni-filtered Cu Kα1 radiation (λ = 1.5406Å). A proportional counter and a 0.02° step size in the 2θ range from 5 to 80°. The assignment of the various crystalline phases is based on the JPDS powder diffraction file cards.

The size of the AuNPs was determined by transmission electron microscopy (TEM). JEM 2100F field emission transmission electron microscope (JEOL) working at 200 kV was used to acquire the images.

The actual Au contents in the catalysts were determined by the ICP-AES technique using ICAP 6300 (Thermo, MA). The sample was dried at 140℃ for 12 h before accurate weighing and digestion process.

3 Results and discussion

3.1 Catalytic performance

Fig. 1 shows the catalytic performance of PI-1Au/C1 and MIV-1Au/C1. Based on the ICP-AES results and Fig. 1(a), calculated specific rate of PI-1Au/C1 (Au 0.983 wt%) was 15.3 mol g^{-1} h^{-1}. For MIV-1Au/C1 (Au 0.924 wt%), a specific rate up to 29.7 mol g^{-1} h^{-1} was reached. Thus, activity of MIV-1Au/C1 was about twice as high as PI-1Au/C1. It should be noted that the mild conditions involved in MIV process had negligible influence on carbon properties crucial to catalytic performance [12]. Therefore, further investigations on active sites will be more convenient.

The selectivity of MIV-1Au/C1 and PI-1Au/C1 were both extremely high (Fig. 1 (b)), cohering with the common results of gold catalysts reported by other researchers [8,15]. PI-1Au/C1 showed an induction period as long as 3 h. By contrast, MIV-1Au/C1 reached its highest efficiency immediately after the reaction being switched on. Such situation implied that MIV-1Au/C1 had adequate active sites at its surface after preparation, whilst PI-1Au/C1 required activation to gain the best performance. From this viewpoint, MIV-1Au/C1 was more suitable than PI-1Au/C1for further study on active sites.

Further experimental results showed that the performance of MIV process was related with the composition of the solvent and the vacuum-drying temperature. As shown in Fig. 2(a), if we change the composition of the impregnating solvent (ethanol/water) by replacing ethanol with water, or acetic acid, or methanol (keep the solution volume at 3.2 times of the total pore volume of C1), the resulting specific rates varied from 12.5 to 21.4 mol g^{-1} h^{-1}, lower than the case when ethanol was used (MIV-1Au/C1). Additionally, lower specific rates of 16.9 and 23.3 mol g^{-1} h^{-1} were gained if the impregnated samples, using ethanol and water as impregnating solvent, were vacuum-dried at 25 and 40℃ respectively instead of 60℃ (Fig. 2(b)).

These findings implied that the option of solvent and drying temperature was crucial for MIV process, probably because solvent could influence the transportation of Au species in the support while drying temperature determined the immobilization of those Au. That is to say, both solvent and vacuum drying temperature had impact on the crystallization process of Au species, which would modify the distribution of Au in different samples. Thus, according to Fig. 2, might it be the case that MIV process is controllable by adjusting the composition of solvents and the vacuum drying temperature. According to current data, the mixture of ethanol and water as well as 60℃ vacuum-drying seemed proper. Additional parameters, namely the volume of the solvent and the vacuum degree, still need further investigations. This will be done in our further work.

3.2 State of gold in the fresh catalysts

Fig. 3 shows the XPS analysis of PI-1Au/C1 and MIV-1Au/C1. It is immediately evident that both of PI-1Au/C1 and MIV-1Au/C1 have no Au^{3+} species [9,12] at their surfaces. As was stated, the emergence of the great amount of Au^0 was associated with the high reducing ability of activated carbon [24,25]. It seemed that without strong oxidants such as aqua regia, Au^{3+} was unstable at the reducible surface of activated carbon. Such phenomenon cohered with the literatures. Usually, only small amount of Au^{3+} could be acquired even if aqua regia was used as the impregnating solvent [8,12,27]. The higher XPS intensity of MIV-1Au/C1 implied that a higher dispersion degree was obtained in it, since XPS is a surface technique and the signal strength is a function of the surface to bulk atoms ratio [9].

Crystal form of Au was then determined by XRD technique. XRD spectra of C1, PI-1Au/C1 and MIV-1Au/C1 catalysts are showed in Fig. 4. The broad peaks in the range of 2θ = 40~48° typical of carbon materials are observed in the XRD pattern of C1, implying its amorphous framework. Besides, weak signals at 2θ of 36.5, 50.1, 60 and 68.1 ° are displayed and assigned to (110), (112), (211) and (203) facets of α-quartz (JCPDS PDF-46-1045). For PI-1Au/C1 and MIV-1Au/C1, very strong peaks at 2θ of 38, 44.3, 64.5, and 77.5° were attributed to the (111), (200), (220) and (311) diffractions of face-centered cubic (FCC) metallic gold (JCPDS PDF-04-0784). The presence of Au^0 peaks cohering with the XPS results.

To determine the dispersion degree of AuNPs in both catalysts, TEM was applied. Representative TEM images of PI-1Au/C1 and MIV-1Au/C1 are displayed in Fig. 5. Plenty of small and isolated AuNPs could be discerned in both samples while some apparent differences could be easily identified. Following PI method, the resulting AuNPs diversified in shape (Fig. 5(a)). This was in line with previously reported Au/C catalysts that synthesized according to impregnation method [8,15]. With more than 60% AuNPs in the size range of 8~12 nm, the mean particle size in PI-1Au/C1 was determined to be 10.6 nm. In stark contrast to PI-1Au/C1, MIV-1Au/C1 showed the most peculiar characteristic of spherical AuNPs (Fig. 5(b)), which might be triggered by the interfacial tension between water and ethanol and their difference in evaporability. Additionally, The mean particle size in MIV-1Au/C1 was determined to be 5.2 nm, much smaller than that in PI-1Au/C1. It should be noted that very small AuNPs with diameters of 2 ~ 6 nm accounted for about 60% of the number of AuNPs in this sample, implying an excellent dispersion of gold. This could be attributed to the rapid evaporation of ethanol under the heated vacuum circumstance, which may cause fast nucleation of gold species rather than growth of the crystallites. Such achievement clearly confirmed that MIV method was effective in synthesis small AuNPs. The resulting AuNPs were preferred for high activity since spherical and smaller AuNPs could provide more surficial atoms and defects for the catalysis process [28].

The most inactive sample in each experimental set of Fig. 2, referred to as H_2O-MIV-1Au/C1 and MIV-25-1Au/C1, were also characterized to illuminate the influence of solvent and vacuum-drying temperature. XPS results (Fig. S2) testified 100% Au^0 in both samples while the signal strength was much smaller than MIV-1Au/C1, implying lower surface/bulk Au ratio in them. TEM further confirmed the XPS results since only big clusters of AuNPs were discerned in both of the two catalysts (Fig. S3), which led to poor gold dispersion. This firmly testified that solvent and vacuum-drying temperature could greatly influence the crystallization process of gold species during the MIV process.

3.3 Evolution of Au^0 during the reaction

Although only Au^0 could be detected in the fresh catalysts, Nkosi [17] and Wittanadecha [14] have mentioned that HCl could oxidize Au^0 to Au^{3+} through coordination with surficial gold atoms. In this viewpoint, active site of the catalysts should be discussed in a more rigorous way. It is necessary to monitor the evolution of Au species during the experimental processes to distinguish the contributions of different Au species to catalytic activity. MIV-1Au/C1 was chosen for such analysis because it was much more active and did not need any activation. The latter feature meant that no transformation of active sites was required to reach the highest catalytic efficiency.

In our experiments, oxidation of Au^0 might take place during the HCl purging process before the reaction being switched on (10 min, subsection 2.2). Additionally, Au^0 might be oxidized during the reaction.

To clarify the initial Au^{3+} content at the starting point of the performance testing, the XPS spectrum of MIV-1Au/C1 after HCl purging was firstly taken. No signal of Au^{3+} exceeded the noise of the equipment was viewed (SI, Fig. S4). Furthermore, after 15 min of acetylene hydrochlorination reaction, no obvious Au^{3+} emerged (SI, Fig. S5). Thus, no apparent transformation of the active sites happened during these short periods. Accordingly, the initial/highest activity of MIV-1Au/C1 was totally attributed to Au^0.

By contrast, as the testing time was lengthened, Au^{3+} content markedly increased at the surface of MIV-1Au/C1, as shown in Fig. 6. This clearly confirmed the oxidation of Au^0 by HCl. However, the increase in Au^{3+} content was much more significant than the decrease in activity (Fig. 6(b) and Fig. S6). That is, the two quantities are not proportional to each other, suggesting that Au^0 was the main active species.

4 Conclusions

An impregnation method involved mixture solvents and vacuum-drying process, referred to as MIV method, was introduced to prepare gold catalysts (MIV-1Au/C1) for acetylene hydrochlorination reaction. With a specific rate up to 29.7 mol g^{-1} h^{-1}, MIV-1Au/C1 appeared to be twice as active as the catalyst prepared by traditional PI method (PI-1Au/C1), testifying that the MIV method was applicable in this subject. The MIV method involved only green solvents and mild conditions; hence, it had negligible influence on the surface properties of the support. Such situation will simplify further investigations on gold active sites. Besides, it was demonstrated that solvent and vacuum-drying temperature were both key parameters in determining the final achievement of MIV process, which made the MIV method adjustable.

Only Au^0 was presented at the surface of the resulting MIV-1Au/C1 catalyst, which was in the FCC form. TEM observations revealed a mean AuNPs size of 5.2 nm in MIV-1Au/C1, which was much smaller than that in PI-1Au/C1. Thus, gold dispersion in MIV-1Au/C1 was much higher. It was proved that Au^0 was the only active species that enabled the initial/highest activity of MIV-1Au/C1. Further analysis testified that Au^0 could be oxidized to Au^{3+} during the reaction. However, the increase in Au^{3+} content was much more significant than the decrease in activity. Such non-proportional relationship suggested that Au^0 was the main active species in our catalyst.

Acknowledgements

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at xxxx.

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Figure captions:

Scheme 1 Schematic representation of MIV process.

Fig. 1 Catalytic performance of PI-1Au/C1 and MIV-1Au/C1: (a) Conversion of acetylene and (b) Selectivity of VCM. Reaction Conditions: C_2H_2 flow rate = 77 mL/min, HCl/C_2H_2 = 1.13, Temp = 180℃, GHSV = 9800 /h.

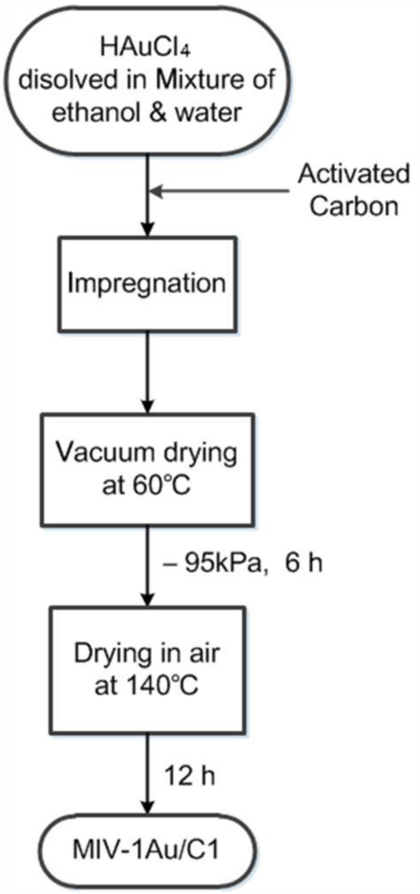
Fig. 2 (a) Influence of solvents on the final catalytic activity following MIV method; (b) Influence of vacuum-drying temperature on catalytic activity when water and ethanol was used as solvents. Reaction Conditions: C_2H_2 flow rate = 77 mL/min, HCl/C_2H_2 = 1.13, Temp = 180℃, GHSV = 9800 /h.

Fig. 3 XPS profiles of fresh PI-1Au/C1 and MIV-1Au/C1 catalysts.

Fig. 4 XRD patterns of bared activated carbon (C1), PI-1Au/C1 and MIV-1Au/C1.

Fig. 5 TEM images and histograms showing the distribution of AuNPs (inset): (a) PI-1Au/C1 and (b) MIV-1Au/C1.

Fig. 6 Valence change of Au: (a) XPS spectra of spent MIV-1Au/C1 after 300 min testing; (b) Evolution of catalytic activity and Au^{3+} content during the testing duration.


HAuCl4
disolved in Mixture of
ethanol & water
Activated
Carbon
Impregnation
Vacuum drying
at 60°C
– 95kPa, 6 h
Drying in air
at 140°C
12 h
MIV-1Au/C1

Scheme 1

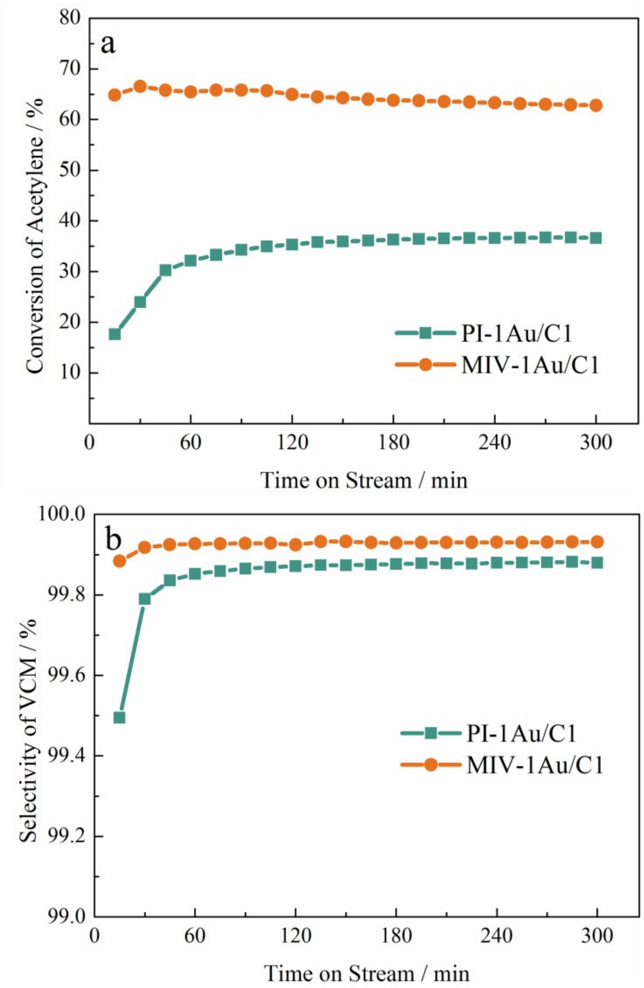
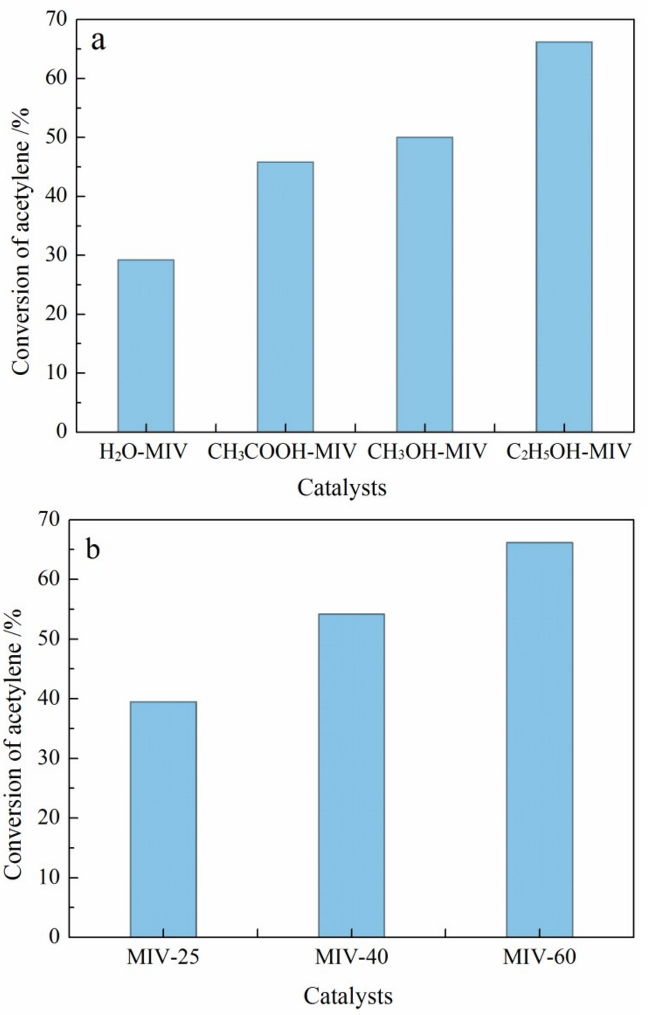

a
Conversion of Acetylene / %
80
70
60
50
40
30
20
10
0
60
120
180
240
300
Time on Stream / min
PI-1Au/C1
MIV-1Au/C1
b
Selectivity of VCM / %
100.0
99.8
99.6
99.4
99.2
99.0
0
60
120
180
240
300
Time on Stream / min
PI-1Au/C1
MIV-1Au/C1

Fig. 1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Conversion of acetylene /%
0
10
20
30
40
50
60
70
H2O-MIV
CH3COOH-MIV
CH3OH-MIV
C2H5OH-MIV
Catalysts
b
Conversion of acetylene /%
0
10
20
30
40
50
60
70
MIV-25
MIV-40
MIV-60
Catalysts

Fig. 2

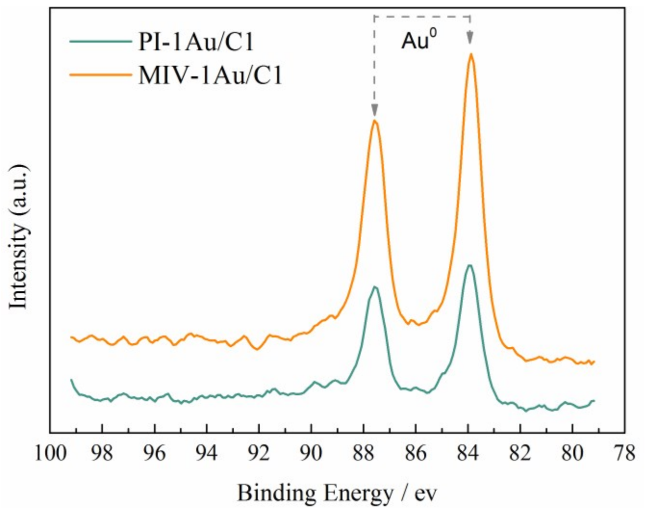
PI-1Au/C1
MIV-1Au/C1
Au^0
Intensity (a.u.)
100
98
96
94
92
90
88
86
84
82
80
78
Binding Energy / ev

Fig. 3

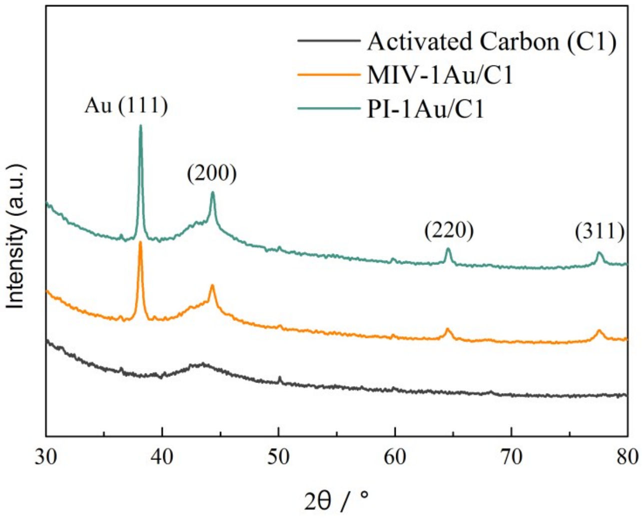
Activated Carbon (C1)
MIV-1Au/C1
PI-1Au/C1
Au (111)
(200)
(220)
(311)
Intensity (a.u.)
30
40
50
60
70
80
2θ / °

Fig. 4

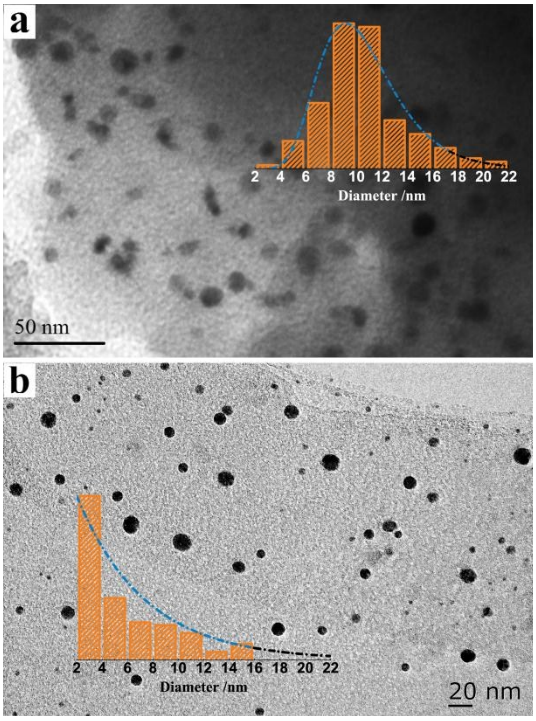
a
2 4 6 8 10 12 14 16 18 20 22
Diameter /nm
50 nm
b
2 4 6 8 10 12 14 16 18 20 22
Diameter /nm
20 nm

Fig. 5

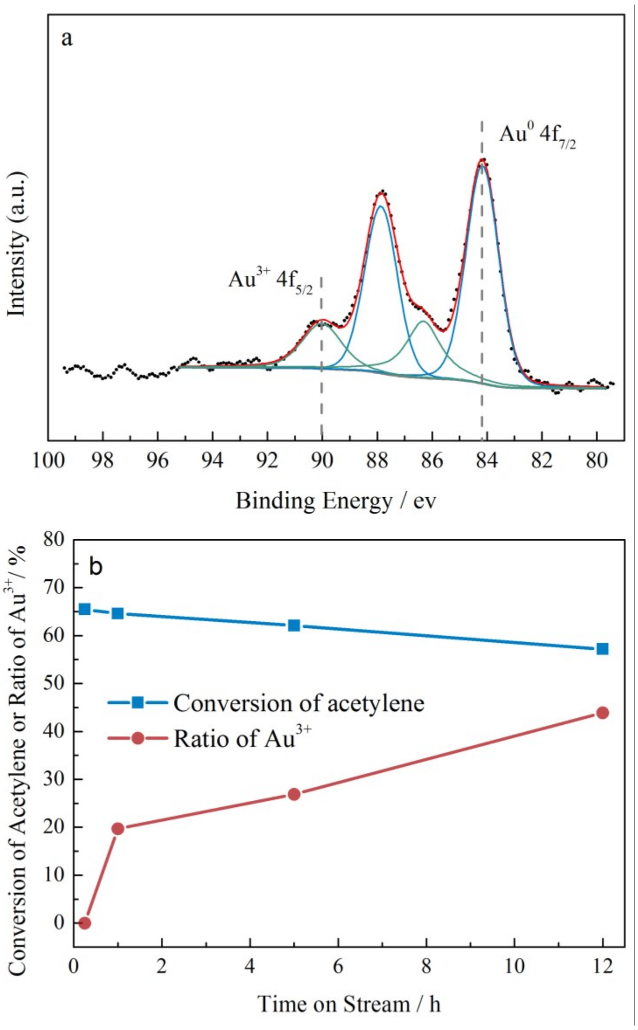
a
Au^{0} 4f$_{7/2}$
Au^{3+} 4f$_{5/2}$
Intensity (a.u.)
100 98 96 94 92 90 88 86 84 82 80
Binding Energy / ev
b
Conversion of Acetylene or Ratio of Au^{3+} / %
0 10 20 30 40 50 60 70 80
Conversion of acetylene
Ratio of Au^{3+}
0 2 4 6 8 10 12
Time on Stream / h

Fig. 6

Efficient Au^0/C catalyst synthesized by a new method for acetylene hydrochlorination reaction

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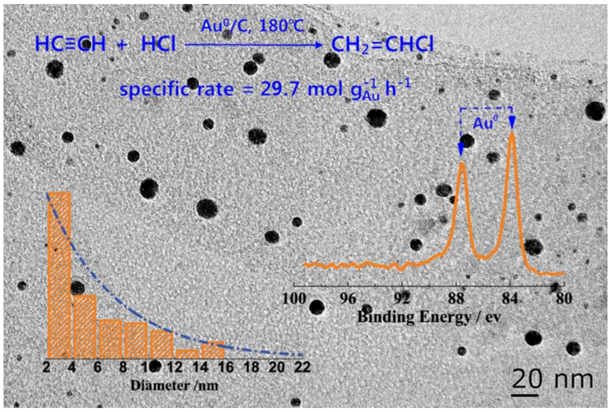
Graphical Abstract:



Au^0/C catalyst for acetylene hydrochlorination reaction was prepared via a novel method, excellent Au dispersion and catalytic activity was obtained.