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Phosphorus-doped Carbon Supports Enhance Gold-based Catalysts for Acetylene Hydrochlorination

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Abstract

The phosphorus-doped carbon, consisting of phosphate groups in the surface, was prepared using triphenylphosphine as the phosphorus source and assessed as the support of Au catalysts for acetylene hydrochlorination reaction, characterized by FT-IR, XPS, Raman, TEM, BET, etc. This P-doped carbon support can enhance both the acetylene conversion and the selectivity to vinyl chloride monomer(VCM) over Au/SAC catalysts. Over the optimal Au/20%P-SAC-700 catalyst, the acetylene conversion is 99.9 % and the selectivity to VCM equals 100 % within 23 h reaction. It is illustrated that the phosphorous groups in the P-doped carbon support, comprised of $(PO_4)^{3-}$and$(PO_3)^-$, can interact with the active gold species Au^{3+} and Au^{1+} so as to improve the dispersibility of catalytic active sites. Andin the catalyst Au/20%P-SAC-700 the interactions of phosphorous groups$(PO_4)^{3-}$and$(PO_3)^-$ can prevent the reduction of active gold species Au^{3+} and Au^{1+}into Au^0, but also retard the coking deposition on catalyst surface, suggesting that the modulation of phosphorus-dopants in the carbon supports is a promising route to explore efficient non-mercuric catalysts for PVC manufacture.

Introduction

Vinyl chloride monomer (VCM) is used to manufacture polyvinyl chloride (PVC), which is one of the top five engineering plastics widely used worldwide. The statistics report showed that 5311 million tons of PVC were consumed over the world in 2012,among which1323.1 million tons were consumed in China.[1]There are two commercialized processes of PVC production, i.e., the ethylene oxychlorination and the acetylene hydrochlorination pathway, respectively. The acetylene hydrochlorination pathway has attracted much more attentions in some countries including China, which experience economic challenges from oil shock but enrich coal resources.[2]Nowadays, about two thirds of PVC production capability is attributed to the acetylene hydrochlorination pathway in China. The current industrial catalysts used in the acetylene hydrochlorination process consist of mercuric chloride,[3] which is toxic and easily volatile so as to result in serious environmental pollutions. According to the emission reduction standard of the United Nations, the application of mercuric chloride will be forbidden over the world in near future.[4] Therefore, it is urgent to explore efficient non-mercuric catalysts for the acetylene hydrochlorination in order to make the supply chain of PVC developed sustainably.

Several non-mercuric catalysts, involving Au, Pd,[5] Ru,[6-7] etc., have been studied for the acetylene hydrochlorination since the pioneer work of Hutchings,[8-13] suggesting that the activity of metal catalysts were associated with the standard electrode potentials of the related metal ions.[14] Later on, gold catalysts supported on carbon (Au/C) were reported to have a high catalytic activity, reaching the acetylene conversion of 75% and the VCM selectivity of 99 %, but become deactivated at the reaction time longer than 2h.[15] It is suggested recently by using DFT simulations that the reduction of Au^{3+} into Au^0 is one probable deactivation reason for the gold catalyst during the acetylene hydrochlorination reaction.[16] In order to inhibit the deactivation and improve the catalytic activity of gold catalysts, the effects of second metallic compounds, involving Pd, Cu, Ir, La, Co, etc,[17-18] have been studied on the Au-based catalysts. For instance, the addition of Co^{III} can enhance the catalytic performance of Au/C catalysts, obtaining the acetylene conversion of 91.6% under the C_2H_2GHSV of 360 h^{-1}at 150°C for 50h.[19]

It is known that the physicochemical properties of supports play an important role in modulating the performance of metallic catalysts, besides the second metal additive. Previously, SiO_2 and TiO_2, with the surface area of 275 m^2g^{-1} and 97 m^2g^{-1} respectively, were studied as the support of Au catalyst for acetylene hydrochlorination, and provided the acetylene conversion less than 1%, much lower than those with the carbon support.[20] Spherical activated carbon (SAC), with an average specific area of 1056 m^2g^{-1}, has been reported to be an efficient catalytic support for acetylene hydrochlorination[6,19]. Recently, the dopants of non-metal elements into the graphene support, including nitrogen, boron and phosphor, have been extensively studied to improve the performance of certain catalysts for the oxygen reduction or CO oxidation reaction.[21-29] The phosphorus dopant was reported to cause the electronical structure change in the network of graphene sheets so as to improve the electrocatalytic activity and the stability of catalysts in oxygen reduction reaction (ORR).[30-32] Additionally, P-doped TiO_2catalysts were found to have higher photocatalytic activity, owing to more structural defects induced by P dopants.[33] However, no report has been found so far on whether or not the P-dopant can improve the activity and the stability of Au-based catalysts for acetylene hydrochlorination.

In this article, a new kind of P-doped carbon support, consisting of the phosphate groups, was prepared using triphenylphosphine (TPP) as the phosphorus source. The effect of this P-doped carbon support was investigated on the catalytic activity of Au-based catalysts for the acetylene hydrochlorination reaction. Through the characterization of FT-IR, XPS, Raman, TPR, TEM, TG, etc., it is indicated that the phosphate groups, comprised of $(PO_4)^{3-}$and$(PO_3)^{-}$, in the P-dopant carbon support can prevent the reduction of catalytic active gold species Au^{3+} and Au^{1+}into Au^0, but also retard the coking deposition on catalyst surface.

Experimental Section

Experimental material

Triphenylphosphine (TPP, the purity>99%, Sinopharm Chemical Reagent Co., Ltd); $HAuCl_4 \cdot 4H_2O$ (the content of Au assay: 47.8%, Tianjin Guangfu Chemical Reagent); Spherical activated carbon (SAC, 20-40 mesh, Shanghai Carbosino Material Co., Ltd); HCl(gas, >99.99%, Tianjin Vista Technology Co., Ltd); C_2H_2(gas, >98%, Tianjin Hexagonal Industrial Gases Distribute Co., Ltd). All these reagents were used without further purification.

Catalyst preparation

The P-doped spherical activated carbon(SAC) supports were prepared using triphenylphosphine(TPP) as the phosphorous source. The ethanol solution with TPP (0.43 g mL-1)was quantitatively added into 10g SAC under stirring, so as to modulate the loading content of TPP (10wt.%, 20wt.%, and 30wt.%).Having been incubated at 60 °C for 21 h and dessicated at 80 °C for 10 h, the SAC-TPP mixture was calcined in a tubular furnace for 1 h at a temperature ranged from 600°C to 800 °C under an Ar atmosphere with a flowrate of 150mL min^{-1}.The obtained P-modified SAC samples were named in terms of the TPP loading content and the calcination temperature, e.g., 20%P-SAC-600, indicating the P-modified SAC sample with the loading TPP content of20%(wt.) and the calcination temperature of 600 °C.

Au-based catalysts were prepared via the incipient wetness impregnation method[34]using the P-modified SAC or the original SAC as the supports. An aqua regia solution containing $HAuCl_4 \cdot 4H_2O$ was quantitatively mixed with the carbon support under stirring to prepare the catalyst with Au loading content of 1% (wt.). Having experienced a sonication for 2.5 h, the mixture was laid aside for 12h at room temperature, followed by an evaporization at 60 °C for 6 h, and then dessicated at 140°C for 18h. Owing to the same loading content of Au, the obtained catalysts were denoted in terms of the support, e.g., Au/10%P-SAC−600 indicates 1% Au catalyst with the P-modified SAC support that has been calcined at 600 °C with the initial TPP loading content of 10%, while Au/SAC indicates 1% Au catalyst supported on the SAC without the TPP additive.

Catalytic performance tests

The catalytic performance was evaluated for acetylene hydrochlorination in a fixed-bed microreacter (i.d.10mm). The reactant of hydrogen chloride (99.9 %) was pretreated using 5 A molecular sieves, while the reactant acetylene using silica gel particles. The reactor was flushed using nitrogen in order to get rid of water vapor and air. The clean HCl and C_2H_2 were fed into a heated reactor containing 5 mL catalysts, and the flowrates were controlled via calibrated mass flow controllers to maintain a volume ratioHCl:C_2H_2 of 1.1:1and a C_2H_2 gas hourly space velocity (GHSV) of 360 h^{-1}.The reaction condition was kept at 170 °C under the atmospheric pressure. The effluent from the reactor was adsorbed with a NaOH aqueous solution and then on-line analyzed using a Beifen GC-3420A gas chromatograph equipped with a hydrogen flame ionization detector (FID).

Catalyst characterization

The Fourier transform infrared spectroscopy(FTIR) was performed with Bruker Vertex70 FT-IR spectrophotometer to acquire the correlated bond vibrations of the carbon supports, with a DTGS detector. The resolution is 4 cm^{-1},while the samples were scanned for 64 times.

Structural deformations of the supports were determined by Raman spectroscopy (Renishaw, UK). A He-Ne laser source was used and the wavelength λ is 633 nm.

Surface areas and pore size distribution were analyzed by N_2 adsorption at 77 K with Quantachrome Autosorb Automated Gas Sorption System(Quantachrome Instruments, USA). Degassed for 4 hours at 250°C, the samples were measured using liquid nitrogen adsorption at -196°C. Surface areas were determined by the BET method, the pore size distribution was calculated by the HK method.

X-ray photoelectron spectroscopy (XPS) measurements of supports and catalysts were performed by PHI5000VersaProbe spectrometer, equipped with monochromatised Al Kα X-ray source (24.2 W), with an analyzer pass energy of 187.85eVfor survey scans and 46.95eV for detailed elemental scans. Binding energies were referenced to the C1s binding energy of carbon, taken to be 284.8eV.The obtained spectra were analyzed using XPS peak software. The cationic Au species can be reduced to the zero-valent state by secondary electron emission during XPS analysis, the Au (4f) region was recorded at the beginning and the end of the analysis. Both Au^{3+} and Au^0 amounts were described as the percentage of the total Au amount.

The total content of Au in the catalysts was determined by inductively coupled plasma (ICP 725), using a Vista Chip Ⅱ CCD detector, and the testing wavenumber is 242.794 nm.

Temperature programmed reduction (TPR) measurements were carried out on a TPDRO 1100 apparatus (Thermo-Finnigan). For each test, a catalyst sample (100 mg) was heated from room temperature to 900°C with a rate (10 $°Cmin^{-1}$), flushing with a 20 $mLmin^{-1}$nitrogen gas containing 5 %(vol) H_2.

Transmission electron microscopy(TEM)was used to observe morphologies of the catalysts. To prepare the samples, the catalyst powder was dispersed inethanol, and then droplets of the suspension were laid and evaporized on a 300-mesh copper TEM grid with a holey carbon film. Bright-field and annular dark-field(ADF) imaging experiments were carried out using a JEM2100F TEM and an FEI Titan 80–300 TEM/STEM equipped with CEOS spherical aberration corrector, respectively.

Thermogravimetric/differential thermal analysis (TG/DTA)was carried out to detect carbon deposition using a Diamond thermogravimetric analysis (Perkin Elmer), under air atmosphere at a flowrate of 100 mL min^{-1}. The temperature was increased from 50 °C to 800 °C with a heating rate of 10 °C min^{-1}.

Results and discussion

Catalytic performance of Au catalysts with P-modified SAC supports

Fig. 1 shows the catalytic performance of Au-based catalysts with the support of SAC and P-modified SAC for acetylene hydrochlorination at 170 ℃ and C_2H_2 GHSV of 360 h^{-1}.Overthe catalyst Au/SAC, the acetylene conversion reaches 97.6% at the first 23 h and then decreases to 88 % at 45 h, whereas the selectivity to VCM is stable at 99.8% within 45 h. For the Au catalysts supported on P-modified SAC, both acetylene conversion and the selectivity to VCM are enhanced. For instance, the acetylene conversion is 99 %over Au/20%P-SAC-600, 99.9 %over Au/20%P-SAC-700and 99.8 % over Au/20%P-SAC-800 at 23 h, while after 45 h it decreases respectively to93%, 97% and 96.6% over Au/20%P-SAC-600, Au/20%P-SAC-700 and Au/20%P-SAC-800(Fig.A1). As shown in Fig.B1, the acetylene conversion is 98.2 % over Au/10%P-SAC-700 and 99.6% over Au/30%P-SAC-700 at 23 h, and then decreases to 92.8 % and 94.1 % respectively after 45 h. However, all the selectivity to VCM over these Au catalysts with P-modified supports are equal to 100% in 45 h (Fig. A2, B2). It is suggested that the P-modified SAC with the TPP dopant of 20% and the calcination temperature of 700 ℃ is the optimal support to enhance the catalytic activity of Au-based catalysts for acetylene hydrochlorination.

We further studied the activity of catalysts with the same support 20%P-SAC-700 but lower gold content, i.e., 0.1%Au/20%P-SAC-700, at 170 ℃ and C_2H_2 GHSV of 180 h^{-1}, as far as the catalyst cost is considered. Over the catalyst 0.1%Au/20%P-SAC-700 the acetylene conversion is 98.2 %at 25 h, and then decreases to 96.7 % after 45 h, while the selectivity to VCM is equal to 100 % in 45 h(Fig. S1). As a control, over the catalyst 0.1%Au/SAC the highest acetylene conversion reaches 86 % at 15 h and drops to 80 % afterwards. Previously, Zhang et al. reported the acetylene conversion of 98% over1%Au-La catalysts at 150 ℃ and the GHSV(C_2H_2)of 360 h^{-1}.[20]Wang et al. reported the acetylene conversion of 60% over1%Au–Cu/C catalysts at 170 ℃ and the GHSV(C_2H_2)of 120 h^{-1}.[35]Conte et al. reported the acetylene conversion about 70% over 1%Au/C catalyst at 180 ℃ and a total GHSV of 740 h^{-1}. [36,37]Therefore, it is indicated that the P-modified carbon support can greatly enhance the acetylene conversion over Au-based catalysts even with lower Au content of 0.1%. In order to disclose the reason that the P-modified SAC is beneficial to increase the catalytic activity of acetylene hydrochlorination, we characterized the physiochemical properties of the P-modified supports.

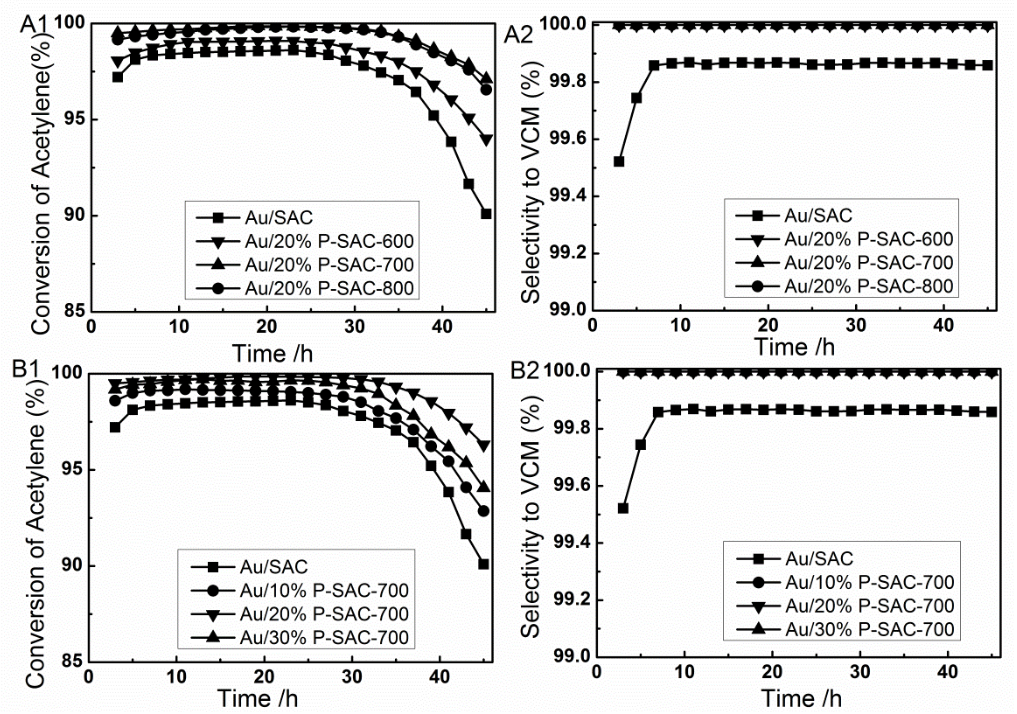

Fig. 1 The acetylene conversion (A1, B1) and the selectivity to VCM (A2, B2) over Au-based catalysts. Reaction conditions: Temperature =170°C, C_2H_2(GHSV) =360 h^{-1}, V_{HCl}:V_{C2H2}=1.1:1.

Characterization of phosphorus-doping SAC supports

Fig. 2 shows the FTIR spectra of P-modified SAC, together with that of SAC, reflecting the functional groups on the surface resulted from the TPP dopant. For the original SAC, the major bands at 3120 cm^{-1} and 1400 cm^{-1} are attributed respectively to the stretching of =C-H aromatic rings[38] and to the C-O stretch in ethers,[39]the band at 3420 cm^{-1} is attributed to O-H stretching vibration of the alcohol,[40] the small peak around 3000 cm^{-1}due to the stretching vibrations of C-H, and the peak at 1580 cm^{-1}due to the C=C stretching vibration of the SAC support.[41] With the doping TPP content of 20 %, as shown in Figure 2A, the band at 3420 cm^{-1} is disappeared but a new band near 1125 cm^{-1} is discerned, and its intensity reaches the maximum for 20%P-SAC-700, which is attributed to the antisymmetrical stretching of P-O.[33,38]It deserves to mention that the FT-IR spectra of P=O is known to have a typical peak near 1400 cm^{-1},[33] which is approximate to the band of C-O in the SAC. Therefore, the relative intensity ratio of I_{1400}/I_{3120} was calculated. For the original SAC, the I_{1400}/I_{3120} value is 1.28. In the presence of the P-dopant, the I_{1400}/I_{3120} value increases in the order: 10%P-SAC-700(1.29)≈20%P-SAC-600(1.29)<20%P-SAC-700(1.60)≈ 30%P-SAC-700 (1.60)<20%P-SAC-800 (2.0). The obvious augment ofI_{1400}/I_{3120}values reflects the existence of P=O in the P-modified SAC, moreover, the higher the calcination temperature the larger amount of P=O in the P-modified SAC. The results illustrate that the phosphorous dopant in SAC is comprised of the chemical bindings of P=O and P-O, which are the major components of phosphate groups, besides the ligation of P-C.

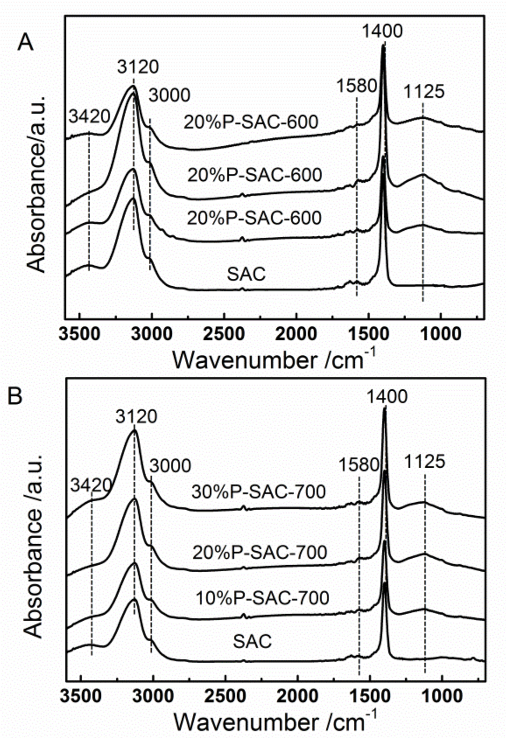

Fig. 2 FTIR spectra of unmodified SAC and phosphorus-doped SAC supports.

XPS spectra of P-doped SAC were analyzed to determine the content and the species of phosphorus in the SAC support. As listed in Table 1, the original SAC consists of 95.7 % carbon and 4.3 % oxygen. With the TPP doping content of 20 %, the phosphorus content is approximate 0.8 % for 20%P-SAC-600, 20%P-SAC-700, and 20%P-SAC-800, whereas the phosphorus content is as low as 0.22 % with the TPP content of 10 %, but increases to 1.06 % at the TPP content of 30 %. The deconvolution of XPS P2p profiles for these P-doped SAC was adopted to discriminate phosphorus species(Fig.S2). The peak at 132.5eV is due to the $(PO_3)^-$species while the peak at133.5eV due to the $(PO_4)^{3-}$species.[42]Table 2 lists the binding energy and the relative amount of each phosphorous species in the P-doped SAC. It is indicated that the relative content of $(PO_4)^{3-}$speciesreaches the maximum (66.7%) in the 20%P-SAC-700, followed in the decreasing order of 20%P-SAC-800(64.0%) > 20%P-SAC-600(61.3%) > 30%P-SAC-700(55.4%) > 10%P-SAC-700(45.7%). In combination with the above catalytic activity of gold-based catalysts, it is suggested that the higher content of $(PO_4)^{3-}$speciesin the P-modified SAC, the more enhanced catalytic activity is obtained over Au-based catalysts for acetylene hydrochlorination.

Table 1 The composition content of SAC and P-modified SAC

Supports	Element content (atom.%)		
	C	O	P
SAC	95.70	4.3	0
20%P-SAC-600	94.71	4.42	0.87
20%P-SAC-700	94.72	4.45	0.83
20%P-SAC-800	94.71	4.70	0.89
10%P-SAC-700	95.28	4.5	0.22
30%P-SAC-700	94.56	4.38	1.06

Table 2 The relative content of phosphorous species in the carbon supports

Supports	$(PO_4)^{3-}$(Area%)	$(PO_3)^{-}$(Area%)
20%P-SAC-600	61.3	38.7
20%P-SAC-700	66.7	33.3
20%P-SAC-800	64.0	36.0
10%P-SAC-700	45.7	54.3
30%P-SAC-700	55.4	44.6

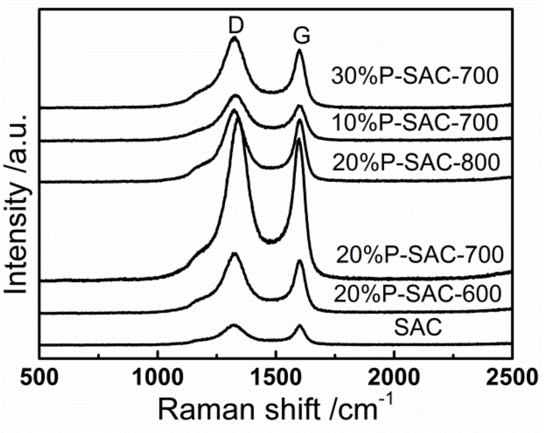

Fig.3 Raman spectra of SAC and phosphorus-doped SAC supports

Table3 I_D/I_G ratio in Raman spectra of P-modified supports.

Supports	SAC	20% P-SAC-600	20% P-SAC-700	20% P-SAC-800	10% P-SAC-700	30% P-SAC-700
I_D/I_G	1.02	1.15	1.22	1.21	1.11	1.18

Raman spectra were recorded to study the influence of P dopant on the interfacial carbon structure of SAC. As shown in Fig. 3, there appear two bands in the Raman spectra, locating near 1320 cm^{-1} due to the D line and 1602 cm^{-1} attributed to the G line. The D line is associated with the structural deformation of graphite. A mild shift of D band between SAC and P-doped SAC appears because of “P defects”[32] and structural distortion. The intensity ratio of the D band and G band (I_D/I_G),as listed in Table 3, is calculated to reflect the disordered structure resulted from P dopants. It is indicated that 20%P-SAC-700 has the highest I_D/I_G value of 1.22, suggesting the highest amount of interfacial phosphorus located in the SAC surface as the heterogeneous defects. Therefore, the more interfacial phosphorous dopants results in the more active sites and consequently the higher catalytic activity.

In addition, N_2 adsorption-desorption isotherms were measured for the P-doped SAC, which show the type-I adsorption isotherm(Fig.S3),[19] suggesting the large amount of micropores. The pore size distribution of these P-doped SAC is similar to that of the original SAC (Fig. S3). Table 4 lists the specific surface area, the pore volume and the average pore diameter of the P-doped SAC. It shows that the original SAC has the largest surface area of 1066 m^2g^{-1} and pore volume of 0.53 cm^3g^{-1}. Experienced the phosphorus doping treatment, both the surface area and pore volume are decreased, and the more amount of phosphorus additives, the smaller the surface area and pore volume, with the maximal decrease amplitude about 17% for 30%P-SAC-700. However, the average pore diameter of P-doped SAC is closely approximate to that of SAC.

Table4 Specific structure parameters of P-modified SAC supports

Supports	S_{BET} (m^2g^{-1})	Pore volume (cm^3g^{-1})	Average pore Diameter (nm)
SAC	1066	0.53	0.50
20%P-SAC-600	939	0.47	0.50
20%P-SAC-700	950	0.47	0.50
20%P-SAC-800	899	0.44	0.50
10%P-SAC-700	984	0.48	0.50
30%P-SAC-700	886	0.43	0.49

Effect of the phosphorus-doping support on gold species

TPR profiles of Au-based catalysts with the support of SAC and P-modified SAC show that the phosphorous dopants greatly influence the reducibility of gold catalysts. As shown in Fig. 4, for the original SAC without phosphorous, there appear the peaks at 270 °C and 310 °C, attributed respectively to the reduction of Au^{3+} and Au^{1+}, [19]accompanying with a broadband from 500 °C to 700 °C due to the reduction of oxygenated groups in SAC.[36]In the case of Au/20%P-SAC-600, Au/20%P-SAC-700 and Au/20%P-SAC-800, the reduction peak of Au^{3+} and Au^{1+} shifts to 240 °C and 265°C respectively. It is worthwhile to note that two new peaks at 450 °C and 680 °Care prominent as the calcination temperature increases from 600 °C to 800 °C, suggesting that the interaction between gold and the P-modified support becomes stronger as the phosphorus content increases. In the presence of much higher phosphorous content, in the case of the catalyst Au/30%P-SAC-700, there is a plateau band in the range of 470 °C -650 °C owing to much stronger interaction between gold and phosphorous species in the P-modified SAC. On the other hand, the band above 600 °C is partially attributed to the reduction of phosphorous species with the valence of +5.[43]Comparing the catalytic activity of Au-based catalysts (Fig. 1) with the phosphorous species in the P-modified SAC supports (Table 2), it is indicated that the improvement of catalytic performance of gold catalysts is not in linear relationship with the phosphorus content, but greatly depends on the content of $(PO_4)^{3-}$species.

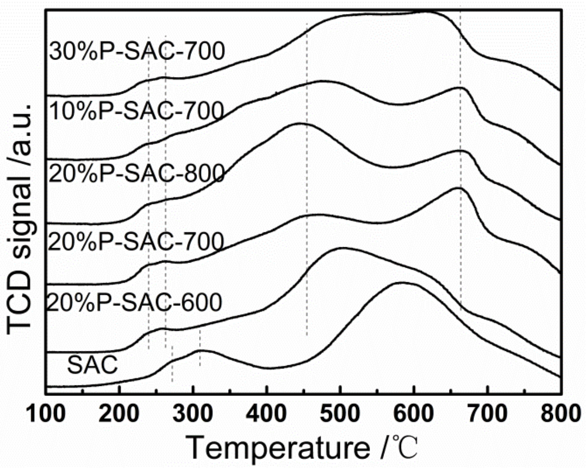

Fig.4 TPR profiles of fresh Au catalysts with unmodified SAC and P-doped SAC supports.

XPS spectra were measured to study the valence variations of gold species in Au-based catalysts with P-modified supports. The deconvolution of Au4f profile was used to distinguish gold species(Fig. S4).[19, 44] Table 5 lists the relative content and binding energy of gold species in the fresh catalysts, based on the deconvolution of XPS spectra. For the Au/SAC catalyst without TPP additive, there exist Au^0 at 83.9eV and 87.5 eV, Au^{1+} at 85.1eV and 88.9 eV, together with Au^{3+} at 87 eV and 90 eV, with the content of these gold species decreasing in the order of Au^0 (80.6 %) >Au^{3+}(10.1%)>Au^{1+} (9.3 %). In the case of Au catalysts with P-modified support, there also exist these three kinds of gold species, however, the content of Au^0 decreases dramatically. As the amount of phosphorus dopants increases, the total amount of Au^{3+} and Au^{1+} increases, while the amount of Au^0 is reduced. For instance, the Au/20%P-SAC-700 catalyst consists of 42.3 % Au^0, 26.9 % Au^{1+} and 30.8 % Au^{3+}. According to the catalytic performance of Au-based catalysts (Fig. 1), it is suggested that the lower content of Au^0, the higher catalytic activity of the Au catalyst.

Table5 The relative content and binding energy of Au species in Au-based catalysts with various supports.

Catalysts	Au^0(Area%)	Au^{1+}(Area%)	Au^{3+}(Area%)
Au/SAC	80.6	9.3	10.1
Au/20%P-SAC-600	45.0	33.6	21.4
Au/20%P-SAC-700	42.3	26.9	30.8
Au/20%P-SAC-800	43.8	27.3	28.9
Au/10%P-SAC-700	67.7	11.1	21.2
Au/30%P-SAC-700	49.5	30.4	20.1

Catalysts	Au^0 (eV)		Au^{1+}(eV)		Au^{3+}(eV)	
	4f7/2	4f5/2	4f7/2	4f5/2	4f7/2	4f5/2
Au/SAC	83.9	87.5	85.1	88.9	—	90.0
Au/20%P-SAC-600	83.9	88	85.0	89.2	87.2	90.3
Au/20%P-SAC-700	83.7	87.6	84.4	89.0	86.4	90.2
Au/20%P-SAC-800	83.6	87.5	84.8	89.0	86.4	90.0
Au/10%P-SAC-700	84	88	—	89.5	87.2	—
Au/30%P-SAC-700	83.9	87.6	85.0	88.7	87.2	90.1

We compared the deconvoluted XPS Au4f profiles of both the fresh and used catalyst of Au/SAC against Au/20%P-SAC-700 (Fig.5). As listed in Table 6, for the Au/SAC catalyst experienced 45 h reaction, the amount of Au^0 is 99.9 %, greatly higher than that in the fresh one (80.6 %). In the case of Au/20%P-SAC-700, the amount of Au^0 in the used catalyst is 56.13 %, which is higher than that in the fresh Au/20%P-SAC-700 (42.3 %) but much lower than that in the fresh Au/SAC (80.6 %). It is illustrated that the P-modified SAC support can significantly inhibit the formation of Au^0 in the reaction process.

Further, the deconvoluted XPS P2p profiles of the fresh and used Au/20%P-SAC-700 catalyst were compared. As shown in Fig.S5, in the fresh Au/20%P-SAC-700 there are two peaks located at 132.7 eV and 133.9 eV respectively, both of which show a blue-shifted binding energy comparing with each peak location in the support of 20%P-SAC-700. It is reasonable to conclude that there occur the interactions between Au^{3+} and $(PO_4)^{3-}$, as well as Au^{+} and $(PO_3)^{-}$in the fresh Au/20%P-SAC-700 catalyst. While for the used Au/20%P-SAC-700 catalyst, besides the former two peaks there appear a new band near 135 eV, which is attributed to the (Cl_3PO) species.[45] As listed in Table 7, after experiencing 45h reaction, the relative content of $Au(PO_4)$decreases from 65.8% to 59.8%, the content of $Au(PO_3)$ decreases from 34.2% to 27.0%, whereas the content of Cl_3PO increases to 13.2%. It is suggested that the phosphorous species establish some extent the interactions with chlorine during the acetylenehydrochlorination reaction, which is detrimental to the interactions between gold ions and the phosphorous species, and consequently gold ions were partially reduced into Au^0in the used Au/20%P-SAC-700 catalyst, resulting in a decrease of acetylene conversion by a fraction of 2.9% after 45h on stream.

In addition, the total Au content in the fresh and used catalysts was measured by ICP. As listed in Table 6, the total Au content in the used catalyst is a little smaller than that in the fresh. For the catalyst Au/SAC, the loss ratio of Au is 1.74% after 45 h reaction while for the Au/20%P-SAC-700 catalyst the loss ratio is 0.86%. It is suggested that with the P-modified SAC support the Au catalyst is much stable owing to the interaction between phosphorous species and gold ions.

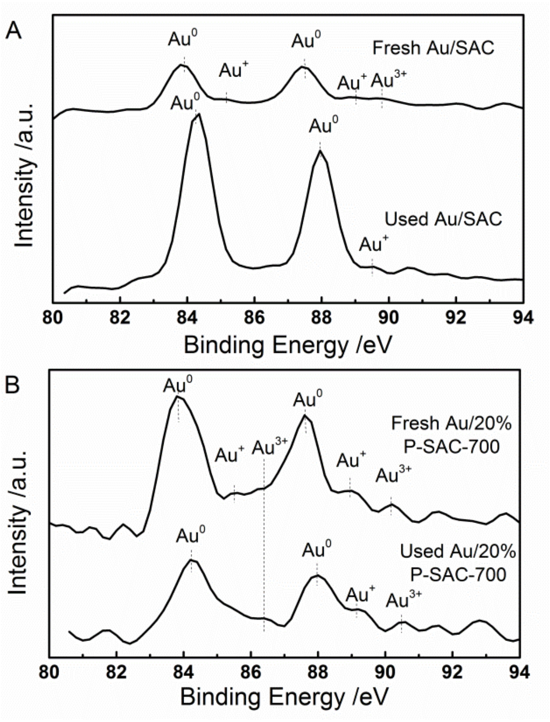

Fig.5 Deconvolution XPS Au4f profiles of the catalyst Au/SAC and Au/20%P-SAC-700.

Table6 The relative content of Au species in the fresh and used catalysts determined by XPS, and the total Au content determined by ICP.

Catalysts	Au^0(Area%)	Au^{1+}(Area%)	Au^{3+}(Area%)
Fresh Au/SAC	80.6	9.3	10.1
Used Au/SAC	99.9	0.1	0
Fresh Au/20 % P-SAC-700	42.3	26.9	30.8
Used Au/20 % P-SAC-700	56.13	17.47	26.4

Catalysts	Total Au(wt.%)		Loss ratio of Au (%)
	Fresh	Used	
Au/SAC	1.15	1.13	1.74
Au/20%P-700-SAC	1.16	1.15	0.86

Table7 The relative content of phosphorous species in the fresh and used Au/20%P-SAC-700 catalyst

Catalyst	$Au(PO_4)$ (Area%)	$Au(PO_3)$ (Area%)	(Cl_3PO) (Area%)
Fresh Au/20%P-SAC-700	65.8	34.2	—
Used Au/20%P-SAC-700	59.8	27.0	13.2

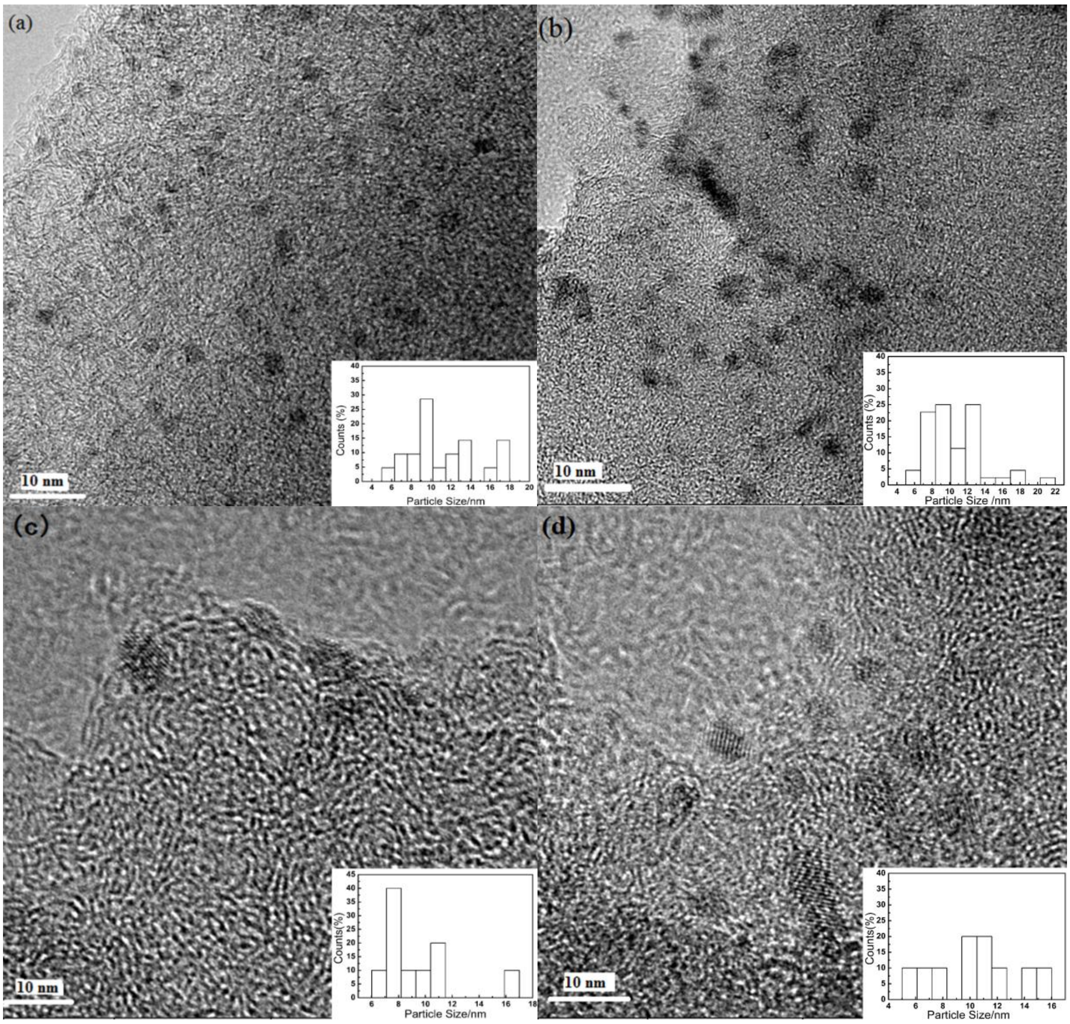

Fig.6 TEM images of the catalyst Au/SAC (a-fresh, b-used)and Au/20%P-SAC-700 (c-fresh, d-used).

Fig. 6 shows the TEM images and the particle size distribution of the fresh and the used catalysts Au/SAC and Au/20%P-SAC-700. For the catalyst Au/SAC, the coverage density of black dots is clearly increased after 45 h reaction, along with the appearance of some larger particles size greater than 20 nm(Fig. 6a and 6b).Whereas for the fresh and used Au/20%P-SAC-700, the nanoparticles with crystal lattice of gold are sparsely located, and the particle size distribution, which are narrower than that in the fresh Au/SAC, shows a little variation after 45 h reaction (Fig. 6c and 6d). It is confirmed that the phosphorous species in the P-modified SAC support can improve the dispersibility of gold elements in the catalysts but also enhance the stability of gold ions during the acetylene hydrochlorination.

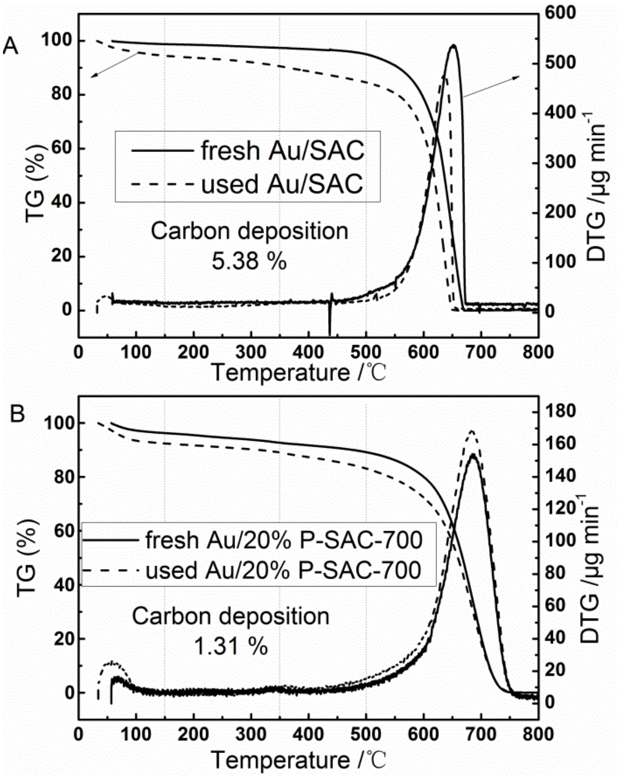

Fig.7 TG and DTG profiles of the catalyst Au/SAC (A) and Au/20%P-SAC-700 (B).

Thermal gravimetric (TG) analysis were performed to study the carbon deposition on the used catalysts Au/SAC and Au/20%P-SAC-700 (Fig. 7). In the case of the used Au/SAC catalyst experiencing 45 h reaction, the slight weight loss before 150 °C is due to the desiccation of adsorbed water, the obvious weight loss in the temperature range of 150-500 °C is associated with the burning of carbon on the catalyst surface. It is the weight loss in the range of 150-500 °C that reflects the amount of coking deposition on the catalyst surface. As shown in Table S1, the weight loss of the used Au/SAC is 9.13 % in the temperature range of 150-500 °C, while it is 3.75 % for the fresh Au/SAC, consequently the carbon deposition of the catalyst surface is about 5.38 % for the used Au/SAC, according to the coke deposition calculation in the same temperature interval.[19]

In the case of Au/20%P-SAC-700 catalyst, the weight loss of the used and fresh catalyst is respectively 8.37 % and 7.06 % in the temperature range of 150-500 °C. Therefore, the carbon deposition of the used Au/20%P-SAC-700 is only 1.3 %. It is indicated that the P-modified SAC support can greatly prevent the coking deposition of the Au catalyst.

In the combination with the TPR, XPS,TEM and TG analysis, it is conclude that the P-modified SAC support can stabilize the catalytic active gold species Au^{3+} and $Au^{1+}$and prevent the formation of Au^0, but also retard the coking deposition on catalyst surface. The optimal catalytic activity was achieved over Au/20%P-SAC-700, with the acetylene conversion of 97%after 45 h under the conditions of 170 ℃ and C_2H_2 GHSV of 360 h^{-1}.

Conclusion

The P-doped spherical activated carbon, consisting of phosphate groups in the surfaces, were prepared using triphenylphosphine as the phosphorus source and assessed as a support of Au catalyst, characterized by FT-IR, XPS, Raman, TPR, BET, TEM and TG analyses. It is indicated that this P-doped carbon support can significantly enhance the catalytic activity of Au/SAC catalyst for acetylene hydrochlorination. For the Au catalysts supported on P-modified SAC, both the acetylene conversion and the selectivity to VCM are enhanced. The acetylene conversion is 99.9 %over Au/20%P-SAC-700for 23 h on stream under the conditions of 170 ℃ and C_2H_2 GHSV of 360 h^{-1}.It is illustrated that the phosphorous species in the P-modified SAC support can improve the dispersibility of gold in the catalysts but also enhance the stability of gold during the acetylene hydrochlorination. There occur the interactions between Au^{3+} and $(PO_4)^{3-}$, as well as Au^{+} and $(PO_3)^{-}$in the Au/20%P-SAC-700 catalyst, which can stabilize the catalytic active gold species Au^{3+} and Au^{1+} whereas prevent the formation of Au^{0}, but also retard the coking deposition on catalyst surface. It is suggested that the P-modified carbon is a promising support to enhance activity of non-mercuric catalysts for acetylene hydrochlorination reaction.

Acknowledgment

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A table of contents entry

Colour Graphic

Text: gold-based catalysts supported on Phosphorus-doped carbon are used in acetylene hydrochlorination to enhance the catalyst activity.