

# Effect of the Basic Surface Sites of Carbons on the Degree of Dispersion of Platinum Catalysts Prepared by $\text{H}_2\text{PtCl}_6$ Adsorption

A. N. Kholodovich<sup>a</sup>, P. A. Simonov<sup>a</sup>, R. I. Kvon<sup>a</sup>, A. V. Bukhtiyarov<sup>b</sup>,  
V. I. Zaikovskii<sup>a</sup>, Yu. A. Chesalov<sup>a</sup>, and A. V. Romanenko<sup>a</sup>

<sup>a</sup> Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia

<sup>b</sup> Novosibirsk State University, Novosibirsk, 630090 Russia

e-mail: spa@catalysis.ru

Received March 28, 2008

**Abstract**—In the synthesis of Pt/C catalysts via  $\text{H}_2\text{PtCl}_6$  adsorption onto a carbon support,  $\text{NH}_4\text{Cl}$  can be formed catalytically during the reduction of the precursor with  $\text{H}_2$  at 250°C. This compound favors the sintering of metal particles. This effect is likely due to the weakening of metal–support bonding because of  $\text{NH}_4\text{Cl}$  adsorption on the Pt surface. The sources of nitrogen and chlorine atoms are basic surface sites of the support, which contain nitrogen atoms in their structure and adsorb  $\text{Cl}^-$  ions from the precursor solution. This effect is typical of active carbons, whose surface contains chemically bound nitrogen as amino groups, and weakens as the Pt/N atomic ratio in the supported catalyst precursors is increased.

**DOI:** 10.1134/S002315840806013X

## INTRODUCTION

The conventional way of preparing Pt/C catalysts with a low metal content (5 wt % and below) is by  $\text{H}_2\text{PtCl}_6$  adsorption onto a carbon support (CS) followed by the reduction of the supported precursors in  $\text{H}_2$  at 250–350°C. It has been established to date that  $\text{H}_2\text{PtCl}_6$  adsorption proceeds via several pathways, namely, the reduction of Pt(IV) chloro complexes by carbon to Pt(II) and  $\text{Pt}^0$ , the formation of  $\pi$  complexes between Pt(II) chloride and surface  $>\text{C}=\text{C}<$  fragments of the carbon framework, and anion exchange on surface basic sites [1–3]. These processes are interrelated and take place in a certain order as the amount of adsorbed platinum per unit area of the surface increases [3]. Redox processes dominate at low amounts of  $\text{H}_2\text{PtCl}_6$  adsorbed [1, 3–5]. Since, at this stage, the amount of supported platinum is comparable with the amount of oxygen-containing functional groups on the CS surface, researchers' attention has been focused on the role of these groups in the formation of platinum catalysts. Most publications have been devoted to the cooperative effect of acid and neutral groups on the degree of dispersion of platinum in 1% Pt/C catalysts [6–13]. The data presented in these publications are summarized in our earlier article [14]. As for basic sites, we failed to find any study dealing with their role in the genesis of the active component of these catalysts.

Here, we report the effect of basic groups of the carbon surface on the degree of dispersion of supported

platinum catalysts. According to an earlier study [15], the basic sites of carbon materials can sorb anions both reversibly and irreversibly (as regards the action of  $\text{NaOH}$ ). The reversible binding of anions is typical of graphitelike materials. A considerable part of the same sites on amorphous carbons (active carbons and soot) is capable of irreversible sorption. In view of this, we selected two types of CSs for our study, namely, active carbons (ACs) of different origins and graphitelike carbon materials of the Sibunit family [16].

## EXPERIMENTAL

The commercial chemicals  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (pure grade),  $\text{HCl}$ ,  $\text{NH}_4\text{Cl}$ ,  $\text{Na}_2\text{CO}_3$  (all special-purity grade), and  $\text{AgNO}_3$  (analytical grade) were used in this study.

The CSs were the commercial Sibunit-family carbon materials Sib55P and Sib1562P (Institute of Hydrocarbon Processing, Siberian Branch, Russian Academy of Sciences, Omsk, Russia) and the active carbons CG-48A (Japan), Sutcliffe AR-2 (coconut, Sutcliffe Speakman Carbons Ltd.), and Norit SGM (peat charcoal, Norit). The ACs were deashed by boiling in 10%  $\text{HCl}$  followed by washing with water and drying. The Sibunit carbons were used as received.

The texture characteristics of CSs (Table 1) were determined by  $\text{N}_2$  adsorption at  $-196^\circ\text{C}$  using an ASAP 2400 instrument (Micromeritics).

Acidic and basic oxygen-containing groups on the CS surface were quantified by back titration with 0.1 M  $\text{NaOH}$  and  $\text{HCl}$  solutions as was suggested by Boehm

**Table 1.** Physicochemical properties of the carbon materials used in the preparation of the Pt/C catalysts

Carbon support	Texture characteristics*					Chemical properties**		
	$S_{\text{BET}}$	$S_{\alpha}$	$V_{\Sigma}$	$V_{\mu}$	$D, \text{\AA}$	$A_{\text{HCl}}$	$A_{\text{NaOH}}$	ash content, wt %
						$\mu\text{mol}/\text{m}^2$		
CG-48A	1105	17.2	0.538	0.511	14.5	0.347	0.274	1.0
Sutcliffe AR-2	1456	592	0.776	0.392	15.3	0.234	0.089	0.6
Norit SGM	1119	485	0.613	0.289	16.2	0.402	0.330	0.4
Sib55P	455	442	0.726	0.008	66.0	0.220	0.088	0.2
Sib1562P	590	542	0.860	-0.035	76.6	0.305	0.051	0.3

\*  $S_{\text{BET}}$  is the BET surface area derived from the initial portion of the  $\text{N}_2$  adsorption isotherm in the pressure range of  $P/P_0 = 0.05\text{--}0.20$ ;  $V_{\Sigma}$  is the total volume of the pores with a diameter of  $<110 \text{ nm}$ , which was determined from the amount of  $\text{N}_2$  adsorbed at  $P/P_0 = 0.98$ ;  $V_{\mu}$  and  $S_{\alpha}$  are the micropore volume and the specific surface area of the mesopores and macropores, respectively, as determined by a comparative method [26];  $D$  is the mesopore diameter calculated using the BET model as  $D = 4V_{\Sigma}/S_{\text{BET}}$ .

\*\*  $A_{\text{HCl}}$  and  $A_{\text{NaOH}}$  are, respectively, the HCl and NaOH adsorption capacities of the carbons in terms of the BET surface area.

[17]. The residual ash content of the carbons was determined gravimetrically after burning their samples at  $800^{\circ}\text{C}$ .

Sib1562P was chlorinated with  $\text{Cl}_2$  at  $100^{\circ}\text{C}$  for 4 h. According to XPS data, the chlorine atom content of chlorinated Sib1562P was  $1.4 \mu\text{mol}/\text{m}^2$  (3 wt %).

Pt/C catalysts containing 0.1–5 wt % Pt were synthesized using CS powders ( $<0.09 \text{ mm}$  size fraction for the ACs and  $0.09\text{--}0.2 \text{ mm}$  for the Sibunits) in a nitrogen atmosphere or in air. A CS was suspended in water at  $20^{\circ}\text{C}$  in a static reactor fitted with a magnetic stirrer. If necessary, the air was replaced with nitrogen. The required amount of  $\text{H}_2\text{PtCl}_6$  was added to the suspension in drops over 1 min under vigorous stirring. Upon contact between the  $\text{H}_2\text{PtCl}_6$  solution and carbon, the entire platinum was sorbed within 1–6 h; nevertheless, the suspension was left standing for 1–4 days. After the completion of the adsorption procedure, the suspension was carefully evaporated by pumping at  $60^{\circ}\text{C}$ , and the resulting carbon with adsorbed precursors was dried at  $100^{\circ}\text{C}$  to a residual pressure of 20 Torr. The adsorbed platinum compounds were reduced in flowing  $\text{H}_2$  ( $30 \text{ ml}/\text{min}$ ) in a flow reactor at  $150^{\circ}\text{C}$  for 1 h and at  $250^{\circ}\text{C}$  for 1 h. The temperature rise rate between these points was  $5 \text{ K}/\text{min}$ .

The overall chemical composition of the platinum compounds adsorbed on a CS was determined as the difference between the Pt (Cl) contents of the  $\text{H}_2\text{PtCl}_6$  solution before and after adsorption (before evaporation). The determination of the total chlorine content of the solution was described elsewhere [18]. Magnesium was added to the solution in order to bring all  $\text{Cl}^-$  ions into one state by breaking the platinum chloro complexes and precipitating Pt as black. The precipitate was separated by centrifugation. An aliquot of the resulting solution was titrated with a 0.1 N  $\text{AgNO}_3$  solution by the Mohr method. In the case of the complete sorption of platinum from the  $\text{H}_2\text{PtCl}_6$  solution,

the residual  $\text{Cl}^-$  content was determined by adjusting the pH of the equilibrium solution to pH 7–7.5 with  $\text{Na}_2\text{CO}_3$  or  $\text{HNO}_3$ .

The chemical state of the CS surface and the electronic state of adsorbed platinum were studied by XPS (VG ESCALAB HP spectrometer,  $\text{Al}K_{\alpha}$  radiation).

The compounds resulting from the reduction of Pt/C catalysts were identified by Fourier transform IR spectroscopy (BOMEM MB-102 spectrometer,  $4\text{-cm}^{-1}$  resolution).

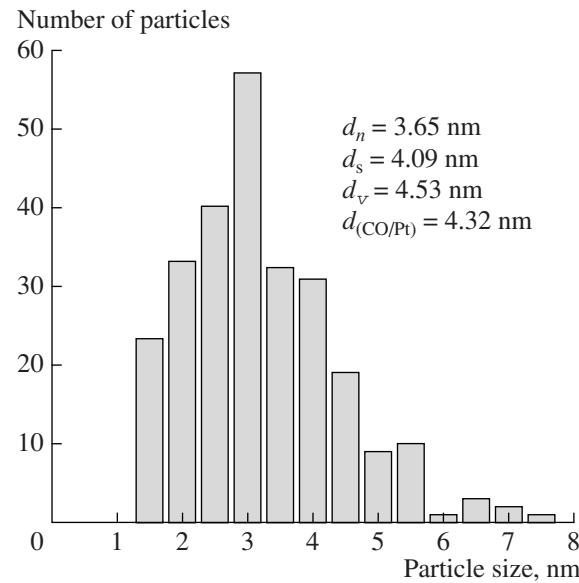
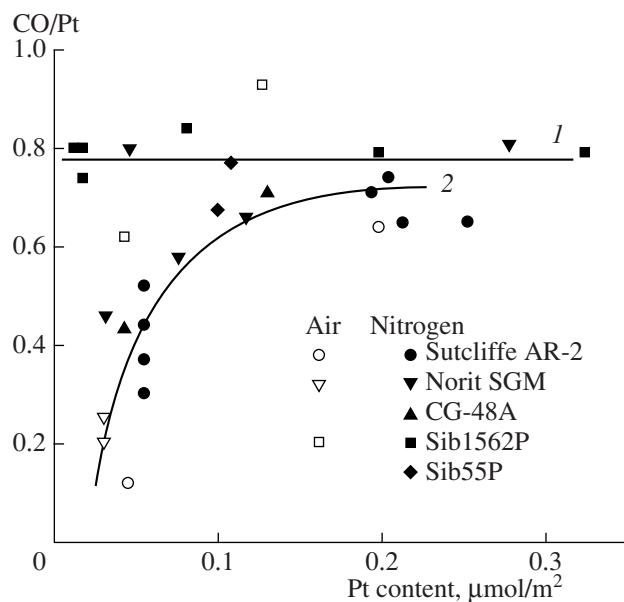
The size of the particles of adsorbed compounds and the size of Pt particles in Pt/C catalysts were determined by high-resolution transmission electron microscopy (HRTEM, JEM-2010 instrument, accelerating voltage of  $200 \text{ kV}$ , lattice resolution of  $1.4 \text{ nm}$ ) and by X-ray diffraction (XRD, HZG-4 diffractometer,  $\text{Cu}K_{\alpha}$  radiation).

The degree of dispersion of platinum in Pt/C catalysts was determined from CO chemisorption at  $20^{\circ}\text{C}$  using a pulse technique under the assumption that one surface Pt atom binds one CO molecule [19]. The degree of dispersion of Pt (CO/Pt) was converted into the apparent surface-average diameter ( $d_s, \text{ nm}$ ) of Pt particles using the formula  $d_s = 1.08/(\text{CO/Pt})$  [6], where CO/Pt is the degree of dispersion equal to the ratio of the number of adsorbed CO molecules to the total number of supported Pt atoms. The information derived from chemisorption data was verified by HRTEM examination of carbon samples containing supported platinum compounds.

## RESULTS AND DISCUSSION

### Platinum Content and Degree of Dispersion of Platinum in the Pt/C Catalysts

Figure 1 illustrates the effect of the supported platinum content on the degree of dispersion of platinum in the Pt/C catalyst for the two CS types. For the Sibunit



family, the degree of dispersion of platinum is high ( $\text{CO/Pt} = 0.78 \pm 0.10$ ) and is almost independent of the surface concentration of the metal. For the active carbons, the degree of dispersion of platinum is extremely low at low platinum concentrations, but, as the platinum concentration is increased, it increases up to values characteristic of Pt/Sibunit. In addition, there is a narrow range of Pt contents of active carbons (0.03–0.06  $\mu\text{mol}/\text{m}^2$ ) in which the CO/Pt values are widely scattered (from 0.13 to 0.80).

The above chemisorption data are in good agreement with HRTEM data (Fig. 2). Therefore, the observed low degree of dispersion of platinum in Pt/AC at  $[\text{Pt}_{\text{ads}}] < 0.15 \mu\text{mol}/\text{m}^2$  is due to the presence of coarse platinum particles in the samples and is not attributable to a decrease in CO chemisorption because of adsorbed impurities (S and others) blocking the platinum surface. The existence of large platinum particles on the AC surface can be explained by the formation of coarse precursor particles at the adsorption stage  $\text{H}_2\text{PtCl}_6$  and by the intensive sintering of Pt particles at the final stage of catalyst preparation, specifically, during the reduction of Pt particles in  $\text{H}_2$ . The latter can be favored by the specific features of the AC surface or by the presence of chemical impurities not typical of Sibunit supports.

#### State of Adsorbed Catalyst Precursors

XRD and HRTEM studies of the carbons containing adsorbed active-component precursors revealed that, throughout the platinum content range examined, these

precursors are finely divided: they are undetectable by the above methods both on the Sibunit supports and on the active carbons. According to XPS data, at  $[\text{Pt}_{\text{ads}}] < 0.15 \mu\text{mol}/\text{m}^2$ , most of these adsorbed precursors are platinum compounds characterized by  $BE(\text{Pt } 4f_{7/2}) = 72.3\text{--}72.6 \text{ eV}$ . For example, the mole fraction of these compounds in the Sutcliffe AR-2 sample containing  $0.0391 \mu\text{mol}/\text{m}^2$  (1.1 wt %) adsorbed platinum is close to 0.9. In the Sib1562P sample with  $[\text{Pt}_{\text{ads}}] = 0.129 \mu\text{mol}/\text{m}^2$  (1.46 wt %), the mole fraction of these compounds is ~0.8 (the rest are platinum compounds with  $BE(\text{Pt } 4f_{7/2}) = 73.9\text{--}74.9 \text{ eV}$ ). The dominant precursor may be  $\text{PtO}$  or the  $[\text{PtCl}_4]^{2-}$  complex [20]. The compound  $\text{PtO}$  can result from the oxidation of  $\text{Pt}^0$  clusters by air [19], and these clusters can result from the reduction of platinum ions by the CS surface upon  $\text{H}_2\text{PtCl}_6$  adsorption. Elution analysis demonstrated that the  $[\text{PtCl}_4]^{2-}$  ions bonded to the CS surface via ion exchange are desorbed under the action of 4 M NaCl [21]. It is most likely that the nonelutable residue is  $\text{PtO}$ . Elution data suggest that, for both types of CSs, the mole fraction of  $\text{PtO}$  in the total amount of adsorbed platinum compounds is ~0.5 for  $[\text{Pt}_{\text{ads}}] = 0.15 \mu\text{mol}/\text{m}^2$  and ~0.8 for  $[\text{Pt}_{\text{ads}}] = 0.05 \mu\text{mol}/\text{m}^2$ . Thus, when the total concentration of adsorbed platinum precursors is below  $0.15 \mu\text{mol}/\text{m}^2$ , their nature and proportions in the two types of supports are rather similar. Therefore, the low degree of dispersion of platinum in the Pt/AC samples at metal contents below  $0.15 \mu\text{mol}/\text{m}^2$  is due to some other factor accelerating the sintering of Pt clusters during the reduction of the catalyst in  $\text{H}_2$ . The strength of this factor declines as the amount of the adsorbed metal precursor increases. This factor does not show itself in the Sibunit-family supports.

**Table 2.** Amounts of heteroatoms on the surface of the initial carbon materials according to XPS data

Carbon support	N/C	O/C	Si/C	Cl/C	S/C	Na/C	Ca/C
Sutcliffe AR-2	0.0033	0.067	0.0017	0.0014	0.00044	—	0.00030
Norit SGM	0.0050	0.060	0.0010	0.0018	0.00033	—	—
Sib1562P	—	0.039	—	—	—	0.0044	—

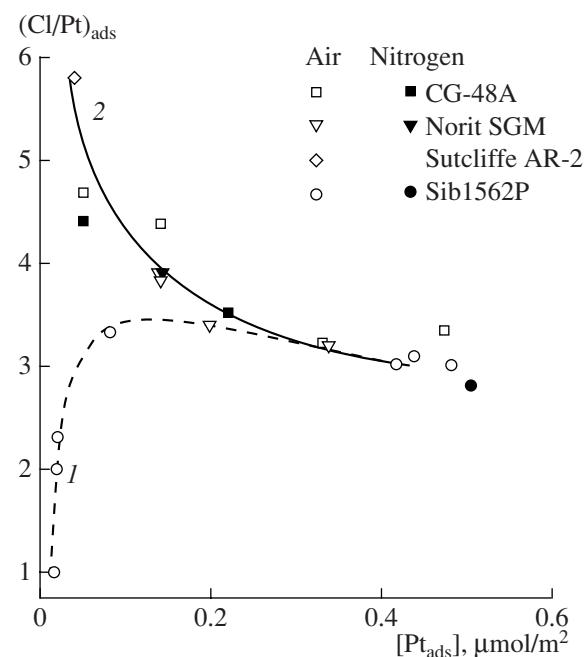
This phenomenon likely arises from the fact that the amount of Pt in the catalysts is comparable with the amounts of various impurities in the ACs. These impurities may be both “genetic” (inherited by the carbon from its organic precursor) and acquired during the synthesis of the catalyst. In the Sibunit-family supports, which are produced by the pyrolysis of gaseous hydrocarbons [16], the impurity level is low. Active carbons, whose precursors are of vegetable origin, usually contain metal compound impurities (primarily compounds of alkali and alkaline-earth metals) removable by acid washing, as well as chemically bonded heteroatoms (N, O, S, etc.). XPS data characterizing the amounts of various elements in the CSs examined are presented in Table 2. As distinct from Sib1562P, the active carbons Sutcliffe AR-2 and Norit SGM contain considerable amounts of nitrogen (0.189 and 0.372  $\mu\text{g-at/m}^2$ , respectively). The corresponding binding energy  $BE(\text{N } 1\text{s})$  is 400.7–400.8 eV, which is characteristic of nitrogen atoms in protonated amino groups [20]. The concentration of chemisorbed oxygen is at least one order of magnitude higher and is nearly the same for all of the ACs.

The presence of nitrogen and oxygen in the structure of the carbon matrix is believed to be due to the existence of anion-exchangeable basic groups on the carbon surface [17]. The carbons examined also contain significant amounts of these groups (Table 1). Figure 3 plots the  $(\text{Cl}/\text{Pt})_{\text{ads}}$  atomic ratio in adsorbed compounds as a function of the total platinum content per unit area of the AC surface. In the  $[\text{Pt}_{\text{ads}}] < 0.1 \mu\text{mol/m}^2$  region, in which  $\text{H}_2\text{PtCl}_6$  adsorption by carbon takes place mainly via the reduction of platinum complexes to  $\text{Pt}^0$ , the released  $\text{Cl}^-$  ions are coadsorbed with platinum. The ACs sorb larger amounts of  $\text{Cl}^-$  than Sib1562P. This is possibly due to the fact that these carbons differ in terms of the hydrolytic stability of the surface compounds between  $\text{Cl}^-$  and basic sites (see Introduction) and that the Sib1562P surface contains sodium compounds (Table 2) favoring hydrolysis.

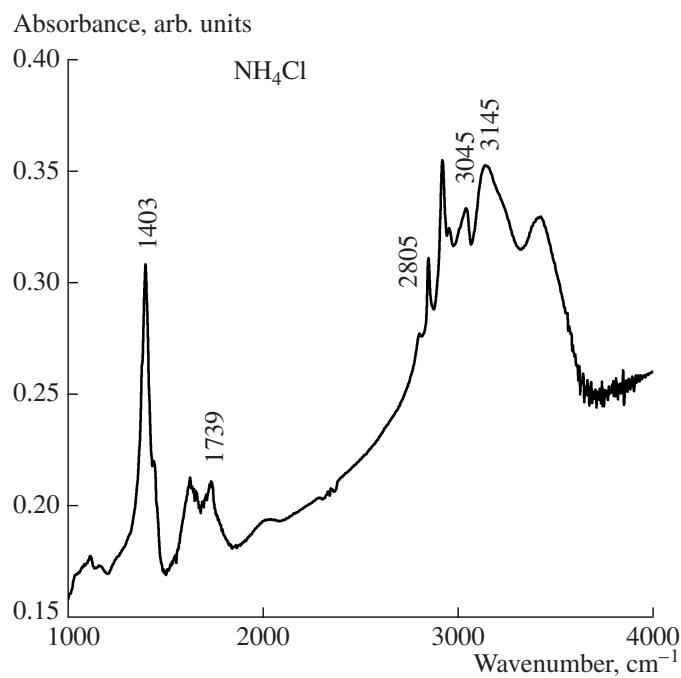
Thus, the adsorbed catalyst precursors in the two types of carbons are in similar physicochemical states, but their chemical environments on the AC and Sibunit surfaces are different.

#### *Role of Nitrogen and Chlorine Atoms Chemically Bonded to the Carbon Surface in the Sintering of Platinum Particles*

Analyses of gases evolved during the reduction of adsorbed platinum compounds with hydrogen demonstrated that, in the case of the activated carbons, HCl is released along with a volatile compound forming a white deposit in the cold zone at the reactor outlet. A qualitative  $\text{AgNO}_3$  test of this compound for the  $\text{Cl}^-$  ion was positive. Using IR spectroscopy, this compound was identified as  $\text{NH}_4\text{Cl}$  (Fig. 4). Only a little, if any,  $\text{NH}_4\text{Cl}$  formed as the initial AC containing HCl (adsorbed in the same way as  $\text{H}_2\text{PtCl}_6$ ) was calcined in  $\text{H}_2$ . Therefore, the presence of platinum compounds is a necessary condition for  $\text{NH}_4\text{Cl}$  formation. In view of this, it can be assumed that nitrogen in the structure of the carbon matrix and the chloride ions adsorbed on the carbon surface react with platinum in a hydrogen atmosphere and can exert an effect on the mobility of platinum clusters.



**Fig. 3.** Atomic ratio  $(\text{Cl}/\text{Pt})_{\text{ads}}$  in the adsorbed compounds as a function of the surface concentration of platinum  $([\text{Pt}_{\text{ads}}])$  on (1) Sibunit and (2) activated carbons. The atmospheres in which  $\text{H}_2\text{PtCl}_6$  was adsorbed onto the supports are specified in the legend.



**Fig. 4.** IR spectrum of the products desorbed by active carbons during the reduction of the platinum compounds adsorbed from  $\text{H}_2\text{PtCl}_6$  solutions. The bands due to  $\text{NH}_4\text{Cl}$  are labeled with their wavenumbers.

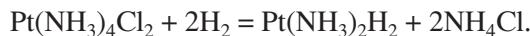
In order to elucidate the actual role of chloride ions in the sintering of platinum particles, we tested the following approaches: in the synthesis of catalysts, the  $(\text{Cl}/\text{Pt})_{\text{ads}}$  ratio in the adsorbed compounds was either increased by using chlorinated Sibunit as the CS or decreased by hydrolyzing the surface compounds with  $\text{Na}_2\text{CO}_3$ . The chloride ions were removed from the AC surface both immediately after  $\text{H}_2\text{PtCl}_6$  adsorption and after drying the samples by heating them in an aqueous  $\text{Na}_2\text{CO}_3$  solution. Next, the samples were washed with water, dried, and reduced with  $\text{H}_2$  according to a standard procedure. After the Pt/C samples containing  $\text{NH}_4\text{Cl}$  were calcined in  $\text{H}_2$ , the changes in their degree of dispersion were determined. Ammonium chloride was introduced by impregnation both into unreduced and into prereduced catalyst samples. The relevant experimental data are listed in Tables 3 and 4.

It is clear from the data presented in Table 3 that a lower degree of dispersion of the Pt particles on chlorinated Sib1562P is observed only at extremely low platinum concentration ( $<0.02 \text{ } \mu\text{mol}/\text{m}^2$ ), when the  $(\text{Cl}/\text{Pt})_{\text{ads}}$  molar ratio is  $\sim 100$  (samples 4 and 5). Raising the Pt content to  $0.042 \text{ } \mu\text{mol}/\text{m}^2$  causes the disappearance of this effect, although the  $(\text{Cl}/\text{Pt})_{\text{ads}}$  ratio remains rather large (sample 7). Data analysis for samples 5, 6, and 9–15 demonstrates that the decomposition of the surface compounds between carbon and chlorine by heating in an alkaline medium raises the degree of dispersion of supported platinum up to its maximum value and that this treatment is effective at any Pt/C catalyst

preparation stage preceding reduction in  $\text{H}_2$ . The treatment of the final catalyst with sodium carbonate exerts no effect on the degree of dispersion of platinum (Samples 16 and 17).

The data presented in Fig. 4 indicate that heating the high-dispersion Pt/C catalysts with supported  $\text{NH}_4\text{Cl}$  in  $\text{H}_2$  causes a marked decrease in the degree of dispersion of platinum (samples 1 and 2). Note that a similar heat treatment of these catalysts without  $\text{NH}_4\text{Cl}$  has no significant effect on the degree of dispersion of platinum. A substantial decrease in the degree of dispersion of platinum is observed after the support containing adsorbed precursors is loaded with  $\text{NH}_4\text{Cl}$  and is then reduced in  $\text{H}_2$  (sample 3). The decrease in the degree of dispersion of Pt results from the sintering of its particles rather from the poisoning of its surface by chloride ions or  $\text{NH}_4\text{Cl}$ . HRTEM studies of the initial Pt/C catalysts and the same catalysts calcined with  $\text{NH}_4\text{Cl}$  demonstrated coarsening of the metal particles. Furthermore, the treatment of the final samples with a hot  $\text{Na}_2\text{CO}_3$  solution in order to remove the residual chlorine or ammonium causes no significant change in the degree of dispersion of platinum in terms of CO chemisorption.

Thus,  $\text{NH}_4\text{Cl}$  resulting from the reduction of the platinum catalysts on active carbons is likely adsorbed by platinum clusters, thereby weakening their interaction with the carbon support surface and accelerating their sintering. A similar effect was observed for Pt/ $\text{Al}_2\text{O}_3$  catalysts [22]. It was demonstrated by HRTEM that the Pt/ $\text{Al}_2\text{O}_3$  catalysts are stable in an  $\text{H}_2$  atmosphere even at  $500^\circ\text{C}$ ; however, on being impregnated with an  $\text{NH}_4\text{Cl}$  solution, they undergo rapid sintering at  $320^\circ\text{C}$ . Further evidence of the adverse effect of  $\text{NH}_4\text{Cl}$  on the degree of dispersion of platinum was provided by studies in which the degree of dispersion of platinum in Pt/C catalysts prepared by impregnation of carbon with a  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2$  solution was found to be low ( $\text{CO}/\text{Pt} < 0.1$ ) for samples reduced with  $\text{H}_2$  without the predecomposition of the adsorbed platinum compounds in a flowing inert gas at  $350^\circ\text{C}$  [10, 23, 24]. However, the authors of those studies believe that the growth of the Pt particles is due to a hypothetical hydride having a high surface mobility:



Evidence against this mechanism of sintering is the fact that, using the chlorine-free complex  $[\text{Pt}(\text{NH}_3)_4](\text{OH})_2$  as the initial platinum compound, it is possible to obtain Pt/C catalysts with a degree of dispersion of 0.8–1.0 [25], although the formation of  $\text{Pt}(\text{NH}_3)_2\text{H}_2$  might seem thermodynamically more favorable because of the binding of protons into  $\text{H}_2\text{O}$ . In addition, we discovered that  $\text{NH}_4\text{Cl}$  accelerates the sintering of metal nanoparticles in Pd/C and Ni/C catalysts as well. Based on these facts, we think that the role of  $\text{NH}_4\text{Cl}$  in the sintering of supported metal catalysts is to cause an adsorption-induced weakening of metal-support adhesion.

**Table 3.** Effects of the chlorination of the Sib1562P surface and of the removal of chemisorbed chlorine from the carbon surface by treatment with  $\text{Na}_2\text{CO}_3$  at different stages of catalyst preparation on the degree of dispersion of platinum in the Pt/C catalysts

Sample no.	Carbon support	Pt content		Heating in a $\text{Na}_2\text{CO}_3$ solution*	CO/Pt
		wt %	$\mu\text{mol}/\text{m}^2$		
1	Sib1562P	0.15	0.013	—	0.80
2		0.19	0.017	—	0.80
3		3.60	0.325	—	0.79
4	Sib1562P/ $\text{Cl}_2$ (1.4 ( $\mu\text{mol Cl}/\text{m}^2$ ))	0.15	0.013	—	<0.20
5		0.18	0.016	—	0.23
6			0.016	After drying	0.62
7		0.48	0.042	—	0.98
8		3.36	0.302	—	0.90
9	Norit SGM	0.67	0.031	—	0.46
10		0.78	0.036	After drying	0.99
11	CG-48A	0.90	0.042	—	0.43
12		0.88	0.041	After drying	0.79
13	Sutcliffe AR-2	0.88	0.031	—	0.20
14		1.10	0.039	After the adsorption of $\text{H}_2\text{PtCl}_6$	1.00
15				After drying	1.00
16		1.51	0.054	—	0.27
17				After reduction with $\text{H}_2$	0.30

\* 85°C, 0.5 h,  $\text{Na}_2\text{CO}_3/\text{H}_2\text{PtCl}_6 = 4 : 1$  mol/mol.

**Table 4.** Effect of  $\text{NH}_4\text{Cl}^*$  on the degree of dispersion of platinum in Pt/C catalysts\*\*

Sample no.	Carbon support	[ $\text{Pt}_{\text{ads}}$ ], wt %	Degree of dispersion (CO/Pt)	
			initial samples	samples heated with $\text{NH}_4\text{Cl}$
1	Norit SGM	0.65	0.78	0.45
2	Sib1562P	5.2	0.80	0.60
3	Sib1562P	3.6	0.79***	0.10

\* N/Pt = 2 at/at;  $\text{NH}_4\text{Cl}$  was introduced by incipient-wetness impregnation.

\*\* Samples 1 and 2 were treated with  $\text{NH}_4\text{Cl}$  after reduction in  $\text{H}_2$  at 250°C for 1 h; sample 3 was treated with  $\text{NH}_4\text{Cl}$  immediately after precursor adsorption and drying and was then reduced.

\*\*\* Degree of dispersion of platinum in the catalyst obtained from these precursors without preimpregnation with an  $\text{NH}_4\text{Cl}$  solution.

## CONCLUSIONS

The low degree of dispersion and poor reproducibility of the Pt/AC catalysts prepared by  $\text{H}_2\text{PtCl}_6$  adsorption at a platinum content of  $<0.06 \mu\text{mol}/\text{m}^2$  is due to the catalytic formation of  $\text{NH}_4\text{Cl}$  during the reduction of supported platinum compounds with  $\text{H}_2$ . The sources of nitrogen and chlorine atoms are basic surface sites of the carbons, which can contain nitrogen atoms in their structure and adsorb  $\text{Cl}^-$  ions from precursor solutions. The resulting  $\text{NH}_4\text{Cl}$  accelerates the sintering of the platinum metal clusters and particles. A likely mecha-

nism of this sintering is  $\text{NH}_4\text{Cl}$  adsorption on the surface of the metal particles, which weakens the metal-support bonding. This causes an increase in the mobility of the particles. The sintering rate is high when the amount of the resulting  $\text{NH}_4\text{Cl}$  is comparable with the amount of supported platinum; that is, as the Pt/N ratio increases, the effect of  $\text{NH}_4\text{Cl}$  weakens. This is likely due to the decreasing  $\text{NH}_4\text{Cl}$  coverage of the metal particle surface. The poor reproducibility of the degree of dispersion of platinum in these catalysts likely arises from the fact that  $\text{NH}_4\text{Cl}$  is removed through sublima-

tion and entrainment with flowing hydrogen and these processes depend on various factors determining mass transfer, including the catalyst bed height in the reactor, the catalyst grain size, the pore structure of the support, the linear velocity of the gas in the bed, and the temperature gradient.

An efficient way of suppressing the adverse effect of the nitrogen-containing impurities in AC is to remove the chloride ions coadsorbed with the catalyst precursors by hydrolysis of their surface compounds.

### ACKNOWLEDGMENTS

This work was carried out under the governmental contract no. 02.513.11.3203, "Development of Technological Principles of Utilizing Nanosize Effects in the Creation of a New Generation of Nanostructured Catalysts for Commercially Significant Oxidation and Hydrogenation Processes."

### REFERENCES

1. Von Czaran, E., Finster, J., and Schnabel, K.H., *Z. Anorg. Allg. Chem.*, 1978, vol. 443, p. 175.
2. Van Dam, H.E. and van Bekkum, H., *J. Catal.*, 1991, vol. 131, p. 335.
3. Simonov, P.A. and Likhobov, V.A., in *Catalysis and Electrocatalysis at Nanoparticle Surfaces*, Wieckowski, A., Savinova, E.R., and Vayenas, C.G., Eds., New York: Marcel Dekker, 2003, p. 309.
4. Fu, R., Zeng, H., Lu, Y., Lai, S.Y., Chan, W.H., and Ng, C.F., *Carbon*, 1995, vol. 33, p. 657.
5. Simanova, S.A., Burmistrova, N.M., Lysenko, A.A., Shchukarev, A.V., Knyaz'kov, O.V., and Kuznetsova, T.V., *Zh. Prikl. Khim.*, 1999, vol. 72, no. 10, p. 1630 [Russ. J. Appl. Chem. (Engl. Transl.), vol 72, no. 10, p. 1722].
6. Prado-Burguete, C., Linares-Solano, A., Rodríguez-Reinoso, F., and Salinas-Martinez de Lecea, C., *J. Catal.*, 1989, vol. 115, p. 98.
7. Prado-Burguete, C., Linares-Solano, A., Rodríguez-Reinoso, F., and Salinas-Martinez de Lecea, C., *J. Catal.*, 1991, vol. 128, p. 397.
8. Kim, K.T., Chung, J.S., Lee, K.H., Kim, Y.G., and Sung, J.Y., *Carbon*, 1992, vol. 30, p. 467.
9. Coloma, F., Sepúlveda-Escribano, A., Fierro, J.L.G., and Rodríguez-Reinoso, F., *Langmuir*, 1994, vol. 10, p. 750.
10. Román-Martínez, M.C., Gazorla-Amorós, D., Linares-Solano, A., Salinas-Martínez de Lecea, C., Yamashita, H., and Anpo, M., *Carbon*, 1995, vol. 33, p. 3.
11. Torres, G.C., Jablonski, E.L., Baronetti, G.T., Castro, A.A., de Miguel, S.R., Scelza, O.A., Blanco, M.D., Peña Jiménez, M.A., and Fierro, J.L.G., *Appl. Catal.*, A, 1997, vol. 161, p. 213.
12. Fraga, M.A., Jordão, E., Mendes, M.J., Freitas, M.M.A., Faria, J.L., and Figueiredo, J.L., *J. Catal.*, 2002, vol. 209, p. 355.
13. Kang, M., Yoon, H.K., Kim, B.H., Song, M.W., and Lee, C.H., *React. Kinet. Catal. Lett.*, 2003, vol. 80, p. 139.
14. Kholodovich, A.N. and Simonov, P.A., *React. Kinet. Catal. Lett.*, 2006, vol. 89, p. 1.
15. Voll, M. and Boehm, H.P., *Carbon*, 1971, vol. 9, p. 481.
16. Yermakov, Yu.I., Surovikin, V.F., Plaksin, G.V., Semikolenov, V.A., Likhobov, V.A., Chuvilin, A.L., and Bogdanov, S.V., *React. Kinet. Catal. Lett.*, 1987, vol. 33, p. 435.
17. Boehm, H.P., in *Advances in Catalysis and Related Subjects*, Eley, D.D., Pines, H., and Weisz, P.B., Eds., New York: Academic, 1966, vol. 16, p. 179.
18. Simonov, P.A., Semikolenov, V.A., Likhobov, V.A., Boronin, A.I., and Ermakov, Yu.I., *Izv. Akad. Nauk SSSR. Ser. Khim.*, 1988, no. 12, p. 2719.
19. Bond, G.C. and Wells, P.B., *Appl. Catal.*, 1985, vol. 18, p. 221.
20. Nefedov, V.N., *Rentgenoelektronnaya spektroskopiya khimicheskikh soedinenii* (X-Ray Photoelectron Spectroscopy of Chemical Compounds), Moscow: Khimiya, 1984.
21. Kholodovich, A.N., Simonov, P.A., and Romanenko, A.V., *Tezisy dokl. V Ross. konf. "Nauchnye osnovy prigotovleniya i tekhnologii katalizatorov"* (Proc. V Russian Conf. on the Scientific Foundations of Catalysts Preparation), Omsk, 2004, p. 142.
22. Zhang, Z.C. and Beard, B.C., *Appl. Catal.*, A, 1999, vol. 188, p. 229.
23. Rodríguez-Reinoso, F., Rodríguez-Ramos, I., Moreno-Castilla, C., Guerrero-Ruiz, A., and López-González, J.D., *J. Catal.*, 1986, vol. 99, p. 171.
24. Moreno-Castilla, C., Porcel-Jiménez, A., Carrasco-Marín, F., and Utrera-Hidalgo, E., *J. Mol. Catal.*, 1991, vol. 66, p. 329.
25. Richard, D., Gallezot, P., Neibecker, D., and Tkachenko, I., *Catal. Today*, 1989, vol. 6, p. 171.
26. Karnaukhov, A.P., Fenelonov, V.B., and Gavrilov, V.Yu., *Pure Appl. Chem.*, 1989, vol. 61, p. 1913.