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Development of a Heterogeneous Non-Mercury Catalyst for Acetylene Hydrochlorination

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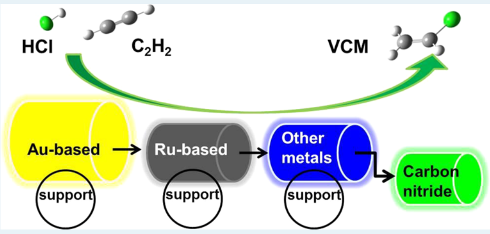
ABSTRACT: Because of the toxicity of mercury catalysts, a nonmercury heterogeneous catalyst for acetylene hydrochlorination has been widely investigated. In this Perspective, we introduce the development of Au-based catalysts, Ru-based catalysts, other metal catalysts, and a carbon nitride catalyst. The effect of the promoter and the carbon support property on the catalytic performance of the $AuCl_3$ catalyst is discussed in detail, and the potential application of other catalysts is also reviewed on the basis of experimental and theoretical studies. At present, it is predicted that a Au-based catalyst may be the optimal candidate catalyst for industrial application in the production of polyvinyl chloride from calcium carbide, but other catalysts should still be further investigated to improve their catalytic performance and their cost advantages.



KEYWORDS: *acetylene hydrochlorination, nonmercury catalyst, heterogeneous catalysis, Au catalyst, Ru catalyst, carbon nitride*

1. INTRODUCTION

The vinyl chloride monomer (VCM) is a very important chemical monomer with an average production of approximately 30 million tons per year[1] and is used mainly for producing poly(vinyl chloride) (PVC), which is a plastic that has the third-highest global volume after polyethylene and polypropylene because of its excellent physical and chemical properties. PVC has many applications, such as water pipes, ceiling tiles, clothes, electric wires, portable electronic accessories, etc. The production capacity of PVC has increased by 5.8% per year globally, and in China, this capacity has increased over 10% annually since 2003.[2] The demand for PVC is expected to total more than 40 million tons in the year 2016.[3]

Two methods are currently employed for the industrial production of VCM. One method is the pyrolysis of dichloroethane, a series of reactions between C_2H_4 and Cl_2,[4−6] whose reaction equations are

$$C_2H_4 + Cl_2 \xrightarrow{FeCl_3} CH_2ClCH_2Cl \quad \Delta H = -171.7\ kJ\cdot mol^{-1} \tag{1}$$

$$CH_2ClCH_2Cl \xrightarrow{450-500\ ^\circ C} CH_2CHCl + HCl \tag{2}$$

$$C_2H_4 + 2HCl + \frac{1}{2}O_2 \xrightarrow{CuCl_2,\ 220-300\ ^\circ C} CH_2ClCH_2Cl + H_2O \quad \Delta H = -251\ kJ\cdot mol^{-1} \tag{3}$$

The other is the calcium carbide method, characterized by the reaction of C_2H_2 with HCl via an acetylene hydrochlorination reaction:[7,8]

$$CaO + 3C \xrightarrow{high\ temperature} CaC_2 + CO \tag{4}$$

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \tag{5}$$

$$2NaCl + 2H_2O \xrightarrow{electocalysis} 2NaOH + H_2 + Cl_2 \quad \Delta H = -251\ kJ\cdot mol^{-1} \tag{6}$$

$$C_2H_2 + HCl \xrightarrow{HgCl_2} CH_2CHCl \quad \Delta H = -124.8\ kJ\cdot mol^{-1} \tag{7}$$

Although largely replaced in many countries by processes based on ethene, acetylene hydrochlorination is one method through which VCM can be manufactured on a commercial scale in locations that have coal-based economies. Indeed, with the current rise in energy costs, the route using acetylene is considered a strong competitor to the process based on ethene as a feedstock because of a renewed interest in coal as a feedstock. A coal feedstock is economically advantageous, and thus, the manufacture of vinyl chloride using acetylene hydrochlorination can be expected to remain an important route of production. Given the advantage of unique coal sources and the relative lack of oil available to China, it is not surprising that the latter route has currently become more important.[9] In addition to the resource factor, the acetylene hydrochlorination has the advantage of being a "one-step" process, whereas ethylene-based processes include several

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reactions that lower the product yield and complicate product separation. As the world's largest PVC-producing country, China synthesizes over 13 Mt per annum of PVC via the calcium carbide method,[10] and this route dominates more than 70% of the gross PVC production in China. This acetylene hydrochlorination production process for PVC is an important industrial route and has attracted considerable attention from both industrial and academic researchers.

In the current industrial process, acetylene reacts with hydrogen chloride gas over a mercuric chloride catalyst supported on activated carbon to produce vinyl chloride. In past decades, attention has been focused on the mercuric chloride catalyst.[11−13] The consumption of Hg in the PVC industry accounts for 50% of the domestic mercury consumption in China and more than 10% of the global consumption. Thus, in the near future, mercury resources would become exhausted as a result of massive mining and consumption. Additionally, in fixed-bed reactors, a low efficiency of heat transfer results in the formation of hot spots and emission of the highly volatile mercury-based catalyst. It is estimated that the production of 1 t of PVC consumes 1.02−1.41 kg of catalyst (with a $HgCl_2$ content ranging from 10 to 15 wt %), of which 25% of the mass of $HgCl_2$ is lost and is not reused.[14]Therefore, HG catalysts have three major shortcomings: (1) activated carbon has a low mechanical strength and is pulverized easily, so it generally cannot be reactivated after deactivation; (2) the catalyst is rapidly deactivated because of the loss of volatile active components, such as $HgCl_2$ and Hg during the reaction; and (3) its high toxicity is harmful to human health and the environment. Thus, the use of carbon-supported $HgCl_2$ as a catalyst is not an environmentally friendly process to obtain VCM.[12,13] Because of these negative characteristics of $HgCl_2$ catalyst, in 2009, the emission reduction standard of the United Nations was enacted, and the application of mercuric chloride will be forbidden worldwide in the near future.[15] Furthermore, in 2013, the Minamata convention on mercury noted that the production, import, and export of products containing mercury would be forbidden worldwide before 2020. More than 140 countries signed this convention and promised to reduce and eventually eliminate mercury pollution.[16]Therefore, it is urgent to explore efficient nonmercuric catalysts for acetylene hydrochlorination to sustainably develop the PVC supply chain, prompting chemical researchers to find and design a nonmercurial catalyst for the hydrochlorination of acetylene.

The research and development of industrial catalysts is system engineering, including studies on reaction and deactivation mechanisms, catalyst design, preparation, deactivation and reactivation, modification, carriers, active component analysis, etc. In this paper, we emphasize the discussion of Au-based, Ru-based, other metal-based, and carbon nitride catalysts.

2. AU-BASED CATALYSTS

In 1968, Smith studied a series of single metal chlorides supported on silica for acetylene hydrochlorination and found that catalytic activity of this reaction might be related to the electron affinity of the metallic cation.[17]In 1975, Shinoda systematized the conversion of acetylene to vinyl chloride over single metallic chlorides supported on activated carbon under similar conditions.[18]They proposed that the conversion of acetylene is related to the metal cations, that the correlation consists of two straight lines, and that its regularity is not obvious. On the basis of previous research, Hutchings further studied the correlation between the activity of a range of single metal chloride (which has 4d and 5d electrons and an outer electron configuration similar to mercury) catalysts and their standard electrode potentials and then gave an improved correlation with the activity approximated by a single line.[11]According to Hutchings' hypothesis, cations with a standard reduction potential greater than that of Hg^{2+} ($E(Hg^{2+})$ = 0.851 V) would be expected to exhibit excellent catalytic activity for this reaction. A range of supported metal chloride catalysts was prepared and tested for acetylene hydrochlorination; the results are given in Table 1.[19] Selectivity for VCM was usually >99% for all of these catalysts, but the initial catalytic activity for these metal chlorides was quite different. It was found that Au^{3+} and Pd^{2+} had better catalytic activity, and this result corresponded to the standard reduction potentials of these two cations ($E(Au^{3+})$ = 1.401 V; $E(Pd^{2+})$ = 0.915 V).

Table 1. Comparison of Catalytic Activity for Acetylene Hydrochlorination[a]

metal	salt	metal loading (% by mass)	initial rate[b]	av decay rate[c] (% conv h^{-1})
Zn	$ZnCl_2$	3.0	15.9[d]	2.2
Cd	$CdCl_2$	0.56	125.3	2.4
		5.1	18.9[d]	2.9
Hg	$HgCl_2$	0.9	164.8	6.6
		1.9	151.1	6.4
		6.7	91.3	8.8
		8.8	78.3[d]	8.8
Cu	$CuCl_2$	3.0	23.8[d]	3.2
Ag	$AgNO_3$	5.0	18.2[d]	3.7
Au	$HAuCl_4$	1.0	461.0	6.0
Au	$HAuCl_4$	1.9	348.3	10.8
Pd	$PdCl_2$	0.64	232.8	6.4
Rh	$RhCl_3$	4.7	79.2[d]	15.4
Ru	$RuCl_3$	4.5	44.3[d]	8.5

[a]Reprinted with permission from ref 19. Copyright 1988, Elsevier. [b]Molhydrogen chloride conv. mol metal^{-1} h^{-1} at 0.5 h reaction time, catalysts reacted at 180 °C, total GHSV 1080 h^{-1}, acetylene: hydrogen chloride = 1:1.1 by volume. [c]Average rate of conversion loss of initial 3 h. [d]Catalysts contain 0.005 mol metal/100 g.

Because carbon-supported $AuCl_3$ displays excellent catalytic activity for acetylene hydrochlorination, subsequent investigations of acetylene hydrochlorination catalysts were focused mainly on the $AuCl_3$/AC catalyst. However, the $AuCl_3$/AC catalyst deactivated rapidly on the stream time,[20] especially compared with $HgCl_2$ catalyst, which can run for 8000 h without an obvious decrease in catalytic performance. The poor stability of the $AuCl_3$/AC catalyst discouraged its industrial application. Therefore, a deep understanding of the reaction and deactivation mechanism of acetylene hydrochlorination for the $AuCl_3$ catalyst is very important and necessary. Many researchers have made great efforts during the past two decades to elucidate the reaction and reduction mechanism of acetylene hydrochlorination. Many factors pertaining to deactivation, including the catalyst preparation method, the loading of gold metal, the gas hourly space velocity, the temperature of the reaction, and the addition of excess HCl, have been considered.[21] On the basis of such studies, it was concluded that the deactivation of the $AuCl_3$ catalyst cannot be ascribed to the leaching of Au elements because there is no obvious difference in metallic composition between fresh and spent $AuCl_3$ catalyst.

Two reasons were given for the deactivation of $AuCl_3$ catalysts. At low reaction temperatures (~60−100 °C), the deposition of carbonaceous residues was the predominant deactivation mechanism. The deposition of carbonaceous residues was assigned with the strong adsorption of C_2H_2. At high reaction temperatures (~120−180 °C), the main deactivation process was ascribed to the reduction of Au^{3+} and possibly of Au^+ to the less active Au^0 during catalysis. The optimum operating temperature for these catalysts was in the range of ~100−120 °C, at which both of these deactivation processes are minimized. Because the acetylene hydrochlorination is carried out at ~150 °C in a fixed-bed reactor in industry, the change in the Au valence may be the main reason for the deactivation of the $AuCl_3$ catalyst. Why can the Au^{3+} active species be reduced to Au^+ and metallic Au^0 with a low valence during the acetylene hydrochlorination process? It is well-known that the adsorption process is important for molecular activation and has a direct impact on heterogeneous catalysis reactions. Therefore, the change in the Au valence may be related to the competitive adsorption properties of the C_2H_2 and HCl reactants on the active sites of the catalyst. Hutchings et al. proposed that the reaction follows a pathway in which C_2H_2 is firmly adsorbed on the active site of $AuCl_3$, and then HCl is adsorbed on the $C_2H_2/AuCl_3$ compound, forming $C_2H_2/AuCl_3/HCl$ reactive intermediates.[22]

In 2012, Zhang et al. carried out more detailed studies on the deactivation mechanism of $AuCl_3$ catalyst during acetylene hydrochlorination. As Figure 1 shows, they proposed two possible paths using the density functional theory (DFT) method. In the main reaction, HCl and a $AuCl_3$ dimer cocatalyze C_2H_2, and a chlorovinyl intermediate is produced. If the HCl in the gaseous phase could not adsorb onto the Au site, it is difficult to desorb chlorovinyl from the catalyst by conversion to C_2H_3Cl. The catalytic activity of $AuCl_3$ would be decreased because the active Au^{3+} sites are occupied. In a side reaction, the $AuCl_3$ catalyst is rapidly deactivated by losing Cl atoms, and with the reduced state of the catalyst, the formed Au_2Cl_4 cannot be reactivated by the HCl purging method.[23] Therefore, the reduction of the Au^{3+} active species can be ascribed to the strong adsorption of C_2H_2 and weak adsorption of HCl in the acetylene hydrochlorination process, which causes the deactivation of $AuCl_3$ by loss of Cl atoms.

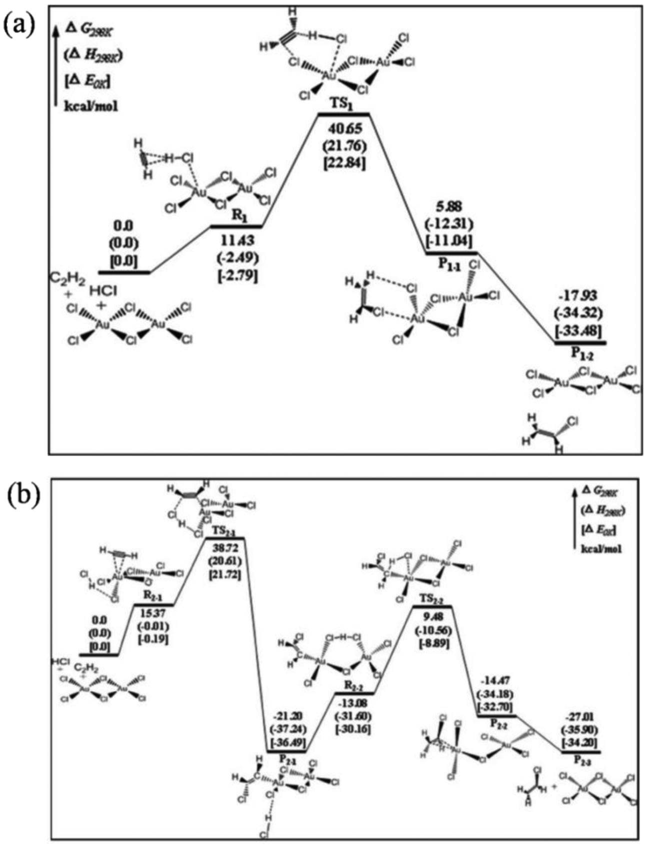

Figure 1. (a) Reaction energy profile for hydrochlorination of acetylene through path 1. (b) Reaction energy profile for hydrochlorination of acetylene through path 2. Reprinted with permission from ref 23. Copyright 2012, Royal Society of Chemistry.

After that, Wang et al. systematically studied the mechanisms of acetylene hydrochlorination to vinyl chloride catalyzed by neutral Au_{3-10} clusters using the DFT method. They thought that the dissociation of hydrogen chloride was the rate-controlling step on the neutral Au_{3-10} cluster catalyst. In addition, they found an "odd−even" rule between the catalytic performance and the atom numbers of gold clusters, that is, odd-numbered atom clusters generally performed better than even-numbered atom clusters in the acetylene hydrochlorination reaction.[24]

Because the reason for the deactivation of $AuCl_3$ catalyst is the reduction of active Au^{3+} species and carbon deposition, two approaches are possible to enhance the catalytic stability of the $AuCl_3$ catalyst. One method is reactivation of the catalyst, and the other is designing a new catalyst with a special physical structure, addition of a promoter, and modifying the carbon support. Nkosi et al. investigated $AuCl_3$ catalyst reactivation by a different reactivation gas according to the deactivation mechanism, and they found that air, Cl_2, NO, and N_2O could be effective for restoring used $AuCl_3$/AC.[25] However, the reactivation mechanisms are different: only air can remove the deposition of carbonaceous residues from the catalyst, but Cl_2, NO, and N_2O oxidize Au^0 to Au^+ and Au^{3+}. Although these methods require considerably longer reactivation times, this online regeneration method is very interesting because it can be carried out in a fixed-bed reactor without migration of the catalyst. Conte et al. also found that the deactivated catalyst can be reactivated by an off-line method. After boiling with aqua regia, Au^+ and metallic Au^0 can be oxidized to an active Au^{3+} species, and the catalytic activity is fully recovered.[26] Both fresh and regenerated catalysts have quite similar activity.

$AuCl_3$ catalyst can be regenerated by online or off-line methods; however, these methods were not convenient to carry out in an actual industrial application. Recently, investigators tried to design a novel catalyst with excellent catalytic stability in the acetylene hydrochlorination process. The common method is the addition of a promotor to change the electronic state of the active Au^{3+} sites. Conte et al. attempted to enhance the gold dispersion and improve the stability of its higher oxidation state by the addition of a second metal (Pd, Pt, Ru, Ir, Rh).[27] Although the results of these synthesized bimetal catalysts are not satisfactory, they concluded that (1) Au−Pd and Au−Pt catalysts increase the initial conversion of acetylene, although the catalysts rapidly become deactivated because of coke deposition; (2) Au−Ir and Au−Rh catalysts could enhance the selectivity of vinyl chloride to some extent; and (3) no matter what conversion of acetylene and selectivity of vinyl chloride were used, Au−Ru has no significant effect.

Subsequently, a series of bimetallic or trimetallic Au-based catalysts, including AuCu,[28] AuLa,[29] AuBa,[30] AuNi,[31] AuCs,[32,33] AuBi,[14] AuTiO$_2$,[34] and AuCoCu,[35] were synthesized and applied to acetylene hydrochlorination by different laboratories; the results are listed in Table 2.

Table 2. Catalytic Performance of Various AuM Catalysts

catalyst	GHSV, h^{-1}	temp, °C	acetylene conv, %	running time, h
AuCu[28]	120	150	97	2
AuLa[29]	360	150	98	50
AuBa[30]	360	200	98.4	50
AuNi[31]	900	170	95.4	46
AuCs[32,33]	740	180	94	50
	1480	180	90.1	50
AuBi[14]	600	180	85	10
AuTiO$_2$[34]	870	180	92	10
AuCoCu[35]	360	150	99.7	50

Among these catalysts, AuCoCu was the most optimal catalyst. As Figure 2 shows, an ~99.7% conversion of acetylene with a selectivity above 99.9% for VCM was obtained over the Au−Co(III)−Cu(II) catalysts with sphere active carbon (SAC) as support. Acetylene conversion then decreased gradually to 48.1% after 270 h. Then, a gas hourly space velocity (GHSV) of C_2H_2 was adjusted to 30 h^{-1}, and this change increased the acetylene conversion to 99.7% within 15 h. Therefore, the lifetime of the ternary catalyst was longer than 6513 h.[35] The rate-determining step of acetylene hydrochlorination was the adsorption of HCl. The strong adsorption of C_2H_2 is disadvantageous for acetylene hydrochlorination because the polymerization of C_2H_2 will cause carbon deposition, and reducibility of C_2H_2 will change the valence of the active Au species. Therefore, the addition of these promoters causes a transfer of electrons between the promoter and the Au active sites, increasing the electron density of the Au^{3+}cation, which further decreases the adsorption of C_2H_2 and increases the adsorption of HCl, thus enhancing the catalytic stability.

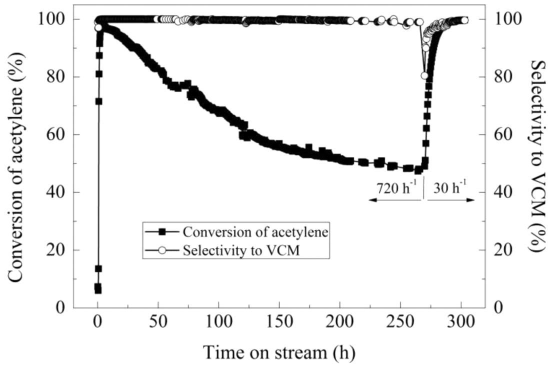

Figure 2. Lifetime estimate for the Au1Co(III)3Cu(II)1/SAC catalyst. Reaction conditions: T = 150 °C, P = 0.1 MPa, VHCl/VC$_2$H$_2$ = 1.15. Reprinted with permission from ref 35. Copyright 2014, Elsevier.

Temperature-programmed desorption (TPD) was an effective method to demonstrate the adsorption of C_2H_2 and HCl on the surface of the catalyst. Thermogravimetric analysis has commonly been used in these investigations to characterize the carbon deposition from acetylene hydrochlorination, despite its imprecision with active carbon (AC) as the catalyst support. X-ray photoelectron spectroscopy (XPS) was carried out to compare the ratio of Au^{3+}/Au^{+}/Au^{0} to demonstrate the effect of the addition of these promotors. However, it must also be noted that this characterization method is also imprecise because the Au 4f peak position in XPS seems insufficient to distinguish the chemical status of Au in these samples.[36] Bimetallic and trimetallic Au-based catalysts exhibited much better stability compared with a single metallic AuCl$_3$ catalyst for acetylene hydrochlorination; however, their prospects for industrial application are not promising, in our opinion. As a noble metal, elemental Au should be recovered after it is taken out of the fixed-bed reactor to decrease the cost. The common method of Au recovery is dissolving the elemental Au with aqua regia. Addition of another metallic promoter, especially elemental K, Cs, etc., which is difficult to deposit from the solution, will increase the recovery cost of the spent AuCl$_3$ catalyst.

The addition of a ligand to the Au^{3+} cation attracted some recent attention because this synthesis method does not include other metallic elements. Elemental Au can be conveniently recovered after acetylene hydrochlorination. Au(III)/Schiff bases[37] have been assessed for their ability to promote acetylene hydrochlorination. Their enhanced catalytic stability was attributed to a change in the electronic structure of the active metal by the second metallic component as a result of electron transfer between Au and another metal chloride. Recently, Wei et al. reported a very interesting catalyst,[38] and they synthesized a well-defined thiocyanate-stabilized Au-complexing catalyst, which showed a high turnover frequency (TOF) of 5.9 s^{-1}. Moreover, a pilot experiment on a 4 t per annum scale was evaluated as shown in Figure 3, and that experiment has been running for over 3000 h. That result is the first report of the industrial application of a Au-based catalyst, and it is of great significance for the development of the industrial application of Au-based catalysts in acetylene hydrochlorination. However, it must also be noted that thiocyanate is toxic, which may discourage the application of that catalyst. Therefore, the selection of another environmentally friendly ligand may be the latest strategy for Au-based catalysts for acetylene hydrochlorination.

The influence of the carbon support on the activity of AuCl$_3$ catalyst for acetylene hydrochlorination is also important. The physical properties of the carbon support include both the functional groups and the pore size of the carbon supports. Dai et al. used multiwall carbon nanotubes (MWCNTs) as the support for the AuCl$_3$ catalyst to investigate the effects of nitrogen doping on the catalytic activity of the AuCl$_3$ catalyst due to the purity and convenience of the modification of MWCNTs.[39] They proposed that the presence of nitrogen atoms on the surface of the MWCTs promoted the adsorption of the HCl reactant and thus somewhat enhanced the catalytic activity of the AuCl$_3$ catalyst. However, MWCNTs are expensive, and the method of nitrogen doping by pyrolysis of polypyr roles is not convenient; therefore, this work is only basic research.

Li et al. reported a very useful nitrogen-doping method for common active carbon. They synthesized a nitrogen-modified active carbon by pretreating it in HNO$_3$ solution and also obtained excellent stability of a AuCl$_3$ catalyst.[40] Why does the presence of a nitrogen functional group improve the stability of the AuCl$_3$ catalyst? Li et al. proposed that the oxygen group played a crucial role in the reduction of the Au^{3+} active species. Phenolic groups could anchor the Au^{3+} cations onto the surface of the active carbon, and the carboxylic group was responsible

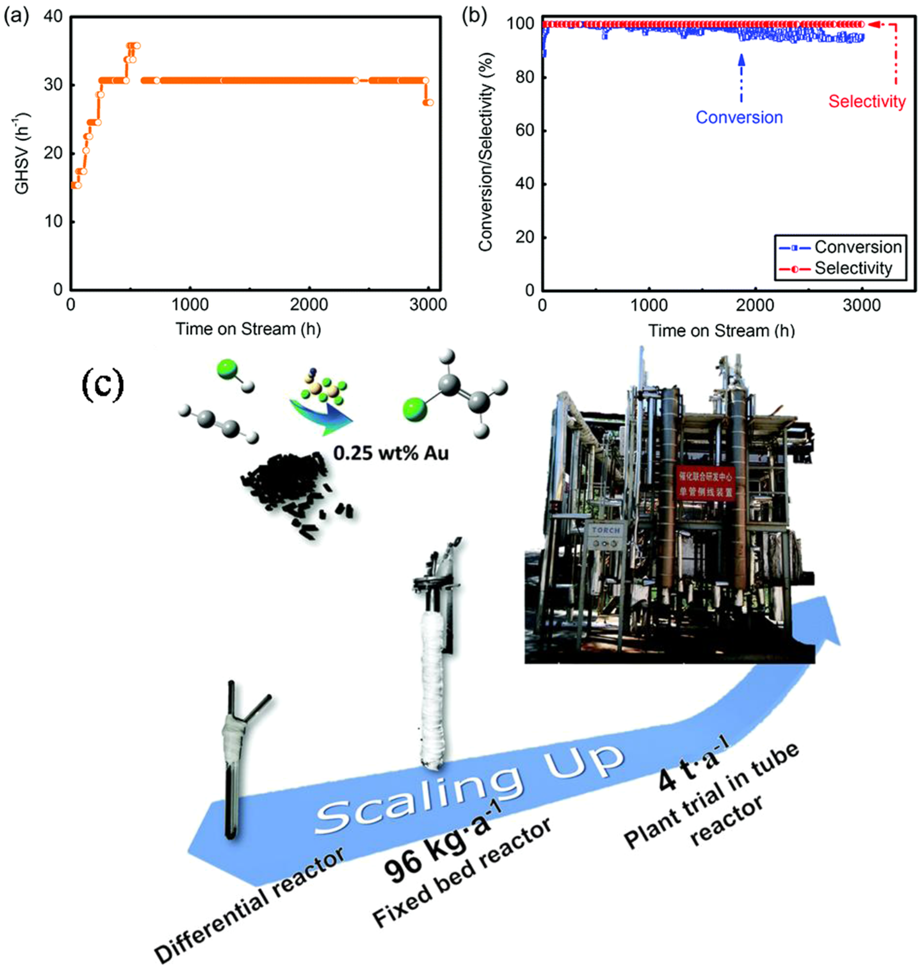

Figure 3. (a) GHSV during the evaluation of the pilot-trial analysis; (b) conversion and selectivity in this 3000 h evaluation. (c) The fixed-bed reactors in different scales: the U-shaped silica tube with 6 mm i.d. loaded with 0.15 g of catalyst, the fixed-bed reactor with 30 mm i.d. loaded with 60 g of catalyst, and the single tube fixed-bed reactor with 80 mm i.d. loaded with 2.5 kg of catalyst. Reprinted with permission from ref 38. Copyright 2015, Royal Society of Chemistry.

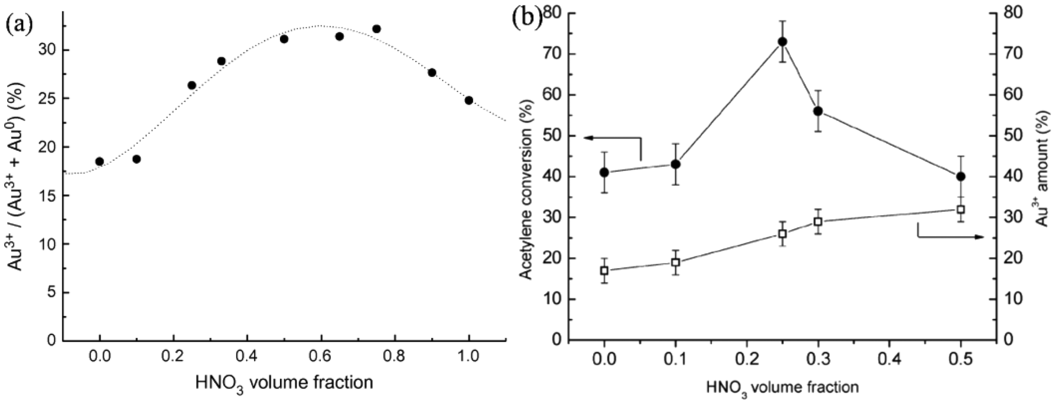

Figure 4. (a) TPR intensities for the reduction of Au^{3+} species for Au/C catalysts prepared using different HNO$_3$ volume fraction in the HCl/HNO$_3$ solvent mixture. All catalysts were dried at 140 °C. Reprinted with permission from ref 42. Copyright 2013, Elsevier. (b)Conversion (●) after 5 h and Au^{3+} amount for Au/C catalysts containing different amounts of Au^{3+}. The catalysts were obtained from impregnation using solutions containing different HNO$_3$ volume fractions in the HCl/HNO$_3$ mixture. Reprinted with permission from ref 43. Copyright 2013, Elsevier.

for the reduction of Au^{3+}. After the pretreating of active carbon with a HNO$_3$ solution, the nitrogen species could also anchor the Au^{3+} cations and enhance the adsorption of the HCl reactants.[41]

Hutchings et al. discussed the effect of the solvent aqua regia on the activity of the Au/C catalyst (Figure 4). They found that the ratio of HCl and HNO$_3$ and the temperature in the impregnation step not only could affect the Au^{3+}/Au^0 ratio but also modified the functional groups of the carbon. On the other hand, they also investigated the effect of the gold oxidation state and carbon structure on the activity of the Au/C catalysts. The activity of the Au/C catalysts was invariably associated

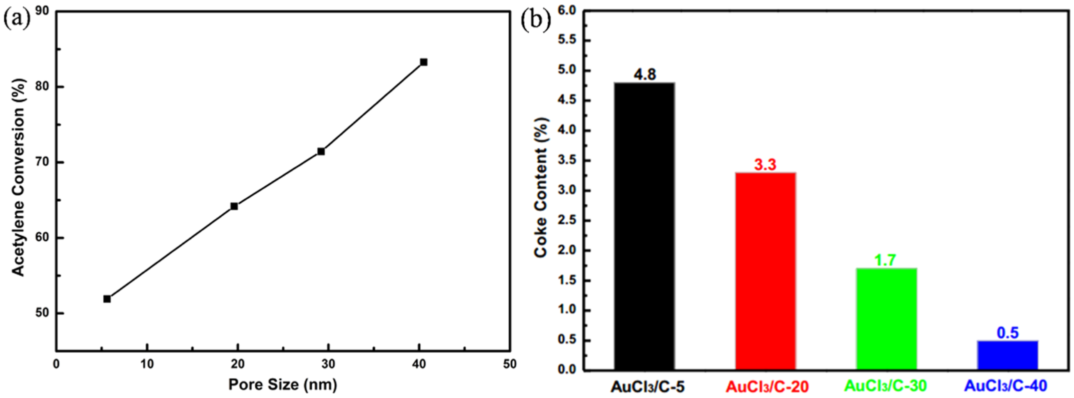

Figure 5. (a) Effect of the pore sizes of the 0.5% AuCl3/C−*x* catalysts on acetylene conversion. (b) Coke content of various 0.5% AuCl3/C−*x* catalysts after acetylene hydrochlorination. Reprinted with permission from ref 46. Copyright 2015, Royal Society of Chemistry.

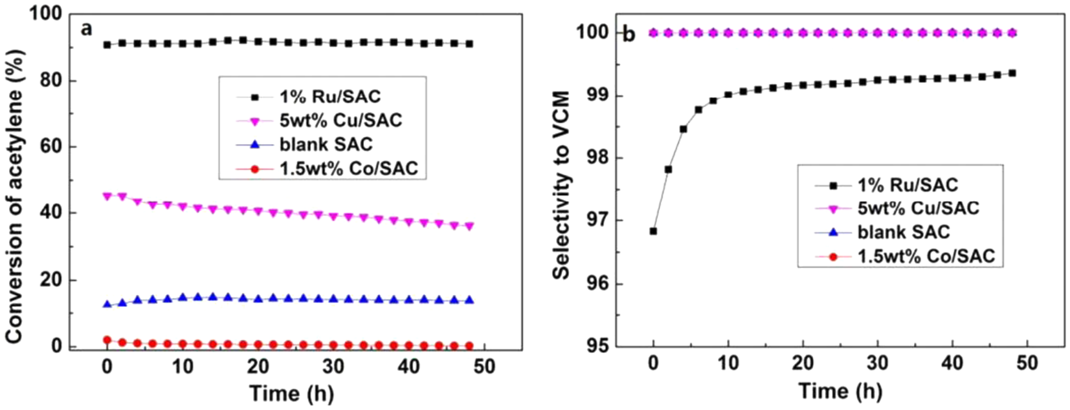

Figure 6. Acetylene conversion (a) and the selectivity to VCM (b) over monometallic Ru, Cu, Co catalysts. Reaction conditions are temperature (T) = 170 °C, C_2H_2 GHSV = 180 h^{-1}, VHCl/VC_2H_2 = 1.1. Reprinted with permission from ref 48. Copyright 2013, Royal Society of Chemistry.

with the presence of the Au^{3+} species and not just its concentration.[42−44] Because nitrogen atom doping can affect the catalytic performance of the $AuCl_3$ catalyst for acetylene hydrochlorination, it can be inferred that other heteroatoms may exhibit similar properties regarding the active carbon support.

Li et al. synthesized phosphorus-doped carbon consisting of phosphate groups on the surface using triphenylphosphine as the phosphorus source.[45] The phosphorus groups in the P-doped carbon support, composed of $(PO_4)^{3-}$and $(PO_3)^{-}$, could interact with the active gold species Au^{3+} and Au^{1+} to improve the dispersion of the catalytic active sites. The interactions of the phosphorus groups $(PO_4)^{3-}$and $(PO_3)^{-}$can prevent the reduction of the active gold species Au^{3+} and Au^{1+} to Au^0 but also retard the coke deposition on the catalyst surface. Apart from the change in the Au^{3+} valence in the $AuCl_3$ catalyst during acetylene hydrochlorination, carbon deposition is another reason for the deactivation of the $AuCl_3$ catalyst, as a result of the strong adsorption of C_2H_2 reactant. An approach to solve this problem is addition of a promoter or the modification of the carbon support. Carbon deposition blocks the pore of the carbon support and inhibits the transfer of the reactant from the gaseous phase to the active site in the pores of the carbon support. If carbon deposition cannot be avoided, another approach to solve this problem is to design mesoporous carbon as a support for the $AuCl_3$ catalyst. Zhu et al. controlled the pore sizes of the carbon support in a range of 5.6−40.5 nm using colloidal silica as a hard template and boric acid as the pore-expanding agent. As Figure 5 shows, the pore size variation significantly affects the initial activity. Larger mesoporous carbon supports could accelerate the reaction rate, resulting in higher acetylene conversion. In addition, the analysis of coke deposition on the catalyst support revealed that the catalytic reaction relies mainly on mesopores, even if the micropores are blocked to some extent. The dependence of regular catalytic performance on pore size is beneficial for acetylene hydrochlorination, which requires fast molecular diffusion to suppress coke formation.[46]

3. RU-BASED CATALYSTS

The price of Ru is much lower than that of Au, so it may be another candidate catalyst for acetylene hydrochlorination because the stand potential of Ru^{3+} is also close to that of the Hg^{2+} cation (($E(Ru^{3+})$ = 0.455 V; $E(Hg^{2+})$ = 0.851 V). In 1988, Nkosi et al. reported that the initial conversion of acetylene with a $RuCl_3$ catalyst was much lower than for other metal chlorides.[19] No other reports about the application of a $RuCl_3$ catalyst for acetylene hydrochlorination were published for 24 years. In 2012, Kang et al. used DFT to calculate the activation barrier for acetylene hydrochlorination and found that it is 16.3, 11.9, and 9.1 kcal/mol over that for $HgCl_2$, $AuCl_3$, and $RuCl_3$, respectively. $RuCl_3$ has been found to be a good candidate catalyst, instead of $HgCl_2$ and $AuCl_3$, for this reaction. Subsequently, much work has been performed to develop the Ru-based catalysts both theoretically and experimentally.[47]

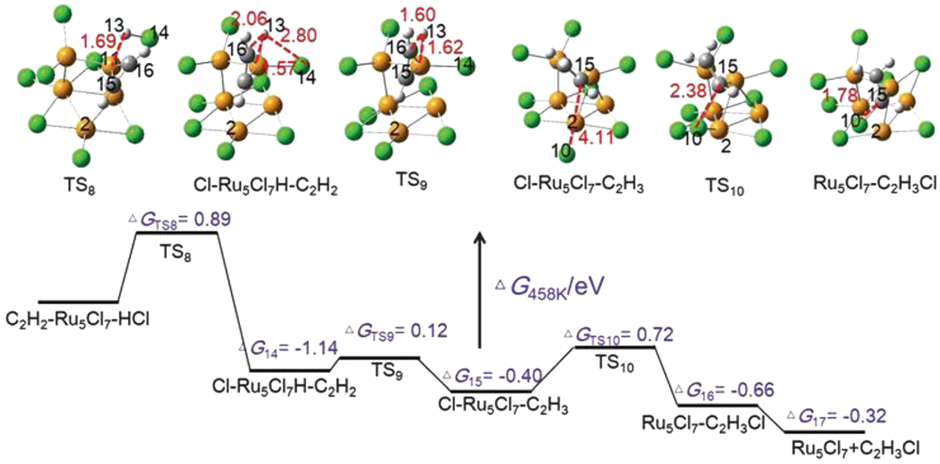

Figure 7. DFT calculated energy surface for acetylene hydrochlorination catalyzed by Ru5Cl7. Reprinted with permission from ref 52. Copyright 2015, Royal Society of Chemistry.

Zhang et al. prepared the Ru/SAC, Ru−Cu/SAC, and Ru−Co/SAC catalysts.[48] As Figure 6 shows, the Ru1Co3/SAC catalyst with a Ru content of 1% gave an optimal conversion exceeding 95% acetylene under reaction conditions of 170 °C and a C_2H_2 hourly space velocity of 180 h^{-1}. The catalytic activity of the RuCo catalyst is very close to that of the $AuCl_3$ catalyst; however, it is not clear which ruthenium species is predominant in this reaction. To answer this question, they treated $RuCl_3$ catalysts at different temperatures and atmospheres to explore the relationship between Ru particle size and the amount of RuO_2 present on the catalysts and the activity of the catalysts.[49] It was demonstrated that (i) a large particle size of Ru decreases the conversion of acetylene; (ii) for similar average-sized Ru particles, the higher the content of RuO_2, the higher the activity of acetylene hydrochlorination; and (iii) two distinct structures of the active ingredients in the oxidative and reductive treatments exist. RuO_2 is the major active ingredient in the oxidative treatment, and metallic Ru and Ru/RuO_y are the major active ingredients in the reductive treatment. In addition, carbon nanotubes (CNT) should be used as a support to prepare Ru catalysts.[50] The Ru-in-CNT catalyst exhibits an activity that is 50% higher than the Ru particles located on the CNT exterior walls, and acetylene conversion is as high as 95%.

To further investigate the Ru-based catalysts, an effective approach is to add K in this reaction.[51] The improved conversion of acetylene can be comprehensively attributed to the increased RuO_2 content, the dispersion of catalysts, and the enhancement of the interaction between the product C_2H_3Cl and the Ru-based catalysts. To gain insight into the relationship between the structure of Ru-based catalysts and their catalytic mechanism at the molecular level, DFT calculations were carried out on Ru_3Cl_9, Ru_3Cl_7, Ru_5Cl_7, Ru_3Cl_3, and Ru_3 clusters.[52] Three different reaction mechanisms for acetylene hydrochlorination exist. On Ru_3Cl_9, the H and Cl atoms of HCl were simultaneously added to C_2H_2 to form C_2H_3Cl, whereas on Ru_3Cl_7, Ru_3Cl_3 and Ru_3, the reaction was divided into two processes: the addition of H to activated C_2H_2 to form C_2H_3 and the addition of Cl to C_2H_3 to produce VCM (the rate-controlling step). On Ru_5Cl_7, a low chloride-coordinated Ru was responsible for activating the reactants and adding H to C_2H_2, and the high chloride-coordinated Ru was responsible for providing Cl to C_2H_3 (Figure 7). Among all of the Ru catalytic models, the Ru_5Cl_7 cluster energy barrier was the lowest. Recently, Li et al.[53] reported a novel catalyst in which the content of Ru is only 400 ppm and also includes 4.24 wt % Cu supported on carbon nanotubes. From the TOF result, its performance is higher than $HgCl_2$ catalysts. Only one question: the mechanism of the synergistic effect between two metals, is not clear. However, the activity of this catalyst should be confirmed.

Ru-based catalysts may be environmentally friendly, inexpensive, and have high activity; however, this catalyst suffers from a simple but fatal flaw: the abundance of Ru is only 0.001 ppm worldwide. An adequate content of the element on Earth is crucial to achieving sustainable human development.

4. OTHER METAL CATALYSTS

In addition to the Ru-based catalysts mentioned above, other noble and nonprecious metal catalysts have also been investigated for acetylene hydrochlorination as predicted by Hutchings on the basis of the standard electrode potentials of the metal chlorides; for example, Ag^+,[19] Pt^{2+},[54,55] Pd^{2+},[27,56] Rh^{3+},[19,25] Ir^{3+},[25] and Cu^{2+}.[57] However, these metal chloride catalysts were significantly deactivated as the reaction time increased because of the loss of the active component and surface carbon deposition, despite that all of these catalysts were able to maintain a high selectivity for VCM throughout the entire reaction period.

Recently, Wang et al.[58] reported on some Pd catalysts by using HY zeolite as the support. They found that the HY zeolite modified with 10 wt % NH_4F exhibited enhanced catalytic performance for acetylene hydrochlorination, with higher acetylene conversion and a slower deactivation rate during the reaction process. The dealumination of the zeolite during fluorination can partially affect the surface acidity of the catalyst and reduce the formation of carbon deposits to some extent, thus improving the catalytic performance of the Pd catalysts.

Although noble metal chloride catalysts exhibit excellent catalytic activity for acetylene hydrochlorination, the poor stability and expense severely restrict further industrial application. Therefore, further exploration of other nonprecious metals as advanced catalysts is significant in both fundamental research and practical application. Advantages of low toxicity, ease of obtainment, low cost, and acceptable catalytic activity of Cu-based catalysts render them good candidates for efficient mercury-free catalysis. In addition to the intrinsic catalytic properties of these catalysts, the support used also plays an

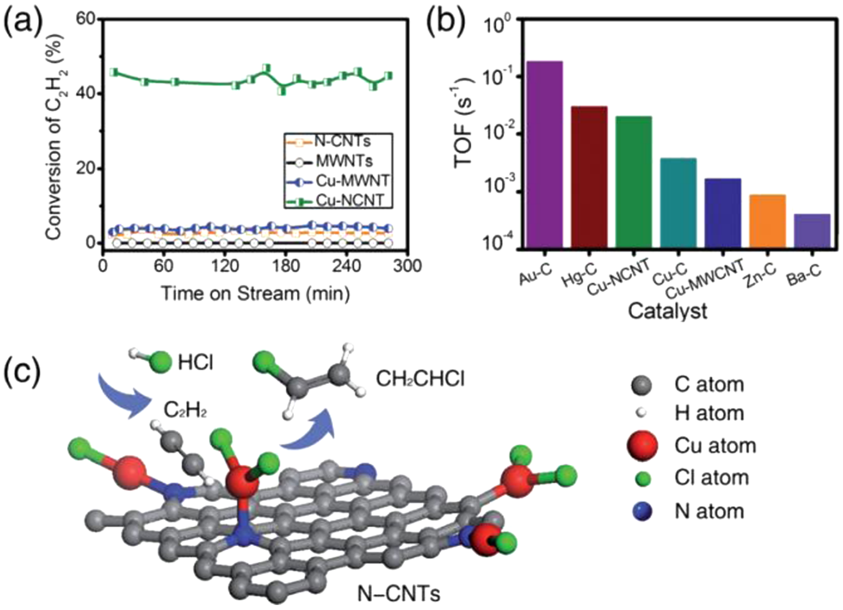

Figure 8. (a) The reactivity evaluation of the catalysts: Cu-NCNT, Cu-MWCNT, N-CNTs, and MWCNTs (T = 180 °C, GHSV = 180 h^{-1}, $Q(HCl)/Q(C2H2)$ = 1.1:1.0). (b) The TOF value for the different catalysts: Au−C, Hg−C, Cu-NCNT, Cu−C, Cu−MWCNT, Zn−C, and Ba−C. (c) The schematic diagram of acetylene hydrochlorination catalyzed by Cu−NCNT. Reprinted with permission from ref 59. Copyright 2014, Royal Society of Chemistry.

important role in determining the catalytic performance. Wei et al.[59] designed a novel catalyst, Cu-NCNT, which consisted of copper chloride nanoparticles (NPs) loaded on nitrogen-doped carbon nanotubes (NCNT). In catalytic studies under the conditions of 180 °C and 180 h^{-1}, they found that Cu-NCNTs exhibited enhanced catalytic activity for acetylene hydrochlorination compared with N-free catalysts; the initial conversion of Cu-NCNTs was 45.8% and stabilized at ~43.5%, whereas Cu-MWCNTs showed an only ~4.0% conversion rate. This significant difference in reactivity suggests that N dopants tune the electron affinity of CNTs. The Cu NPs can coordinate with N, that is, a Cu−N−C hybrid served as the active reaction center for acetylene hydrochlorination and the further adsorption of C_2H_2 on the catalyst surface, contributing to higher activity, as the schematic in Figure 8 shows.

Bimetallic or trimetallic Cu bases have also been applied to catalysts for acetylene hydrochlorination. For instance, $SnCl_2$−$BiCl_3$−CuCl ternary metal chloride[60] supported on AC was an efficient catalyst, giving an initial 97% conversion rate and 95% selectivity at a reaction temperature of 140 °C and a GHSV of 30 h^{-1}. However, both $SnCl_2$ and $BiCl_3$ show severe losses because of their low boiling points during the reaction process; the stability of the $SnCl_2$−$BiCl_3$−CuCl ternary metal catalyst was relatively poor. Recently, Wei et al.[6] developed a Bi/Cu/H_3PO_4 series catalyst supported on silica gel, for which H_3PO_4 promotes catalyst regeneration and inhibits active component loss. Experiments of 700 h and 10 t per annum toward industrial production were operated on a fluidized-bed reactor, and the catalyst exhibited good catalytic performance, maintaining a conversion rate of ~80% in 200 h trials.

5. CARBON NITRIDE CATALYSTS

Metal-based hybrids as catalysts have exhibited significantly high catalytic activities for acetylene hydrochlorination. However, metal-based catalysts often suffer disadvantages such as high cost, poor stability, etc. Therefore, the development of fully metal-free catalysts is of great importance for the production of the monomer vinyl chloride. Recently, heteroatom doping of carbon materials became the “Big Thing of Concern” in materials science, further proving to be versatile functional materials with a wide range of heterogeneous catalysis, including oxygen reduction reactions,[61] biomass conversion,[62] and acetylene hydrochlorination.[63−68] In particular, the carbon nitride materials enriched with nitrogen content have garnered a great deal of attention over the past few years. Many researchers have proved that the heteroatom doping changes not only the carbon surface chemistry, such as basicity, but also the electronic structure by donating a lone pair of electrons on the undoped carbon lattice. To date, a number of carbon nitride nanocomposites have been proposed in which nitrogen is impregnated into porous activated carbon,[63,67] pitch-based spherical activated carbon,[64] multiwalled carbon nanotubes,[65] silicon carbide[66] or graphene[68] by chemical vapor deposition, heat-treatment with nitrogen sources, or direct carbonization of N-containing precursors. Carbon nitride nanocomposites applied to acetylene hydrochlorination as metal-free catalysts and their respective nitrogen contents are summarized in Table 3.

As for carbon nitride materials, multiple types of N species are often introduced simultaneously; thus, it is hard to dope carbon materials with a single N species. Although both theory and experiments indicate that carbon atoms bound with nitrogen are the active sites for acetylene hydrochlorination, it is still difficult to determine a positive correlation between catalytic activity and the exact N species. Li et al.[63] successfully fabricated the g-C_3N_4-based carbon nitride catalyst (g-C_3N_4/AC) by using porous activated carbon as a support and cyanamide as a precursor. Through the synthetic process, the produced nonmetallic g-C_3N_4/AC catalyst not only had a high surface area and a high nitrogen content but also improved the conversion of acetylene to 76.52% under the reaction conditions of 180 °C and GHSV of 50 h^{-1}. The authors demonstrated that C_3N_4 could enhance the adsorption of hydrogen chloride and activate acetylene, and the hydrogen

Table 3. Carbon Nitride Catalysts and Their Nitrogen Contents

catalyst	preparation method	precursor	nitrogen content, %	ref
g-C_3N_4/AC	thermal annealing	AC, cyanamide	7.39	63
PSAC-N	thermal annealing	PSAC, melamine	4.93	64
NCNTs	CVD	Ar, H_2,C_2H_4, NH_3	4.4	65
SiC@N−C	thermal annealing	SiC, CCl_4, NH_3	7.1	66
PANI-AC	thermal annealing	AC, aniline	2.39	67
N-G	thermal annealing	GO, NH_3	5.47	68
B,N-G	thermal annealing	GO, H_3BO_3, NH_3	10.96	68

chloride molecules were more readily adsorbed at the active site of pyridinic nitrogen.

In another case, through a chemical vapor deposition (CVD) growth process, Zhou et al.[65] successfully synthesized a NCNT catalyst with a TOF value of $2.3 \times 10^{-3} s^{-1}$. Here, the TOF was calculated on the basis of the quaternary nitrogen atoms, with the quaternary N species employed as important active sites instead of pyridinic or pyrrolic N. Such nitrogen-containing NCNTs showed enhanced catalytic activity for acetylene hydrohalogenation. This study revealed that nitrogen doping enhances the adsorption of the C_2H_2 molecule compared with the undoped state, and the adsorption of hydrogen chloride is very weak. In addition, it has also been demonstrated that nitrogen doping increases the nucleophilicity of CNTs and enhances the interaction between the highest occupied molecular orbital of NCNTs and the lowest unoccupied molecular orbital of acetylene.

To overcome this disadvantage, such as difficulty of shaping and low-mechanical strength, Bao et al.[66]successfully fabricated a SiC-based carbon nitride (SiC@N−C) catalyst and found that the hybrid had excellent catalytic properties for acetylene hydrochlorination, giving an acetylene conversion rate as high as 80% during a 150 h test at 200 °C at atmospheric pressure and a space velocity of 30 h^{-1}. In the report, the authors found that carbon materials doped with pyrrolic N species are active for the reaction and that acetylene hardly adsorbs on the quaternary and pyridinic N. On the other hand, DFT calculations indicate that the pyrrolic-N-induced electronic state possesses a higher energy level and density, which benefits the adsorption of acetylene. In a later study, Zhang et al.[67] found that the catalytic activity for acetylene hydrochlorination of the N-doped AC catalyst depended strongly on the various

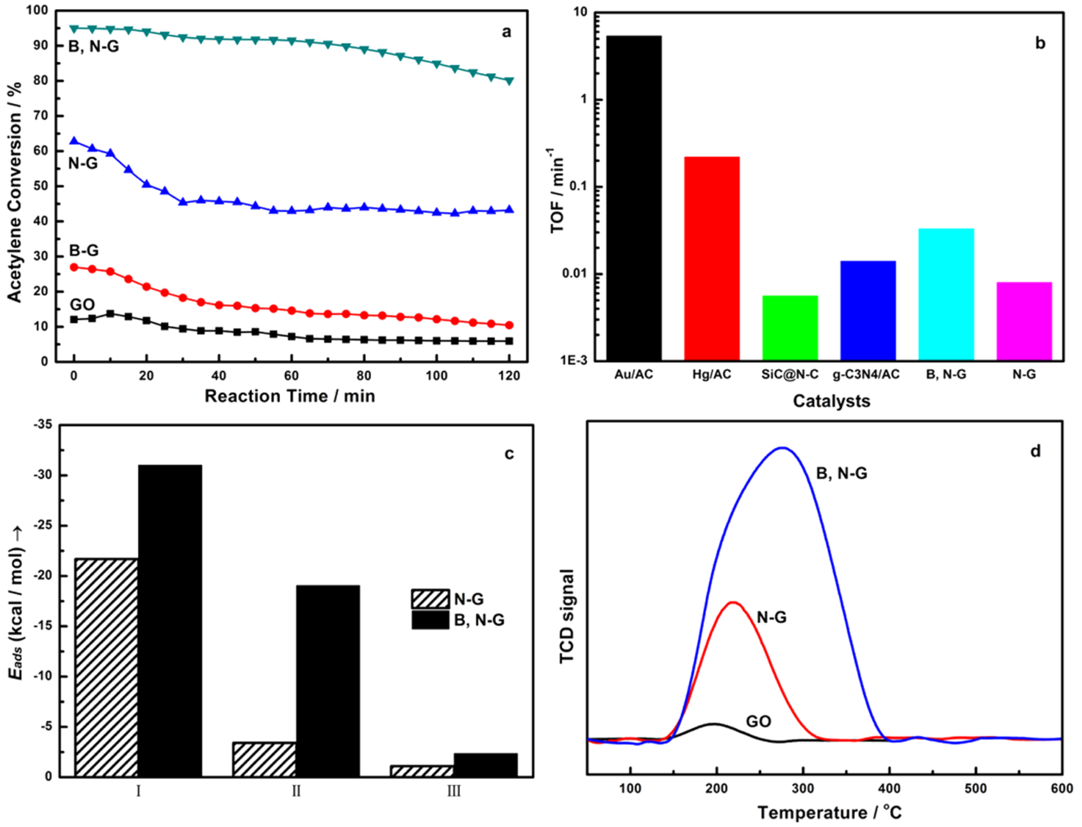

Figure 9. (a) Catalytic reactivity evaluation of GO, B-G, N-G, and B,N-G. Reactions were carried out at 150 °C, atmospheric pressure, a gas hourly space velocity (GHSV) of 36 h^{-1}, and HCl/C_2H_2 = 1.15/1 (volume ratio). (b) The TOFs for different catalysts: Au/AC,[59] Hg/AC,[59] SiC@N−C,[66] g-C_3N_4/AC,[63] B,N-G,[68] and N-G.[68] (c) E_{ads} of HCl on different types of active sites in N-G and B,N-G. (I) The carbon atoms bonded with pyridinic N species. (II) The carbon atoms bonded with pyrrolic N species. (III) The carbon atoms bonded with graphitic N species. (d) TPD profile of GO, N-G, and B,N-G. The samples were preadsorbed by HCl gas for 2 h at a flow rate of 20 mL/min in the microreactor, which was heated to 150 °C. Then it was taken out of the microreactor when the sample was cooled to room temperature. Subsequently, a temperature-programmed desorption TPD was conducted using a Micromeritic ASAP 2720 instrument. Reprinted with permission from ref 68. Copyright 2015, American Chemical Society.

nitrogen species, in the sequence pyrrolic *N* > graphitic *N* > pyridinic N. On the basis of the TPD experiments, a positive correlation between the pyrrolic N content and the capability for adsorbing hydrogen chloride and acetylene was obtained.

The dual-doping of multiple species of foreign atoms may generate new properties or create synergistic effects. Recently, we synthesized a dually doped N,B graphene (B,N-G)[68] catalyst via a two-step method and studied its catalytic activity for acetylene hydrochlorination. As shown in Figure 9a,b, the dually doped B,N-G catalyst significantly enhanced acetylene conversion to 94.98%; the TOF value of B,N-G is ∼15% of Hg/AC and 6‰ of the Au/AC catalyst. Both DFT calculations and HCl-TPD studies showed that the presence of B heteroatoms dramatically increased the absorption of the hydrogen chloride molecule. Theoretical results also demonstrated that the carbon atoms bonded with pyridinic N dominate the HCl adsorption, and the transition of the pyrrolic N group from "inactive" to "active" after B in corporation is also very favorable for the outstanding activity of the B,N-G catalyst.

6. CONCLUSION AND PROSPECT

Nonmercury catalysts for acetylene hydrochlorination are very important for PVC production from calcium carbide because of the toxicity of Hg catalysts. This Perspective aimed to introduce the development of heterogeneous catalysts for acetylene hydrochlorination. At present, we can draw five conclusions and predict the prospects of these catalysts on the basis of the reported literature.

(i) Addition of other metal chlorides as a promotor can improve the stability of the $AuCl_3$ catalyst. A trimetallic AuCo(III)Cu(II) catalyst has optimal catalytic performance, and it can function for 6513 h without a significant decrease in acetylene conversion. However, in the presence of other metals, the recycling of elemental Au from spent catalyst may be problematic for industrial application. A thiocyanate-stabilized Au-complexing catalyst can function for 3000 h for acetylene hydrochlorination; however, thiocyanate is toxic, and exploration of another environmentally friendly ligand as a promoter for the $AuCl_3$ catalyst may be a developing strategy in this area of research.

(ii) Doping with nitrogen and phosphorus atoms can enhance the stability of the $AuCl_3$ catalyst, and a mesoporous carbon support can inhibit coking of the catalysts. The functional group and pore size of the carbon support should be further modified in the future to obtain optimal stability.

(iii) Ru-based catalysts displayed a similar catalytic performance compared with Au-based catalysts. However, in our opinion, these may not be widely applied in acetylene hydrochlorination because of a lack of abundance.

(iv) At present, the catalytic activities of Pd-based and Cu-based catalysts are not suitable for industrial application in acetylene hydroclorination. However, the investigation of these catalysts is very important for nonmercury heterogeneous catalysts for acetylene hydrochlorination because of their low cost.

(V) Carbon nitride is another candidate catalyst for acetylene hydrochlorination. However, the TOF of this catalyst is much lower than for Au and Hg catalysts, and serious carbon deposition occurs on the catalyst surface. The detailed reaction mechanism of acetylene hydroclorination should be investigated, which may be helpful for designing novel carbon nitrides with better catalytic activity and stability.

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Weissermel, K.; Arpe, H. *Industrial Organic Chemistry*, 4th ed.; Wiley-VCH: Weinheim, 2003, p 217.

(2) Allsopp, M. W.; Vianello, G. *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2000.

(3) Saeki, Y.; Emura, T. *Prog. Polym. Sci.* **2002**, *27*, 2055−2131.

(4) Clegg, I. M.; Hardman, R. U.S. Patent 5,763,710, 1998.

(5) Speight, J. G.; Speight, J. *Chemical and Process Design Handbook*; McGraw-Hill: New York, 2002, 2542.

(6) Zhou, K.; Jia, J.; Li, X.; Pang, X.; Li, C.; Zhou, J.; Luo, G.; Wei, F. *Fuel Process. Technol.* **2013**, *108*, 12−18.

(7) Matar, S.; Hatch, L. F. *Chemistry of Chemical Processes*, 2nd ed.; Butterworth-Heinemann: Woburn, MA, 2001.

(8) United States Environmental Protection Agency. Entry file *EPA/600/X-84/178*, U.S. EPA: Washington, DC, 1988.

(9) Wei, X.; Shi, H.; Qian, W.; Luo, G.; Jin, Y.; Wei, F. *Ind. Eng. Chem. Res.* **2009**, *48*, 128−133.

(10) Bing, J.; Li, C. *Polyvinyl Chloride* **2011**, *39*, 1−8.

(11) Hutchings, G. J. *J. Catal.* **1985**, *96*, 292−295.

(12) Hutchings, G. J.; Grady, D. T. *Appl. Catal.* **1985**, *16*, 411−415.

(13) Hutchings, G. J.; Grady, D. T. *Appl. Catal.* **1985**, *17*, 155−160.

(14) Zhou, K.; Wang, W.; Zhao, Z.; Luo, G.; Miller, J.; Wong, M.; Wei, F. *ACS Catal.* **2014**, *4*, 3112−3116.

(15) Nairobi. *Decisions and information on the 25th session of the UNEP Governing Council/Global Ministerial Environment Programme*; to be found under http://www.unep.org/gc/gc25/, 2009.

(16) Minamata Convention Agreed by Nations www.unep.org/newscentre/default.aspx?DocumentID=2702&ArticleID=9373, EP News Centre; 2013.

(17) Smith, D. M.; Walsh, P. M.; Slager, T. L. *J. Catal.* **1968**, *11*, 113−130.

(18) Shinoda, K. *Chem. Lett.* **1975**, 219−220.

(19) Nkosi, B.; Coville, N. J.; Hutchings, G. J. *Appl. Catal.* **1988**, *43*, 33−39.

(20) Nkosi, B.; Coville, N. J.; Hutchings, G. J. *J. Chem. Soc., Chem. Commun.* **1988**, 71−72.

(21) Nkosi, B.; Coville, N. J.; Hutchings, G. J.; Adams, M. D.; Friedl, J.; Wagner, F. E. *J. Catal.* **1991**, *128*, 366−377.

(22) Conte, M.; Carley, A. F.; Heirene, C.; Willock, D. J.; Johnston, P.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. *J. Catal.* **2007**, *250*, 231−239.

(23) Zhang, J.; He, Z.; Li, W.; Han, Y. *RSC Adv.* **2012**, *2*, 4814−4821.

(24) Wang, Y.; Zhu, M.; Kang, L.; Dai, B. *RSC Adv.* **2014**, *4*, 38466−38473.

(25) Nkosi, B.; Adams, M. D.; Coville, N. J.; Hutchings, G. J. *J. Catal.* **1991**, *128*, 378−386.

(26) Conte, M.; Carley, A. F.; Hutchings, G. J. *Catal. Lett.* **2008**, *124*, 165−167.

(27) Conte, M.; Carley, A. F.; Attard, G.; Herzing, A. A.; Kiely, C. J.; Hutchings, G. J. *J. Catal.* **2008**, *257*, 190−198.

(28) Zhao, J.; Zeng, J.; Cheng, X.; Wang, L.; Yang, H.; Shen, B. *RSC Adv.* **2015**, *5*, 16727−16734.

(29) Zhang, H.; Dai, B.; Wang, X.; Xu, L.; Zhu, M. *J. Ind. Eng. Chem.* **2012**, *18*, 49−54.

(30) Zhang, H.; Li, W.; Li, X.; Zhao, W.; Gu, J.; Qi, X.; Dong, Y.; Dai, B.; Zhang, J. *Catal. Sci. Technol.* **2015**, *5*, 1870−1877.

(31) Pu, Y.; Zhang, J.; Wang, X.; Zhang, H.; Yu, L.; Dong, Y.; Li, W. *Catal. Sci. Technol.* **2014**, *4*, 4426−4432.

(32) Zhao, J.; Zhang, T.; Xu, X.; Xu, J.; Xu, J.; Ni, J.; Li, X. *ChemPlusChem* **2015**, *80*, 196−201.

(33) Zhao, J.; Xu, J.; Xu, J.; Zhang, T.; Di, X.; Li, X.; Ni, J *RSC Adv.* **2015**, *5*, 6925−6931.

(34) Huang, C.; Zhu, M.; Kang, L.; Li, X.; Dai, B. *Chem. Eng. J.* **2014**, *242*, 69−75.

(35) Zhang, H.; Dai, B.; Li, W.; Wang, X.; Zhang, J.; Zhu, M.; Gu, J. *J. Catal.* **2014**, *316*, 141−148.

(36) Su, Y. S.; Lee, M. Y.; Lin, S. D. *Catal. Lett.* **1999**, *57*, 49−53.

(37) Huang, C.; Zhu, M.; Kang, L.; Dai, B. *Catal. Commun.* **2014**, *54*, 61−65.

(38) Zhou, K.; Jia, J.; Li, C.; Xu, H.; Zhou, J.; Luo, G.; Wei, F. *Green Chem.* **2015**, *17*, 356−364.

(39) Li, X.; Zhu, M.; Dai, B. *Appl. Catal., B* **2013**, *142−143*, 234−240.

(40) Zhao, J.; Xu, J.; Xu, J.; Zhang, T.; Di, X.; Ni, J.; Li, X. *Chem. Eng. J.* **2015**, *262*, 1152−1160.

(41) Xu, J.; Zhao, J.; Xu, J.; Zhang, T.; Li, X.; Di, X.; Ni, J.; Wang, J.; Cen, J. *Ind. Eng. Chem. Res.* **2014**, *53*, 14272−14281.

(42) Conte, M.; Davies, C. J.; Morgan, D. J.; Davies, T. E.; Elias, D. J.; Carley, A. F.; Johnston, P.; Hutchings, G. J. *J. Catal.* **2013**, *297*, 128−136.

(43) Conte, M.; Davies, C. J.; Morgan, D. J.; Davies, T. E.; Carley, A. F.; Johnston, P.; Hutchings, G. J. *Catal. Sci. Technol.* **2013**, *3*, 128−134.

(44) Conte, M.; Davies, C. J.; Morgan, D. J.; Carley, A. F.; Johnston, P.; Hutchings, G. J. *Catal. Lett.* **2014**, *144*, 1−8.

(45) Wang, B.; Yu, L.; Zhang, J.; Pu, Y.; Zhang, H.; Li, W. *RSC Adv.* **2014**, *4*, 15877−15885.

(46) Chen, K.; Kang, L.; Zhu, M.; Dai, B. *Catal. Sci. Technol.* **2015**, *5*, 1035−1040.

(47) Zhu, M.; Kang, L.; Su, Y.; Zhang, S.; Dai, B. *Can. J. Chem.* **2013**, *91*, 120−125.

(48) Zhang, J.; Sheng, W.; Guo, C.; Li, W. *RSC Adv.* **2013**, *3*, 21062−21068.

(49) Pu, Y.; Zhang, J.; Yu, L.; Jin, Y.; Li, W. *Appl. Catal., A* **2014**, *488*, 28−36.

(50) Li, G.; Li, W.; Zhang, H.; Pu, Y.; Sun, M.; Zhang, J. *RSC Adv.* **2015**, *5*, 9002−9008.

(51) Jin, Y.; Li, G.; Zhang, J.; Pu, Y.; Li, W. *RSC Adv.* **2015**, *5*, 37774−37779.

(52) Han, Y.; Sun, M.; Li, W.; Zhang, J. *Phys. Chem. Chem. Phys.* **2015**, *17*, 7720−7730.

(53) Xu, J.; Zhao, J.; Zhang, T.; Di, X.; Gu, S.; Ni, J.; Li, X. *RSC Adv.* **2015**, *5*, 38159−38163.

(54) Mitchenko, S. A.; Khomutov, E. V.; Shubin, A. A.; Shul'ga, Y. M. *J. Mol. Catal. A: Chem.* **2004**, *212*, 345−352.

(55) Mitchenko, S. A.; Krasnyakova, T. V.; Mitchenko, R. S.; Korduban, A. N. *J. Mol. Catal. A: Chem.* **2007**, *275*, 101−108.

(56) Krasnyakova, T. V.; Zhikharev, I. V.; Mitchenko, R. S.; et al. *J. Catal.* **2012**, *288*, 33−43.

(57) Wang, S.; Shen, B.; Song, Q. *Catal. Lett.* **2010**, *134*, 102−109.

(58) Wang, L.; Wang, F.; Wang, J. *Catal. Commun.* **2015**, *65*, 41−45.

(59) Zhou, K.; Si, J.; Jia, J.; Huang, J.; Zhou, J.; Luo, G.; Wei, F. *RSC Adv.* **2014**, *4*, 7766−7769.

(60) Deng, G.; Wu, B.; Li, T. *Polyvinyl Chloride* **1994**, *6*, 5−9 (in Chinese)..

(61) Zheng, Y.; Jiao, Y.; Ge, L.; Jaroniec, M.; Qiao, S. *Angew. Chem.* **2013**, *125*, 3192−3198.

(62) Tessonnier, J. P.; Villa, A.; Majoulet, O.; Su, D.; Schlögl, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 6543−6546.

(63) Li, X.; Wang, Y.; Kang, L.; Zhu, M.; Dai, B. *J. Catal.* **2014**, *311*, 288−294.

(64) Wang, X.; Dai, B.; Wang, Y.; Yu, F. *ChemCatChem* **2014**, *6*, 2339−2344.

(65) Zhou, K.; Li, B.; Zhang, Q.; Huang, J.; Tian, G.; Jia, J.; Zhao, M.; Luo, G.; Su, D.; Wei, F. *ChemSusChem* **2014**, *7*, 723−728.

(66) Li, X.; Pan, X.; Yu, L.; Ren, P.; Wu, X.; Sun, L.; Jiao, F.; Bao, X. *Nat. Commun.* **2014**, *5*, 3688−3694.

(67) Zhang, C.; Kang, L.; Zhu, M.; Dai, B. *RSC Adv.* **2015**, *5*, 7461−7468.

(68) Dai, B.; Chen, K.; Wang, Y.; Kang, L.; Zhu, M. *ACS Catal.* **2015**, *5*, 2541−2547.