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Preparation of carbon supported platinum catalysts: role of π sites on carbon support surface

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Abstract The role of the π sites in the adsorption of anionic platinum precursor ($PtCl_6^{2-}$) on the carbon surface was studied. A set of carbon supports was prepared by the oxidative treatments of a commercial carbon black in liquid or thermal treatment in a nitrogen gas flow. The supports obtained had similar physical structure, but were different in their surface chemistry, e.g., the types and the amount of the surface functional groups. The Pt/C catalysts were prepared by the impregnation of the supports with an aqueous solution of hexachloroplatinic acid. N_2 adsorption, acid-base titration, X-ray photoelectron spectrometry (XPS), ICP, and TEM were used to characterize the supports and the catalysts. It was found that the absence of the surface acidic groups led to a higher platinum loading amount on the supports; and platinum loading amount would decrease when the higher H_2PtCl_6 impregnating solution concentration was used. The π sites in the basal planes play a more important role than the surface acidic groups in $PtCl_6^{2-}$ ions adsorption on the carbon surface. Upon impregnation, the delocalized π electrons form coordination bonds with the platinum precursors, and further cause the reduction of Pt(IV) complex to Pt(II) complex, which was strongly chemisorbed on the surface of the supports. $PtCl_6^{2-}$ ions adsorbing at the surface acidic groups would easily desorb during the washing process. However, when the impregnating solution was used at a higher concentration, a large amount of H_3O^+ was firstly adsorbed in the π sites, leading to a decrease of the amount of strong $PtCl_6^{2-}$ ions adsorption on the supports.

Introduction

Carbon materials as the support for noble metal catalysts have found their applications in various fields [1–5], due to their unique properties, such as the existence of various forms of the surface functional groups, strong corrosion resistance, and especially, good electrical conductivity. These properties make it ideal for the use in the electrocatalyst in fuel-cell systems [4, 6–8], where platinum is required to disperse highly on the surface of the carbon black as an electrode material. Several previous works related the Pt/C electrocatalyst performance to the carbon properties such as the surface area [9], the pore structure [10] and the surface oxygen groups [11].

One of the most popular ways to get highly dispersed platinum particles on the carbons is the impregnation-reduction method, which includes the following steps: adsorption of the platinum precursor ions on the surface of the carbon supports and their subsequent reduction with hydrogen flow at an appropriate temperature. During the impregnation step, the interactions of the carbon support surface with both the metal precursor and the solvent greatly influence

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metal uptake and dispersion [11]. These interactions are governed by the polarity of the solvent, the pH value of the impregnating solution, the cationic or anionic nature of the metal precursor and the surface charge in the solution of the carbon support. The surface chemistry of the carbon black greatly depends on various functional groups on the surface (e. g., carboxylic and hydroxyl groups), which can act as the adsorption sites for the metal precursor. These groups can be obtained by the oxidation treatments, or progressively destroyed by the thermal treatments [12], which make the support more hydrophilic, allowing a better accessibility of the impregnating aqueous solution to the carbon surface. In aqueous solution, the carboxylic or hydroxyl groups behave as the amphoteric species being dissociated or protonated depending on the pH value of the solution [13]. Thus, the impregnation with an anionic precursor like $PtCl_6^{2-}$ is favored in the acidic solution, whereas the cationic precursors such as $[Pt(NH_3)_4]^{2+}$should be used in the basic solutions.

The importance of the surface oxygen groups has been approved in several previous works [11, 14, 15], showing a direct relationship between the platinum uptake or the dispersion and the amount of the surface oxygen groups on the carbon black. However, it was observed that the highly platinum dispersions were obtained when the carbon black supports were heated in helium at 2273 K, without any further oxidation treatment before the impregnation with H_2PtCl_6 [16]. In this case, although $PtCl_6^{2-}$ adsorption would be favored by the higher IEP [15] of the pregraphitized supports, the absence of the surface oxygen groups on the carbon led to the idea of the existence of other adsorption sites for the platinum precursor. These sites could be the π sites in the basal planes of the graphite crystallites, which are capable of acting as the electron donors to form a coordination bond with the platinum precursor [17]. It was well known that after impregnation of the carbon supports with an aqueous H_2PtCl_6 solution and drying in air, Pt(IV) complex was reduced to Pt(II) complex, even metal platinum by carbon [11, 17, 18]. These works have hinted that the π sites would play an important role in adsorption of $PtCl_6^{2-}$ ions on the surface of the carbon black.

The aim of this paper is to study the role of the π sites in the adsorption of $PtCl_6^{2-}$ ions on the carbon black surface during the preparation of the carbon supported platinum catalysts by studying the impregnation of the carbon blacks, with different amount of surface oxygen groups but same physical texture, and different hexachloroplatinic acid aqueous solution concentration.

Experimental

Supports

Four kinds of supports were prepared according to the following procedure: support S0 was a commercial carbon black (Vulcan XC-72R, Cabot Corp.), which was used as received. Support S1 was prepared by the thermal treatment of Vulcan XC-72R carbon black at 1273 K for 3 h under a nitrogen flow, with heating rate of 10 K/min. Support S2 or S3 were obtained by oxidizing Vulcan XC-72R carbon black in liquid: 1.0 g of Vulcan XC-72R carbon black was immersed in 50 ml of 30% H_2O_2 or 65% HNO_3 aqueous solution, and the slurry so formed was stirred for 48 h at room temperature. The oxidized samples were washed with the distilled water to eliminate the excess of the oxidant and dried in air at 383 K.

Supports were firstly characterized by the elemental analysis, with a LECO CHN-2000 elemental analyzer for the C, H and N content, and an S-144DR elemental analyzer for the S content, respectively. The specific surface area of the supports was determined by the Brunauer-Emmett-Teller (BET) method using physical adsorption of nitrogen at 77 K on a Quantachrome NOVA-2000 physical adsorption apparatus. Wettability measurement was obtained based on the weight increase after permitting the carbon samples to stand for 10 h in contact with the saturated water vapor at 323 K [19]. The acidity of the aqueous carbon slurries (pH values) was measured with a PHS-25 standard pH meter. The slurries were prepared by placing 1.0 g of carbon support and 10 ml of pre-boiled deionized water in a flask and heated to boil for 15 min. Then the slurries were cooled down to room temperature in the stoppered flask to avoid dissolution of atmospheric carbon dioxide. Finally, the pH values of the slurries were measured after calibration of the pH meter with standard buffers. Chemical-shift analysis of the C1s in the XPS was used to elucidate the different kinds of functional groups on the surface of the supports. The amount of the surface acidic groups on the supports was determined by acid-base titration [6]. The total acidic groups were titrated using a strong base (NaOH); however, the strong acidic groups like carboxylic groups were titrated using a very week base such as $NaHCO_3$.

Catalysts

Catalysts were prepared by the impregnation of the supports with the aqueous solutions of hexachloroplatinic acid (Grikin, Beijing) at room temperature. The procedure was as followed: 0.2 g of the support was immersed in 10 ml of aqueous H_2PtCl_6 solution under agitation for 48 h. The resulted suspension was filtered to remove the excess of the solution, and the remained solid was washed with 500 ml of distilled water. The catalyst samples were dried at 383 K in air, and then reduced using a hydrogen flow at 453 K for 4 h.

To determine the platinum loading amount, the carbon supported platinum catalysts was calcined in air at 1073 K until the carbon support was burnt away, and then the platinum residue was dissolved in the aqua regia. The obtained solutions were heated, and the resulted platinum complex solids were diluted with the distilled water. The analysis was carried out using an inductively coupled plasma optical emission spectrometry (ICP-OES, VISTA-MPX). The surface electronic states of the platinum species in the fresh catalysts were studied by X-ray photoelectron spectrometry (XPS) using a Perkin-Elmer PHI1600 ESCA system with an Al $K\alpha$ radiation (1486.6 eV). The surface morphology of the catalysts was determined using a Philips Tecnai G^2 F20 electron microscopy system.

Results and discussion

Supports

The results of the elemental analysis on the supports are summarized in Table 1. The H and C content of the support S1 is lower than that of the support S0. During the thermal treatment, the surface oxygen groups on the carbon black were progressively destroyed, desorbing as CO and CO_2. The H and O content of the support S2 and S3 shows obvious increase due to the liquid oxidation of H_2O_2 or HNO_3. The content of N and S for all supports is similar. This indicate that hydrogen and oxygen containing-functional groups such as the hydroxyl and carboxylic groups were formed on the surface of the support S2 and S3 due to liquid oxidation, while nitrogen and sulfur containing-functional groups were scarcely. X-ray photoelectron spectra (no shown) showed that the surface of the support S3 consists only of carbon and oxygen (and hydrogen). Hence, nitric acid oxidation did not introduce significant amounts of nitrogen.

Table 1 Elemental analysis of the supports

Support	Elemental content (wt%)					
	C	H	O	N	S	Ash
S_0	98.42	0.11	0.59	0.20	0.58	0.10
S_1	99.09	0.09	0.06	0.12	0.51	0.14
S_2	97.39	0.22	1.47	0.18	0.57	0.16
S_3	95.95	0.23	2.90	0.32	0.52	0.08

It is well known that there are various kinds of functional groups on the carbon black surface. They are classified as the acidic, neutral, or basic groups. Carboxylic and anhydride are considered as strongly acidic groups, while lactone, phenolic, carbonyl, quinine, and ether groups are weakly acidic or neutral. Basic complexes are mainly the pyrone and chromene groups [20]. Among these, the carboxylic group has a particularly easily dissociable hydrogen ion (H^+) and serves to dominate the pH value of the carbon slurry.

As seen from Table 2, the analysis of the acid–base titration shows that the amount of the surface acidic groups of the support S_1 subjected to the thermal treatment is very low. However, the oxidation causes different increases in the amount of the surface acidic groups, depending on the type and strength of the oxidant. After the oxidation with an aqueous solution of nitric acid, the amount of carboxylic groups and total acidic groups increased to 0.195 and 0.257 mmol/g, respectively, and the pH value decreases to 3.30. The titration results indicate that the HNO_3-treatment of the carbon black produces higher amount of both strong and weak acidic groups than H_2O_2-oxidaton treatment. From the pH values and the wettability results in Table 2, it also can be seen that the increase of the surface acidic groups leads to a decrease of the pH values of the aqueous carbon slurry and also the hydrophobicity of the carbon supports, thus making the aqueous solutions more accessible to their surface.

N_2 adsorption measurements also show that the specific surface area of all supports is almost similar; this means that neither the heat treatment in N_2 flow nor the liquid oxidation of H_2O_2 or HNO_3 obviously

Table 2 Some characteristics of the supports

Support	S_{N_2} (BET) (m^2/g)	pH	Wettability (mg/g)	Amount of surface acidic groups (mmol/g)	
				Carboxylic acid groups[a]	Total acidic groups[b]
S_0	221.1	8.40	39.52	0.001–0.005	0.008–0.010
S_1	218.4	8.50	38.12	—[c]	—[c]
S_2	205.3	4.52	44.26	0.068	0.089
S_3	191.6	3.00	63.86	0.195	0.257

[a] Obtained by titration with $NaHCO_3$

[b] Obtained by titration with NaOH

[c] The amount of surface acidic groups is too low to be determined by acid-base titration

changed the physical structure of the carbon black. So, it is concluded that these supports treated with the different methods have largely identical physical structure, but different in the surface chemical properties. The amount of the surface acidic groups can be set in the following sequence: $S_3 > S_2 > S_0 > S_1$.

π sites on carbon supports

Oxidized carbons always contain the surface basic sites in addition to the acidic groups. But, their number is usually smaller than that of the original and the heat-treated carbons. These surface basic groups are frequently associated with pyrone or chromene-like structures, and decompose thermally at ~1050–1200 K, generating CO [17, 21, 22]. However, other authors consider that the surface basic sites are essentially of Lewis type and are associated with π-electron-rich regions within the basal plane [23–25]. According to Leon y Leon et al. [25], the protonation of such oxygen-free basic carbon sites would lead to an electron-donor-acceptor complex (Fig. 1), where C_π is probably a graphitized carbon surface platelet in which single π electron pairs may become partially localized as a result of the H_3O^+ addition. A π site has been defined as "a graphitized carbon surface platelet having maximum itinerant π electrons" [11]. These delocalized π electrons have been used to account for the basicity of the carbons without (or with a low amount) of the surface oxygen groups, through the expression in Fig. 1. The presence of the surface oxygen groups near these π sites decreases the Lewis basicity due to an electron-withdrawing effect which destroys the electron delocalization.

When the original or heat-treated carbons are used as the supports, the importance of the π sites should be taken into account. In this case, the amount of the surface acidic groups is much lower than that of the oxidized carbons, causing the increase of basicity of the carbons. The nature of carbon support was studied by XPS, and the XP spectra of the supports are shown in Fig. 2. The C1s spectrum has asymmetrical peaks showing long tails at the higher binding energy side of the main peak. The asymmetry shows the presence of different kinds of binding between carbon and oxygen. The overall spectra may be deconvoluted into three Gaussian peaks. The main peak situated at 284 1eV corresponds to the binding energy of aromatic carbon (C=C), which forms the basal planes of the graphite crystallites. However, the two components at 285.7 and 288.3 eV can be assigned to hydroxyl groups (–C–OH) and carboxylic groups (–C=O), respectively, by the reference to the reported C1s chemical shift data [26].

$$C_\pi + H_3O^+ \rightleftharpoons [C_\pi - H_3O]^+$$

$$C_\pi + 2H_2O \rightleftharpoons [C_\pi - H_3O]^+ + OH^-$$

Fig. 1 Protonation of oxygen-free basic carbon sites

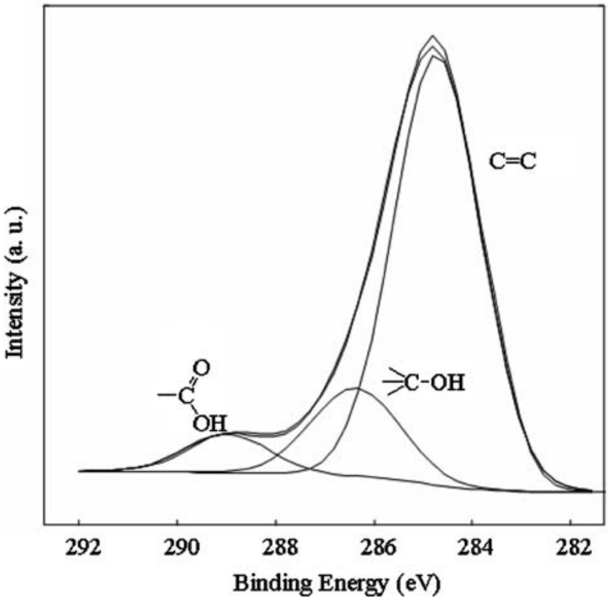

Fig. 2 XP C1s spectra of the support S_3

Table 3 shows the results of XPS analysis. The contents of C and O were calculated from the corresponding peak areas. The reconstruction of the C1s peak gives approximate information on the nature of the surface oxygen groups. The oxidized carbons (supports S_2 and S_3) show a low aromatic carbon (C=C) content on the surface, while the thermal treatment increases the surface aromatic carbon content. In this paper, the amount of the π sites is defined to be in direct proportion to the content of the aromatic carbon (C=C). So, the results in Table 3 confirm the existence of a large amount of π sites on the surface of the original or heat-treated carbons, even the oxidized carbons. The amount of the π sites

Table 3 XPS results for the C1s region, values given in % of the total amount

Support	Binding energy (eV)			C_{total}	O_{total}
	284.0 (C=C)	285.7 (–C–OH)	288.3 (–C=O)		
S_0	73.68	10.46	5.27	89.4	10.6
S_1	84.09	7.28	3.34	90.7	5.3
S_2	62.23	15.42	7.45	85.1	14.9
S_3	50.64	19.23	11.52	81.4	18.6

on the surface of the supports can array in a decreasing sequence: $S_1 > S_0 > S_2 > S_3$.

Catalysts

TEM pictures of the catalyst samples are shown in Fig. 3. Small platinum particles homogeneously dispersed on the surface of the carbon supports are observed, with the main particle diameter of platinum ranging from 2 to 4 nm.

Figure 4 shows the platinum loading amount on the carbon supports with the different surface chemistry. The platinum loading amount was determined by ICP-OES analysis. The different points of the curves were obtained by changing initial H_2PtCl_6 impregnating solution concentration. The shape of the curves indicates that H_2PtCl_6 adsorption on the carbon surface is not a simple process. According to the curves, it can be concluded that as the H_2PtCl_6 solution concentration increased, the platinum loading amount first increased and then decreased slightly, and the that platinum loading amount also changed with the treatment of the supports. Since all supports have similar physical structure, the different behavior toward H_2PtCl_6 adsorption may determine by the different surface chemistry of the supports as a consequence of the thermal and oxidation treatments. Thus, the heat-treated carbon (support S_1) shows the highest platinum loading amount, followed by the original carbon (support S_0), and in a decreasing sequence, the H_2O_2-treated carbon (support S_2) and finally the HNO_3-treated one (support S_3).

Figure 5 shows the correlation of the platinum loading amount of the catalysts with the content of aromatic carbon (C=C) (see Table 3) on the surface of the corresponding supports. Thus, a similar correlation between the platinum content of the catalysts and the amount of the π sites on the surface of the corresponding supports was also obtained from the consistency of the amount of the π sites with the content of aromatic carbon. The curves could satisfactorily display that as the amount of the π sites increases, the platinum loading amount on the support increases accordingly.

Role of π sites

In order to explain the adsorption behaviors of $PtCl_6^{2-}$ on the supports, the surface chemistry of the carbons should be taken into account. It has been recognized that the surface functional groups affect the chemical properties of the carbons. The surface aicdic groups make the support more hydrophilic, allowing a better

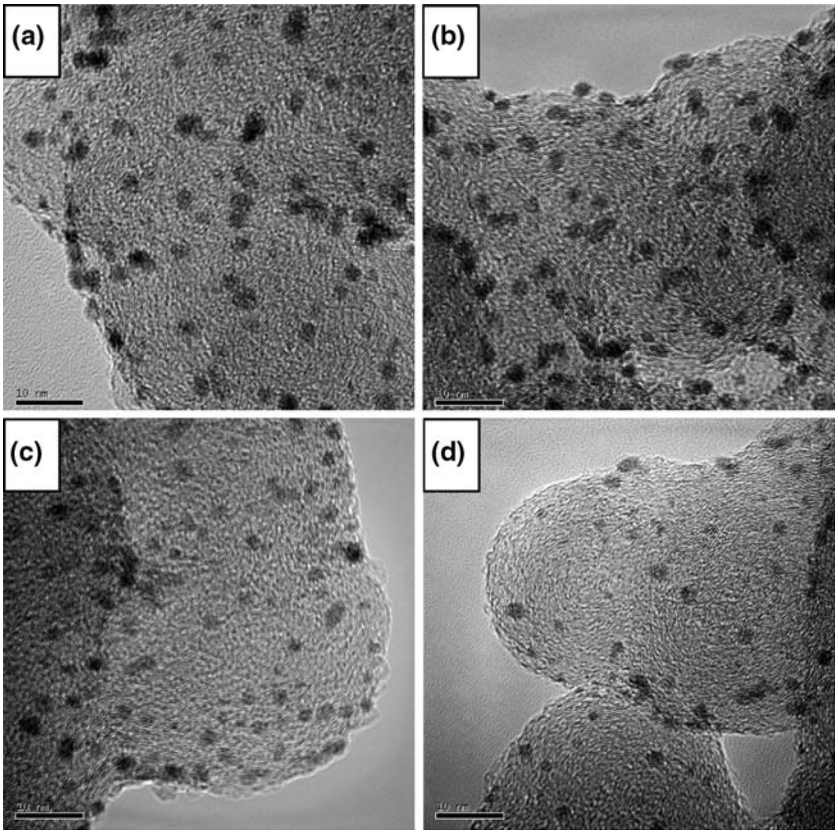

Fig. 3 TEM micrographs of the different catalyst samples. Supports: (**a**) S_0; (**b**) S_1; (**c**) S_2; (**d**) S_3; H_2PtCl_6 solution concentration: 1.1 g[Pt]/l

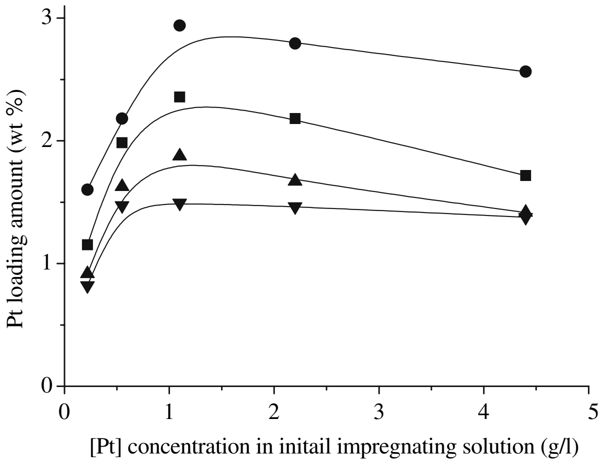

Fig. 4 Pt loading amount on the supports: (■) S_0; (•) S_2; (▲) S_2; (▼) S_3

accessibility of the impregnating aqueous solution to the carbon surface and leading to a better metal dispersion. On the other hand, they can alter the surface-metal precursor interaction by the modification of the ‘‘surface charge’’ properties of the support. In the aqueous solution, the surface oxygen groups behave as amphoteric oxides, being dissociated or protonated depending on the pH value of the solution, according to the equations [13] in Fig. 6. Thus, impregnation with an anionic precursor like $PtCl_6^{2-}$ is favored in the acidic solution, especially when the impregnating solution is more acidic than the aqueous slurry of the supports [27]. In the acidic solution, the protonated groups ($–OH_2^+$) serves as the adsorption sites for the anionic precursor-$PtCl_6^{2-}$. But, due to amphoteric properties of these groups, the adsorbed platinum precursor would possibly desorb from support surface during the water-washing process.

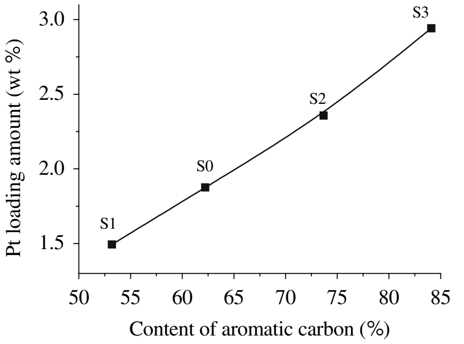

Fig. 5 Correlation of Pt loading amount with the content of aromatic carbon on the surface of the supports. H_2PtCl_6 solution concentration: 1.1 g[Pt]/l

$$\underline{C}OH_2^+ \xleftrightarrow{-H^+} \underline{C}OH \xleftrightarrow{-H^+} \underline{C}O^-$$

Fig. 6 Amphoteric surface oxygen groups

However, Fig. 4 shows that the support S_1, which major fraction of the acidic groups is destroyed by the thermal treatment, displays the highest platinum loading amount. This result agrees well with those obtained by van Dam [17] and Torres [12]. In this case, the absence of the surface acidic groups would decrease the amount of the adsorbed weakly platinum precursor on the carbon surface to a great extent, so it is tenable that other adsorption sites for the platinum precursor must exist on the surface of the carbon. These sites could be the π sites in the basal planes of the graphite crystallites, which are capable of acting as the electron donors to form a coordination bond with the platinum precursor. Then, a more realistic model for the oxidized carbon surface would be one based on the independent acid and basic groups, which ionize according to equilibria of the type shown in Fig. 7, where $\underline{\mathbf{A}}$ and $\underline{\mathbf{B}}$ denote the sites of the carbon solid matrix or the surface oxygen groups [28]. Thus, two types of the adsorption sites have been known during the impregnation of the carbons, with a hexachloroplatinic acid solution: the surface acidic groups at the basal plane edges and the π structures in the carbon basal plane. However, the protonation of the undissociated conventional acidic oxygen groups present on the carbon surfaces is unlikely to take place in the aqueous solutions, due to the low pK_a values of these groups [29] shown in Fig. 8. So, combination of the results from Fig. 4 with the model described by Fig. 7 leads to the conclusion that the surface acidic groups should not be considered as the strong adsorption sites for the platinum precursors, and the π sites on the carbon surface should play a more dominant role than the surface acidic groups in $PtCl_6^{2-}$ ions adsorption during the impregnation.

On the other hand, according to van Dam and van Bekkum [17], it is observed that partial reduction of the platinum precursors during the impregnation. This

$$\mathbf{H\underline{A}} \longleftrightarrow \mathbf{\underline{A}^- + H^+}$$
$$\mathbf{\underline{B} + H^+} \longleftrightarrow \mathbf{\underline{B}H^+}$$

Fig. 7 Model with independent acid and basic groups

$$\mathbf{\mathit{R}COOH + H^+ \longrightarrow \mathit{R}COOH_2^+} \quad (pK_a = -6.0)$$
$$\mathbf{ArOH + H^+ \longrightarrow ArOH_2^+} \quad (pK_a = -6.4)$$

Fig. 8 Protonation of undissociated acidic groups is cannot be explained by above-mentioned mechanism, which assigns the acidic groups as the weak adsorption sites for the platinum precursors. Therefore, the chemistry of both hexachloroplatinic acid and the carbon surface during the impregnation should be taken into account. Due to the existence of a large amount of π sites on the surface of whether the oxidized carbons or the heat-treated carbon, the delocalized π electrons in the basal planes can act with $PtCl_6^{2-}$ ions and cause the reduction of Pt(IV) complex to Pt(II) complex by the carbon [17]. Then the Pt(IV) complex is coordinatively bound to the surface of the carbon strongly by a C–O–Pt linkage [30]. The reduction of Pt(IV) species has been confirmed by XPS characterization of the fresh impregnated catalyst samples (see Fig. 9). In addition, the weak adsorption of $PtCl_6^{2-}$ ions on the π sites also takes place simultaneously. Because the π sites belong to the basic site, they can adsorb H_3O^+ anions to form the $C_\pi(H_3O)^+$ groups, as defined in Fig. 1. These $C_\pi(H_3O)^+$ sites will be incapable of serving as the weak adsorption sites for the platinum precursor, causing a interaction of Pt(IV) complex with the carbon surface. The two different adsorption types are described in Fig. 10. But it must be indicated that the equations of Fig. 10 should not be taken as stoichiometric ones, and the ratio of Fig. 10a, b affected by the pH values of the impregnating H_2PtCl_6 solutions. Moreover, the oxidative pretreatments of the carbons would decrease the amount of the basic surface sites (π sites), leading to the decrease of the amount of the strong chemically adsorption described in Fig. 10b. So, the decrease of the platinum loading amount on the oxidized carbon can also be explained through this mechanism.

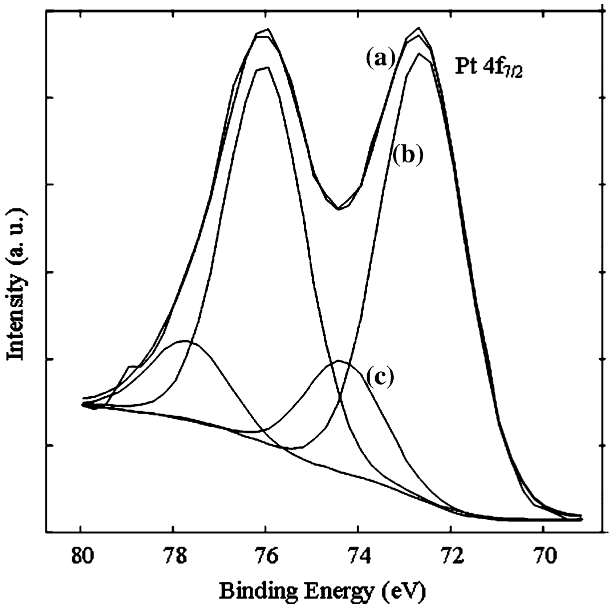

Fig. 9 Pt 4f spectra of the fresh catalyst supported on the support S_3 impregnated with an aqueous solution of 1.1 g-Pt/l H_2PtCl_6. (**a**) Experimental spectrum. After deconvolution: (**b**) E_B: 72.6 eV; (**c**) E_B: 74.3 eV (Pt $4f_{7/2}$: Pt^0 71.0–71.3 eV; $K_2Pt(II)Cl_4$ 72.8–73.4 eV; $K_2Pt(IV)Cl_6$ 74.1–74.3 eV [17])

$$\textbf{(a)}\ \ Pt(IV)Cl_6^{2-} + C_\pi(H_3O)^+ \longrightarrow [C_\pi - OH_3 - Pt(IV)Cl]_6^{\ -}$$

$$\textbf{(b)}\ \ Pt(IV)Cl_6^{2-} + C_\pi + H_2O \longrightarrow [C - O - Pt(II)Cl_4]^{2-} + 2HCl$$

Fig. 10. Adsorption of $PtCl_6^{2-}$ ions on the π sites

In Fig. 4, we can also see that at higher H_2PtCl_6 impregnating solution concentration ranges, the platinum loading amount on the supports decreases as increasing the solution concentration. In this case, the lower pH values of the impregnating solution would lead to a larger amount adsorption of H_3O^+ ions on the π sites, causing the equation of Fig. 10a happening at higher ratio to that of Fig. 10b. However, this weak adsorption of $PtCl_6^{2-}$ ions in Fig. 10a is easily destroyed at medium pH value during the washing process with the distilled water after the impregnation. Therefore, it is reasonable that the decrease of the amount of the strong chemisorption on the π sites would decrease the platinum loading amount on the supports.

Conclusion

Carbons subjected to the oxidative or thermal treatment had largely identical physical structure, but different their surface chemistry. The oxidative treatments increase the carbon's hydrophilicity, thus making the aqueous metal precursor solutions more accessible to its surface. Both the surface oxygen groups at the basal plane edges and the π sites in the carbon basal plane can serve as the adsorption sites for $PtCl_6^{2-}$ ions, but with the different adsorption mechanisms. Due to the low pK_a values, the surface acidic groups cannot be considered as the strong adsorption sites for the platinum precursors. XPS characterization confirms the existence of a large amount of the π sites on the surface of the original or heat-treated carbons, even the oxidized carbons. These π sites on the carbon surface should play a more dominant role than surface acidic groups in $PtCl_6^{2-}$ ions adsorption during the impregnation. The delocalized π electrons in the π sites can react with $PtCl_6^{2-}$ ions and cause the reduction of Pt(IV) complex to Pt(II) complex by the carbon, and then the Pt(II) complex is coordinatively bound to the surface of the carbon strongly by a C–O–Pt linkage. This strong interaction of the platinum species with the carbon surface would hold out the conclusion that the platinum loading amount on the carbon increases with the increase of the amount of the π sites on the carbon surface. However, at higher H_2PtCl_6 impregnating solution concentration ranges, the lower pH values of impregnating solution would lead to a larger amount adsorption of H_3O^+ ions on the π sites, causing weak adsorption of Pt(IV) complex at H_3O^+ sites, which is easily destroyed at medium pH value during the washing process with the distilled water after the impregnation. Therefore, in this case platinum loading amount on the supports decreases as increasing solution concentration.

Reference

1. Aksoylu AE, Faria JL, Pereira MFR, Figueiredo JL, Serp P, Hierso JC, Feurer R, Kihn Y, Kalck P (2003) Appl Catal A Gen 243:357
2. Fuente AM, Pulgar G, González F, Pesquera A, Blanco C (2001) Appl Catal A Gen 208:35
3. Sepúlveda-Escríbano A, Collma F, Rodríguez-Reinoso F (1998) Appl Catal A Gen 173:247
4. Prabhuram J, Zhao TS, Wong CW, Guo JW (2004) J Power Sources 134:1
5. Auer E, Freund A, Pietsch J, Tacke T (1998) Appl Catal A Gen 173:259
6. Yasuda K, Nishimura Y (2003) Mater Chem Phys 82:921
7. Tian JH, Wang FB, Shan ZhQ, Wang RJ, Zhang JY (2004) J Appl Electrochem 34:461
8. Kim H, Subramanian NP, Popov BN (2004) J Power Sources 138:14
9. Takasu Y, Kawaguchi T, Sugimoto W, Murakami Y (2003) Electrochimica Acta 48:3861
10. Park GG, Yang TH, Yoon YG, Lee WY, Kim CS (2003) Inter J Hydrogen Energy 28:645
11. Coloma F, Sepúlveda-Escribano A, Fierro JLG, Rodríguez-Reinoso F (1994) Langmuir 10:750
12. Torres GC, Jablonski EL, Baronetti GT, Castro AA, de Miguel SR, Scelza OA, Blanco MD, Peňa Jiménez MA, Fierro JLG (1997) Appl Catal A Gen 161:213
13. Noh JS, Schwarz JA (1990) Carbon 28:675
14. Prado-Burguete C, Linares-Solano A, Rodríguez-Reinoso F, Salinas-Martínez de Lecea C (1989) J Catal 128:98
15. Solar JM, Leon y Leon CA, Osseo-Asare K, Radovic LR (1990) Carbon 28:369
16. Prado-Burguete C, Linares-Solano A, Rodríguez-Reinoso F, Salinas-Martínez de Lecea C (1991) J Catal 128:397
17. van Dam HE, van Bekkum H (1991) J Catal 131:335
18. Czaran E, Finster J, Schnabel KH (1978) Z Anrog Allg Chem 433:175
19. Li X, Horita K (2000) Carbon 38:133
20. Radmilovic V, Gasteiger HA, Ross PN Jr (1995) J Catal 154:98
21. Suh DJ, Park TJ, Ihm SK (1993) Carbon 31:427
22. Polania-L A, Papirer E, Donet JB, Dagois G (1993) Carbon 31:473
23. Lopez-Ramon MV, Stoekli F, Morena-Castilla C, Carrasco-Marin F (1999) Carbon 37:1215
24. Barton SS, Evans MJB, Halliop E, MacDonald JAF (1997) Carbon 35:1361
25. Leon y Leon CA, Solar JM, Calemma V, Radovic LR (1992) Carbon 30:797
26. Amine K, Mizuhata M, Oguro K, Takenaka H (1995) J Chem Soc Faraday Trans 91:4451
27. Román-Martínez MC, Cazorla-Amorós D, Linares-Solano A, Salinas-Martínez de Lecea C (1994) Carbon 33:3
28. Carrott PJM, Carrott MMLR, Candeias AJE, Ramalho JPP (1995) J Chem Soc Faraday Trans 91:2179
29. Fraga MA, Jordão E, Mendes MJ, Freitas MMA, Faria JL, Figueiredo JL (2002) J Catal 209:355
30. Lambert JF, Che M (2000) J Mol Catal A Gen 162:5