

Review

Progress and Challenges of Mercury-Free Catalysis for Acetylene Hydrochlorination

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Abstract: Activated carbon-supported HgCl_2 catalyst has been used widely in acetylene hydrochlorination in the chlor-alkali chemical industry. However, HgCl_2 is an extremely toxic pollutant. It is not only harmful to human health but also pollutes the environment. Therefore, the design and synthesis of mercury-free and environmentally benign catalysts with high activity has become an urgent need for vinyl chloride monomer (VCM) production. This review summarizes research progress on the design and development of mercury-free catalysts for acetylene hydrochlorination. Three types of catalysts for acetylene hydrochlorination in the chlor-alkali chemical industry are discussed. These catalysts are a noble metal catalyst, non-noble metal catalyst, and non-metallic catalyst. This review serves as a guide in terms of the catalyst design, properties, and catalytic mechanism of mercury-free catalyst for the acetylene hydrochlorination of VCM. The key problems and issues are discussed, and future trends are envisioned.

Keywords: vinyl chloride monomer; acetylene hydrochlorination; mercury-free catalysts; noble metal catalyst; non-noble metal catalyst; non-metallic catalysts

1. Introduction

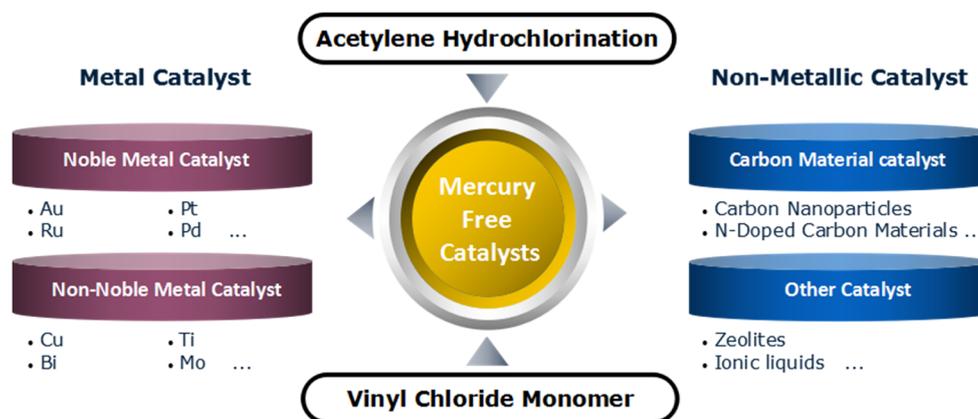
Polyvinyl chloride (PVC) is one of the most important general purpose plastics. It is widely used in daily necessities and industrial application. It has the advantages of cheap and affordable features while also having superior comprehensive performance [1]. PVC is used in building materials, floor leather, packing materials, wires and cables, commodities, and other aspects [2]. In 2016, the global demand for PVC exceeded 45 million tons, among which China's PVC production exceeded 23 million tons, making it the world's largest producer and consumer of PVC [1]. PVC is a polymer made from vinyl chloride monomer (VCM) through the free radical polymerization mechanism. At present, the synthesis of VCM is mainly divided into three kinds: Ethane oxychlorination, ethylene oxychlorination, and acetylene hydrochlorination, respectively. Ethane oxychlorination started with natural gas resources, which is a new clean production process [1]. The lack of catalyst with good performance, especially high selectivity, is one of the main limiting factors restricting the method [3]. Ethylene oxychlorination is an environmentally benign process that depends on petroleum fossil fuels. Acetylene hydrochlorination is an important alternative process for the production of VCM in the coal-rich areas and the country [4–6]. In recent years, the increasing price of crude oil has highlighted the economic advantages of acetylene hydrochlorination. In the reaction of acetylene

hydrochlorination to VCM, the atomic utilization of reactants is 100% [1]. The reaction process is as follows:



This reaction is exothermic with high selectivity, and the optimum reaction temperature is 170–180 °C [6]. For more than 60 years, almost all the catalysts used in this process in industry are mercury-containing catalysts, with the dosage of HgCl_2 ranging from 5 wt % to 12 wt % [7]. However, Hg catalysts have several disadvantages. HgCl_2 is a linear triatomic aggregate, which is easily sublimed during the hydrochlorination reaction. The life cycle of the catalyst is correlated to the amount of HgCl_2 catalyst loaded on the support [8]. During the acetylene hydrochlorination reaction, high temperature (180–220 °C) and pressure induces the desorption and sublimation of the HgCl_2 . This not only causes a loss of HgCl_2 from the support but also poses a serious pollution problem [7]. The high temperature generates hot spots that aggravate the situation, resulting in a significant amount of mercury loss [9]. As a cumulative toxin, HgCl_2 is extremely toxic and harmful. Therefore, the loss of HgCl_2 will not only lead to the deactivation of the catalysts but also cause serious environmental issues [10]. Although efforts have been taken to recycle the losing mercury, about 25% of it is released directly into the environment [11]. In order to solve this issue, worldwide, the Minamata Convention has agreed on controlling the mercury emission reduction act in 2013 by the United Nations Environment Protection Committee. The agreement came into effect on 16th August 2017.

In order to reduce the mercury compounds released from the hydrochlorination process, it is urgent and of paramount importance to develop environmentally friendly green mercury-free catalysts as substitutes. In this review, we discuss the recent research progress and challenges for mercury-free catalysts (Scheme 1). Perspectives and future trends for the development of greener and cleaner processes for VCM production with mercury-free catalysts are also discussed.



Scheme 1. Mercury-free catalysts for acetylene hydrochlorination.

2. Noble Metal Catalysts

The research of acetylene hydrochlorination catalysts supported by metal has been going on for 50 years. Smith et al. reported compound metal (Hg, Bi, Ni, Zn, Cd, Cu, Mn, and Ca) catalysts supported on silica for acetylene hydrochlorination in 1968 [12]. In 1975, Shinoda prepared metal chloride catalysts with activated carbon as the support. In their work, the results revealed that the catalytic activity of metal chloride was well correlated to the electron affinity of metal cations (Figure 1) [13]. One class of metal cations had its catalytic activity increase with the increase of electron affinity. Meanwhile, another class

of metal cations demonstrated the opposite trend, and this was considered to be due to cations forming complexes with HCl of the type $H_m[MCl_{n+m}]$, which were Friedel–Crafts-type catalysts [14].

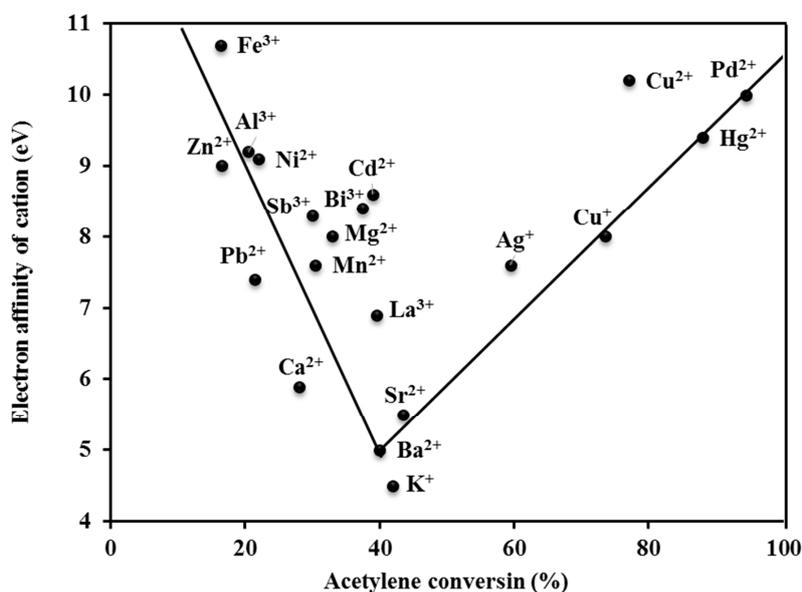


Figure 1. The relationship between acetylene hydrochlorination activity of metal chlorides and electron affinities of metal cations. Adopted from Ref [13].

In 1985, Hutchings evaluated a series of supported metal chloride catalysts analyzed by Shinoda and made different attribution associations. Hutchings reported that the interaction between acetylene and metal chloride may involve the transfer of more than one electron. Therefore, the standard reduction potential was considered to be a more appropriate parameter to correlate catalytic activity. Except for a few metals such as K, Ba, Mg, and La, most of the metals showed a positive correlation between its activity and the standard electrodes potential in acetylene hydrochlorination (Figure 2) [14]. The proposed correlation has certain guiding significance to the research of acetylene hydrochlorination. Based on these results, a large number of studies on mercury-free catalysts are conducted on noble metals.

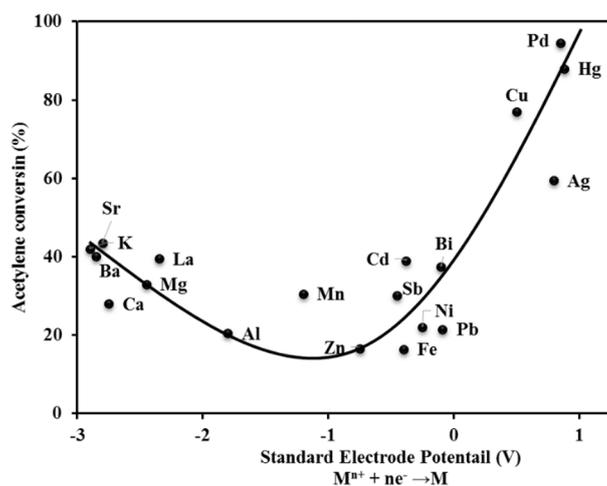


Figure 2. The relationship between acetylene hydrochlorination activity of metal chlorides and standard reduction potential [14].

2.1. Au Catalysts

In 1985, Hutchings predicted that Au might have good activity for acetylene hydrochlorination [14]. The prediction was verified in the article reported in 1988 [8]. Figure 3 further confirmed the correlation with the standard electrode potential. Since then, studies on supported Au catalysts have been increasing. The earliest method for preparing Au catalysts was to dissolve the gold of high purity in aqua regia and on the carbon support, which could minimize the introduction of impurities and avoid the adverse effects of impurities on the catalysts [8,15,16].

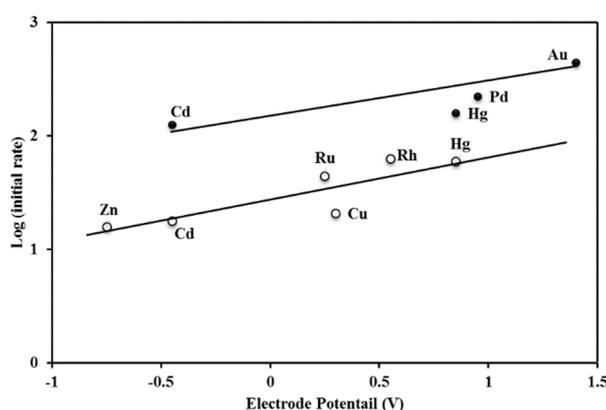


Figure 3. The correlation between catalytic activity and standard electrode potential of metal cations in acetylene hydrochlorination [16].

2.1.1. Auⁿ⁺ Catalysts

Most studies on the catalytic mechanism of Au catalysts showed that the amount of Au³⁺ had a great correlation with the catalytic activity and was considered as the active species for acetylene hydrochlorination. For Au species, the order of catalytic activity was Au³⁺ > Au⁺ > Au⁰. Although it has also been reported that AuCl can be used as a catalytic active species [17], due to the poor stability of AuCl in aqueous solution and reaction conditions, a disproportionation reaction occurs, resulting in the formation of AuCl₃ and elemental Au:



Since the equilibrium constant of the reaction is very large (10^{10} orders of magnitude), it can be considered that there is almost no free Au⁺ in aqueous solution, and it is difficult to prepare supported AuCl catalysts using conventional preparation methods. Therefore, Au³⁺ catalyst is the most studied and applied catalyst.

Conte et al. demonstrated that exposure to HCl before reaction led to enhanced catalyst activity, whereas exposure to acetylene resulted in a decrease of catalyst activity [5]. It was proposed that the catalytic activity of Au³⁺ could be explained by two possible mechanisms: (a) a nucleophilic electrophilic interaction between the Au³⁺ center and a triple bond of acetylene through π -coordination; and (b) the acidic protons of the terminal alkyne facilitated σ -coordination [5,18,19]. The reaction mechanism of HAuCl₄ (Au³⁺) as the active species was proposed in Figure 4 [5]. This mechanism involved the presence of both acetylene and HCl for a six-member ring. In the six-member ring, the alkyne axially coordinated to the Au³⁺ center. Density functional theory (DFT) calculations implied that it was unlikely that the simultaneous coordination of acetylene and HCl to the Au³⁺ center would occur. The transition state for HCl addition to the π -complex of acetylene with AuCl₃ by calculation predicted that the stereochemistry of Cl addition was controlled by a hydrogen bond between HCl and a Cl ligand of Au. The anti-addition of HCl observed experimentally was a consequence of a sequential addition of Cl and H to the acetylene [5,6,20–23].

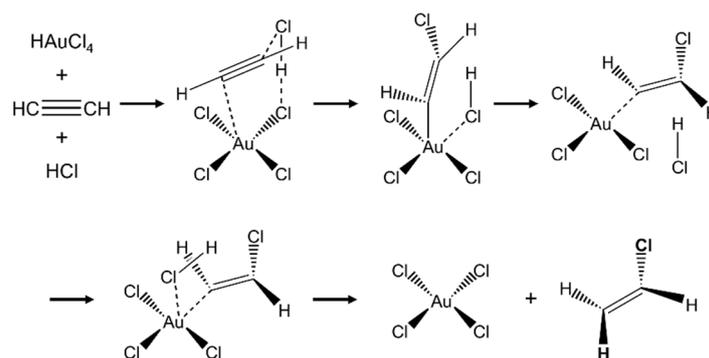


Figure 4. Acetylene hydrochlorination model of Au^{3+} catalyst [5].

The preparation method of catalysts has an important influence on its performance and activity. Conte et al. showed that Au could be highly dispersed on support with acid as the solvent [24]. They found that aqua regia was the most effective solvent for preparing the catalyst, while catalysts prepared using HCl or HNO_3 individually were less active. The superior activity of the catalyst prepared in aqua regia was proposed to be a combination of the oxidizing effect of HNO_3 and the nucleating effect of HCl. Both of these are helpful to promote the high dispersion of Au [5,7,25]. Although aqua regia is an effective solvent, it is extremely corrosive and dangerous, causing negative impacts on the environment and threatening the safety of the process. In addition, there are many difficulties in the treatment, recovery, and disposal of the used aqua regia, so it is not suitable for industrial application [26,27]. Therefore, researchers began to develop a similar activation protocol that could be realized by using other environmentally friendly solvents.

The general mechanism of catalyst deactivation is the reduction of Au^{3+} to Au^0 . It is urgent to improve the stability of active Au^{3+} species and extend the service life of the catalyst. Zhao et al. reported that organic aqua regia (OAR, 1:10 SOCl_2 : DMF) could be used as a substituent for conventional aqua regia to activate Au/AC catalyst with Au^{3+} as the active center. OAR could promote Au oxidation and help achieve high disparity. The content of Au^{3+} species in Au(H_2O)/AC(OAR) was greater than that in the Au(aqua regia)/AC sample, indicating that OAR treatment could partially promote the oxidation of Au^0 into Au^{3+} . Residual S and N stabilized the Au^{3+} species and generated a more thermally stable catalyst by forming Au–S complexes, increasing the electron density of the Au center through electron transfer, enhancing the reduction temperature of Au^{3+} , and promoting the effective adsorption of HCl on the Au catalyst (Figure 5) [28].

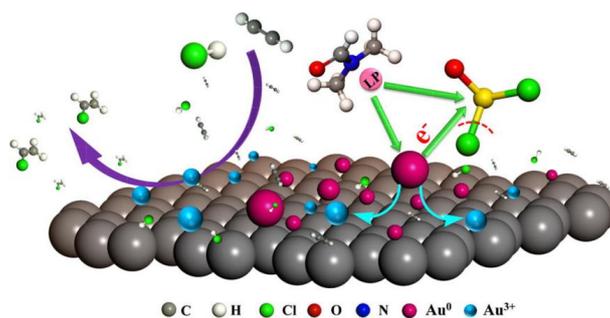


Figure 5. Au catalysts prepared by organic aqua regia [28].

Huang et al. studied the effect of the 1,10-phenanthroline ligand on Au catalyst performance. With an appropriate ligand, the $[\text{AuCl}_2(\text{phen})]\text{Cl}$ catalyst achieved excellent acetylene conversion (90%) after 40 h of operation. The enhanced catalytic stability was attributed to the presence of

the phen ligand; electron transfer from the phen species to the Au^{3+} center increased the Au^{3+} electron density, which inhibited the active Au^{3+} component deactivation [29].

Chao et al. prepared Au catalysts using activated carbon pretreated at different temperatures. It was shown that thermal treatments can change the surface functional groups on activated carbon. Ketone, lactone, and carbonyl tended to anchor Au on the surface with a good dispersion state. The phenolic and alcohol groups can easily reduce Au^{3+} to Au^0 , which is not active for the reaction. Surface functional groups may be a constituent part of the active sites adsorbing and activating acetylene. This indicated that both Au^{3+} and the surface functional groups work in synergy as the active sites [30].

2.1.2. Au^0 Catalysts

There are some studies that have reported that Au^0 is the active center of Au catalysts. The catalytic efficiency of Au^0 catalysts is closely related with the dispersion degree of Au nanoparticles (Au NPs). Some researchers have demonstrated that the various edges or defects of multiple-twinned or polycrystalline particles formed on the surface of the Au NPs catalyst have high surface stress and are easily broken to reduce their surface energy, thus providing active sites for acetylene hydrochlorination.

Zhang et al. revealed that Au^0 catalyst activity was strongly associated with the properties of the used solvent. It was found that the catalyst's activity increased with the decreased polarity of solvents. Compared to polar solvents such as water and aqua regia, less polar solvent alcohols would influence the formation of crystallization of Au NPs. The mean particle size in Au-x/AC (x = alcohol) catalysts was determined to be 3.9–4.7 nm and showed peculiar characteristic of spherical Au NPs, demonstrating good dispersity on the catalysts. Au NPs exhibited good catalytic activity. Polycrystalline particles formed with various edges or defects could act as active sites. Weakly polar alcohols facilitated the interfacial interaction between the support and Au^0 species, made the active species highly dispersed, and anchored and inhibited the agglomeration and loss during the reaction. Moreover, the interaction also enhanced catalytic activity by increasing the adsorption capacity on the catalyst's surface [31].

Different preparation methods including ultrasonic, microwave, and incipient wetness impregnation were also studied and compared for acetylene hydrochlorination. Wittanadecha et al. investigated the catalytic performance of Au^0 catalysts using different preparation routes. It was found that the ultrasonic-assisted method improved the dispersion of the active component and increased the pore volume and aperture of the support. Noticeably and interestingly, only the initial activity of the catalyst was affected with different pretreatment processes, while the overall catalyst activity was almost unaffected. They suspected that the active Au species is Au^0 . The Cl-containing substance is chemically adsorbed and reacts with acetylene to form a VCM [32].

Tian et al. prepared an Au catalyst (MIV-1Au/C1) with significantly increased activity. The catalysts were synthesized using mixed solvents and vacuum drying instead of the traditional impregnation method. Au^0 with a mean size of 5.2 nm was in the face-centered cubic form and was the only active species of MIV-1Au/C1 at the initial/highest point of the testing. The active species of Au^0 could be oxidized to Au^{3+} and became deactivated during the acetylene hydrochlorination reaction. The particle size of Au NPs prepared by this method was much smaller than that by the immersion method [33].

2.1.3. Modification of Au Catalysts

Efforts were devoted to improving the efficiency and enhancing the stability of active sites of Au catalysts. Adding synergistic metals, forming ligand coordination, and support modification have been attempted to solve the problems of catalysts deactivation, coke deposits, and Au particles aggregation (Scheme 2).



Scheme 2. Modification of Au catalysts.

Addition Synergistic Metal

Au^{3+} catalysts suffer from poor stability both during preparation and application. One way to solve this problem is to dope Au with other elements so that the electronic state of the active sites can be tuned. In 2008, Conte et al. studied the effect of different metal additives on the catalytic performance of Au^{3+} catalysts. The metals used include Pd, Pt, Ir, Rh, and Ru. The results showed that dispersed pure Au was actually the most active one for acetylene hydrochlorination in a long run. The addition of other metals did not improve the catalytic reactivity [34]. However, in recent years, studies have shown the opposite observations and conclusions when Au was doped with other elements, such as La, Cu, Bi, Sn, Ce, Sr, etc. to modified Au catalysts, which may have higher catalytic stability due to synergy effects [35]. On the one hand, the loading capacity of Au can be reduced, which led to reducing the cost of catalyst by adding metal additives. On the other hand, these metal additives provide electrons to Au^{3+} , absorb more oxidizing HCl, and slow down the reduction of Au^{3+} . Table 1 lists some AuM catalysts prepared with HAuCl_4 in collaboration with other synergistic metal precursors. The results show that the addition of metal additives can improve the dispersion of Au^{3+} , stabilize the chemical valence of the active center, enhance the electron cloud density of the Au^{3+} active center, inhibit carbon deposition, and finally improve the catalytic efficiency for acetylene hydrochlorination.

Table 1. Performance of AuM catalysts for acetylene hydrochlorination.

Year	Catalyst	Synergistic Metal	Au (wt %)	GHSV (h^{-1})	Temp ($^{\circ}\text{C}$)	Acetylene Conv. (%)	Running Time (h)	Ref.
2019	AuCe	CeO_2	0.1	60	180	99.9	70	[4]
2016	AuCe	CeO_2	1.0	852	180	98.4	20	[36]
2017	AuY	YCl_3	1.0	800	180	87.8	10	[37]
2016	AuSn	SnCl_2	0.9	720	170	95	48	[38]
2017	AuCu	CuCl_2	0.1	740	180	98.5	500	[39]
2016	AuCu	CuCl_2	0.1	120	150	97	4	[40]
2015	AuCu	CuCl_2	0.25	120	150	97	2	[41]
2017	AuCuK	CuCl_2/KCl	0.2	40	165	89	1600	[42]
2014	AuCoCu	$\text{Co}(\text{NH}_3)_6\text{Cl}_3/\text{CuCl}_2$	1.0	720	150	99	5	[43]
2018	AuSr	SrCl_2	1.0	1806	180	99.7	180	[44]
2016	AuSr	SrCl_2	1.0	762	180	87.7	20	[45]
2015	AuBa	BaCl_2	1.0	360	200	98.4	50	[46]
2015	AuCs	CsCl	1.0	740	180	94	50	[47]
2015	AuCs	CsCl	1.0	1480	180	90.1	50	[48]
2015	AuInCs	$\text{CsCl}/\text{InCl}_3$	1.0	1480	180	92.8	50	[49]
2014	AuBi	BiCl_3	1.0	600	180	85	10	[17]
2014	AuBi	BiCl_3	1.0	120	150	96	10	[50]
2014	AuTi	TiO_2	1.0	870	180	92	10	[51]
2014	AuNi	NiCl_2	1.5	900	170	95.4	46	[52]
2013	AuCo	$\text{Co}(\text{NH}_3)_6\text{Cl}_3$	1.0	360	150	99.9	36	[53]
2012	AuLa	LaCl_3	1.0	360	150	98	50	[54]

Ligand Coordination

It is a common modification method to introduce suitable ligands to stabilize the high valence Au^{3+} in Au catalysts. Results showed that the activity and stability of the Au^{3+} catalyst could be

significantly improved with the addition of chelating donors and N-containing ligands. The donor groups include thiosulfate, thiocyanate, thiourea, and cyanides [55,56]. The catalyst complexes can be prepared by synthesizing complexes and then loading them on the support; or they can be formed by directly adding the precursor of the complexes to the HAuCl_4 during the preparation process and then forming the Au complexes with catalytic activity in situ. Zhou et al. reported an Au catalyst with thiocyanate ($-\text{SCN}$) donors with 0.25 wt % Au loading. The donor significantly decreased the electrode potential of Au^{3+} from 0.926 to 0.662 V. Complexion prevented Au catalyst deactivation by increasing the reaction energy barrier [57]. Table 2 shows some Au catalysts prepared with different ligand precursors; Au^{3+} has high catalytic activity for acetylene hydrochlorination.

The catalytic activities of Au^0 catalysts (Au NPs) could be influenced by many factors. These factors include the Au cluster size and shape [58,59], the cluster charge [60,61], the structure of the support material [62], and the ligand [63]. Recently, it was found that doped Au clusters can form distinctive structures and achieve enhanced properties. Zhao et al. proposed a mechanism for pristine Au_7 and Au_8 clusters catalysts and, on the Si-doped Au clusters, Au_6Si and Au_7Si based on DFT. The results showed that the reaction process of acetylene hydrochlorination catalyzed by Au^0 involved two steps. In the first step, HCl disassociated and Cl was added, which was followed by H addition through the transfer of protons from the Au cluster to acetylene chloride. Doping can not only change the size and shape of Au clusters but also improve the efficiency for acetylene hydrochlorination [64].

Table 2. Au catalysts prepared with different ligand precursors.

Year	Catalyst	Ligand	Au (wt %)	GHSV (h^{-1})	Temp ($^{\circ}\text{C}$)	Acetylene Conv. (%)	Running Time (h)	Ref.
2016	Au/TCCA	Trichloroisocyanuric acid	0.2	90	180	98	24	[65]
2015	$\text{HAu}(\text{C}_3\text{Cl}_3\text{-N}_3\text{O}_3)_3\text{Cl}$	Trichloroisocyanuric acid	1.0	500	130	52	24	[8]
2015	$\text{Au}(\text{CS}(\text{NH}_2)_2)$	Thiourea	0.1	500	130	95	24	[8]
2015	Au/SCN	KSCN	0.25	1200	180	99	10	[57]
2014	$[\text{AuCl}_2(\text{phen})]\text{Cl}$	1,10-phenanthroline	0.49	603	180	90	40	[29]
2013	$\text{AuCl}_3/\text{PPy-MWCNT}$	Pyrrole	1.47	120	150	90	10	[66]

Support Modification

Support is an important component of catalysts and has a great influence on the performance of Au catalysts. Choosing an appropriate support material is crucial under rigorous reaction conditions. The catalysts need to be robust and stable enough at high temperature. Support is also critical in view of stabilizing the highly dispersed metal chloride and preventing the agglomeration of active components [7]. For supported metal catalysts, support modification is common to increase the guest–host interaction. One example is to dope carbon support with heteroatoms such as N, B, and P.

The catalytic performance of supported metal catalysts is greatly dependent on the properties of the support. Carbon materials are recognized as ideal supports because of their large surface area and good electrical conductivity. Chen et al. observed that mesoporous carbon supports could increase the activity of Au^{3+} catalysts prepared with an HAuCl_4 precursor. The pore size of supports was important because large pore sizes allowed rapid diffusion and suppressed coke formation [67]. Jia et al. reported that the addition of a B species was favorable for the stabilization of active Au^{3+} species and the inhibition of a transition from Au^{3+} to Au^0 . In addition, the B species also inhibited carbon deposition and catalyst sintering during the reaction [68].

Zhang et al. reported several Au–bimetallic catalysts for acetylene hydrochlorination. The catalysts were prepared with HAuCl_4 and LaCl_3 precursors on different supports. The results indicated that compared with SiO_2 and TiO_2 , coconut shell activated carbon and pitch-based spherical activated carbon were desirable. These supports showed more developed pore structures and had larger specificity. Pitch-based spherical activated carbon was found to be more desirable for acetylene hydrochlorination than coconut shell activated carbon because it had a higher N content. Au particles' aggregation and the loss of Au^{3+} would decrease the catalyst activity. Furthermore, the valence change of Au^{3+} and

carbon deposition were also responsible for catalyst deactivation. The addition of La to Au can help stabilize Au^{3+} by inhibiting the valence change and carbon deposition [54].

N-doped carbon is one of the hot topics in support modification. N-doped carbon material as a non-metal catalyst has shown promising properties for acetylene hydrochlorination [69,70]. The introduction of N species changed the electronic structure of the adjacent carbon atoms so to adsorb HCl or acetylene easily, thereby enhancing the catalytic activity of carbon-supported catalysts. Dai et al. reported AuCl_3/PPy -multiwall carbon nanotubes (MWCNTs) with enhanced catalytic performance compared with $\text{AuCl}_3/\text{MWCNTs}$. This was attributed to electron transfer from polypyrrole to the Au^{3+} center, which facilitated the adsorption of HCl (Figure 6) [66]. Zhao et al. incorporated N-containing functional groups into carbon support by the post-modification of activated carbon with urea. The results showed that electron transfer from N atoms to the Au^{3+} center accelerated the adsorption of HCl by increasing the electron density of Au^{3+} [71].

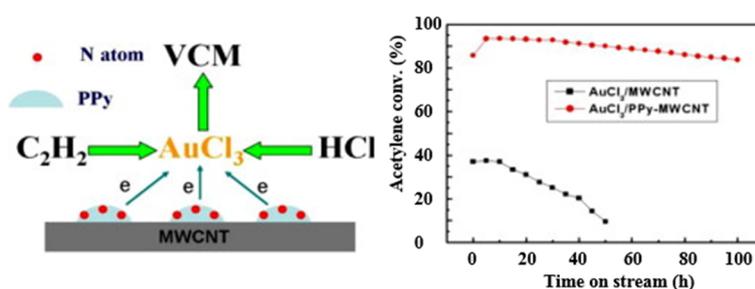


Figure 6. AuCl_3/PPy -multiwall carbon nanotube (MWCNT) catalyst for acetylene hydrochlorination [66].

ILs (Ionic liquids) are also used to stabilize Au^{3+} catalysts. Zhao et al. obtained Au^{3+} complexes, Au ILs (1-propyl-3-methylimidazolium tetrachloroaurate ($[\text{Pmim}]\text{AuCl}_4$)). The Au^{3+} -IL/C catalyst showed higher activity and stability than IL-free Au/C [72]. Zhao et al. reported that the reduced Au^0 could be regenerated in situ to Au^{3+} by CuCl_2 and further stabilized by the electron transfer from Cu^{2+} to these active species. The Au^{3+} - Cu^{2+} -IL/C catalyst demonstrated excellent activity. With this catalyst, over 99.8% selectivity was achieved for the VCM product (Figure 7) [39].



Figure 7. Au^{3+} - Cu^{2+} -IL/C catalyst for acetylene hydrochlorination [39]. IL: Ionic liquid.

Modification of the support can also improve the activity of the Au^0 catalyst. Tian et al. found that amorphous silica could be dispersed on the carbon surface uniformly as spherical particles. Silica deposition achieved a better distribution of Au NPs, which improved the catalytic activity of the Au^0 catalyst, although the surface area was decreased [73]. Dai et al. found that a mesoporous carbon nitride material can control the Au NPs sizes and was active for acetylene hydrochlorination [74]. Kang et al. reported that graphene substrate can improve the adsorption of HCl and C_2H_2 , and N-doping significantly weakened the interaction with the Au_3 cluster for acetylene hydrochlorination [75]. Gong et al. reported that adding the heteroatom N to Au embedded in graphene (AuG) could reduce the reaction activation energy based on DFT calculations (Figure 8).

With N-doping in AuG-SAC, the adsorption ability was increased, and the interaction between the starting materials HCl and acetylene was significantly enhanced. The energy band gap (ΔE_g) between the Highest Occupied Molecular Orbital (HOMO) of AuG- N_n -acetylene and the Lowest Unoccupied Molecular Orbital (LUMO) of the HCl, N-doped AuG-SACs decreased. Overall, this could reduce the activation energy of acetylene hydrochlorination [76].

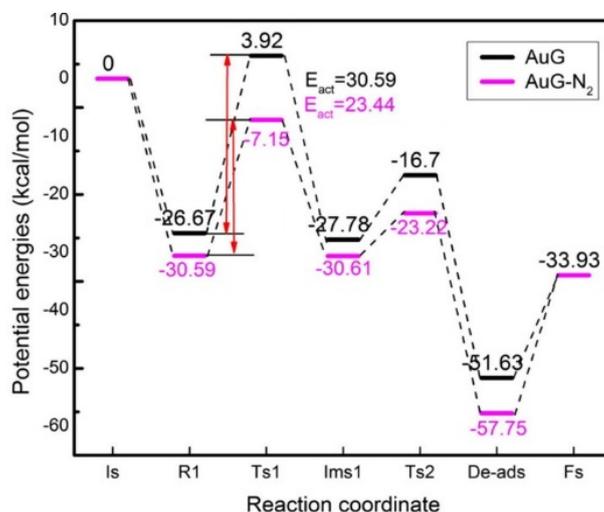


Figure 8. Energy diagrams of acetylene hydrochlorination on AuG and AuG- N_4 spheric active carbons (SACs) [76].

2.1.4. Deactivation and Regeneration of Au Catalysts

In 1988, Hutchings et al. investigated the reactivation by treatment of used catalysts in situ in the reactor with HCl. This treatment was applied to Au^{3+} and Hg^{2+} catalysts (Figure 9). The results indicated that the Hg catalyst cannot be reactivated, and 25% of the mercury had been lost from the catalyst. However, the activity of Au catalysts treated with HCl can be restored to the initial activity and the Au content of the deactivated catalyst did not decrease [16].

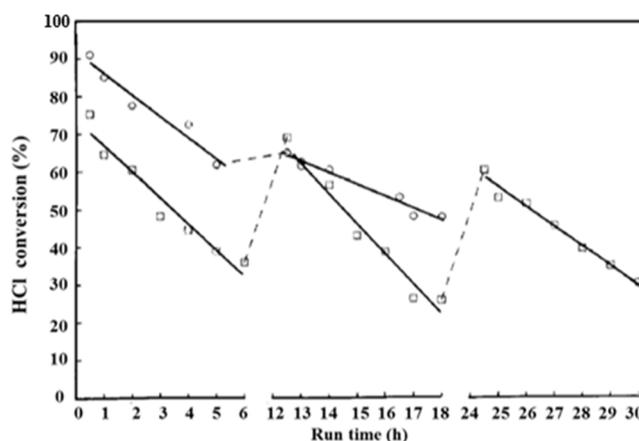


Figure 9. Effect of reactivation of catalyst with HCl treatment; \circ $HgCl_2/C$, 9% Hg; \square $HAuCl_4/C$, 1.9% Au; (—) HCl treatment [16].

The deactivation of a supported Au catalyst with Au^{3+} as the active species can be attributed to the following factors: the reduction, aggregation of the active particles of the Au catalyst, and the carbon deposition on the catalyst surface area, which may occur simultaneously [9,77]. Nkosi et al. reported that at low temperature (60–100 °C), carbon deposition led to the deactivation of the Au catalyst. At higher

temperatures (120–180 °C), the active component $\text{Au}^{3+}/\text{Au}^+$ was reduced to Au^0 , resulting in the deactivation of the Au catalyst (Figure 10) [78]. It was also observed that a minimum deactivation rate occurred at 100 °C. However, at this temperature, the activity of the Au catalyst was very low; it was not the optimum reaction temperature [26,31,79]. The deactivation of Au catalysts caused by a reduction of active components can be explained from the reaction mechanism of Au catalysts. Conte et al. reported that AuCl_3 could absorb acetylene and HCl, but the adsorption on acetylene was stronger. Acetylene has higher reducibility, which was one of the reasons for catalyst deactivation [5].

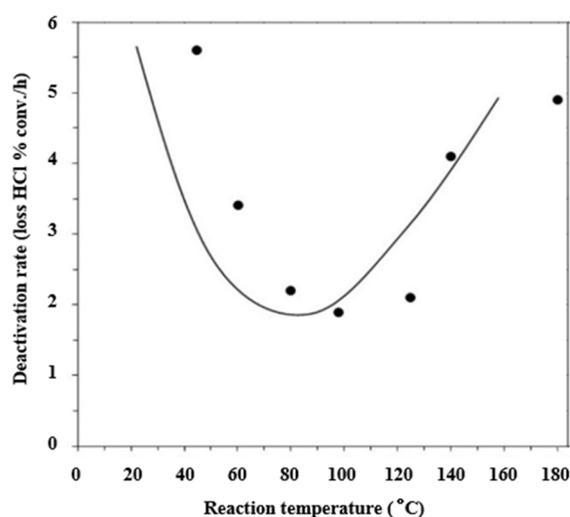


Figure 10. Effect of reaction temperature on rate of Au^{3+} catalyst deactivation [78].

For catalysts with Au^{3+} as the active center, the reduction of Au^{3+} is observed to be detrimental to catalyst activity [80]. One approach to improve the stability of Au^{3+} catalysts is to reactivate them. A large number of studies have shown that the deactivated Au catalyst can be regenerated by re-oxidation. Conte et al. demonstrated that a used catalyst can be regenerated by boiling aqua regia and a deactivation of Au catalyst was due to a loss of Au^{3+} , which was restored by the aqua regia treatment [81]. Cl_2 , NO, and N_2O have been found to be effective in re-oxidation. These oxidants could alleviate the deactivation rate of catalyst [80]. Although Au^{3+} catalyst can be regenerated, the actual industrial application is still limited for various reasons.

The main reason for the deactivation of Au NPs with Au^0 as the active species is the aggregation of Au NPs during acetylene hydrochlorination [82]. Malta et al. reported that single-site Au was the active site, but the formation of metallic Au particles by single-site Au^0 was one reason for catalyst deactivation. Inelastic neutron scattering studies of Au^0 catalysts exposed to acetylene showed that an oligomeric acetylene species formed on the catalyst surface. These oligomers could be precursors for carbon formation and become a deactivation process, thus significantly slowing down the reaction process (Figure 11) [83].

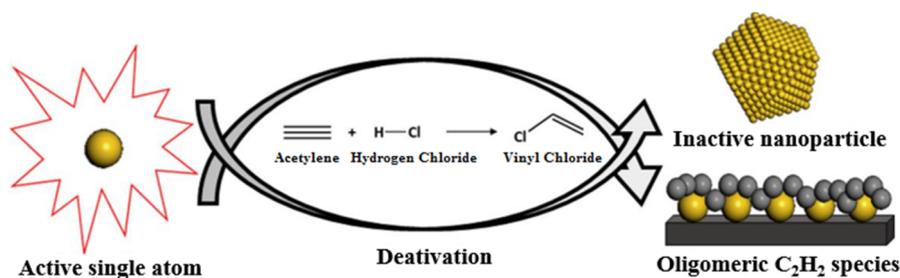


Figure 11. Deactivation of a single-site Au^0 catalyst [83].

2.2. Ru Catalysts

The research on Ru catalysts has drawn considerable attention. In 2013, Zhu et al. calculated the activity parameters of Au, Hg, and Ru for acetylene hydrochlorination by DFT. The results showed that the calculated activation barrier was 16.3, 11.9, and 9.1 kcal mol⁻¹ for HgCl₂, AuCl₃, and RuCl₃, respectively. These results indicated that RuCl₃ was a good candidate for the hydrochlorination of acetylene [84]. Table 3 summarizes and shows the performance of some Ru catalysts for acetylene hydrochlorination.

Table 3. Performance of Ru catalysts for acetylene hydrochlorination.

Year	Catalyst	Material	Ru (wt %)	GHSV (h ⁻¹)	Temp (°C)	Acetylene Conv. (%)	Running Time (h)	Ref.
2018	Ru(III)-ChCl/AC	RuCl ₃ + ChCl	0.2	900	170	99.3	25	[85]
2018	Φ-P-Ru/AC-HNO ₃	RuCl ₃ + tris-(triphenylphosphine) ruthenium dichloride	1	180	180	99.2	48	[86]
2018	RuCl ₃ -A/AC	RuCl ₃ + NH ₃ ·H ₂ O	2	100	180	95.8	8	[87]
2017	(NH ₄) ₂ RuCl ₆ /AC	(NH ₄) ₂ RuCl ₆	1	180	170	90.5	12	[88]
2017	TPAP/AC-HCl	C ₁₂ H ₂₈ NO ₄ Ru	1	180	180	97	48	[89]
2016	Ru/N-AC	RuCl ₃	1	57	250	95.2	180	[90]
2013	Ru ₁ Co ₃ /SAC	RuCl ₃ + CoCl ₂	1	180	170	95	48	[91]
2014	Ru/SAC-C300	RuCl ₃	1	180	170	96.5	48	[92]
2016	Ru-Co(III)-Cu(II)/SAC	RuCl ₃ + CuCl ₂ + Co(NH ₃) ₆ Cl ₃	0.1	180	170	99	48	[93]
2017	Ru10%[BMIM]BF ₄ /AC	1-Butyl-3-methylimidazolium tetrafluoroborate	1	180	170	98.9	24	[94]

Zhang et al. reported a series of Ru catalysts for acetylene hydrochlorination. Monometallic Ru, bimetallic Ru-Cu, and Ru-Co were prepared on spherical active carbon (SAC) support. It was proposed that the addition of Co could enhance the catalytic activity and Ru species (RuO₂, Ru⁰, RuO_x, and RuCl₃) of the Ru catalyst [91]. It was found that the active ingredient of RuO₂ was critical for improving the catalytic performance of Ru catalysts [92]. A series of trimetallic Ru-Co³⁺-Cu²⁺/SAC catalysts were synthesized and evaluated for acetylene hydrochlorination. Compared with the monometallic and bimetallic catalysts, the trimetallic Ru-Co³⁺-Cu²⁺/SAC catalyst with 0.1 wt % Ru loading showed a superior catalytic performance with the acetylene conversion of 99.0%. It was found that the addition of Co³⁺ and Cu²⁺ can help form highly dispersed Ru on the support, and Cu²⁺ species can not only inhibit the reduction of RuCl₃ precursors but also facilitate the formation of Co³⁺ from Co²⁺ or Co⁰ (Figure 12) [93].

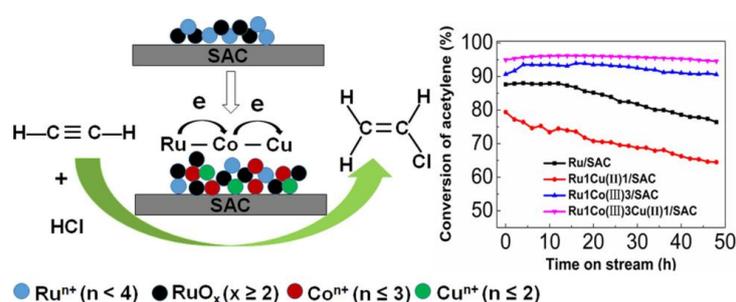


Figure 12. Ru-Co³⁺-Cu²⁺/SAC catalyst for acetylene hydrochlorination [93].

In 2017, imidazolium-based ILs (IBILs) were reported. The optimal Ru10% [BMIM]BF₄/C catalyst achieved the acetylene conversion of 98.9% and the selectivity to VCM of 99.8%. It was proposed that IBILs additives could improve the dispersion of Ru species and prevent coke deposition due to the interactions between Ru species and [BMIM]BF₄. Moreover, the O-containing functional groups on the carbon support were involved in the interactions between Ru species and [BMIM]BF₄ [94].

2.3. Pt Catalysts

There are a few reports on the catalytic hydrochlorination of acetylene by Pt catalysts, and the research mainly focuses on the catalytic mechanism. Mitchenko et al. conducted a series of studies on Pt catalysts. In their study, K_2PtCl_6 salt was treated under acetylene, ethylene, or propylene atmosphere to form a heterogeneous catalyst. It was shown that with this approach, the formation of Pt^{2+} complexes and Pt complexes with vacancies were observed. It was hypothesized that the active centers were defected in the form of impure Pt^{2+} ions in the K_2PtCl_6 matrix [95]. In 2004, Mitchenko et al. found that trans-d-VCM was formed in the DCl atmosphere. According to the established catalytic reaction mechanism on the active sites, a K_2PtCl_6 lattice that defected in the form of topologically bound coupled $PtCl_4^{2-}$ – $PtCl_5^-$ was formed by mechanical pre-activation under acetylene. Acetylene chloroplatination started first by coordination with an unsaturated Pt^{4+} complex producing an intermediate β -chlorovinyl Pt^{4+} derivative. The reduction of this intermediate yielded a Pt^{2+} organometallic derivative. The catalytic mechanism of acetylene hydrochlorination over the Pt catalyst is shown in Figure 13 [96].

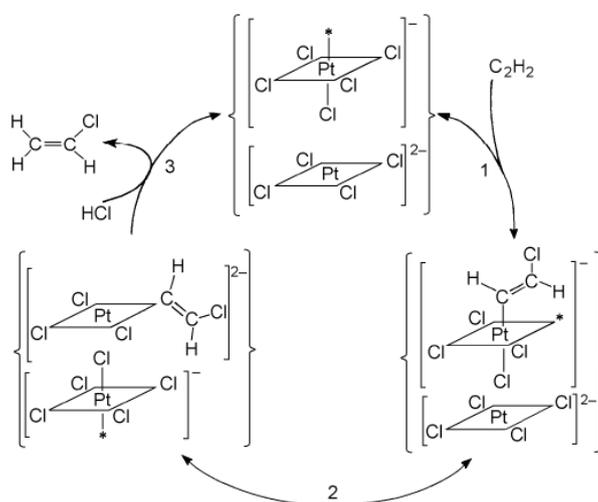


Figure 13. Catalysis mechanism of acetylene hydrochlorination over the Pt catalyst [96].

Mitchenko et al. also found that the catalytic reaction of acetylene chloroplatination proceeds in the form of π -acetylene complexes. The limiting step of the reaction was acetylene chloroplatination. It involved a π -acetylene complex and HCl , producing a new π -acetylene Pt^{2+} complex and an intermediate β -chlorovinyl Pt^{2+} derivative. The protonolysis of the intermediates resulted in VCM formation [23]. In 2014, Mitchenko et al. reported that HCl was involved in two steps of acetylene hydrochlorination. With K_2MCl_4 ($M = Pt$ or Pd) and K_2PtCl_6 catalysts, the intermediate β -chlorovinyl derivative of Pt^{2+} was observed in protodemetalation over the Pt-containing catalysts [97].

2.4. Pd Catalysts

In 1985, Hutchings made Pd catalysts supported on carbon with relatively high initial activity for acetylene hydrochlorination but also found that Pd catalysts would be rapidly deactivated due to Pd^{2+} being reduced into Pd^0 and carbon deposition [14]. Nkosi et al. reported that Pd catalysts were found to be as active as Hg catalysts on a mole basis. However, loadings of $PdCl_2$ catalysts with durable stability were very low (<1 wt %). At higher loadings, $PdCl_2$ was rapidly lost from the catalyst presumably as a result of the formation of a volatile Pd acetylene complex. The loss of the average rate of conversion was 6.8% conv. h^{-1} during the first 3 h [16]. Strebelle et al. reported that 57.3% yield and a 96% selectivity for VCM was achieved with $PdCl_2$ catalyst without a detailed description of catalyst stability [98].

Table 4 shows the performance of some Pd catalysts for acetylene hydrochlorination, in which the Pd²⁺ species is the active species.

Table 4. Performance of Pd catalysts for acetylene hydrochlorination.

Year	Catalyst	Material	Pd (wt %)	GHSV (h ⁻¹)	Temp (°C)	Acetylene Conv. (%)	Running Time	Ref.
2016	Pd/PANI-HY	H ₂ PdCl ₄ + polyaniline	0.9	110	160	95	300 h	[99]
2016	Pd-K/NFY	PdCl ₂ + KCl + NH ₄ F	0.9	110	160	99	50 h	[100]
2015	Pd/NH ₄ F-HY	PdCl ₂ + NH ₄ F	0.9	110	160	99.92	400 min	[101]
2013	Pd/HY	H ₂ PdCl ₄	0.5	110	160	95	160 min	[102]
2010	PdCl ₂ -KCl-LaCl ₃ /C	PdCl ₂ + KCl + LaCl ₃	0.9	120	160	99	3 h	[103]

Wang et al. reported that the presence of NH₄F in Pd/HY catalysts can significantly improve the catalyst performance (acetylene conversion >95% and VCM selectivity >90%). The hypothesis was that NH₄F could partially enhance the surface acidity, prevent carbon deposition, and slow down the loss of Pd (Figure 14) [101]. Wang et al. prepared a Pd catalyst (Pd/HY) with Y zeolite (HY) support. The catalyst exhibited excellent catalytic performance with >95% acetylene conversion and >90% VCM selectivity. The results showed that with the aid of ultrasonic-assisted impregnation, Pd was uniformly dispersed on the Y zeolite surface [102].

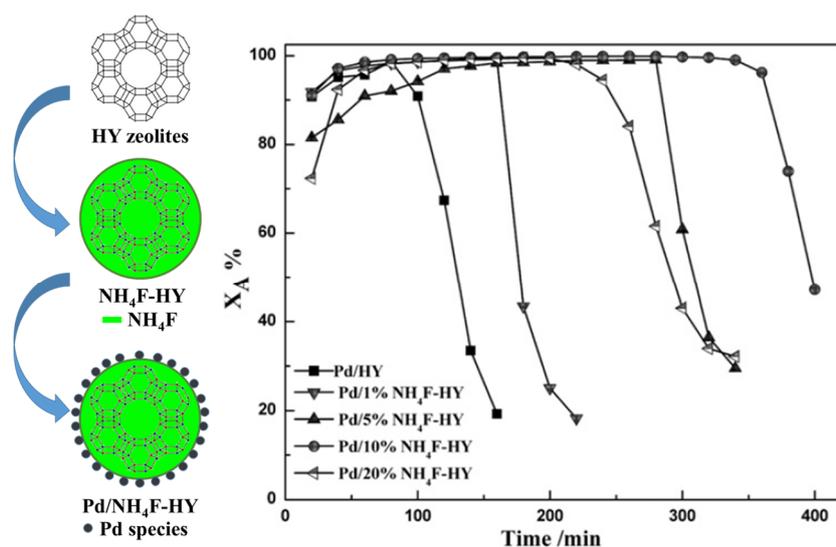


Figure 14. Pd/HY catalysts modified with NH₄F for acetylene hydrochlorination. Adopted from Ref [101].

Song et al. reported that the deactivation of Pd catalysts were mainly from the loss of an active component, surface carbon deposition, and decrease in specific surface area. The results showed that the addition of KCl and LaCl₃ can reduce the loss of PdCl₂, increase the conversion of acetylene, and improve the selectivity of VCM. When the used PdCl₂-KCl-LaCl₃/C catalyst was treated with HNO₃ and HCl, it can be re-activated to some extent by oxidation, but it is not as good as the original one [103].

N-doped carbon materials and ILs were used to improve the catalytic performance of Pd catalysts. Li et al. demonstrated that N doping can prevent carbon deposition and improve the catalyst stability. The doped N atoms can act as a ligand, stabilizing PdCl₂ and improving the surface activity [104]. Yang et al. reported IL-stabilized metal NPs (NPs@IL)-cosolvent liquid-liquid biphasic Pd NPs catalysts with improved performance for acetylene hydrochlorination. The NPs@IL droplets served as microreactors. The low viscosity organic phase enabled the rapid mass transfer. The acetylene conversion of 98% and VCM selectivity of 99.5% were achieved with this type of Pd catalyst [105]. Zhao et al. chose 1-butyl-3-methylimidazolium chloride ([Bmim]Cl) IL and activated carbon support

to immobilize volatile catalytically active Pd complexes. The 0.5Pd-10IL/C catalyst showed superior performance with 98.6% conversion of acetylene and above 99.8% selectivity to VCM. The influence of IL on the catalyst properties such as activity and stability was mainly due to the stabilization and dispersion of active Pd species in the IL layer, the possible coordination of the IL to the Pd atoms, and the confinement of Pd complexes within the pore's supports (Figure 15) [99].

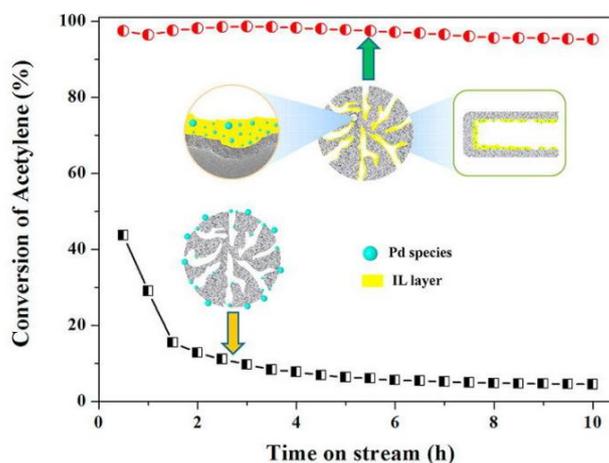


Figure 15. Supported IL-Pd catalyst for acetylene hydrochlorination [106].

2.5. Challenge of Noble Metal Catalysts

For the noble metal catalysts, the main problems of their industrialization are the high cost and short service life. There are mainly two problems that need to be solved: On the one hand, reducing the load of noble metals, which needs to be optimized from the catalyst formulation, and on the other hand, improving the stability of the noble metal catalyst. Therefore, the industrial application of noble metal catalysts should consider the reduction of noble metal catalyst loading capacity; at the same time, it should include a comprehensive consideration of support optimization, activated carbon pretreatment, additives, and catalyst preparation methods.

3. Non-Noble Metal Catalysts

Supported noble metal catalysts have the characteristics of high price and poor stability. Even the relatively good performance of Au catalyst is not able to meet the industrialization requirements for the economy and effect. Non-noble metal catalysts have become one of the catalysts with great potential for industrialization due to their advantages of being cheap and easy to obtain. At present, researches on non-noble metals are mainly focused on supported catalysts with Cu, Bi, and Sn as active centers.

3.1. Cu Catalysts

Compared with noble metals, Cu has the advantage of low price and easy availability with good thermal stability. Its price is relatively low, even in non-noble metals. In Hutchings' study, Cu^{2+} has a high potential of catalyzing acetylene hydrochlorination due to its high electrode potential. Cu is often used as an auxiliary agent in the modification of other metal active center catalysts [14]. In fact, acetylene hydrochlorination with Cu as the main active center has been reported as early as in 1933. US patent 1934324 first introduced CuCl catalyzed acetylene hydrochlorination as an active component [107]. Table 5 shows the performance of some Cu catalysts for acetylene hydrochlorination.

Table 5. Performance of Cu catalysts for acetylene hydrochlorination.

Year	Catalyst	Material	Cu (wt %)	GHSV (h ⁻¹)	Temp (°C)	Acetylene Conv. (%)	Running Time	Ref.
2018	Cu-Cs/AC	CuCl ₂ + CsCl	1	50	200	92	200	[108]
2016	Cu-g-C ₃ N ₄ /AC	CuCl ₂ + dicyan-diamide	4.15	72	180	79	450 min	[109]
2015	Cu ₂ P ₂ O ₇ /SAC	Cu ₂ P ₂ O ₇	15	180	140	40.5	500 min	[110]
2015	Cu400Ru/MWCNTs	CuCl ₂ + RuCl ₃	4.24	180	180	51.6	6 h	[111]
2014	Cu-NCNT	CuCl ₂ + N-doped carbon nanotubes	5	180	180	45.8	4 h	[112]

Zhao et al. found that Cu-g-C₃N₄/AC significantly improved catalytic performance compared to the catalyst without N doping. The authors hypothesized that after doping, pyrrolic N promoted the adsorption of HCl and acetylene, and it inhibited the coke deposition on the catalyst surface [109]. Li et al. reported that the P-doped Cu demonstrated good stability and catalytic activity. The amount of P used was critical and significantly influenced the catalyst activity. It was assumed that P doping enhanced the interaction between metal and support, improved the dispersity of Cu, retarded the reduction of the active components (Cu²⁺/Cu⁺) to Cu⁰, and effectively prevented the aggregation of Cu particles [110]. Zhou et al. reported that N-doped carbon nanotubes (N-CNTs) improved the electron conductivity ability of the carbon sheets as well as the interaction between Cu and N-CNTs, and the improvement of the adsorption capacity of acetylene led to high catalytic activity and excellent VCM selectivity. The active components were proposed to be a mixture of Cu⁺ and Cu²⁺. It was speculated that acetylene hydrochlorination preferred to take place at binding sites of Cu and N (Figure 16) [112].

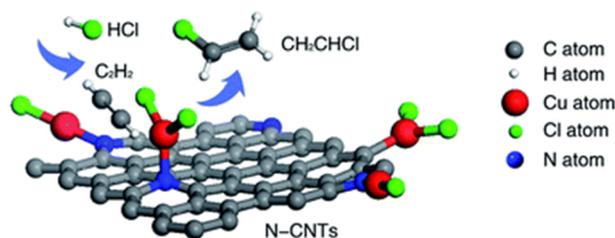


Figure 16. Cu-N-CNT catalyst for acetylene hydrochlorination [112]. N-CNT: N-doped carbon nanotubes.

In the preparation of Cu catalysts, the addition of promoters such as metal chlorides and rare earth oxides can improve the catalytic performance. Shi et al. reported that the catalyst La_{1.7}K_{0.3}NiMnO₆-CuCl₂/γ-Al₂O₃ doped with K had a large amount of Mn⁴⁺ and surface-adsorbed oxygen. These species accelerated the oxidation of Cu⁺ and released Cl₂ [3]. Xu et al. reported a catalyst consisting of 400 ppm Ru and 4.24 wt % Cu. Carbon nanotubes were chosen as the support. The synergistic effect between Ru and Cu led to a high activity (TOF = 1.81 min⁻¹) [111]. Zhai et al. synthesized a perovskite-like catalyst for acetylene hydrochlorination. The CsCuCl₃ NPs were supported on activated carbon with 1 wt % Cu content, which exhibited superior performance compared with a pure Cu catalyst without Cs. The formation of the perovskite-like CsCuCl₃ complex structure stabilized the active Cu²⁺ [108].

In order to improve the performance of Cu catalysts, efforts were attempted by modifying the support and adding promoters for improving the dispersion of Cu. The modification did not change the structure of the Cu active center. The preparation of a highly dispersed Cu catalyst is complex and is limited for large-scale industrial production. The addition of expensive noble metals can increase the catalytic activity of Cu catalysts; however, the advantage of cheap and easy availability of non-noble metal catalysts has been lost.

3.2. Other Non-Noble Metal Catalysts

Zhou et al. synthesized a Bi/Cu/H₃PO₄ catalyst supported by silica gel. The catalyst exhibited acceptable initial activity (30% activity of Hg catalyst) and stability at 200 °C and GHSV 360 h⁻¹. The catalyst could be recovered by a two-step regeneration method [11]. Hu et al. found that the doping of S increased the Brunauer-Emmett-Teller (BET) surface areas and decreased the active species particle size of the Bi catalyst, which led to more accessible active sites and consequently boosted the catalytic activity in hydrochlorination. The main active components of the catalyst is BiOCl crystal particle, and the coke deposition was responsible for the deactivation of the Bi catalyst [113].

Dai et al. developed a series of transitional metal catalysts. In their work, Mo and Ti were chosen as the active ingredients in a catalyst for acetylene hydrochlorination. With this catalyst, 89% acetylene conversion and >98.5% VCM selectivity can be obtained. The doping of Mo and Ti reduced the adsorption capacity for acetylene while increasing the adsorption of HCl [114]. The authors reported three transition metal nitride VN/C, Mo₂N/C, and W₂N/C catalysts on activated carbon. With these catalysts, 98% VCM selectivity was achieved [115]. For W₂N, two catalysts were prepared. The first was prepared by depositing W onto activated carbon, whereas the second was prepared in the same procedure except for extra plasma treatment. The author claimed that plasma treatment increased the interaction between active ingredients and support material. The results showed that plasma treatment increased the number of W–N bonds and restricted the deposition of coke, thus enhancing the catalytic performance [116]. They found that the Co–N–AC catalyst effectively improved the adsorption of HCl. The presence of Co–N_x played a major role in acetylene hydrochlorination (Figure 17) [117].

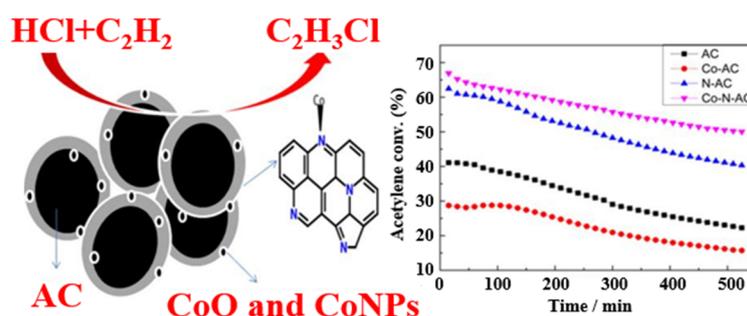


Figure 17. Co–N–AC catalyst for acetylene hydrochlorination [117].

3.3. Challenge of Non-Noble Metal Catalysts

At present, the research of non-noble metals catalysts is largely confined to the laboratory stage. Non-noble metal catalysts are constantly modified and improved to increase their activity and stability by adding additives or using bimetallic or trimetallic catalysts. However, there are still challenges and limitations, such as low monomer conversion rate, poor selectivity of VCM, severe carbon accumulation, loss of catalytic activity over time, unsatisfactory stability, and short lifetime.

4. Non-Metallic Catalysts

An alternative approach to replace Hg catalysts is to develop the non-metallic catalysts. Non-metallic catalysts are newly emerging green catalytic materials that have attracted much attention in recent years due to their advantages of environmental friendliness and low cost.

4.1. Carbon Material Catalysts

The research of carbon catalysts is mainly about the structural defect sites, the regulation of functional groups on the carbon materials surface, and the doping of heteroatoms. Non-metallic nanocarbon materials for acetylene hydrochlorination have been intensively investigated by many researchers (Table 6).

Table 6. Performance of carbon material catalysts for acetylene hydrochlorination.

Year	Catalyst	Material	GHSV (h ⁻¹)	Temp (°C)	Acetylene Conv. (%)	Running Time (h)	Ref.
2019	ND@G	Nanodiamond + graphene	300	220	50	10	[118]
2018	ZIF-8/SAC	ZIF-8 + spherical activated carbon	30	220	81	2	[119]
2018	NS-C-NH ₃	S + N-doped carbon + NH ₃	35	220	80	9	[120]
2017	p-BN	H ₃ BO ₃ + melamine + NH ₃	-	280	99	50	[121]
2016	Z4M1	ZIF-8 + melamine	50	180	60	20	[122]
2015	B,N-G	Graphene oxide + H ₃ BO ₃ + NH ₃	360	150	94.87	4	[123]
2014	N-OMC-700	N-doped ordered mesoporous carbon	-	200	77	100	[124]
2014	N-CNTs	C ₂ H ₄ + NH ₃	180	180	7.2	3	[125]
2014	g-C ₃ N ₄	Activated carbon + cyanamide	50	180	76.52	7	[69]
2014	PSAC-N	Pitch-based spherical activated carbon + melamine	120	250	68	-	[126]

Efforts have been devoted to improving the activity and stability of catalysts by modifying carbon-based catalysts. The most common materials studied are N-doped carbon materials. N-containing carbon materials are often prepared by heating different N-containing precursors under N₂ atmospheres or direct carbonization [7,70]. It was hypothesized that the incorporation of N atoms could tune the basicity of carbon materials surface. The N atoms could also provide available lone pairs, which can facilitate a hydrochlorination reaction.

Li et al. prepared a series of zeolitic imidazolate framework (ZIF)-derived N-doped carbon using melamine as N sources. Additions of melamine not only facilitated forming a special morphological structure and pore structure but also adjusted the relative content ratio of three N species in ZIF-derived N-doped carbon materials [122]. Li et al. reported that N-doped ordered mesoporous carbon (N-OMC) with high surface areas processed high activity and stability. A 77% acetylene conversion and 98% VCM selectivity was obtained over the 100 h test period. The N-OMC activity increased with the increasing of the catalyst surface area and N content [124]. Wang et al. prepared an N-doped pitch-based spherical activated carbon catalyst (PSAC-N) with melamine. The active site of PSAC-N had a special N-6v structure in which quaternary N bonded between two 6-membered rings. Compared to controls, the adsorption capacity of HCl on PSAC-N was the highest, which was beneficial for acetylene hydrochlorination. The reaction energy of N-6v(7) was calculated as 236.2 kJ mol⁻¹ [126]. Li et al. reported that the g-C₃N₄/C catalyst prepared with cyanamide as a precursor displayed considerable catalytic performance. C₃N₄ was able to adsorb and activate acetylene and HCl simultaneously, and the strong C(1)-C(2) interaction led to the formation of a stable CHCl=CH-C₃N₄H unit that provided a rate-controlling step ($E_{act} = 77.94$ kcal mol⁻¹ [69]). Qian et al. synthesized a g-C₃N₄ framework with rich N defects using melamine formaldehyde as a precursor. The fragmentary g-C₃N₄ showed high catalytic activity with 94.5% acetylene conversion, which was 30 times higher than that of pure g-C₃N₄. The improvements were attributed to the etching of the g-C₃N₄ framework by O species in the melamine formaldehyde resin. Moreover, DFT calculations showed that the N defects in the g-C₃N₄ framework greatly improved the adsorption of HCl and acetylene and brought down the energy barrier from 62.0 to 38.1 kcal mol⁻¹ [127]. Zhang et al. reported that the N-doped carbon catalyst with polyaniline had significantly improved catalytic activity and stability (Figure 18). The catalytic performance of this catalyst was closely related to pyrrolic N (pyrrolic N > graphitic N > pyridinic N) [128].

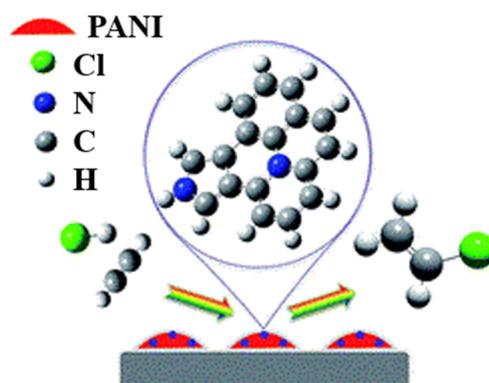


Figure 18. N-doped active carbon catalyst for acetylene hydrochlorination [128].

Lan et al., reported nanodiamond–raphene composed of a nanodiamond core and graphitic shell with defects. The catalyst showed pretty high catalytic activity, which was comparable with metal catalysts for acetylene hydrochlorination. Figure 19 shows that the defects on the carbon surface and edge were assumed to be desirable for acetylene hydrochlorination [118]. Zhou et al. found that N-CNTs featured good catalytic activity ($\text{TOF} = 2.3 \times 10^{-3} \text{ s}^{-1}$) and high VCM selectivity (>98%). There was an observable correlation between the quaternary N content and acetylene conversion. DFT calculation revealed that N doping enhanced the interaction between acetylene and N-CNTs compared with the CNTs without N [125]. Cyanamide and its derivatives are common raw materials for preparing N-doped carbon catalysts. Li et al. reported ZIF-8-derived NPs featuring more active sites, which were easily accessible for reactants HCl and acetylene. Bamboo-shaped CNTs promoted the efficiency of active site N, changed the porosity of the catalyst, and inhibited the formation of coke deposition [119]. Zhao et al. proposed that the defects in graphene could be useful to improve the catalytic performance for acetylene hydrochlorination based on the DFT calculated [129].

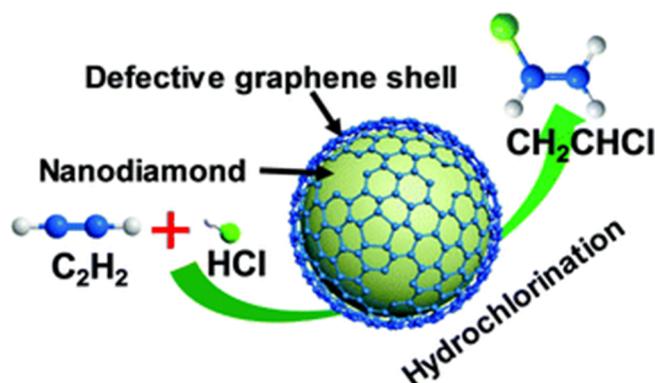


Figure 19. Defective nanodiamond–graphene catalyst for acetylene hydrochlorination [118].

Dual heteroatom doping was also attempted for catalyst design. Dong et al. reported that an S and N co-doped carbon catalyst exhibited a higher acetylene conversion than the N-doped carbon. The C atoms adjacent to pyridinic N were found to be active sites, and S improved the pyridinic N content in N-doped carbon materials (Figure 20) [120]. Li et al. reported that porous boron nitride (p-BN) was active for acetylene hydrochlorination. The activity of p-BN was originated from the defects and edge sites. Particularly, the armchair edges of p-BN can polarize and activate acetylene, which react with HCl to form VCM [121]. Dai et al. synthesized B and N heteroatoms dual doped on a graphene oxide (B,N-G) catalyst. With this catalyst, acetylene conversion is near 95%, which is significantly higher than that of singly B- or N-doped graphene. The authors proposed that the synergistic effect of B and N doping promoted HCl adsorption (Figure 21) [123]. Li et al. reported an

N-doped carbon nanocomposite derived from silicon carbide. It was found that the catalyst activated acetylene directly in which C atoms bonded with pyrrolic N were the active sites [130]. Zhao et al. found that the doping of C atoms on boron nitride (BN) cages can significantly promote the adsorption ability of the acetylene molecule compared with the BN cages without doping. Acetylene was adsorbed onto $B_{12-n}N_{11+n}C$ ($n = 0, 1$) clusters prior to HCl and then formed three adsorption states: two *trans* configuration and one *cis* configuration. The energy barrier of the minimum energy pathway based on $B_{11}N_{12}C$ catalyst was as low as $36.08 \text{ kcal mol}^{-1}$ [131].

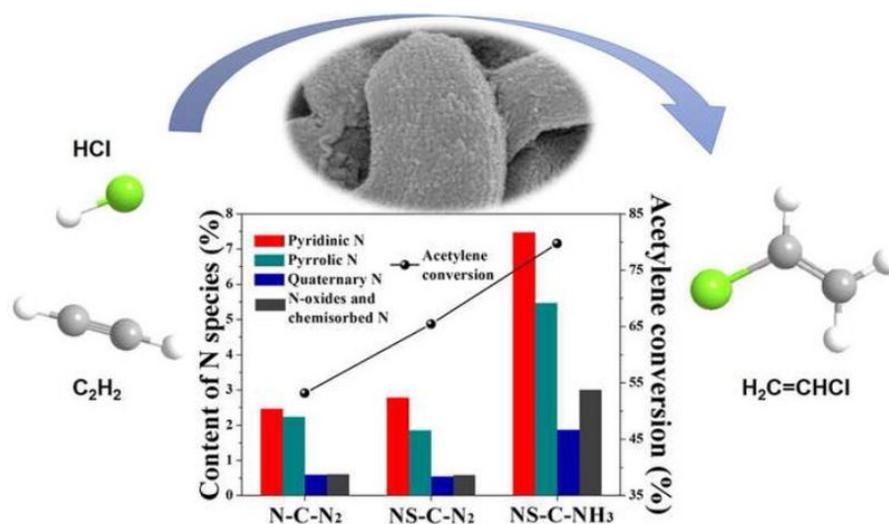


Figure 20. S and N co-doped carbon catalyst for acetylene hydrochlorination [120].

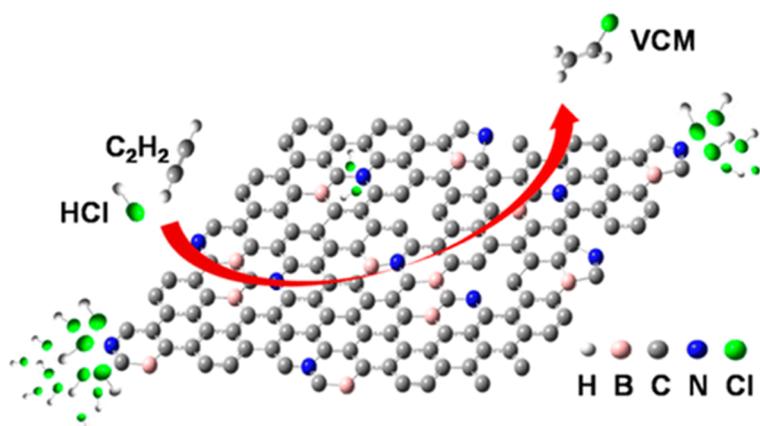


Figure 21. B,N-graphene catalyst for acetylene hydrochlorination [123].

The deactivation mechanism of N-doped carbon catalysts has been studied. Li et al. reported that a PDA/SiC composite with high activity and stability can be prepared by coating silicon carbide with polydopamine (PDA). The catalyst deactivation was caused presumably by the carbon deposition, which can be regenerated with NH_3 treatment at high temperature [132]. Chao et al. reported that C atoms adjacent to the pyridinic N were the active sites of N-doped carbon catalyst derived from ZIF-8. Coke deposition over pyridinic N was responsible for catalyst deactivation [133].

4.2. Other Non-Metallic Catalysts

Zeolites not only have a large specific surface area and unique pore structure, but also have abundant active sites and acid centers. Therefore, zeolites are widely adopted as catalysts in the chemical industry. Song et al. investigated the activity of faujasite (FAU) zeolite 13X for

acetylene hydrochlorination without loading any metal. It was found that the FAU zeolite 13X demonstrated observable activity presumably from its abundant micropores and unique supercage; acetylene conversion was up to 98.5%. Na cations in the zeolite framework could facilitate acetylene hydrochlorination. The deactivation of 13X was probably due to the collapse of its crystal structure and severe carbon deposit. The spent catalyst could be partly regenerated by calcination [134].

ILs are well-known green solvents. They have unique physicochemical properties involving high solubility, high thermal stability, and negligible volatility, and they have been applied in many fields including catalysis, adsorption, and organic synthesis. Li et al. found that tetraphenylphosphonium bromide (TPPB) ILs exhibited strong adsorption for HCl but weak adsorption for acetylene. At the catalytic active site of TPPB, the activation energy of acetylene hydrochlorination was $21.15 \text{ kcal mol}^{-1}$, which is much lower than that without a catalyst ($44.29 \text{ kcal mol}^{-1}$). During the reaction, the H-Cl bond was preferentially activated through the electrons transfer from the anion of TPPB; then, acetylene was activated to undergo the addition of H and Cl. Such unique preferential activation toward the H-Cl bond significantly promoted the catalytic activity and the stability of TPPB catalysts. The catalyst has good catalytic activity and stability, and the highest acetylene conversion rate was 97.1% [135]. Wang et al. investigated the catalytic performance of imidazolium-based ILs 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim][BF₄]) (IL/CaX) for acetylene hydrochlorination with a nearly 90% acetylene conversion. The reaction proceeded via a two-site mechanism. HCl adsorbed on the Ca²⁺ in zeolite reacted with acetylene adsorbed on IL cations to form VCM. The catalytic reaction occurred at the IL/CaX interface, while the IL/CaX in the upper interphase had no activity. Catalyst deactivation was mostly caused by by-products dissolved in the IL and can be reactivated by a simple vacuum process [136]. Moreover, Zhou et al. reported that 1-alkyl-3-methylimidazolium-based ILs as metal-free catalysts have to consist of the chloride anion due to its participation in acetylene hydrochlorination with the formation of [HCl₂]⁻ by the activation of HCl molecules. The structural modification of conjugated cation in ILs was the key to promote the catalytic activity (Figure 22) [137].

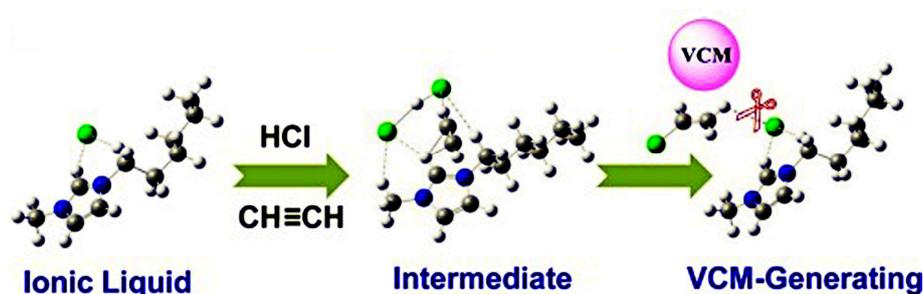


Figure 22. ILs catalyst for acetylene hydrochlorination [137].

4.3. Challenge of Non-Metallic Catalysts

The design and development of non-metallic catalysts for acetylene hydrochlorination has been widely studied in recent years. It is worth looking forward to the application of non-metallic catalysts in industry as an economical and environmentally friendly approach. However, most of the non-metallic catalytic materials reported at present have some intrinsic disadvantages, which limit the practical industrial applications. Researchers are working vigorously to meet the needs and requirements of viable catalysts in the production of the VCM industry. Although non-metallic doped catalysts, especially N-doped carbon catalysts, have been used in many reactions, there are still some problems and hurdles for acetylene hydrochlorination. The first is that the reaction mechanism of different N species (pyridine N, pyrrole N, and graphite N) has not yet been determined. In addition, the highest conversion rate of acetylene for N-doped carbon catalysts is about 95%, which reasonably matches the industrial space velocity. Compared with the acetylene conversion rate of Hg or even Au catalyst

approaching 100% at extreme space velocity, a significant amount of work needs to be done to improve both acetylene conversion and VCM selectivity.

Compared with solid-phase catalysts, ILs have some advantages in activity and stability. However, it is difficult to separate the reaction products from the catalysts, and there are also issues in the recovery and reuse of deactivated catalysts.

5. Future Prospects

Acetylene hydrochlorination is an important reaction in the traditional coal (chlor-alkali) chemical industry. The main problems of mercury-free catalyst with noble metals are the high application cost and short catalyst life.

High cost has become the biggest issue to the industrial application of noble metal catalysts. Reducing the content of noble metal alongside improving the stability and life of the catalysts are very critical in the research and development of noble metal catalysts. The following aspects of research need to be strengthened as well. The first is to develop or find better support materials. The commonly used activated carbon has well-developed pores. The distribution of pores is very extensive, and the existence of functional groups is very rich. At present, research on the microstructure and internal properties of activated carbon are relatively few. It is necessary and meaningful to continue to develop high-performance carbon supports that are suitable for acetylene hydrochlorination with a large specific surface area, appropriate pore size, and suitable internal chemical properties. At the same time, it is important to find ways to improve the reaction efficiency of noble metal catalysts by actively developing new supports other than carbon materials. The second is to look for non-noble metal additives that could be substituents of noble metal active components. By adding non-noble metal active components or additives, one would expect to see coordination and collective effects in improving catalyst performance. Meanwhile, the use of noble metals can also be reduced to lower the cost of the catalyst. The third is to find a better way to support the noble metal components so as to have dispersity at the nanometer level while maintaining durable stability and robustness. It is easy for the traditional simple impregnation method to cause the aggregation and agglomeration of the active components, which quickly bring down the catalytic activity of noble metal species and limit their applications. A reasonable loading mode can provide more active centers for noble metal components per unit mass, so as to improve the catalytic efficiency of noble metal particles and reduce noble metal content. Finally, the regeneration and recycling of noble metal catalysts are also very important. If the noble metal can be reused well, the problem of high price and high cost of catalyst may be solved.

The problems of non-noble metal and non-metallic catalysts are that although they are cheap, they suffer from poor stability and selectivity, low activity, and a low conversion rate. An in-depth study of the reaction mechanisms of the catalytic process would be very helpful. The interaction and collaboration between active components and supports, in other words, the multi-component composite catalysts may be prepared to further improve the catalysts' performance. Optimizing the formula and loading process of active components with a well-established computational approach and artificial intelligence is challenging and exciting. The traditional production process of VCM adopts the fixed bed reaction technology, which is well established and mature; however, the catalysts in this process suffer large loss, easily get pulverized, and suffer poor heat transfer, which limits the catalytic performance of the catalysts.

With continuing efforts and deeper understanding of the catalytic mechanism, the design and development of non-mercury catalysts with satisfactory performance is viable. The industrial application of mercury-free acetylene hydrochlorination catalysts is expected to be realized in the near future.

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