Applied Catalysis A: General 467 (2013) 386–393

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

The influence of acid treatment of carbon nanofibers on the activity of palladium catalysts in the liquid-phase hydrodechlorination of dichlorobenzene

O.V. Netskina[a,*], O.V. Komova[a], E.S. Tayban[a], G.V. Oderova[a], S.A. Mukha[a], G.G. Kuvshinov[b], V.I. Simagina[a,b]

[a] Laboratory of hydrides investigation, Boreskov Institute of Catalysis SB RAS, Pr. Akademika Lavrentieva 5, Novosibirsk 630090, Russia
[b] Department of Chemical Engineering, Novosibirsk State Technical University, Pr. Karla Marksa 20, Novosibirsk 630092, Russia

ARTICLE INFO

Article history:
Received 19 February 2013
Received in revised form 19 July 2013
Accepted 22 July 2013
Available online xxx

Keywords:
Carbon nanofibers
Acid treatment
Surface function groups
Adsorption
Hydrodechlorination
Palladium catalyst

ABSTRACT

Palladium catalysts on the basis of acid treated carbon nanofibers (CNF) were studied. Using physicochemical methods of investigation (low-temperature nitrogen adsorption–desorption, FTIR spectroscopy and Boehm titration) it has been shown that under the action of HCl and HNO_3 there take place a reduction in the specific surface area and the volume of pores and an increase of the concentration of surface functional groups. This has a substantial influence on the adsorptive properties of CNF, the dispersion of palladium and the catalytic activity in the liquid-phase hydrodechlorination of 1,2-dichlorobenzene. The reaction rate was observed to be the highest in the presence of Pd/CNF-HCl. Treatment of CNF by HCl gives the highest dispersion of palladium on the external surface of CNF. There is also an increase in the adsorption capacity for 1,2-dichlorobenzene and a decreased adsorption of the solvents on the surface of the acid-modified CNF.

1. Introduction

Carbon materials provide optimal supports of catalysts for the low-temperature hydrogenation of organic molecules, including the liquid-phase hydrodechlorination of chlorinated organic compounds [1–3]. These materials are characterized by a high adsorption capacity for organochlorine compounds [4] and are resistant to the action of hydrochloric acid that forms in the course of the hydrodechlorination [5]. However, when choosing a carbon material for a support application its porosity should be taken into consideration since the presence of the chlorine atom in the benzene ring makes impossible chlorobenzene adsorption in pores smaller than 0.36 nm [6,7]. Therefore, in such applications carbon materials with a minimum volume of micropores should preferably be used.

Accessibility of the nanofibrous carbon surface to large organic molecules and almost absolute absence of micropores make it attractive catalyst support for hydrodechlorination of chloroaromatic compounds. [8,9]. By varying the synthesis conditions the nanofibrous materials supports with different characteristics can be obtained [10,11]. The support properties can also be modified by a treatment in an oxidizing or a reducing medium. [12–15].

Inorganic acid treatment is generally considered to be a means of controlling the adsorptive properties of carbon materials by varying the concentration and nature of the oxygen-containing groups on their surface [16–21]. In spite of the fact that an extensive literature is available on the adsorption properties of oxidized carbons, the studies of support acid treatment effects on Pd catalysts activity are not numerous [22–28]. It has been suggested [25,29,30], that acid treatment of activated carbon not only has an influence on the adsorption properties of the final catalyst but also on the dispersion of metal active component.

The purpose of this work was to investigate the activity of Pd catalyst in the liquid-phase hydrodechlorination of 1,2-dichlorobenzene (1,2-DCB) by molecular hydrogen depending on the physicochemical properties of carbon nanofibers (CNF) supports subjected to a treatment by nitric (CNF-HNO_3) and hydrochloric (CNF-HCl) acid. The choice of CNF as the object of investigation was determined by the absence in them of a developed structure of micropores which is an essential requirement for catalytic reactions involving large organic molecules [31].

2. Experimental

2.1. Material

The CNF samples ($V_{\Sigma pore} = 0.32\ cm^3/g$; $S_{BET} = 151\ m^2/g$) were prepared by the pyrolysis of a (C_1–C_3) fraction over a nickel catalyst

---

* Corresponding author. Tel.: +7 383 330 74 58; fax: +7 383 330 76 91.
E-mail address: netskina@catalysis.ru (O.V. Netskina).

0926-860X/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcata.2013.07.046

in a quartz flow microreactor at 550 °C [10]. A nickel catalyst was prepared by coprecipitation of hydroxide mixtures from nickel and aluminum salt solutions. Sediment was filtered, washed and dried at 120 °C and then decomposed in nitrogen at 350 °C. The sample was reduced with pure hydrogen at 550 °C for 3 h. According to the chemical analysis the nickel content was 90 ± 3 wt.%. Gas (C_1–C_3) flow rate was set to meet the following conditions: 110 L of gas per 1 h per 1 g of Ni in the catalyst.

The CNF fraction of 0.04–0.08 mm was used for further experiments.

2.2. Acid treatment of CNF

Treatment of CNF by acids was performed at room temperature using solutions containing 10% (w/w) of the corresponding (HCl and HNO_3) acid. 5 g of CNF was placed into a 50 mL flask and 25 mL of acid solution were added. The mixture was agitated with a magnetic stirrer for 20 h after which it was quickly warmed up to 80 °C and kept at this temperature for an hour. The acid-treated CNFs were repeatedly washed with distilled water. The acid treatment procedure was repeated three times for each CNF sample and the treated samples were dried under vacuum for two hours at 75 °C.

2.3. Study of the adsorption of 1,2-DCB, toluene and 2-propanol from organic phase of reaction mixture

The adsorption of 1,2-dichlorobenzene (1,2-DCB), toluene and 2-propanol from the organic phase of the reaction medium was studied by the static method at room temperature using the following concentrations: $C_{1,2\text{-DCB}} = 0.2$ mol/L, $C_{\text{toluene}} = 5.87$ mol/L and $C_{2\text{-propanol}} = 4.65$ mol/L. 1 g sample of the original or acid-treated carbon nanofibers was placed into a 60 mL flask and then 50 mL of reaction mixture (1,2-DCB, toluene or 2-propanol) was added. Changes in concentrations of the organic compounds during the adsorption cycle were monitored using a GC–MS instrument Agilent 7000 Triple Quadrupole GC/MS, column Agilent 19091S-433:HP-5MS 5% Phenyl Methyl Silox. To obtain reliable data each experiment was repeated for at least three times. The differences between the experimental values did not exceed ±3%.

2.4. Catalyst preparation

Supported palladium catalysts were prepared by incipient wetness impregnation from hydrochloric solutions of palladium chloride ($PdCl_2$). The catalysts were dried at temperatures from 130 to 150 °C for two hours. The reduction of the catalyst was performed at room temperature by adding an aqueous solution of sodium borohydride (the Pd:$NaBH_4$ molar ratio was 1:3) [32]. The palladium loading of the catalyst was 1 ± 0.05 wt.% according to the chemical analysis.

2.5. Experimental procedure

The apparatus for the liquid-phase hydrodechlorination of 1,2-DCB consisted of two main parts: a rector unit and a volumetric block. The reaction was carried out under constant stirring (1200 rpm), at 50 °C and constant pressure of hydrogen of 0.1 MPa. At stirring rates of higher than 800 rpm the influence of the external diffusion processes was shown to be negligible [32]. To obtain reliable data each experiment was repeated for at least three times. The differences between the experimental values did not exceed ±4%.

To 11 cm^3 of a solution of 1,2-DCB in an organic phase containing of 7 cm^3 of toluene and 4 cm^3 of 2-propanol were added 4 cm^3 of a 50% (w/w) solution of potassium hydroxide in water to neutralize the forming HCl [32,33]. Thus, the reaction medium was made up of two immiscible fluids. In some experiments a organic phase consisted from 7 cm^3 of toluene, 4 cm^3 of 2-propanol and 2.5 mL of 1,2-DCB.

The products of hydrodechlorination in the organic phase were analyzed on a “Crystall-2000” chromatograph (JSC KUPOL, Russia) with a flame-ionization detector. The instrument was operated under an Ar carrier gas, using a hydrogen flame, in the temperature range from 60 to 120 °C (heat rate is 10 °C/min), a column length of 2 m and column diameter of 2.5 mm. The filling sorbent was Chromaton N-AW.

Hydrodechlorination performance is quantified in terms of dechlorination degree (X_{Cl}):

$$X_{\text{Cl}} = \frac{[1,2\text{-DCB}]_0 - [1,2\text{-DCB}] - 0.5[\text{CB}]}{[1,2\text{-DCB}]_0} \quad (1)$$

where $[1,2\text{-DCB}]_0$ is the initial concentration of 1,2-DCB; [1,2-DCB] is the value of concentration of 1,2-DCB at reaction time *t* and [CB] is the concentration of chlorobenzene (CB) at reaction time *t*.

2.6. Investigation methods

The specific surface area and pore volume were based on N_2 adsorption isotherms, determined with a Micrometritics ASAP 2000 surface analyzer.

The content of impurities in CNF and of palladium in catalysts was determined by X-ray fluorescence analysis on a VRA-30 instrument with a Cr anode of the X-ray tube. The relative error of determination was ±5%.

The transmission IR spectra were taken in air at ambient temperature on a Bomem MB-102 Fourier spectrometer. For these measurements 1.5 mg of a catalyst sample was mixed with 800 mg of CsJ and pressed to a pellet.

The content of acidic functional groups on CNF surface was investigated by the acid–base titration method proposed by Boehm using $NaHCO_3$, Na_2CO_3, NaOH or sodium ethoxide solutions [34,35]. One gram of the carbon and 70 mL of a 0.05 N solution of bases were mixed in a conical flask and agitated at 100 rpm for 24 h at 298 K under argon. Then a 18 mL aliquot of this solution was acidified by the addition of 18 mL of HCl (0.05 N) and the sample was back-titrated with NaOH (0.05 N). Adsorption from 0.1 N NaOEt in ethanol was determined analogously. The points of neutralization were detected by potentiometric titration using an ATP-02 automatic titrator (Akvilon, Russia). Each sample was analyzed three times and the average value was employed for further analysis.

Temperature-programmed desorption (TPD) is used to measure the surface acidic groups of the CNF-HCl and CNF-HNO_3. It was carried out in a tabular quartz reactor of 3.00 mm in diameter and 100 mm in length, which coupled to quadrupolar mass spectrometer (NETZSCH QMS 403 C Aëolos). The sample (60 mg) was heated in the reactor from room temperature to 1000 °C at rate of 10 °C/min under a flow of argon (40 cm^3/min). CO and CO_2 desorbed from the sample were monitored by a mass spectrometer at an m/e of 28 for CO and 44 for CO_2.

The high-resolution transmission electron microscopy (HR TEM) studies of the catalysts were carried out using a JEM-2010 (JEOL, Japan) instrument with a lattice resolution of 1.4 Å and an accelerating voltage of 200 kV. The local elemental analysis was performed by the EDX method on an Energy-dispersive X-ray Phoenix Spectrometer equipped with a Si (Li) detector with an energy resolution of at least 130 eV or higher. The samples were fixed on “holey” carbon films supported on copper grids and examined with an electron microscope. To construct the particle size distribution diagrams the diameter of at least 300 particles has been determined. The mean Pd particle sizes are quoted [36] as both a number average diameter ($\bar{d}_n$),

$$\overline{d_n} = \frac{\sum_i n_i d_i}{\sum_i n_i}. \tag{2}$$

and surface area-weighted diameter ($\bar{d}_s$),

$$\overline{d_s} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2}, \tag{3}$$

where n_i is the number of particles of diameter d_i.

3. Results

As has been described in Section 1, treatment of carbon materials by acids has a considerable influence on their physicochemical properties. The resulting changes in the nature of surface functional groups, the structure of surface layers, porosity and specific surface area and the removal of impurities may have an influence on the catalytic properties of Pd supported on an oxidized carbon. A study of acid-treated carbon nanofibers has been performed and the obtained data were compared with those for an untreated CNF.

3.1. Characterization of acid-treated carbon nanofibers

3.1.1. Chemical composition

According to X-ray fluorescence data (Table 1) treatment of CNF by hydrochloric and nitric acids decreases the amount of impurities in the samples. In the case of CNF-HNO_3 the content of nickel was reduced by a factor of 5 as compared with the untreated CNF. In the case of CNF-HCl the amount of nickel was reduced only by a factor of 2.5. Carbon materials are capable of a strong adsorption of nitrate and chloride ions. X-ray fluorescence analysis confirmed an enhanced content of chloride ions in CNF-HCl. The nitrogen impurities could not be detected because of the limitations of this technique.

3.1.2. Textural characteristics

In Fig. 1 are shown the low-temperature nitrogen adsorption-desorption isotherms and pore size distribution for CNF, CNF-HCl and CNF-HNO_3. It can be seen that they are practically identical to each other and are indicative of a mesoporous structure of the samples under study. The irreversible capillary condensation in mesopores is supported by the presence of a hysteresis loop at $P/P_0 > 0.4$ (the desorption curve runs above the adsorption curve). An analysis of the shapes of the observed hysteresis loops using the IUPAC classification allows their assignment the H1 type, a type characteristic of uniformly packed globules having close volumes. [37]. For all of the CNF samples the determined volume of micropores does not exceed 1–2% of the total pore volume (Table 1).

Fig. 1B shows the pore size distribution in the regions of meso- (from 20 to 500 Å) and macro- (>500 Å) pores. It can be seen that treatment by acids did not lead to any essential changes in the porous structure of CNF. All the samples show the typical bimodal pore size distribution-peaks at 145 Å and 390 Å. The total pore volume is equal to 0.32, 0.28 and 0.27 cm^3/g for CNF, CNF-HCl and CNF-HNO_3, respectively. This is consistent with the reduced values of the specific surface area in the CNF samples kept in 10% (w/w) solutions of acids. Thus, for CNF, CNF-HCl and CNF-HNO_3 the values of the specific surface area are equal to 151, 143 and 145 m^2/g, respectively. An analogous decrease in the specific surface area of activated carbon upon treatment by nitric and hydrochloric acids has been observed in [38,39].

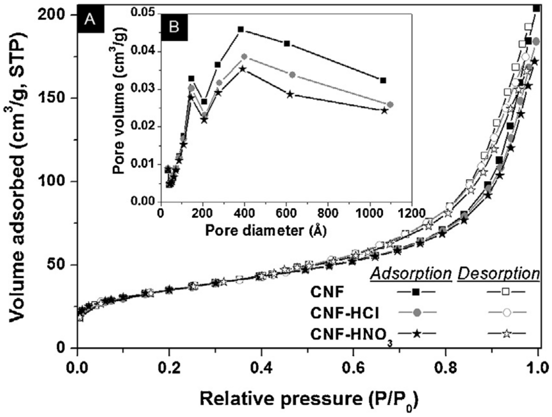

Fig. 1. Nitrogen adsorption–desorption isotherm at 77 K (A) and pore size distribution (B) for the initial CNF, CNF-HCl and CNF-HNO_3.

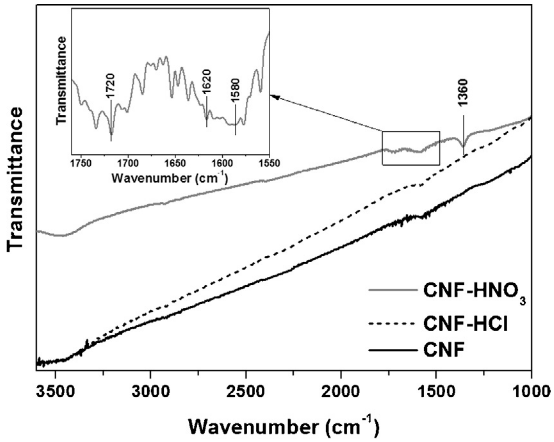

Fig. 2. FTIR-spectra CNF, CNF-HCl and CNF-HNO_3.

3.1.3. Surface group determination

To determine the composition of the surface functional groups in the CNF, CNF-HCl and CNF-HNO_3 samples were studied by FTIR spectroscopy, Boehm titration and TPD.

The IR spectra of the CNF, CNF-HCl and CNF-HNO_3 samples are shown in Fig. 2. It is seen that there are no substantial differences between the spectra of CNF and CNF-HCl but in the spectrum of CNF-HNO_3 there appear new lines at 1720, 1620 (sh.), 1580 and 1360 cm^{-1}. There is an increase in the amount of the adsorbed water as indicated by increased relative intensities of the absorption bands at 3450 and 1620 (sh.) cm^{-1} due to the vibrations of water molecules [40]. The absorption band at 1720 cm^{-1} indicates the presence on the sample surface of carbonyl (C=O) and carboxyl

Table 1
Physicochemical properties of CNF before and after treatment by hydrochloric and nitric acids.

Sample	Contents of impurities (wt.%)					Pore volume (cm^3/g)		
	Ni	Fe	Cl	Al	S	Micropores	Mesopores	Macropores
CNF	0.94	0.014	–	0.08	0.01	0.003	0.242	0.074
CNF-HCl	0.39	<0.01	0.11	–	–	0.002	0.218	0.060
CNF-HNO_3	0.18	<0.01	–	–	<0.01	0.006	0.211	0.053

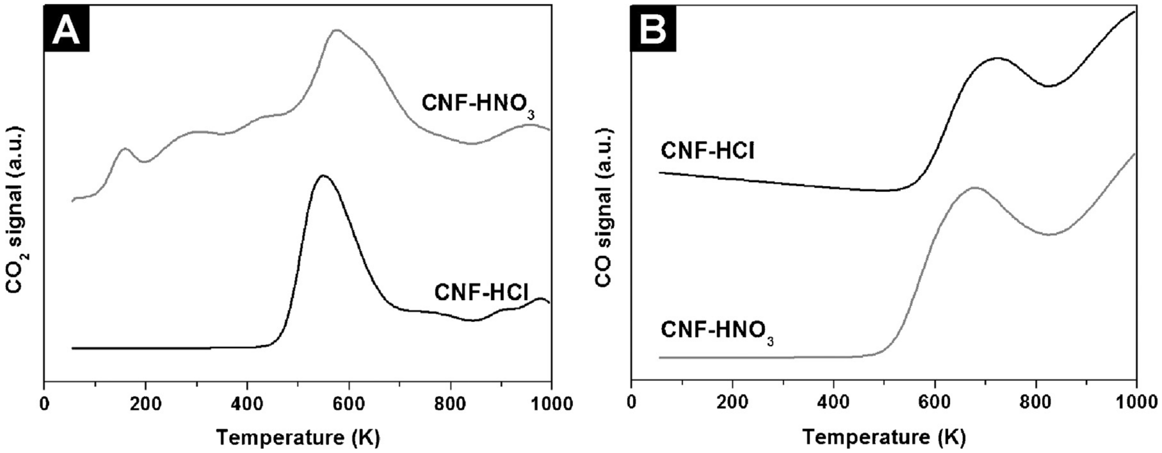

Fig. 3. CO_2 (A) and CO (B) releases during the TPD of the CNF-HCl and CNF-HNO_3 samples.

Table 2
Acidic surface oxides of CNF, CNF-HCl and CNF-HNO_3 (according to the Boehm's titration method).

Sample	Titration using (µmol/g)			
	NaOEt	Na_2CO_3	$NaHCO_3$	NaOH
CNF	112 ± 9	22 ± 5	12 ± 3	69 ± 6
CNF-HCl	179 ± 11	42 ± 7	26 ± 5	82 ± 8
CNF-HNO_3	294 ± 8	165 ± 8	126 ± 9	233 ± 12

(—COOH) functional groups [41]. The absorption band at 1580 cm^{-1} is assignable to the stretching vibrations of the aromatic ring [42]. The absorption band at 1360 cm^{-1} appears to be due to $NO_3{}^-$ vibrations [43,44] indicating that there takes place adsorption of nitrate ions. This is in good agreement with the results of a FTIR study of oxidized carbon nanofibers [45].

The concentration of acidic sites on the carbon surface after its acid-treatments was studied by Boehm's method [34,35]. It is assumed that sodium bicarbonate ($pK_a = 6.7$) neutralizes carboxylic acids, sodium carbonate ($pK_a = 10.25$) neutralizes carboxylic acids and lactones, sodium hydroxide ($pK_a = 15.74$) neutralizes carboxylic acids, lactones, and phenols, whereas sodium ethoxide ($pK_a = 20.58$) reacts with all oxygen species, even extremely weak acids [12,46]. According to the Boehm titration data (Table 2) the content of surface functional groups in the acid-treated CNF was increased. The carbon surface was enriched by weakly acidic oxygen-containing groups (carbonyl, phenolic, lactone or lactol groups) under action of hydrochloric acid. In case of CNF treatment by nitric acid the concentration of strongly acidic groups such as carboxylic acids and phenolic groups was increased several times but the amount of weakly acidic oxygen-containing groups changes little.

The difference in the surface chemistry between CNF-HCl and CNF-HNO_3 is most clearly demonstrated by TPD. The CO and CO_2 profiles for the oxidized CNFs are shown in Fig. 3. An analysis of this data shows that CNF treated by HCl mainly contain carbonyl and lactone groups and on the surface of the CNF-HNO_3 the prevailing species are carboxyl groups and carboxylic anhydrides (Table 3). This is in agreement with the data obtained by the Boehm method.

3.2. Study of the adsorption of 1,2-DCB, toluene and 2-propanol from organic phase of reaction mixture

Changes of the physicochemical properties of carbon materials will certainly have an influence on the adsorption of the reaction mixture components in the liquid-phase catalytic reactions. Adsorption of 1,2-DCB, toluene and 2-propanol from the organic phase of the reaction medium was used to compare the adsorption properties of studied CNFs depending on the applied acid treatment. The changes in the composition of the reaction medium were determined by gas chromatography–mass spectrometry. According to the obtained results (Table 4), treatment by hydrochloric acid increases the adsorption of 1,2-DCB on CNF-HCl and decreases the adsorption of 2-propanol, especially in the early stages of the process (the adsorption equilibrium of 1,2-DCB on studied CNFs is attained within the first 5 min). The adsorption of 1,2-DCB and toluene on CNF-HNO_3 was decreased.

Thus, it has been established that changes in the physicochemical properties of acid-treated CNFs may have a substantial influence on the adsorption process of 1,2-DCB in the cause of the catalytic conversion, especially in the case of CNF-HCl-based catalysts.

3.3. Study of Pd catalysts based on untreated CNF and acid-treated CNF

Palladium catalysts on the basis of CNF, CNF-HCl, CNF-HNO_3 have been prepared. After their reduction by sodium borohydride at room temperature the particle size of the active component was studied by HR TEM. It can be seen from Fig. 4 that the particle size of Pd does not exceed 10 nm. A detailed examination of the particle size distribution of Pd has shown the metal dispersion to decrease in the order Pd/CNF-HCl < Pd/CNF < Pd/CNF-HNO_3. In the Pd/CNF catalyst Pd particles were present not only on the CNF surface but also inside the channels (Fig. 5). This makes them inaccessible to the large molecules of the reagents. Thus, pretreatment of CNF by

Table 3
Acidic surface oxides of CNF, CNF-HCl and CNF-HNO_3 (according to TPD method).

	Surface functional groups (µmol/g)					
	Carboxylic anhydrides	Carboxyl acid groups	Lactone groups	Carboxylic anhydrides	Phenol groups	Carbonyl groups
CNF-HCl	23	–	34	Negligible	112	482
CNF-HNO_3	86	35	28	76	597	340

Table 4
Adsorption of 1,2-DCB, toluene and 2-propanol from organic phase of reaction medium in the presence of the CNF, CNF-HCl and CNF-HNO_3 samples.

Sample	Concentration (mol/L)								
	1,2-DCB			Toluene			2-Propanol		
	Initial	5 min[a]	60 min[b]	Initial	5 min[a]	60 min[b]	Initial	5 min[a]	60 min[b]
CNF	0.20	0.28	0.28	5.87	5.80	5.87	4.65	2.60	2.34
CNF-HCl	**0.20**	**0.18**	**0.18**	**5.87**	**6.14**	**6.18**	**4.65**	**3.91**	**3.67**
CNF-HNO_3	0.20	0.24	0.23	5.87	5.91	5.97	4.65	3.26	3.35

[a] The beginning of process

[b] The adsorption reaches equilibrium in 15 ± 5 min.

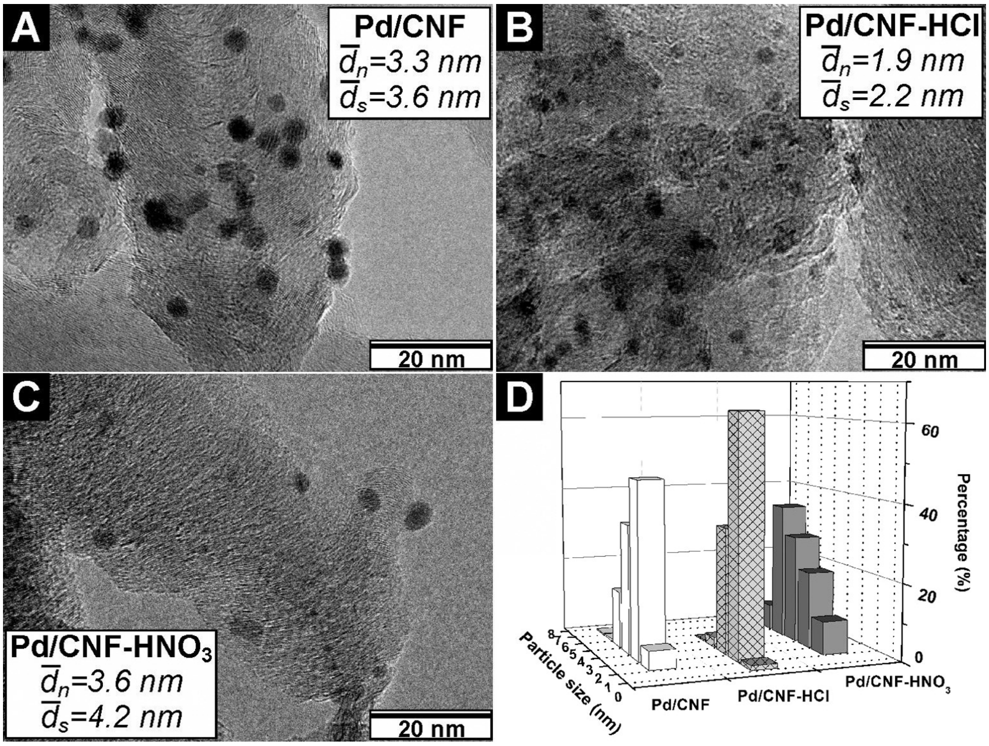

Fig. 4. TEM image of reduced Pd/CNF (A), Pd/CNF-HCl (B), Pd/CNF-HNO_3 (C) catalysts and Pd nanoparticle size distribution (D).

mineral acids ensues that Pd is present only on the surface of CNF. So, the changes in the surface chemistry of carbon materials have a substantial influence not only on the adsorption properties of the materials but also on the particle size of the active component as reported for activated carbons [27,47].

3.4. Catalytic hydrodechlorination of 1,2-DCB

The 1,2-DCB hydrodechlorination was carried out in a medium consisting of two immiscible liquid phases. The reactor contains a 50% (w/w) aqueous solution of KOH and an organic phase consisting

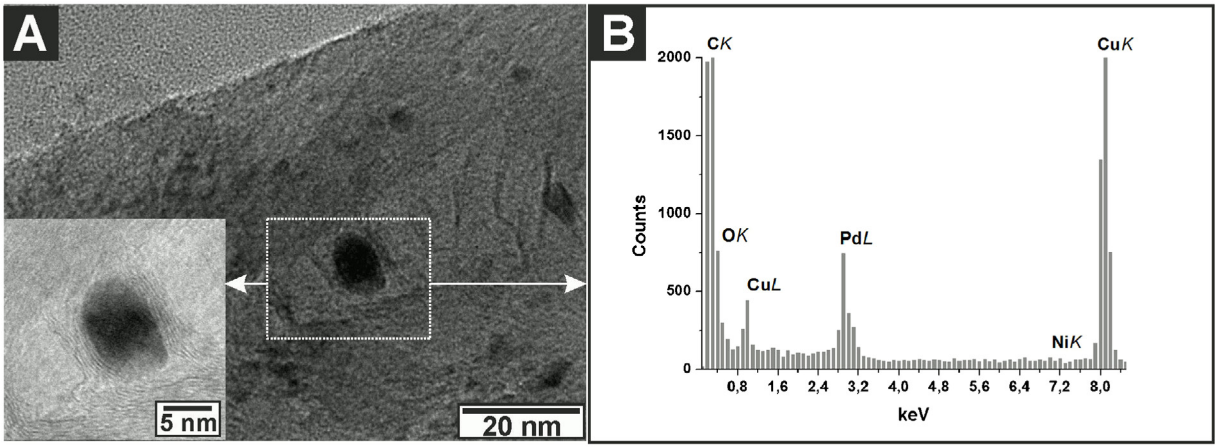

Fig. 5. TEM image (a) and EDX spectrum (b) of palladium particle in a CNF channel of Pd/CNF. Dash line indicates EDX analysis region.

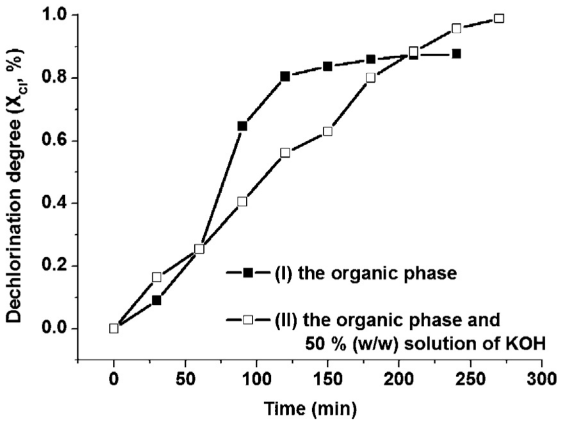

Fig. 6. The reaction medium of catalytic hydrodechlorination of 1,2-DBC.

of toluene, 2-propanol and 1,2-DCB. The presence of an alkali is necessary to bind the hydrogen chloride which forms in the course of the hydrodechlorination to prevent deactivation of the catalyst and possibly shifting the reaction equilibrium toward the formation of the products (Fig. 6). In the alkali-free organic medium the rate of the reaction was higher but a 100% conversion of 1,2-DCB could not be achieved. With the addition of a further portion of 1,2-DCB to the alkali-free reaction medium no hydrodechlorination was observed. The full loss in activity of the Pd/CNF was caused by the palladium being washed away into the reaction medium: 1.02 wt.% Pd before the reaction and 0.18 wt.% Pd after the reaction. In the reaction in the two-phase medium the decrease in the catalyst's content of palladium was inconsiderable from 1.04 wt.% to 0.93 wt.%. Therefore, even for a Pd:C–Cl molar ratio of 1:1000 the full conversion of 1,2-DCB reached after 4.5 h (Fig. 6).

It should be noted that in this reaction medium the catalyst based on untreated CNF was usually at the interface of the two phases as shown in Fig. 7. Such a behavior was also observed for the Pd/CNF-HCl catalyst but the granules of Pd/CNF-HNO_3 catalyst were located exclusively in the aqueous phase. It was not possible to make Pd/CNF-HNO_3 go to the organic phase even with an intense stirring of the reaction medium. Therefore for these experimental conditions treatment by nitric acid has a negative effect on the hydrodechlorination rate of 1,2-DCB (Fig. 8). Treatment of CNF in a 10% (w/w) solution of hydrochloric acid increases the activity of the palladium system and the 1,2-DCB dechlorination was fully complete within 30 min.

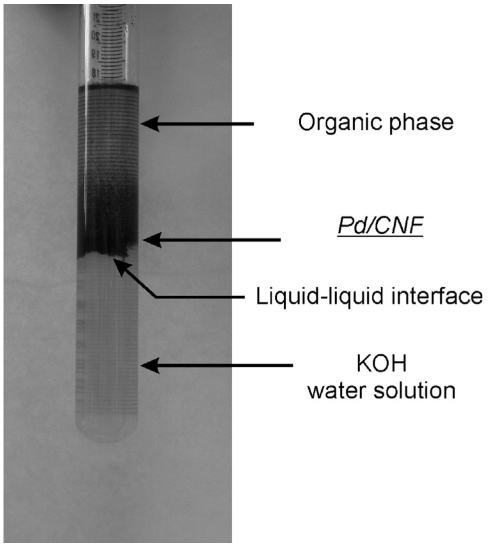

Fig. 7. The liquid-phase 1,2-DCB hydrodechlorination in different reaction medium: (■) the organic phase; (□) the organic phase and 4 mL 50% (w/w) solution of KOH. The organic phase: 4 mL 2-propanol, 7 mL toluene and 2.5 mL 1,2-DCB. Molar ratio of Pd:C–Cl = 1:1000. Temperature was 50 °C. Pressure of hydrogen was 0.1 MPa. Stirring rate was 1200 rpm.

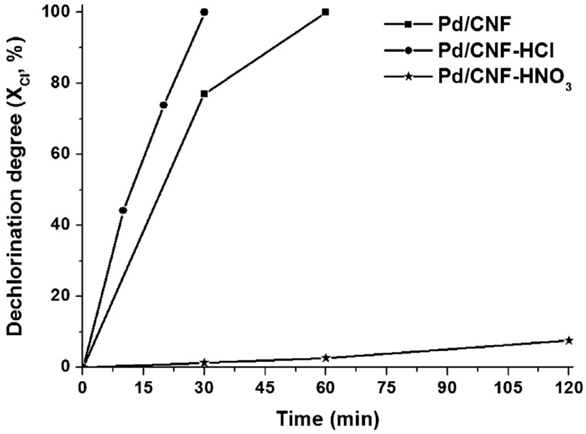

Fig. 8. The influence of acid treatment of the CNF on the activity of palladium catalysts in the liquid-phase hydrodechlorination of 1,2-DCB. Reaction medium: 4 mL 2-propanol, 7 mL toluene and 4 mL 50% (w/w) aqueous solution of KOH. The 1,2-DCB concentration was 0.2 mol/L. Molar ratio of Pd:C–Cl = 1:100. Temperature was 50 °C. Pressure of hydrogen was 0.1 MPa. Stirring rate was 1200 rpm.

Thus, our study of the hydrodechlorination of 1,2-DCB over Pd/CNF, Pd/CNF-HCl and Pd/CNF-HNO_3 catalysts has shown that treatment of nanofibrous carbons by inorganic acids has an influence on their activity (Fig. 8).

4. Discussion

Physicochemical properties of nanofibrous carbons have been studied before and after their treatment by nitric and hydrochloric acids. According to the chemical analysis data (Table 1) treatment by inorganic acids leads to the removal of nickel from the samples and the surface becomes enriched with oxygen-containing groups as is seen from Boehm titration (Table 2), TPD (Table 3) and IR spectroscopy data (Fig. 2). It can be suggested that functionalization of the pores surfaces leads to their narrowing and is the main reason for the decreased pore volume of the samples (Fig. 1) as was described in [48]. A second reason may be the blocking of channels by anions of the acids [49]. The presence of chlorine and nitrate-ions in the acid-treated CNFs was confirmed by the chemical analysis (Table 1) and IR spectroscopy (Fig. 2). It appears that these chloride- and nitrate-ions may fill the channels of the CNF and thus prevents active component precursor penetration into these channels at the stage of the catalyst synthesis. This explains the absence of palladium particles in the channels of the acid-treated CNFs (Fig. 4B and C).

The enrichment of CNF surfaces with oxygen-containing functional groups may be the reason for the differing dispersions of the active component in the Pd/CNF, Pd/CNF-HCl, Pd/CNF-HNO_3 catalysts (Fig. 4D). Thus, in Refs. [23,27] the particle size of palladium on activated carbon surfaces has been shown to be dependent on the content and nature of oxygen-containing functional groups, with the dispersion of the active component being strongly influenced by the carbon treatment conditions. [28]. According to TEM and chemisorption data [23] the dispersion of Pd increases as the surface becomes richer in weakly acidic oxygen-containing groups (phenolic, lactonic and carbonyl groups). At the same time, predomination on activated carbon surfaces of the more acidic phenolic and carboxylic groups, as in the case of 5.6 M HNO_3 treatment, shifts the particle size distribution to larger sizes. In our work, it

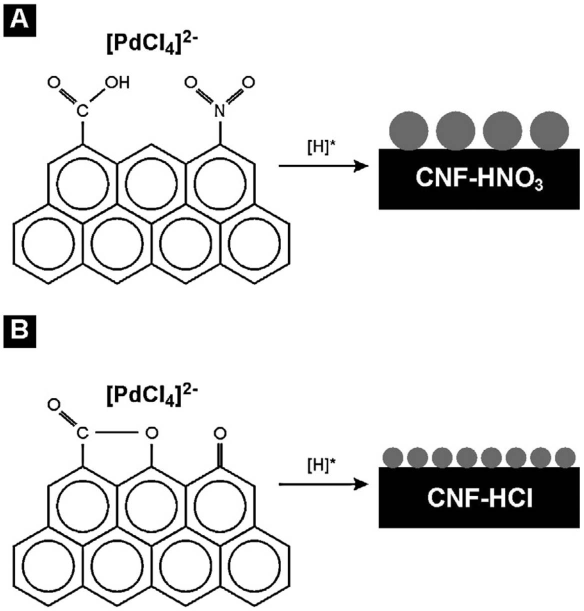

Fig. 9. Schematic representation of interactions between the oxygen surface groups and $[PdCl_4]^{2-}$ anion.

was found that the more acidic groups are present on the CNF surface the larger the size of the particles of the active component are formed. Thus, the Pd/CNF-HNO_3 catalyst shows the lowest values of Pt dispersion (Fig. 4D) and the highest concentration of strongly acidic surface groups (Tables 2 and 3) whose IR adsorption bands are observed in the regions 1730–1720, 1670–1570 and 1400–1340 cm^{-1} (Fig. 2). At the same time, the predominance of weakly acidic oxygen-containing groups (Tables 2 and 3) on the CNF-HCl surfaces leads to a higher dispersion of Pd in the Pd/CNF-HCl catalyst (Fig. 4D). The influence of surface functional groups nature on the active component dispersity may be explained by the electrostatic interaction between oxygen-containing groups and palladium anion ($[PdCl_4]^{2-}$) at the impregnation step, as described for platinum and palladium catalysts based on activated carbon [2,24,25]. When carbon surface has been enriched with strongly acidic oxygen-containing groups (acidic phenolic, carboxylic and nitro groups), electrostatic repulsion of $[PdCl_4]^{2-}$ anions from CNF-HNO_3 surface takes place. This leads to the formation of bigger palladium particles (Fig. 9). Enrichment of CNF-HCl surface by lactone and carbonyl groups increases electrostatic attraction $[PdCl_4]^{2-}$ anions with surface (Fig. 9). These groups act as anchoring centers hinter agglomeration and surface diffusion of the active component.

A detailed study of both the initial supports CNF, CNF-HCl, CNF-HNO_3 supports and the Pd/CNF, Pd/CNF-HCl, Pd/CNF-HNO_3 catalysts by physicochemical methods may help find reasons for their differing catalytic activities in the liquid-phase 1,2-DCB hydrodechlorination by molecular hydrogen in a water–organic liquid medium. Thus, the high activity of the Pd/CNF-HCl catalyst in the 1,2-DCB hydrodechlorination is, first of all, accounted for by a more highly dispersed state of the catalyst whose particle are located only on CNF-HCl external surfaces. Moreover, the high activity of the Pd/CNF-HCl catalysts in the liquid-phase hydrodechlorination of 1,2-DCB can be related the increased rate of the 1,2-DCB adsorption from the reaction medium and the decreased adsorption of 2-propanol (Table 4). This demonstrates an important role of the surface functional groups on the carbon in the adsorption processes during catalytic reactions carried out in a liquid phase as described for gas phase dechlorination of chlorobenzene and 1,3-dichlorobenzene over Pd and Ni [50,51].

The somewhat lower activity of the Pd/CNF system as compared with Pd/CNF-HCl may be explained by the fact that some of the palladium particles become blocked in the channels of the CNF, which makes them inaccessible to the reagents. At the same time, the low activity of the Pd/CNF-HNO_3 catalysts is determined not by the particle size of palladium but is the result of the hydrophilic character of its surface caused by a high concentration of acidic surface groups. As for palladium catalysts based on oxide supports Al_2O_3 and SiO_2 [3,33,52,53] hydrophobic organic compounds interact weakly with the hydrophilic surface of CNF-HNO_3 (Tables 2 and 3). Therefore, the CNF-HNO_3 and the Pd/CNF-HNO_3 catalyst mainly remain in the aqueous phase, as in the case of H_2O/hexane mixture [45]. The Pd/CNF-HNO_3 catalyst does not go to the organic phase even after an intense stirring. This makes the Pd/CNF-HNO_3 catalyst inaccessible for the 1,2-DCB molecules and the hydrodechlorination in the water–organic liquid medium does not take place (Fig. 8).

5. Conclusion

Physicochemical properties of CNF before and after their treatment by hydrochloric and nitric acid have been studied by chemical analysis, low-temperature adsorption–desorption of nitrogen, FTIR spectroscopy, Boehm titration and temperature-programmed desorption. Summing up the results for CNF, CNF-HCl, and CNF-HNO_3 obtained by different techniques it can be concluded that treatment of carbon nanofibers by inorganic acids leads to changes in (I) the content of impurities, (II) the concentration of the surface functional groups and (III) their textural characteristics (porosity and specific surface area).

Palladium catalysts based on CNF, CNF-HCl and CNF-HNO_3 have been prepared by incipient wetness impregnation from hydrochloric solutions of palladium chloride – $H_2[PdCl_4]$. It was shown that changes of the physicochemical properties of CNF occurring under the action of acids have a substantial influence on palladium activity in the liquid-phase hydrodechlorination of 1,2-dichlorobenzene. It was shown that palladium particles dispersion and their location, acidity of the CNF surface and its adsorption properties are the main factors determinated the efficiency of applied palladium catalyst. So, pretreatment of CNF by a hydrochloric acid leads to a higher dispersion of the active component and an increased rate of the 1,2-DCB adsorption from the reaction medium as compared with untreated Pd/CNF catalyst. This makes Pd/CNF-HCl the most active catalyst among Pd/CNF, Pd/CNF-HCl and Pd/CNF-HNO_3.

Acknowledgements

This work was supported by the Russian Foundation for Basic Research (grant nos. 10-03-00372 and 12-03-31517). The authors are thankful to A.V. Ischenko for the HR TEM study.

References

[1] E. Auer, A. Freund, J. Pietsch, T. Tacke, Appl. Catal., A 173 (1998) 259–271.
[2] F. Rodríguez-Reinoso, Carbon 36 (1998) 159–175.
[3] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A 173 (2001) 329–345.
[4] E.G. Furuya, H.T. Chang, Y. Miura, K.E. Noll, Sep. Purif. Technol. 11 (1997) 69–78.
[5] Z.M. de Pedro, E. Diaz, A.F. Mohedano, J.A. Casas, J.J. Rodriguez, Appl. Catal. B 103 (2011) 128–135.
[6] V.B. Fenelonov, M.S. Melgunov, N.A. Baronskaya, React. Kinet. Catal. Lett. 63 (1998) 305–312.
[7] V.B. Fenelonov, V.A. Likholobov, A.Yu Derevyankin, M.S. Mel'gunov, Catal. Today 42 (1998) 341–345.
[8] V.V. Shinkarev, V.B. Fenelonov, G.G. Kuvshinov, Carbon 41 (2003) 295–302.
[9] P. Serp, M. Corrias, P. Kalck, Appl. Catal., A 253 (2003) 337–358.
[10] G.G. Kuvshinov, YuI. Mogilnykh, D.G. Kuvshinov, D.Yu. Yermakov, M.A. Yermakova, A.N. Salanov, N.A. Rudina, Carbon 37 (1999) 1239–1246.
[11] T.V. Reshetenko, L.B. Avdeeva, Z.R. Ismagilov, V.V. Pushkarev, S.V. Cherepanova, A.L. Chuvilin, V.A. Likholobov, Carbon 41 (2003) 1605–1615.
[12] H.P. Boehm, Carbon 32 (1994) 759–769.

[13] P. Albers, K. Deller, B.M. Despeyroux, A. Schäfer, K. Seibold, J. Catal. 133 (1992) 467–478.
[14] J.L. Figueiredo, M.F.R. Pereira, M.M.A. Freitas, J.J.M. Órfão, Carbon 37 (1999) 1379–1389.
[15] W. Shen, Z. Li, Y. Liu, Recent Patents Chem. Eng. 1 (2008) 27–40.
[16] A. Derylo-Marczewska, B. Buczek, A. Swiatkowski, Appl. Surf. Sci. 257 (2011) 9466–9472.
[17] F. Yu, J. Ma, Y. Wu, J. Hazard. Mater. 192 (2011) 1370–1379.
[18] T. Karanfil, J.E. Kilduff, Environ. Sci. Technol. 33 (1999) 3217–3224.
[19] L. Li, P.A. Quinlivan, D.R.U. Knappe, Carbon 40 (2002) 2085–2100.
[20] B. Cabal, T. Budinova, C.O. Ania, B. Tsyntsarski, J.B. Parra, B. Petrova, J. Hazard. Mater. 161 (2009) 1150–1156.
[21] H. Tamon, M. Okazaki, Carbon 34 (1996) 741–746.
[22] D.J. Suh, P. Tae-Jin, I. Son-Ki, Carbon 31 (1993) 427–435.
[23] V.Z. Radkevich, T.L. Senko, K. Wilson, L.M. Grishenko, A.N. Zaderko, V.Y. Diyuk, Appl. Catal., A 335 (2008) 241–251.
[24] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, J. Hazard. Mater. 161 (2009) 842–847.
[25] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodríguez, Ind. Eng. Chem. Res. 44 (2005) 6661–6667.
[26] E.J.A.X. van de Sandt, A. Wiersma, M. Makkee, H. van Bekkum, J.A. Moulijn, Appl. Catal., A 173 (1998) 161–173.
[27] V.I. Simagina, O.V. Netskina, E.S. Tayban, O.V. Komova, E.D. Grayfer, A.V. Ischenko, E.M. Pazhetnov, Appl. Catal., A 379 (2010) 87–94.
[28] A.L. Dantas Ramos, P. da Silva Alves, D.A.G. Aranda, M. Schmal, Appl. Catal., A 277 (2004) 71–81.
[29] P. Albers, K. Deller, B.M. Despeyroux, G. Prescher, A. Schafer, K. Seibold, J. Catal. 150 (1994) 368–375.
[30] P. Albers, R. Burmeister, K. Seibold, G. Prescher, S.F. Parker, D.K. Ross, J. Catal. 181 (1999) 145–154.
[31] M. Gurrath, T. Kuretzky, H.P. Boehm, L.B. Okhlopkova, A.S. Lisitsyn, V.A. Likholobov, Carbon 38 (2000) 1241–1255.
[32] A.G. Gentsler, V.I. Simagina, O.V. Netskina, O.V. Komova, S.V. Tsybulya, O.G. Abrosimov, Kinet. Catal. 48 (2007) 60–66.
[33] G. Yuan, M.A. Keane, Appl. Catal. B 52 (2004) 301–314.
[34] S.L. Goertzen, K.D. Thériault, A.M. Oickle, A.C. Tarasuk, H.A. Andreas, Carbon 48 (2010) 1252–1261.
[35] A.M. Oickle, S.L. Goertzen, K.R. Hopper, Y.O. Abdalla, H.A. Andreas, Carbon 48 (2010) 3313–3322.
[36] C. Amorim, G. Yuan, P.M. Patterson, M.A. Keane, J. Catal. 234 (2005) 268–281.
[37] S. Brunauer, L.S. Deming, W.E. Deming, E. Teller, J. Am. Chem. Soc. 62 (1940) 1723–1732.
[38] G.R. Heal, L.L. Mkayula, Carbon 26 (1988) 803–813.
[39] L.B. Okhlopkova, A.S. Lisitsyn, V.A. Likholobov, M. Gurrath, H.P. Boehm, Appl. Catal., A 204 (2000) 229–240.
[40] B. Viswanathan, P. Indra Neel, T.K. Varadarajan, Methods of Activation and Specific Applications of Carbon Materials, National Centre for Catalysis Research, Indian Institute of Technology, Madras, 2009.
[41] U.J. Kim, C.A. Furtado, X. Liu, G. Chen, P.C. Eklund, J. Am. Chem. Soc. 127 (2005) 15437–15445.
[42] D.B. Mawhinney, V. Naumenko, A. Kuznetsova, J.T. Yates, J. Liu, R.E. Smalley, J. Am. Chem. Soc. 122 (2000) 2383–2384.
[43] R.A. Marcus, J.M. Fresco, J. Chem. Phys. 27 (1957) 564–568.
[44] D. Forney, W.E. Thompson, M.E. Jacox, J. Chem. Phys. 99 (1993) 7393–7403.
[45] T.G. Ros, A.J. van Dillen, J.W. Geus, D.C. Koningsberger, Chem. Eur. J. 8 (2002) 1151–1162.
[46] T.J. Bandosz, in: P. Serp, J.L. Figueiredo (Eds.), Carbon Materials for Catalysis, John Wiley & Sons, Inc., Hoboken, New Jersey, 2009, pp. 45–92.
[47] C. Prado-Burguete, A. Linares-Solano, F. Rodriguez-Reinoso, C. Salinas-Martinez de Lecea, J. Catal. 115 (1989) 98–106.
[48] A. Gil, G. de la Puente, P. Grange, Microporous Mater. 12 (1997) 51–61.
[49] H.P. Boehm, A. Vass, R. Kollmar, Proc. 18th Biennial Conf. on Carbon, July 19–24, 1987, pp. 86–87.
[50] S. Jujjuri, M.A. Keane, Chem. Eng. J. 157 (2010) 121–130.
[51] X. Wang, N. Perret, M.A. Keane, Chem. Eng. J. 210 (2012) 103–113.
[52] G. Yuan, M.A. Keane, J. Catal. 225 (2004) 510–522.
[53] W. Wu, J. Xu, R. Ohnishi, Appl. Catal. B 60 (2005) 129–137.