

Probing Pd–carbon interaction in Pd/C catalysts by EXAFS

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Abstract

The Pd/C catalyst prepared by PdCl₂ impregnation was examined with extended X-ray absorption fine structure (EXAFS) analysis. The model of precursor anchoring by surface oxygen groups is not supported by EXAFS. A Pd–C interaction at around 3.6 Å can be included in the fitting of the fresh catalyst. This Pd–C interaction remained after the fresh PdCl₂/C was washed and reduced by NaBH₄. However, a further hydrogen treatment at 338 K removed this Pd–C interaction and Pd sintering was indicated with increasing hydrogen treatment temperature. This Pd–C interaction was originally proposed [B.L. Mojet, M.S. Hoogenraad, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, J. Chem. Soc., Faraday Trans. 93 (1997) 4271] for Pd(NH₃)₄Cl₂/C and was also found in the Pd/C prepared by Pd(NO₃)₂ impregnation in this study. This suggests a similar Pd–C interaction while preparing Pd/C catalyst from cationic, anionic and neutral Pd species.
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1. Introduction

Supported noble metal catalysts are used widely in chemical industries. Carbon-supported noble metal catalysts are frequently used because of the high activity and, in addition, the easy metal recovery. However, carbon-supported metal catalysts seem less understood than oxide-supported catalysts. Explanation and attribution in catalysis by oxide-supported metal catalysts are often extended to carbon-supported metal catalysts. Carbon supports, not like oxides, are hydrophobic unless they are subjected to oxidative treatment. Acid boiling is one of the popular treatments, as well as thermal treatment, under oxidative environments [2,3]. Such oxidative treatments result in surface oxygen via the formation of functional groups like carboxylic, phenolic and lactone groups [3,4]. The presence of surface oxygen can improve the metal dispersion on carbon support. The higher the surface oxygen content, the better the metal dispersion is [2,5–8]. This is usually explained by the interaction between surface oxygen and noble metal, in analogy to oxide-

supported metal catalysts. According to the surface charge model, the interaction between metal precursor and surface functional groups on carbon surface is determined by the pH of the metal loading environment. Simonov and co-workers [9–11] argued against the above scenario in their preparation of Pd/C catalysts from PdCl₂. They proposed that PdCl₂ can either be reduced by carbon surface to form metal particles or interact directly with carbon surface via C=C bond. The former mechanism resulted in larger Pd aggregates but took only a minor portion of the loaded Pd. The majority of the loaded Pd came from the PdCl₂ interaction with carbon surface. Three types of interaction were proposed, i.e., on graphitic planes, on edges of graphitic planes and in between graphitic planes. The PdCl₂ coordinated to the edges and in between planes are considered strongly bound and lead to well-dispersed Pd after reduction.

The Pd/C catalyst is of interest in this study not only because of its catalytic activity but also of its peculiar behaviors reported earlier. Palladium metal is known to form stable hydride phase and carbide phase under certain conditions. Interstitial and surface carbon were attributed for the suppressed chemisorption of the Pd/C prepared from Pd(acac)₂ [12,13] but this was not observed on that prepared from PdCl₂

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[14]. This attribution is by no doubt indicating the important role of Pd–C interactions. Extended X-ray absorption fine structure (EXAFS) is a well-known technique capable of detecting short-range bonding morphology of a specific element. It has been widely used to characterize supported metal catalysts. XAFS modeling can provide information of metal–support interaction when the metal is dispersed well on the support. This is because that EXAFS generates only volume-average information. EXAFS has been used to study stable PdC_x phase [15–17], $\text{Pd}(\text{NH}_3)_4\text{Cl}_2/\text{C}$ [1], PdCl_2/C [18] and Pd/fullerene [19]. Among these studies, bonding models of Pd–C interaction were proposed only for $\text{Pd}(\text{NH}_3)_4\text{Cl}_2/\text{C}$ [1] and Pd/fullerene [19]. Since PdCl_2 is more often used as the precursor for Pd catalysts, understanding the interaction between PdCl_2 and carbon surface would be beneficial towards more active Pd/C catalysts. Therefore, this study reports the EXAFS examination of the Pd–C interaction within the Pd/C catalyst prepared from PdCl_2 and the extension to that prepared from $\text{Pd}(\text{NO}_3)_2$.

2. Experimental

The Pd/C catalyst was prepared by an incipient wetness impregnation method from $\text{HCl}_{(\text{aq})}$ solution of PdCl_2 (Aldrich, 99.999%) or aqueous solution of $\text{Pd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (Merck, 99.99%) and carbon black support (Cabot, XC72R, after 1273 K passivation under N_2 and a following activation with O_2 at 673 K). The carbon support after O_2 activation was titrated by means of the Boehm's method [2] and was found to contain mainly acidic oxygen groups that are titratable with NaOH. The catalyst was then dried in an oven at 373 K for 4 h. The fresh catalyst was dispersed in excess deionized water, agitated, aged, filtered and dried in oven to become the washed sample. The washed sample was redispersed in deionized water, reduced by dropwise-addition of NaBH_4 (0.5%, diluted from Merck 99%), then filtered, washed with deionized water and dried in oven. The NaBH_4 -reduced sample was further treated with H_2 (San-Fu, 99.995%, flown through dryer and oxy-trap columns) at elevated temperatures.

X-ray absorption spectra were recorded ex situ at room temperature, at Pd *K*-edge using BL12B2 beam line at Spring-8 (Japan). The monochromator employed double Si(3 1 1) crystals for energy selection. A transmission mode was adopted in which the intensities of both incident and transmitted X-ray beams were measured by gas ionization chambers. The energy was scanned from 200 eV below the edge to 1000 eV above the edge. The raw absorption data, with pre-edge and post-edge backgrounds subtracted, were normalized to the edge jump to yield the EXAFS function. After being weighted by k^3 to compensate the damping of the EXAFS oscillations with increasing k (the photoelectron wave number), the EXAFS function was Fourier transformed to *r*-space in which a nonlinear least-squares fitting algorithm was applied. All the computer programs were implemented

in the UWXAFS package [20]. The backscattering amplitude and phase shift for specific atom pairs were theoretically calculated with FEFF7 code [21]. The amplitude factor was calibrated against measured data of reference samples such as Pd foil and PdCl_2 and it was found to be within 7% error. Therefore, the amplitude factors from fitting were used without further correction.

3. Results

A high Pd loading of 10% by weight is used for the Pd/C in this study such that all possible Pd–C interactions can be presented. On the other hand, EXAFS requires good Pd dispersion to get meaningful models for short-range bonding morphology. The Pd dispersion was examined by TEM as shown in Fig. 1. It is clear from Fig. 1 that very well-dispersed phase presents. The small aggregates averaged to ca. 2 nm size. The numerous small particles suggest that EXAFS analysis on the prepared PdCl_2/C should be applicable.

The EXAFS plots in both the *r*- and the *k*-space are shown in Fig. 2 for the fresh PdCl_2/C . The Pd–Cl shell is the major contribution to this catalyst. The Pd–Cl coordination number falls between 3.5 and 3.8 from all the models we tested. This is slightly lower than the expected coordination number of 4 for PdCl_2 . It suggests that most of the loaded PdCl_2 remained intact while a small portion of it changed its chemical identity. The possibility of PdCl_2 particle formation in this sample is excluded because a second-shell Pd at 3.34 Å cannot fit, even to the EXAFS data recorded at 77 K.

In order to probe the PdCl_2 –C interaction, different regression models were composed and tested. Mojet et al. [1] observed Pd–C coordination at both $r = 3.6$ and 4.3 Å in the

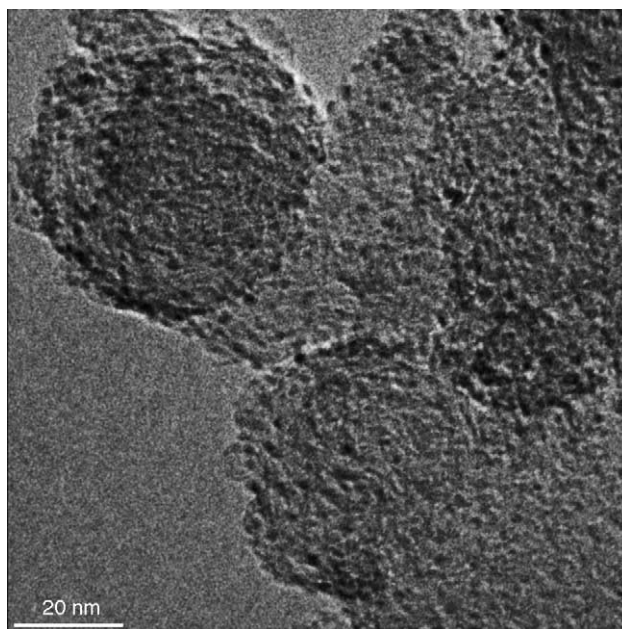


Fig. 1. High-resolution TEM image of the fresh PdCl_2/C catalyst.

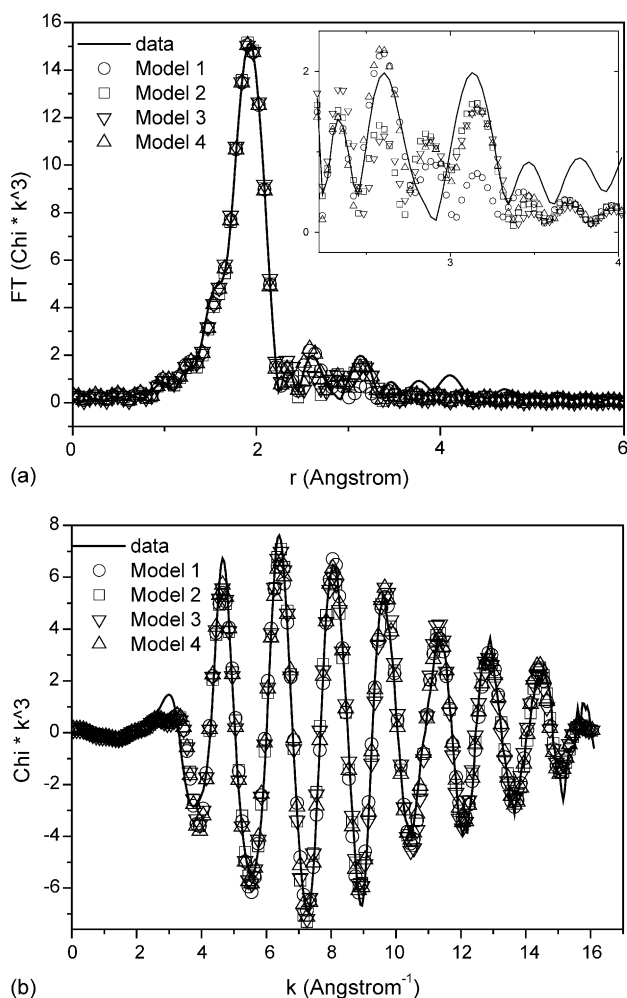


Fig. 2. EXAFS plots of the fresh PdCl₂/C catalyst fitting to Model 1: Pd–Cl+Pd–Pd (○), Model 2: Pd–Cl+Pd–C+Pd–C (□), Model 3: Pd–Cl+Pd–O+Pd–C (▽) and Model 4: Pd–Cl+Pd–Pd+Pd–C (△) in (a) the *r*-space and (b) the *k*-space (see text for details). Lines represent raw data.

fresh Pd(NH₃)₄Cl₂/C-fibril and at *r* = 2.6 Å in the reduced Pd/C-fibril. Chenov et al. [19] reported Pd–C shells at *r* = 2.3 and 3.3 Å in the PdC₆₀ prepared from an organometallic precursor. Jones et al. [15] reported Pd–C shells at *r* = 1.95 and

3.46 Å in PdC_{0.15} powders but McCauly [16,17] did not observe such a Pd–C coordination in his PdC_{0.13}. Table 1 and Fig. 2 compare four regression models of better agreement and better physical meaning. Model 1 analyzes the contributions of both Pd–Cl and Pd–Pd if the latter is formed during the PdCl₂ loading as reported earlier [9,22]. Model 2 leaves out the Pd–Pd coordination but includes two Pd–C shells in analogy to that proposed for Pd(NH₃)₄Cl₂/C [1]. Model 3 depicts the surface oxygen anchoring mechanism by including both Pd–O and Pd–C shells; the latter assumes a bond length as the sum of Pd–O and C–O in carboxylic group. Model 4 is hypothesized, which includes the Pd–Cl (unreduced), Pd–Pd (reduced) and a Pd–C (as proposed in [1]). All four models show statistically indifferent agreement to the measured data in Fig. 2. Fitted parameters in Table 1 show consistent Pd–Cl and Pd–Pd first shells, indicating that only a small portion of Pd is reduced while most retain Cl neighbors. In the case of Model 3, a Pd–Pd second shell at 3.4–3.6 Å was further examined to account for the possible formation of PdO but the fitting results reject this possibility. A *k*³-weighting was used in these model regressions. The effect of *k*-weighting on the fitting results with Model 4 is shown in Fig. 3. Both the Pd–Pd shell and the Pd–C shell at 3.6 Å cannot be identified in the fitting with *k*¹-weighting. It seems that the Pd–C contribution can be identified only when the contribution from the Pd–Pd shell is unambiguously contained. The fitting parameters obtained by using *k*²- and *k*³-weighting are almost indistinguishable.

Most interestingly, the presence of a Pd–C shell at ca. 3.6 Å was found in Models 2, 3 and 4 as shown in Table 1. Though theoretically C and O neighbors cannot be distinguished in EXAFS, our fitting with a Pd–O shell at 3.6 Å resulted in erroneously abnormal fitted parameters. Fig. 4 compares the fittings with a Pd–C at 3.6 Å and that with a Pd–O shell at 3.6 Å based on Model 4. The difference file technique [23] is used and the fitting parameters are included in Fig. 4 for comparison. The use of a Pd–O shell at 3.6 Å in Model 4 resulted in a negative amplitude factor which is not acceptable. In addition, a Pd–C shell at 3.6 Å has better physical meaning than a Pd–O shell at 3.6 Å. As proposed [1], a Pd center sitting above a hexagonal C-ring resulted in

Table 1
Model regressions of the fresh 10% Pd/C prepared from PdCl₂

Model	Shell	<i>r</i> (Å)	C.N.	σ ²	E ₀ (eV)	<i>r</i> -Factor
1	Pd–Cl	2.316 ± 0.004	3.65 ± 0.26	0.004 ± 0.0004	6.4 ± 1.0	0.020
	Pd–Pd	2.762 ± 0.022	0.53 ± 0.57	0.008 ± 0.005		
2	Pd–Cl	2.313 ± 0.007	3.51 ± 0.31	0.004 ± 0.0004	5.7 ± 1.9	0.018
	Pd–C	2.628 ± 0.031	1.1 ± 1.8	0.002 ± 0.007		
	Pd–C	3.553 ± 0.039	3.2 ± 3.3	0.006 ± 0.007		
3	Pd–Cl	2.319 ± 0.015	3.8 ± 3.8	0.004 ± 0.002	8.6 ± 6.5	0.021
	Pd–O	2.25 ± 0.50	1.6 ± 3.5	0.008 ± 0.030		
	Pd–C	3.574 ± 0.071	3.3 ± 3.6	0.006 ± 0.009		
4	Pd–Cl	2.316 ± 0.004	3.65 ± 0.23	0.004 ± 0.0004	6.4 ± 1.0	0.016
	Pd–Pd	2.759 ± 0.023	0.47 ± 0.58	0.007 ± 0.006		
	Pd–C	3.553 ± 0.034	2.1 ± 2.2	0.003 ± 0.006		

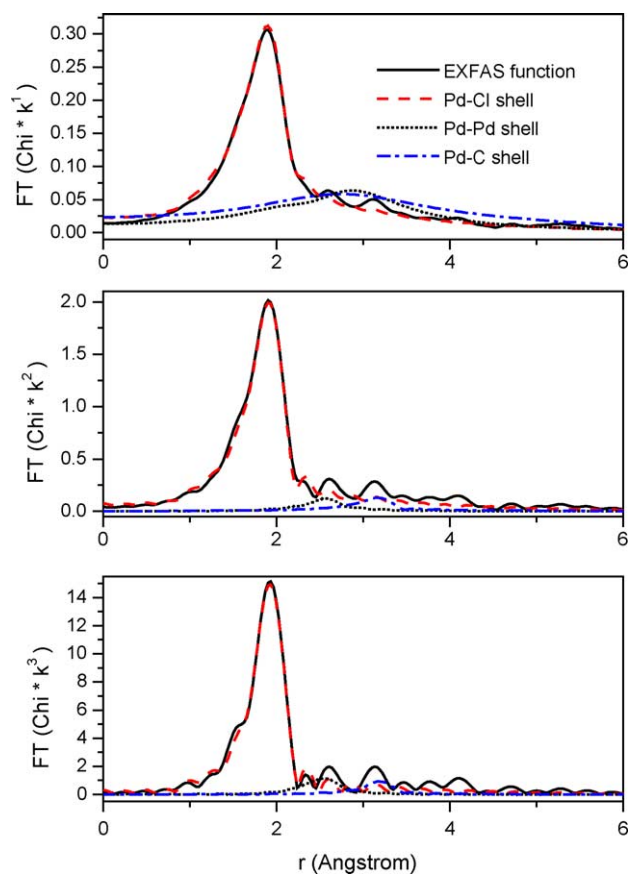


Fig. 3. Effect of k -weighting on the fitting of the fresh PdCl₂/C catalyst using Model 4. From top to bottom, the figure shows the fitting with k^1 -, k^2 - and k^3 -weighting.

this Pd–C shell, whereas a Pd–O at 3.6 Å would need to be PdO particle formation which is rejected as described above. Therefore, we conclude that a Pd–C interaction is a better assignment than a Pd–O interaction. These fitting results suggest that the PdCl₂–C interaction is similar to that proposed for Pd(NH₃)₄Cl₂/C [1]. Comparing the fitting results in Table 1 and the inset of Fig. 2(a), the two smaller peaks at $r = 2.6$ and 3.2 Å (before phase correction) seem attributable to Pd–Pd and Pd–C, respectively. Including a Pd–C shell at 2.3 or 3.3 Å, as that reported in PdC₆₀ [19], resulted in inconsistent fitting. The Model 4 in Table 1 appears to be the more suitable model though Model 3 cannot be dismissed at this moment.

The fresh PdCl₂/C catalyst is further tested by EXAFS after a series of pretreatment as shown in Table 2 and Fig. 5. Loosely bound PdCl₂ may present in this high-loading fresh PdCl₂/C catalyst and a washing step would remove these loosely bound species. The Model 4 in Table 1 still explained the data of the washed sample well but Model 3 cannot fit the measured data. This indicates that the model of Pd anchoring via surface oxygen can be dismissed. Interestingly, a coordination number close to 6 for the Pd–C at ca. 3.6 Å was observed in the washed sample. This coordination number is similar to the coordination number observed in

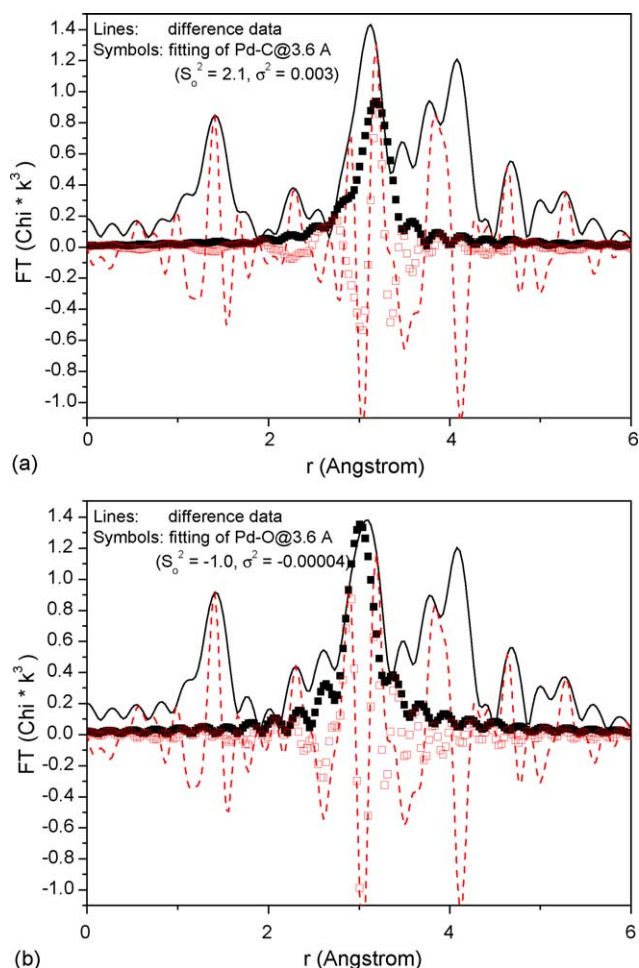


Fig. 4. The EXAFS plots in the r -space of the difference file and (a) the fitted Pt–C at the rate 3.6 Å or (b) the fitted Pd–O at the rate 3.6 Å based on Model 4. Lines represent the difference file which is obtained by the subtraction of fitted Pt–Cl and Pt–Pt contributions from raw spectra.

Pd(NH₃)₄Cl₂/C [1]. It suggests that the morphology of the PdCl₂–C interaction can be explained by a similar coordination model. The washing procedure simultaneously resulted in a decrease in Pd–Cl and an increase in Pd–Pd coordination numbers. This can be explained by a lower fraction of the unreduced PdCl₂ and a higher fraction of the reduced Pd after washing. During washing, the washed liquid showed color similar to PdCl₂. It indicates that weakly bound PdCl₂ in the fresh sample was removed. If the already reduced Pd clusters and strongly adsorbed PdCl₂ are supposed not changed, the fraction of PdCl₂ on carbon surface would decrease due to washing. This would result in a reduced average Pd–Cl coordination number and an increased averaged Pd–Pd coordination number as observed in Table 2.

When the washed sample was further reduced by NaBH_{4(aq)}, the Pd–Cl shell was completely removed. The Pd–Pd and the Pd–O become the main first-shell contributions. Though the Pd–O shell can be substituted by a Pd–C shell at ca. 2.0 Å, we would tentatively leave it as the Pd–O for the time being. The Pd–C shell at ca. 3.6 Å remained after

Table 2
Model regressions of the morphology changes of PdCl₂/C during pretreatment

Sample	Shell	r (Å)	C.N.	σ^2	E_o (eV)	r -factor
Fresh	Pd–Cl	2.316 ± 0.004	3.65 ± 0.23	0.004 ± 0.0004	6.4 ± 1.0	0.016
	Pd–Pd	2.759 ± 0.023	0.47 ± 0.58	0.007 ± 0.006		
	Pd–C	3.553 ± 0.034	2.1 ± 2.2	0.003 ± 0.006		
+Washing	Pd–Cl	2.311 ± 0.005	3.12 ± 0.28	0.005 ± 0.006	6.0 ± 0.9	0.013
	Pd–Pd	2.763 ± 0.005	1.81 ± 0.46	0.006 ± 0.001		
	Pd–C	3.617 ± 0.043	5.1 ± 4.9	0.011 ± 0.011		
+NaBH ₄	Pd–O	2.017 ± 0.007	2.14 ± 0.31	0.004 ± 0.001	3.6 ± 1.0	0.016
	Pd–Pd	2.752 ± 0.004	3.17 ± 0.36	0.007 ± 0.0005		
	Pd–C	3.637 ± 0.032	4.3 ± 3.5	0.008 ± 0.008		
+H ₂ , 338K	Pd–O	2.000 ± 0.011	1.54 ± 0.38	0.006 ± 0.002	1.0 ± 0.7	0.016
	Pd–Pd	2.744 ± 0.003	4.97 ± 0.41	0.007 ± 0.0004		
+H ₂ , 523K	Pd–O	2.004 ± 0.013	1.19 ± 0.37	0.005 ± 0.002	1.1 ± 0.7	0.013
	Pd–Pd	2.743 ± 0.003	5.93 ± 0.43	0.007 ± 0.0004		

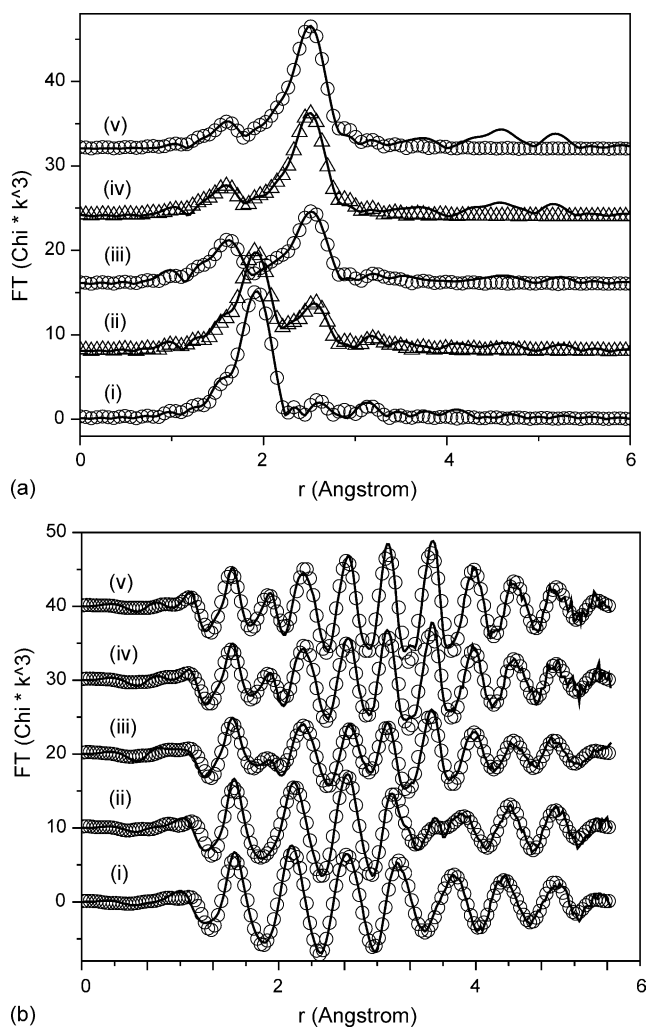


Fig. 5. Effect of treatment conditions on the EXAFS plots of the fresh PdCl₂/C catalyst: (i) fresh, (ii) washed, (iii) NaBH₄ reduction of the washed sample, (iv) H₂ treatment at 338 K of the NaBH₄-reduced sample and (v) H₂ treatment at 523 K of the NaBH₄-reduced sample in (a) the r -space and (b) the k -space. Lines represent raw data and symbols represent fitting according to models listed in Table 2.

NaBH₄ reduction although its averaged coordination number decreased. When the NaBH₄-reduced sample was further treated with hydrogen at 338 K, the Pd–C shell was removed. At the same time, the Pd–Pd coordination increased and the average Pd–O coordination number decreased. This can be explained by that the H₂ treatment eliminated the Pd–C interaction, leading to Pd agglomeration and subsequently less oxygen adsorption when air-exposed. Increasing the hydrogen treatment temperature to 523 K resulted in even more aggregation.

Fig. 6 compares the EXAFS fittings of the 10% Pd/C prepared by Pd(NO₃)₂ impregnation. The fitting shows a coordination number of Pd–O and Pd–Pd as 3.1 ± 0.9 and 0.8 ± 0.8 , respectively. It indicates a mostly unreduced precursor in the fresh catalyst, even when the Pd–O shell can be alternatively replaced by a Pd–N shell of the same bond distance. Again, the fitting indicates the presence of a Pd–C shell at ca. 3.6 Å. The results suggest that the Pd–C interaction model proposed in Ref. [1] is applicable for Pd/C prepared from different precursors.

4. Discussion

From this study, a model of PdCl₂ interaction with carbon surface can be composed. A small fraction of the PdCl₂ precursor was reduced to Pd clusters after impregnation and oven drying. This was proposed earlier [9,22] as due to the reducing ability of carbon surface. The Pd–Pd coordination number around 0.5 suggests that only a small fraction of PdCl₂ was reduced to metallic state. Most of the loaded PdCl₂ remained chemically intact, according to the average Pd–Cl coordination number being close to 4. Washing the fresh sample resulted in PdCl₂ loss, which should be the weakly bound PdCl₂. The presence of reversibly adsorbed PdCl₂ on carbon was reported in Ref. [9]. Washing also caused a decrease in Pd–Cl and an increase in Pd–Pd coordination number. It is not sure whether this is due to a severe loss of PdCl₂ or

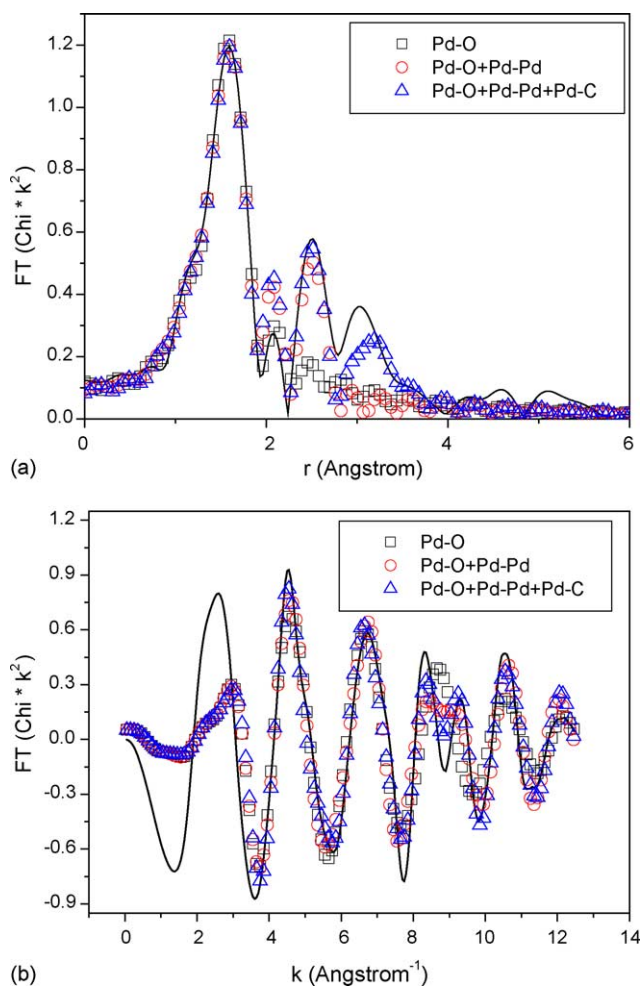


Fig. 6. EXAFS plots of the fresh $\text{Pd}(\text{NO}_3)_2/\text{C}$ catalyst fitting to Pd–O (\square), Pd–O + Pd–Pd (\circ) and Pd–O + Pd–Pd + Pd–C (\triangle) in (a) the r -space and (b) the k -space. Lines represent raw data.

more PdCl_2 was reduced to Pd clusters. If no further reduction occurred due to washing, the changes in the Pd–Cl and Pd–Pd coordination numbers can be explained by a reduced PdCl_2 fraction in the washed sample. No Pd–O coordination can be included in the fitting of the washed sample. This indicates that its contribution, if any, is relatively small compared to the Pd–Cl shell. Reduction with NaBH_4 nicely removed all Pd–Cl bonds and generated highly dispersed Pd clusters with an average Pd–Pd coordination number around 3. However, a following H_2 treatment caused Pd clusters to sinter; the higher the treatment temperature is, the more sintering is indicated.

The presence of a Pd–C interaction is indicated from EXAFS in this and previous [1] studies. Such interaction is important because it will play a role in stabilizing Pd adspecies during catalyst preparation. In the fresh PdCl_2/C , a Pd–C coordination with the bond length of 3.55 Å was observed. This Pd–C distance was originally proposed for $\text{Pd}(\text{NH}_3)_4\text{Cl}_2/\text{C}$ where $\text{Pd}(\text{NH}_3)_4$ sits 3.3 Å above the center of a hexagonal ring of the graphite plane [1]. A coordination

number of 6 is required for this proposed model, but it was not found in our fresh PdCl_2/C catalyst. Instead, the proposed Pd–C coordination number was found in the washed sample. This suggests that only the more strongly bound PdCl_2 adspecies are consistent with such a Pd–C interaction pattern. That a Pd–C coordination number around 2 found in the fresh PdCl_2/C suggests that only approximately one-third of the loaded Pd atoms have this kind of Pd–C interaction.

The surface oxygen anchoring mechanism (Model 3 in Table 1) is not supported by this study. This model could not fit the EXAFS data of the washed sample although it fits the fresh sample. However, the fitted parameters of Model 3 in Table 1 have higher statistical errors (e.g., coordination numbers of first shells) than other applicable models. The fitted Pd–O bond distance is about 10% longer than a typical Pd–O (at 2.02 Å) in palladium oxide. Previous EXAFS results, mostly of oxide-supported metal catalysts, show metal–oxygen interactions characterized by both short (2.0–2.2 Å) and long (2.5–2.8 Å) distances. [24] Vaarkamp et al. [25] proposed that the long metal–oxygen distance is due to the presence of hydrogen in the metal–support interface because this distance shortened from 2.6 to 2.2 Å in $\text{Pt}/\text{Al}_2\text{O}_3$ after H_2 desorption. This model of having interface hydrogen between Pt and C was recently applied to explain the Pt–support interaction in Pt/C [26]. The Pd–C at 2.6 Å presented in the reduced Pd/carbon fiber [1] may also be interpreted analogously. We did examine if a Pd–C(O) at 2.2–2.6 Å can be included in the fitting, but the results were negative. Including this Pd–C(O) at 2.6 Å shell generated a somewhat better match to the measured data of the NaBH_4 -reduced sample, but the fitting Debye–Waller factor of this shell was negative. The Pd–O at 2.02 Å is typically observed in both chemisorbed oxygen and palladium oxide. The fitted Pd–O shell at 2.2 Å in Model 3 suggests that this bond is not oxidic and that it would imply the presence of a strong metal–support interaction [24–26]. It is somewhat difficult to expect that the acidic H_2PdCl_4 would have a strong interaction with acid groups (e.g., carboxylic) on the carbon surface. Furthermore, that a mild H_2 reduction at 338 K removed this Pd–C shell indicates its not-so-strong interaction. Consequently, the Pd–C interaction model proposed by Ref. [1] is considered more suitable than the surface oxygen anchoring model. In addition, that no Pd–O shell can be included in the fitting of the washed sample also suggests that the surface oxygen anchoring model is not applicable.

For the $\text{Pd}(\text{NH}_3)_4\text{Cl}_2/\text{C}$ [1], its Pd–C coordination at 3.65 Å disappeared after a H_2 reduction and a new Pd–C coordination at 2.6 Å was included in its EXAFS fitting. This is consistent with the loss of that Pd–C in our catalyst after H_2 treatment. However, we did not find the new Pd–C shell at 2.6 Å in our samples. On the other hand, this metal–carbon shell at 2.6 Å is also reported in the reduced Pt/C [26] and Ru/C [27]. Zhang et al. [26] reported that this Pt–C distance shortened from 2.6 to 2.0 Å after evacuation, in analogy to the bond shortening due to the removal of interface hydrogen observed in $\text{Pt}/\text{Al}_2\text{O}_3$ [25]. This Pt–C at 2.6 Å is accompanied

by a Pt–C at 3.6 Å in the reduced Pt/carbon black but the latter Pt–C was not observed in the carbon nanofiber-supported Pt [26]. The authors proposed that the Pt–C at 3.6 Å occurs on the graphitic basal plane while the Pt–C at 2.6 Å is attributable to the presence of hydrogen in between Pt and C. The loss of the Pt–C interactions in Pt/carbon black is accompanied by particle sintering [26], as that observed in the Pd/C in this study.

The first-shell Pd–O observed in our reduced sample may be, as mentioned earlier, due to the O₂ adsorbed in ex situ EXAFS measurement or to some new Pd–C at 2.0 Å since it is indistinguishable from Pd–O. This question may be answered if the particle size can be estimated. For a cubo-octahedral particle about 2 nm with chemisorbed O₂, the numbers of surface and total atoms suggests an average Pd–O coordination number around 0.6. With smaller particle size, the Pd–O coordination number will increase significantly. For the three reduced samples in Table 2, the Pd–O coordination increases with decreasing Pd–Pd coordination. This is qualitatively consistent with the dispersion effect. For the Pd/C after H₂ reduction at 523 K, the Pd–Pd coordination number about 6 suggests an average particle size less than 2 nm even when the possible errors in this size evaluation are considered [28–31]. Its Pd–O coordination number of 1.2 ± 0.4 implies that it can be mostly contributed from chemisorbed O. A further in situ EXAFS measurement also indicated the absence of such Pd–O (or Pd–C) coordination [32]. Thus, no new Pd–C coordination is considered in the reduced samples in this study.

The Pd–Pd coordination number increased when the Pd–C coordination was removed by reduction. It implies that the Pd–C coordination at 3.65 Å can stabilize the Pd clusters on carbon surface. The extent of Pd sintering increases with increasing H₂-reduction temperature, as indicated by the higher Pd–Pd coordination number in Table 2 and by the decreased CO chemisorption [33]. The Pd–C coordination at 3.65 Å was proposed originally for Pd(NH₃)₄Cl₂/C [1]. It was found in this study to appear in the fresh Pd/C prepared from both PdCl₂ and Pd(NO₃)₂. This suggests a similar Pd–C interaction within differently prepared Pd/C catalysts. These three precursors have cationic, anionic and neutral Pd species, respectively, in precursor solutions. The similar Pd–C interaction found in these three Pd/C catalysts indicates that electrostatic interaction between precursor species and carbon surface is absent. Our EXAFS analysis indicates that Pd agglomeration occurred concurrently when such Pd–C interaction disappeared. The presence of such a Pd–C interaction during catalyst preparation, treatment and reaction obviously is important for catalyst stability.

5. Conclusion

The 10% Pd/C catalyst prepared by PdCl₂ impregnation was found to contain both weakly and strongly bound PdCl₂; the former can be removed by a washing procedure.

EXAFS analysis on the fresh, washed, NaBH₄-reduced and further H₂-treated samples was performed. The fresh sample is best fitted with a model containing a Pd–Cl (unreduced), a Pd–Pd (reduced) and a Pd–C interaction at around 3.6 Å. This Pd–C interaction remained in the washed PdCl₂/C and that reduced by NaBH₄. However, a further hydrogen treatment at 338 K removed this Pd–C interaction and Pd sintering was indicated with the increased Pd–Pd coordination number. The Pd–C coordination at 3.6 Å was proposed originally for Pd(NH₃)₄Cl₂/C-fibril [1] as Pd centers sitting 3.3 Å above hexagonal C-ring. It was also found in this study in the fresh Pd/C catalysts prepared from PdCl₂ and Pd(NO₃)₂. These three precursors have cationic, anionic and neutral Pd species, respectively, in precursor solutions, but the similar Pd–C interaction was found. This indicates that the conventional electrostatic interaction model of precursor anchoring by surface oxygen groups is not supported by these EXAFS results.

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