

An Alternative Carbon Carrier in Green Preparation of Efficient Gold/Carbon Catalyst for Acetylene Hydrochlorination

Huixia Lai,^[a] Bolin Wang,^[a] Yuxue Yue,^[a] Gangfeng Sheng,^[a] Saisai Wang,^[a] Feng Feng,^[a] Qunfeng Zhang,^[a] Jia Zhao,^{*[a]} and Xiaonian Li^{*[a]}

Au catalysts supported with carbon-based carriers have been extensively studied for the hydrochlorination of acetylene and expected to replace toxic mercury catalysts. However, removal of the highly corrosive agua regia used in the preparation of carbon-based catalysts while maintaining catalytic activity and stability remains a key challenge. Herein, we present a green technology carrier, activated carbon fibers (ACF), to support gold catalysts for the hydrochlorination of acetylene. TPD and XPS analyses confirmed the presence of surface oxygencontaining functional groups (SOGs) and pyrrolic N species on

Introduction

The energy structure of China's rich coal and lean oil dictates that the production of vinyl chloride monomer (VCM) by acetylene hydrochlorination is the best route for large-scale production of polyvinyl chloride (PVC).^[1] Considerable research efforts have been devoted to developing mercury-free catalysts, such as AC-supported AuCl₃,^[2-4] PdCl₂,^[5-7] RuCl₃,^[8,9] and CuCl₂^[10,11] to replace conventional Hg-based catalysts in the hydrochlorination of acetylene because of the mercuric chloride lost from the catalyst can disperse into the environment, which will seriously endanger human health. Hutchings and coworkers showed that Au catalysts are the most promising mercury-free catalysts. In regards to the sustainability of a catalyst, the instability of Au species significantly limits the development of gold catalysts.^[2,12] Many studies have reported improving the Au stability by adding ligands such as $\mathsf{IL}^{\scriptscriptstyle[13,14]}$ and additives.^[15-19] In addition, the selection of new materials such as oxides,^[20] nanotubes,^[21,22] and graphene^[23] to overcome the Au instability problem has been reported. Compared to such materials, however, carbon-based carriers are much more suitable carriers because of their advantages of higher chemical stability and easy combustion to recover the supported metals.^[24]

[a]	H. Lai, B. Wang, Y. Yue, G. Sheng, S. Wang, F. Feng, Q. Zhang,
	Prof. Dr. J. Zhao, Prof. Dr. X. Li
	Industrial Catalysis Institute
	Laboratory Breeding Base of Green Chemistry-Synthesis Technology
	Zhejiang University of Technology
	Hangzhou 310014 (P.R. China)
	E-mail: jiazhao@zjut.edu.cn
	xnli@zjut.edu.cn
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the ACF. The Au/ACF-H₂O catalyst exhibited better catalytic activity and stability than Au/ROX0.8(AQ)-H₂O. Characterization results revealed that the catalytic properties of Au/ACF-H₂O could be attributed to the anchoring and stabilization of gold active species on the SOGs, leading to atomic dispersion, and to the improvement of HCl adsorption with the synergistic effect of electron-donating pyrrolic N groups. The results indicated that usage of this green carrier can be considered as the a new approach to reduce or eliminate the use of strong oxidizing reagents in the preparation of Au catalysts.

At present, for the synthesis of vinyl chloride from acetylene, strong acid-treated activated carbon is used to support HgCl₂ catalysts.^[25-27] Among the possible alternatives, there is no direct material that can achieve the effect of activated carbon treated with aqua regia. Unfortunately, the activated carbon carrier will cause considerable harm to the ecological environment during the strong acid treatment process. More importantly, handling and recycling/disposal of such a large amount of aqua regia and waste acid present a significant economic and technical challenge, which may prevent or delay the commercialization of these catalysts.^[27] Although acid-treated activated carbon offers the advantages of low ash content and introduction of surface oxygencontaining functional groups (SOGs),^[28,29] the mechanical strength of the activated carbon after acid treatment is significantly reduced.^[30] Moreover, it can be easily pulverized under a high temperature and reaction gas flow, resulting in blockage of the reactor and a very hazardous dust explosion. Furthermore, the SOGs introduced by the acid-treated activated carbon are too difficult to effectively control, and the cost and actual benefits may negate the advantages offered by the acidtreated activated carbon. In order to avoid these issues, it is necessary to find a greener and more efficient catalyst to replace the current preparation methods.

Herein, we propose an environmentally friendly strategy to avoid the use of a hazardous reagent from the perspective of changing the carrier material while also ensuring good catalytic performance. That is, we proposed the use of activated carbon fibers (ACF), which contain phenolic and carbonyl groups and nitrogen species, to support Au catalysts for acetylene hydrochlorination. Compared to the conventional acid-treated activated carbon carrier, ACF offers the advantages of no harmful acid treatment, high effective functional group content, pyrrolic



N species, low ash content, a microporous structure and high mechanical strength in addition to greener production technology. STEM, XRD, XPS, TPD, and HCI-breakthrough curve analyses were used to examine the surface properties of the Au/ ACF–H₂O catalyst and suggested that the presence of SOGs (such as phenol and carbonyl groups) and pyrrolic N species on the ACF. Furthermore, the enhanced catalytic performance of Au/ACF–H₂O could be attributed to both the anchoring and stabilization of gold active species by SOGs, leading to atomic dispersion, and the improvement of HCI adsorption with the synergistic effect of electron-donating pyrrolic N species.^[4,22,31] In addition, the development and design of a new green material such as ACF that replaces acid-treated activated carbon as a green catalyst carrier is essential for the sustainable development of the PVC industry.

Results and Discussion

Characterization of the Au-Based Catalysts

The dispersion of Au species on the catalysts was investigated by STEM-HAADF analyses as shown in Figure 1. In the highly magnified images of the fresh Au/ACF–H₂O catalysts shown in Figure 1a, the Au species were observed to mainly appear as isolated atoms having a diameter of less than 2 nm with minor occasional sub-nano clusters on the support areas. Thus, it was confirmed that the preparation of the Au catalysts with such supports could significantly improve the dispersion of Au species. After use, some occasional Au nanoparticles larger than 2 nm in diameter appeared in the supports, but the Au species size of less than 2 nm was predominantly maintained, as shown



Figure 1. Aberration-corrected STEM-HAADF images of the (a) fresh Au/ACF–H₂O, (b) used Au/ACF–H₂O, (c) fresh Au/ROX0.8–H₂O and (d) used Au/ROX0.8–H₂O catalysts.

in Figure 1b. In contrast, from the images of the fresh Au/ ROX0.8-H₂O catalysts, the Au species predominantly existed as metallic-Au nanoparticles in the 6-10 nm size range and contained a very low content of dispersed Au species (as shown in Figure 1c). However, after use, the support areas contained no atomically dispersed Au species with clusters in the 15-50 nm size range (as shown in Figure 1d), thus indicating that the Au particles could be easily sintered during reaction. Recently, Hutchings and co-workers reported that a Au/C-H₂O catalyst was nearly devoid of any atomically dispersed species, which was consistent with our results.^[25] Moreover, they observed active sites for acetylene hydrochlorination, proving that the atomically dispersed Au species were critical for the enhanced catalytic activity.^[32] Thence, the Au/ACF-H₂O catalyst, having a large amount of atomically dispersed Au species on the support, exhibited high activity.

In addition to the atomically dispersed Au species, the surface properties of the carrier also contributed to the enhanced catalytic activity, such as the presence of SOGs, nitrogen species, specific surface area, and pore structure.^[33-35] Table 1 shows that the specific surface area of the ACF was slightly higher than that of ROX0.8. The most obvious difference was that a rich microporous structure existed on the ACF in contrast to ROX0.8, which may have a positive effect on the activity of the catalyst. In fact, Brasquet et al. reported that ACF with an abundant microporous structure and specific surface area exhibit highly effective adsorption capacity.^[36] Overall, these findings demonstrated that such a rich structure may provide a suitable platform for the dispersion of the active Au species as well as better conditions for the diffusion of the substrate. This behavior will be further clarified by catalyst characterization.

Figure 2a shows the X-ray diffraction patterns of fresh and used Au/ACF-H₂O and Au/ROX0.8(AQ)-H₂O catalysts. The data showed that the diffraction peaks at 77.48°, 64.48°, 44.26°, and 38.13° could be attributed to the (311), (220), (200), and (111) planes of Au⁰, respectively.^[3,4,22] The fresh and used Au/ ROX0.8(AQ)-H₂O catalyst clearly showed a typical characteristic peak of Au⁰, while the Au/ACF-H₂O samples only showed the carbon diffraction peak. The XRD results revealed that the active sites of cationic gold (AuCl_x) species were highly dispersed on the ACF surface and that the unique surface chemistry properties of the ACF affected the anchoring of Au species, thereby leading to the inhibition of sintering.^[37] XPS results shown in Figure 2b were in agreement with the above-mentioned XRD results. According to the literature, the Au 4f_{7/2} peaks appearing at the binding energies of 84.0 eV, 85.0 eV, and 87.0 eV (\pm 0.2 eV) can be attributed to Au^0 , Au^+ , and Au^{3+} , respectively.[3,12,38]

Table 1. Texture parameters calculated by BET method from the low-temperature $N_{\rm 2}$ adsorption/desorption experiments.							
Sample	$S_{BET} \left[m^2/g \right]$	V [cm³/g]	D [nm]	Micropore volume [%]			
ACF ROX0.8	1265 1020	0.56 0.56	2.15 2.22	89.3 51.8			

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Figure 2. (a) X-ray diffraction (XRD) patterns: fresh Au/ACF–H₂O, used Au/ACF–H₂O, fresh Au/ROX0.8(AQ)–H₂O and used Au/ROX0.8(AQ)–H₂O catalysts (b) Au 4f XPS spectra: fresh Au/ACF–H₂O and fresh Au/ROX0.8(AQ)–H₂O catalysts.

Table 2. Relative contents and binding energies of Au species.							
Sample	Au spe Au ³⁺	cies [%] Au ⁺	Au ⁰	Bindin Au ³⁺	g energy Au ⁺	/ [eV] Au⁰	
Fresh Au/ACF–H ₂ O Fresh Au/ROX0.8(AQ)–H ₂ O	49.1 39.0	10.7 13.2	40.2 47.8	86.8 86.9	84.9 85.1	84.0 84.0	

The relative contents and binding energies of Au species obtained from XPS are listed in Table 2. For the fresh Au/ROX0.8(AQ)–H₂O samples, the relative contents of Au³⁺, Au⁺, and Au⁰ were 39.0%, 13.2%, and 47.8%, respectively. A large amount of Au⁰ existed in fresh Au/ROX0.8(AQ)–H₂O, which may have been caused by the reduction of Au³⁺ to Au⁰ by carboxylation at the ROX0.8 surface.^[39] Compared to that of the fresh Au/ROX0.8(AQ)–H₂O catalysts, the total AuCl_x (x=1, 3) species content (the amount of Au³⁺ and Au⁺) in the fresh Au/ACF–H₂O catalysts was increased from 52.2% to 59.8%, indicating the strong anchoring and stabilization of AuCl_x species on the surface of the ACF. This was consistent with the observations from XRD and STEM.

To elucidate the oxidation states of Au species in the Au/ ACF-H₂O and Au/ROX0.8(AQ)-H₂O catalysts, H₂-TPR analysis was performed, as shown in Figure 3. The hydrogen consumption peak in the high temperature region represents the reduction of the oxygen-containing functional groups, and at the low temperature represents the reduction of Au species.^[4] Details of the TPR profiles in the region 200-420°C (AuCl_x reduction) and procedure for the TPR area peaks determination were provided in Figure S1 and Figure S2. In deed, the analyses was determined from the TCD signal with a CuO standard and the fitting parameters of H₂-TPR profiles of the samples were listed in Table S1. For our catalysts, the fresh Au/ACF-H₂O sample presents a characteristic hydrogen consumption peak between 310-420 °C (with center at 364 °C, Figure 3 and Figure S1), which was diagnostic of AuCl_x species. The calculation method of TPR analysis was consistent with the research of Hutchings.^[40] Clearly, comparing with the TCD signal with a standard, it was estimated that the total AuCl_x species content in fresh Au/ACF-H₂O catalysts amounted to 59.2% of the total



Figure 3. TPR profiles of the fresh Au/ACF– H_2O , used Au/ACF– H_2O , fresh Au/ROX0.8(AQ)– H_2O and used Au/ROX0.8(AQ)– H_2O catalysts.

Au loading, which was higher than the 39.5% in fresh Au/ ROX0.8(AQ)-H₂O catalysts (Table S1). Moreover, the reduction temperature of fresh Au/ACF-H₂O catalysts was 78°C higher than that of fresh Au/ROX0.8(AQ)-H₂O, indicating that the unique surface properties of the ACF may make Au species more difficult to reduce because of the stronger interaction between the ACF surface and the Au species. To further analyze the performance of the catalysts, comparative H₂-TPR analysis of the used Au/ACF-H₂O and used Au/ROX0.8(AQ)-H₂O catalysts was also conducted, and the results are shown in Figure 3. It was estimated that the total AuCl_x species content in the used Au/ACF-H₂O catalysts amounted to 53.1% of the total Au loading and the reduction temperature of Au species was 352 °C, which was similar to that of the fresh Au/ACF-H₂O catalysts. In contrast, the total AuCl_x species content in the used Au/ROX0.8(AQ)–H₂O catalysts was significantly reduced to 12.5% after the reaction. These results further proved that the unique surface properties of the ACF may make Au species



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Figure 4. TPD evolution profiles: (a) CO and (b) CO₂ evolved in the TPD-MS of the ACF, Au/ACF–H₂O, ROX0.8(AQ), Au/ROX0.8(AQ)–H₂O and ROX0.8 samples.

Table 3. Amounts of different SOGs and the total amounts of SOGs on catalysts (obtained from the CO-TPD curves).							
Sample	Peak 1 ^[a] Adsorptive CO	Peak 2 Carboxylic anhydride	Peak 3 Phenol	Peak 4 Ether	Peak 5 Carbonyl	Total	
ACF	/ ^[b]	21.2	274.4	/	215.6	511.2	
Au/ACF-H ₂ O	/	13.8	60.3	/	51.5	125.6	
ROX0.8(AQ)	/	/	7.3	622.8	169.7	799.8	
Au/ROX0.8(AQ)–H ₂ O	/	/	4.7	520.3	118.1	643.1	
ROX0.8	/	/	/	/	/	/	

Sample	Peak 1 ^[a] Carboxyl	Peak 2 Carboxylic anhydride	Peak 3 Peroxide	Peak 4 Lactone 1	Peak 5 Lactone 2	Total
ACE	12.8	10.6	/[b]	16.4	11.0	50.8
Au/ACF-H ₃ O	9.2	8.4	,	12.8	6.3	36.7
ROX0.8(AQ)	141.0	147.8	/	90.0	/	378.8
Au/ROX0.8(AQ)-H2O	41.9	111.8	/	47.7	/	201.4
ROX0.8	/	/	/	/	/	/

[a] The amount of SOGs in µmol/g. [b] No SOGs were observed.

more difficult to reduce because of the stronger interaction, which was consistent with the XRD analyses. In addition, the results of STEM-HAADF analysis for used Au/ACF–H₂O catalysts revealed the presence of highly dispersed Au species on the ACF after reaction, which was consistent with the atomic Au deposition of fresh Au/ACF–H₂O catalysts.

Hence, the above-mentioned structural characterization results further confirmed the high stability of the Au/ACF–H₂O catalysts, which can be possibly attributed to its unique surface properties. To support these results, we further investigated that whether the AuCl_x species stabilized by specific supports were the active sites for the acetylene hydrochlorination.

Study of Carrier Surface Chemistry and the Au-C Interface

It is well known that the surface properties of a carrier offer a characteristic feature that affects the catalytic performance.^[41-43]

In order to analyze the induction of Au deposition and nucleation effected by SOGs on different supports, TPD analysis was carried out. This technique involves the evaluation of all types and various amounts of gas released, such as CO, CO₂, and H₂O, at different decomposition temperatures,^[44,45] as shown in Figure 4.

Figures 4a and 4b show the CO and CO₂ TPD-MS evolution profiles, respectively, of the ACF, Au/ACF–H₂O, ROX0.8(AQ), Au/ ROX0.8(AQ)–H₂O, and ROX0.8. ROX0.8 exhibited small amounts of CO and CO₂ evolved, which confirmed that it contained a very low SOG content. However, a high amount of SOGs was introduced into ROX0.8 though the pretreatment with aqua regia, as shown by the significantly increased amounts of CO and CO₂ evolved (Tables 3 and 4). In particular, a large amount of phenol and carbonyl groups (490.0 μ mol/g) existed on the ACF, and its amount was higher by 313.0 μ mol/g than that on ROX0.8(AQ) (177.0 μ mol/g), which were introduced by the aqua regia pretreatment, as shown in Figure 4a and Table 3. On the





Figure 5. (a) N 1s XPS spectra of Au/ACF–H₂O catalysts (b) schematic diagram of N species.

other hand, CO₂ curves (Figure 4b) showed that ROX0.8(AQ) had a large amount of carboxyl and carboxylic anhydride groups. It was obvious that the amount of CO₂ decomposed from the ACF was 50.8 μ mol/g, which was 328.0 μ mol/g less than that from ROX0.8(AQ) (378.8 µmol/g), as shown in Table 4, implying that the amount of carboxyl, carboxylic anhydride, and lactone groups on the ACF was lower than that on ROX0.8(AQ). Bulushev et al. have proved that phenolic groups could interact with the Au³⁺ precursor by stabilizing the AuCl_x species according to $O-OH + Au^{3+} \rightarrow O-O^{-}Au^{3+} + H^{+}$. In addition, the Au³⁺ precursor could be reduced by the carboxyl functional groups at the carbon surface according to ©-COOH $+Au^{3+}\rightarrow O +Au^{0} +H^{+} +CO_{2}^{[39]}$ As such, it was demonstrated that the AuCl_x species tended to gradually form clusters. However, the AuCl_x species could be stable on a metal oxide surface that had hydroxyl groups.[46] Specifically, based on the strong anchoring and stabilization of the AuCl_x species on the carrier, the nature of the support and its interaction with the gold species are considered to be important factors for the catalytic reaction.[4]

Hence, TPD-MS analyses were also carried out for the Au/ ACF-H2O and Au/ROX0.8(AQ)-H2O catalysts in order to gain more insight into the support chemistry and the effect of SOGs on Au deposition. The data acquired for Au/ACF-H₂O and Au/ ROX0.8(AQ)-H₂O samples are shown in Figure 4 and Tables 3 and 4. As shown in the CO curve (Figure 4a), the amount of phenol and carbonyl groups obviously decreased for the Au/ ACF-H₂O sample upon Au deposition and was significantly more than that for Au/ROX0.8(AQ)-H₂O. The specific amounts of CO decomposed before and after Au was supported on the carriers were 511.2 µmol/g (CO, ACF), 125.6 µmol/g (CO, Au/ ACF-H₂O), 799.8 µmol/g (CO, ROX0.8(AQ)), and 643.1 µmol/g (CO, Au/ROX0.8(AQ)-H₂O). In addition, Figure 4b shows that the amount of carboxyl, carboxylic anhydride, and lactone groups significantly decreased on the ROX0.8(AQ) surface after Au deposition. Meanwhile, for Au/ACF-H₂O, it could be observed that the CO₂ curve was almost unaffected after Au was supported. To explain this observation consequence, we considered that the Au deposition probably lead to the obvious reduction in SOGs decomposed, as a result of the anchoring on

Table 5. Relative contents and binding energies of nitrogen species.						
Sample	Pyridinic N	Pyrrolic N	Graphitic N	Other N species		
Au/ ACF—H₂O	20.02 % ^[a] (398.3 eV) ^[b]	79.98% (400.4 eV)	/ ^[c]	/		
Au/ ROX0.8–H ₂ O	1	1	/	/		
[a] The content of N species. [b] Binding energy. [c] No N species were observed.						

the functionalized surface sites of the support.^[47] The TPD-MS analyses performed for the Au/ACF–H₂O catalysts in this study confirmed that the AuCl_x species directly interacted with phenol and carbonyl groups on the ACF surface. In contrast, the AuCl_x species may bond to all of the SOGs, especially the carboxyl, carboxylic anhydride, and lactone groups, on the Au/ROX0.8(AQ)–H₂O samples. Therefore, the higher amount of phenol and carbonyl groups as well as the lower amount of carboxyl, carboxylic anhydride, and lactone groups on the ACF than on ROX0.8(AQ) may facilitate the anchoring and stabilization in the atomic deposition of Au.

In addition to the apparent influence of SOGs, nitrogen species also played an important role in imparting unique surface properties to the catalysts, which was corroborated by XPS N 1s spectra. Figure 5a shows that the curve of Au/ ACF-H₂O could be well deconvoluted into two individual peaks at 398.3 and 400.4 eV, demonstrating the coexistence of pyridinic N and pyrrolic N, respectively.[48-51] Moreover, the relative contents and binding energies of the existing nitrogen species in the catalysts according to XPS are summarized in Table 5, which shows that the content of pyrrolic N of Au/ ACF-H₂O was as high as 79.98% of the N species, but no N species were observed in the spectra of the Au/ROX0.8-H₂O catalysts. The schematic diagrams in Figure 5b show that fractional N species were observed. As previously reported,^[52] pyrrolic N species are considered to be important for the performance of N-doped carbon catalysts in the hydrochlorination of acetylene. The Au $4f_{7/2}$ signal of the Au/ACF–H₂O catalyst from XPS analysis, corresponding to Au³⁺, was negatively





Figure 6. HCI-breakthrough profiles of: blank, Au/ACF–H₂O catalyst and Au/ ROX0.8–H₂O catalyst.

shifted from the standard binding energy (BE) of 87.0 eV to 86.8 eV (Table 2). Meanwhile, the same changes took place for the peak corresponding to the pyrrolic N species of the Au/ ACF-H₂O catalyst, which was 0.4 eV higher than the standard BE of 400.0 eV (Table 5).^[53–55] Considering that the N-containing species could cause the negative shift of Au³⁺ (Figure 2b), this phenomenon may be attributed to the electron transferred from pyrrolic N to the Au³⁺ center. A compound structure possibly formed though a π - σ coordination bond between Au³⁺ and pyrrolic N.^[22,56] As can be seen from Figure 5, the pyrrolic N content was relatively high for the Au/ACF-H₂O catalyst. The pyrrolic N served as electron donors, thus enhancing the catalytic activity, as had already been reported in our previous paper.^[56] In order to thoroughly investigate the catalytic properties of the nitrogen-rich ACF, the HCl adsorption properties of the Au/ACF-H₂O and Au/ROX0.8-H₂O catalysts were analyzed. As shown in Figure 6, the HCl adsorption efficiency of Au/ ACF-H₂O was significantly higher than that of the Au/ ROX0.8–H₂O samples, because of the longer breakthrough time of HCI.^[57] Several excellent reports discussing this issue are available in the literature, including those stating that catalysts exhibited excellent adsorption capacity possibly due to the coordination of the electron-donating pyrrolic N species, which can increase the electron density of the single-site ${\rm AuCl}_{\rm x}$ species.^[22] Besides, Zhang et al.^[33,58-60] reported that the Ndoped support can stabilize the gold species and increase the catalytic activity. Dai et al.^[61-63] demonstrated that pyrrolic N is the most important nitrogen species and pointed out that pyridinic N is also positive for acetylene hydrochlorination. Indeed, the active AuCl_x species of the catalyst were easily deactivated because of the loss of CI atoms from AuCl_x owing to the acetylene atmosphere and AuCl_x was a good electron donor that could adsorb HCl easily during reaction. Thus, sufficient adsorbed HCl on the Au/ACF-H₂O catalyst might effectively supply the consumption of Cl atoms and improve the catalytic performance. Moreover, the adsorbed HCl on the active AuCl_x species could further activate the further adsorbed C_2H_2 , which leads to a decrease in the activation energy of the



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Figure 7. Catalytic performances of the different catalysts. Reaction conditions: temperature = 180 °C, P = 0.1 MPa, GHSV (C_2H_2) = 1480 h^{-1} , and V (HCI)/V(C_2H_2) = 1.2.

reaction.^[56] Overall, the above results and the experimental phenomena reported in the literature indicate that the presence of pyrrolic N species is beneficial to the catalytic performance to some extent.

Catalytic Study of Acetylene Hydrochlorination

Figure 7 shows the catalytic performances of the different catalysts as well as those of catalyst supports in acetylene hydrochlorination. The selectivity for VCM of all catalysts was higher than 99%. The results illustrated that the highest activity of above 79% conversion could be obtained with the Au/ ACF-H₂O samples consisting of unpretreated ACF carbon. In contrast, the Au/ROX0.8(AQ)-H₂O catalysts had lower activity than the Au/ACF–H₂O catalysts. Further, the activity of the Au/ ACF-H₂O catalysts showed almost no decrease over 10 h, while the Au/ROX0.8(AQ)-H₂O catalysts were completely deactivated. The pure ACF-H₂O and ROX0.8(AQ)-H₂O samples were used as controls with lower conversions in order to rule out the influences of the carriers themselves. It should be noted that catalysts prepared using deionized water on the untreated ROX0.8 carbon without SOGs were nearly inactive. In summary, the results showed that the superior performance of the Au/ ACF-H₂O catalysts was likely due to the abundant microporous structure, compared to that of Au/ROX0.8(AQ)-H₂O catalysts, despite having similar specific surface areas. Moreover, the specific surface oxygen ligands (such as phenol and carbonyl groups) incorporated obtained on the ACF evaluated by TPD may be the essential factor that can be linked to the stabilization of the atomic Au deposition and the presence of the single-site AuCl_x species suggested by the combined analyses of STEM, XRD, and XPS. In addition, we further studied the impact of pyrrolic N species on the ACF, and demonstrated that the synergistic effect of electron-donating pyrrolic N species generated an active catalysts. Therefore, it was clear that the ACF without acid treatment are greener than the



conventional acid-treated activated carbon carriers as well as provided enhanced catalytic performance. Moreover, ACF could establish more suitable surface properties than aqua regia treatment preparation methods of supported Au catalysts.

Possibility of Using ACF Carrier to Reduce/Eliminate Strong Oxidizing Reagents in the Production Technology

For achieving economical and green production methods for Au catalysts, the immediate challenge has been to eliminate strong corrosive and environmentally unfriendly aqua regia from catalyst preparation schemes. Some literature has been reported that aqua regia is important for Au deposition and nucleation on supports and closely related to high catalytic activity.^[26,27] Recently, Zhang et al.^[64] reported that the activity of a catalyst is closely related to the intrinsic properties of the solvents, and that specific solvents can enhance the interaction between the carrier and the Au species, thereby inhibiting aggregation and the loss of active sites during reaction. In our study, we applied ACF to support Au catalysts as a direct material without any harmful technology that can achieve the same effect of using preparation methods involving different strong oxidizing reagents, as evident from the following catalytic performance comparison.

The catalysts were evaluated in the hydrochlorination of acetylene, and the results are presented in Figure 8. It was found that the catalytic activity of Au/ACF–H₂O was lower than those of typical strong oxidant-prepared catalysts Au/ROX0.8–AQ, Au/ROX0.8–AP, and Au/ROX0.8–OAR. The selectivity for VCM of all catalysts was higher than 99%. On one hand, this result may be attributed to the prevalence of atomic dispersion of Au species on catalysts prepared using strong oxidizing agents, which may be superior to catalysts prepared in water. On the other hand, the high activity was considered to be based on these strong oxidant-prepared catalysts perhaps having higher total $AuCI_x$ species contents than $Au/ACF-H_2O$. Indeed, Hutchings et al. observed that catalysts treated with



Figure 8. Catalytic performances of the different catalysts. Reaction conditions: temperature = 180 °C, P = 0.1 MPa, GHSV (C_2H_2) = 1480 h⁻¹, and V (HCI)/V(C_2H_2) = 1.2.

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aqua regia contained very high cationic Au species contents (> 50%).^[26] Furthermore, we recently reported a novel catalyst that was treated with a H₂O₂/HCl mixture, that contained a relative content of cationic Au species as high as 47.3%.^[4] In general, a catalyst prepared using strong oxidizing agents could basically have high contents of highly dispersed cationic Au species. However, it was worth noting that Au/ACF-H₂O was superior to the typical aqua regia-treated catalysts in terms of stability over 15 h. The reason for this superior performance was speculatively based on the influence of surface chemistry and could be the presence of SOGs and pyrrolic N species, which may have served as anchoring sites for Au species on the ACF. Recently, Kaiser et al.^[65] reported that N species have a stabilizing effect on single Au atoms, which was consistent with our results. Accordingly, the results in this study suggest that ACF is the carrier that has the potential to reduce/eliminate the use of strong oxidizing reagents in catalyst synthesis schemes and highlight the direction of green catalyst development for industrial applications.

Conclusions

In this paper, we presented an environmentally friendly strategy for developing carrier materials, using ACF to support Au catalysts for acetylene hydrochlorination. In particularly, these Au/ACF-H2O catalysts exhibited higher activity than Au/ ROX0.8(AQ)-H₂O catalysts, whose carriers were pretreated with aqua regia, and better stability than the typical impregnation solvent-treated carbon catalysts. It was confirmed that the superior catalytic performance of Au/ACF-H₂O could be due to both the anchoring and the stabilization of atomic Au deposition on SOGs (such as phenol and carbonyl groups) and the improvement of HCl adsorption with the synergistic effect of electron-donating pyrrolic N species on the ACF. Furthermore, we performed a series of characterization analyses on the Au/ACF-H₂O and Au/ROX0.8(AQ)-H₂O catalysts, including STEM, XRD, XPS, TPD, and HCI-breakthrough analyses. In addition, the development and design of a new green material such as ACF, which could be a substitute for acid-treated activated carbon and reduce/eliminate the use of strong oxidizing reagents, as a catalyst carrier is essential for the sustainable development of the PVC industry. However, the specific composition and structure of the active species could not be fully defined and further systematic investigation will be required.

Experimental Section

Catalysts Supports Preparation

Viscose fibers (Thornel-25) and activated carbon (Norit ROX0.8) were chosen to prepare carriers. Before carbonization viscose fibers were pre-soaked in an aqueous solution (NH₃,H₂O 3.3 g/l) for 24 h and dried at 120 °C for 18 h. The pre-soaked fibers were then heated to 950 °C at the speed of 5 °C/min for carbonization under nitrogen gas protection, then naturally cooled to room temper-



ature. For comparison, the ROX0.8 carbon was pretreated with aqua regia (3:1 HCl (>36 wt%): HNO₃ (>65 wt%)) at room temperature for 12 h to remove ash and to create SOGs. After that, both pretreated fibers and pretreated ROX0.8 carbon were washed by deionized water to neutral, eventually dried at 120 °C for 18 h, to obtain ACF and ROX0.8(AQ), respectively.

Catalysts Preparation

The obtained ACF and HAuCl₄ aqueous solution were mixing in deionized water. The mixture was impregnation for 12 h and then dried at 120 °C for 18 h, was designated Au/ACF–H₂O, Au loading of 1.0 wt.%. For comparison, ROX0.8(AQ) and ROX0.8 supports were also prepared in the same method and was designated Au/ROX0.8(AQ)–H₂O and Au/ROX0.8–H₂O. In addition, catalysts without Au prepared on the ACF and ROX0.8(AQ) supports were labeled ACF–H₂O and ROX0.8(AQ)–H₂O, respectively. Furthermore, the ROX0.8 and HAuCl₄ aqueous solution were mixing using aqua regia and green aqua regia (1:3 H₂O₂ (30 wt%): HCI (36 wt%)) as solvent and prepared by the same method and was designated Au/ROX0.8–AQ and Au/ROX0.8–AP respectively and the Au/ROX0.8–H₂O treated by organic aqua regia (1:10 SOCl₂ (> 99.5%): DMF (> 99.9%)) was labeled as Au/ROX0.8–OAR.

Catalytic Reaction Evaluation

The catalysts were tested in a fixed-bed micro-reactor (10 mm diameter). The mass of the catalysts were 0.2 g, the reaction temperature was 180 °C at a heating rate of 10 °C/min, and it was treated under a hydrogen chloride atmosphere for 30 minutes firstly. Then, a mixed gas of acetylene and hydrogen chloride was introduced into the reactor. The total C₂H₂ GHSV was 1480 h⁻¹. The reaction product was sent into a bottle of NaOH solution to remove hydrogen chloride and then analyzed by the FID detector to test the catalytic performance.

Characterization of Catalysts

Scanning Transmission electron microscopy (STEM) analyses were analyzed by the Cs-corrected FEI Titan G2 60-300 Microscope operating at 300 kV with an HAADF detector. Brunauer-Emmett-Teller (BET) parameters were evaluated using a Micromeritics ASAP 2020 instrument. X-ray diffraction (XRD) detection was adopted by the PANalytical-X'Pert PRO generator using Cu K α radiation ($\lambda =$ 0.1541 nm). X-ray photoelectron spectroscopy (XPS) was carried by the Kratos AXIS Ultra DLD spectrometer using monochromatized aluminum X-ray source (1486.6 eV). Temperature-programmed reduction (TPR) was performed in a micro-flow reactor fed with hydrogen (10% in Ar, 45 mL/min) and hydrogen consumption was measured from TCD signal using CuO as a standard. Temperatureprogrammed desorption-mass spectrometry (TPD-MS) was obtained by automated AMI-200 equipment (Altamira Instruments) to evaluate the qualitative and quantitative determination of SOGs. The mass of the samples were 100 mg and the temperature was raised to 900°C at a heating rate of 5°C/min under a helium atmosphere (30 mL/min). CO and CO₂ signals were performed by the quadrupole mass spectrometer (Dymaxion 200, Ametek). The HCI-breakthrough curves was achieved by the Omnistar GSD320 (Pfeiffer Vacuum, Germany) mass spectrometer.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: acetylene hydrochlorination · activated carbon fibers · phenolic and carbonyl groups · pyrrolic N species

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