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Formation of active component particles in platinum catalysts on α- and γ-alumina

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The sizes of platinum particles in Pt/Al_2O_3 catalysts prepared by the impregnation of α- and γ-alumina with platinum nitrate solutions are determined by the composition of precursor solution and the calcination temperature, whereas the chemical state of an active component also depends on the crystal modification of alumina and its pretreatments.

The platinum-based catalysts are widely applied in the oil industry, the deep oxidation of hydrocarbons, organic synthesis, *etc.*[1–4] Alumina is a traditional support for the deposition of platinum nanoparticles.[5–9] A wide set of crystalline forms of Al_2O_3,[10] possibilities of its surface modification and the diversity of active component precursors make it possible to prepare Pt/Al_2O_3 catalysts with diverse characteristics and catalytic behaviors.[5,11–15] The detailed investigation of the mechanisms of formation of the active component particles and the factors affecting their interaction with the support is the key to developing the approaches to stabilize nanoparticles and to designing the highly active and highly stable catalysts. In this work we prepared a set of platinum catalysts supported on α- and γ-Al_2O_3. The samples were characterized by X-ray photoelectron spectroscopy (XPS), small angle X-ray scattering (SAXS) and high resolution transmission electron microscopy (HRTEM).

The platinum on alumina catalysts with different Pt particle sizes were prepared using published methods.[11] To prepare the catalysts with large platinum particles, predried α-Al_2O_3 (S_{BET} = = 12.2 $m^2\ g^{-1}$) and γ-Al_2O_3 (S_{BET} = 198 $m^2\ g^{-1}$) were wet impregnated with a dilute solution of commercial platinum nitrate with tetramethylammonium hydroxide (TMA). After drying, the samples were calcined at 600 °C for 2 h in air (Pt-8 set). To prepare the samples with small platinum particles (Pt-1 set), two sets of the supports were used. The first set included predried oxides. For the second set, predried supports were impregnated with glacial acetic acid for 24 h with the subsequent drying. Both of the support sets were then wet impregnated with a platinum nitrate solution. After drying, the samples were calcined at 400 °C for 4 h in air. The elemental analysis data showed that the Pt content of all samples was ~1 wt%. The results of HRTEM indicate that the application of TMA-stabilized Pt nitrate solution yields the samples with the mean sizes of platinum particles of about 8 nm, whereas pure nitrate solution provides considerably smaller Pt particles (mean size of $\leqslant$ 1.5 nm).

To study the influence of the preparation conditions on the chemical composition of the supports, blank experiments, in which the supports were treated with HNO_3 + TMA (original alumina supports) and HNO_3 (both original and acetic acid pretreated supports) solutions, were performed. Table 1 shows that the treatment of α-alumina with the solutions does not affect the surface composition. In the case of γ-Al_2O_3 under the given conditions, the surface is modified due to both the introduction of acetic acid residues and hydroxylation.

Table 1 XPS data for α-Al_2O_3 and γ-Al_2O_3 supports.

Sample	Atomic ratio	
	O/Al	$C_{carboxyl}$/Al
α-Al_2O_3 original	1.8	–
α-Al_2O_3/HNO_3 + TMA + H_2O	1.8	–
α-Al_2O_3/$AcOH_{glacial}$	1.8	–
α-Al_2O_3/$AcOH_{glacial}$/HNO_3 + H_2O	1.8	–
γ-Al_2O_3 original	1.9	–
γ-Al_2O_3/HNO_3 + TMA + H_2O	2.0	–
γ-Al_2O_3/$AcOH_{glacial}$	2.5	0.33
γ-Al_2O_3/$AcOH_{glacial}$/HNO_3 + H_2O	2.2	0.16

A similar behavior under alumina treatments with dilute HNO_3 was observed for various types of Al_2O_3.[16] For the supports treated with the TMA solution, nitrogen from the tetramethylammonium cation was detected by XPS. No N 1*s* peaks corresponding to the nitrate species were found in the samples of supports or catalysts.

The SAXS data [Figure 1(*a*)] evidenced the existence of rod-like particles in the initial platinum nitrate solution (Pt-NO_3) and the solution stabilized by TMA (Pt-TMA).[17] The data are well fitted by the model of polydisperse cylinders with a fixed diameter of 1.2 nm, similar for both solutions. However, the particles in the Pt-NO_3 solution have a larger size as compared with the Pt-TMA solution.

The next stage was the SAXS study of the supports after impregnation with the precursor solutions. The contrast technique was used for this purpose.[18] Under support impregnation with the precursor solution, the shape of platinum-containing particles changes. If the particles of ‘platinum nitrate’ in the solution have the oblong shape, they form compact particles best fitted by sphere distribution after deposition. For the comparison of the samples at each preparation step, the radius of gyration, a common parameter for SAXS studies, was applied.[17] In the sequence Pt-TMA–Pt-8(precursor)/γ-Al_2O_3–Pt-8/γ-Al_2O_3, the radius of gyration changed as follows: 2.0±0.1, 3.0±0.1 and 4.7±0.2 nm, respectively. Thus, the SAXS data show that a gradual enlargement of platinum particles is observed after deposition, drying and calcination [Figure 1(*b*)]. In case of the samples prepared from ‘platinum nitrate’ solution, a quite different process is observed. Thus, in the sequence Pt-NO_3–Pt-1(precursor)/γ-Al_2O_3–Pt-1/γ-Al_2O_3, the radius of gyration changed as follows: 3.1±0.1, 1.0±0.4 and 1.3±0.4 nm, respectively. Figure 1(*b*) shows a particle

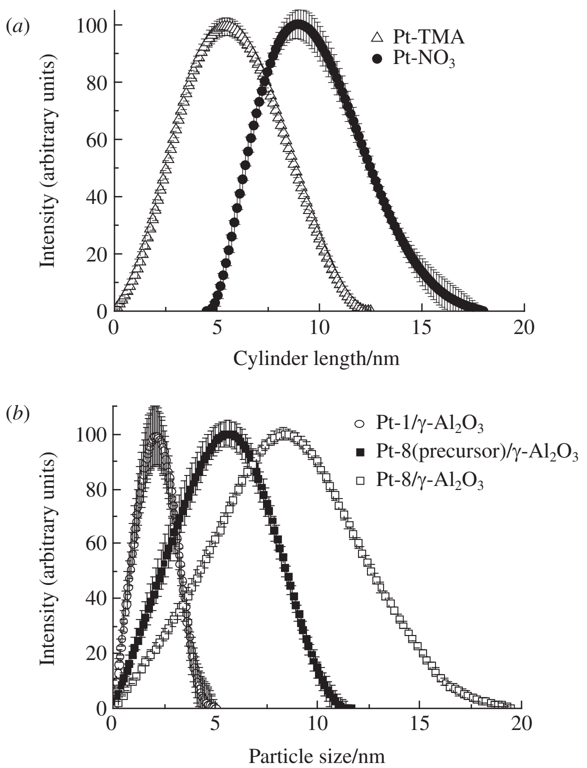

Figure 1 SAXS data: (*a*) cylindric particle length distribution for precursor solutions; (*b*) particle size distributions obtained for Pt-8/γ-Al_2O_3 sample after precursor deposition and for Pt-8/γ-Al_2O_3 and Pt-1/γ-Al_2O_3 after air calcination.

size distribution only for Pt-1/γ-Al_2O_3 since SAXS data taken for Pt-1(precursor)/γ-Al_2O_3 are rather noisy. Generally, the SAXS technique has low sensitivity to small particles (less than 3 nm). The formation of highly dispersed platinum from the 'platinum nitrate' precursor can be explained by the lower stability of Pt-contained complexes in Pt-NO_3 solutions in comparison with the solution stabilized by TMA. It can be assumed that the interaction of Pt-NO_3 solution with the support leads to the decomposition of these polynuclear species forming smaller particles with the mean size close to the diameter of the initial polydisperse cylinders in the impregnated solution.

According to the XPS data, in all impregnated non-calcinated samples, one state of platinum was found with a binding energy of 74.2–74.4 eV, which corresponds to Pt^{4+} in $Pt(OH)_4$.[19] As in the case of the corresponding supports, TMA nitrogen was found in Pt-8/α-Al_2O_3 and Pt-8/γ-Al_2O_3 samples. However, a detailed study showed no connection of this nitrogen with the platinum. The carboxyl groups were present on the surface of Pt-1/(Ac)/γ-Al_2O_3 after the precursor deposition, but they disappeared when heated.

Air calcination of the samples with impregnated precursor decreases the Pt/Al atomic ratio. This can be interpreted as the particle substance density increase in the course of precursor decomposition and the sintering of particles. This effect is manifested stronger in the samples heated at a higher temperature, which favors the sintering.

Calcination of all studied samples in air shifts the Pt 4*f* line by ~0.5 eV towards the lower binding energies (Figure 2 and Table 2). This state can be interpreted as Pt^{4+} in PtO_2.[19] For all samples other than Pt-1/γ-Al_2O_3, air calcination results in the partial reduction of platinum to Pt^0. For the Pt-1 samples on α-Al_2O_3, the Pt^{4+}/Pt^0 ratio does not depend on the support pre-treatment, whereas for γ-Al_2O_3 the pre-treatment with glacial acetic acid is of key importance. On the surface of Pt-1/γ-Al_2O_3, along with Pt^{4+}, the state of platinum with a Pt $4f_{7/2}$ peak binding energy of 72.5 eV corresponding to Pt^{2+} in PtO was found.[19]

According to the obtained data, the fundamental possibility to prepare the samples of Pt/Al_2O_3 catalysts differing greatly in the mean size of the active component particles is determined by

Table 2 HRTEM and XPS data for the catalysts after calcination in air.

Sample	Particle size/nm (HRTEM)	State portion		
		Pt^{4+}	Pt^{2+}	Pt^0
Pt-8/α-Al_2O_3[a]	8.1±2.1	~0.20	–	~0.80
Pt-8/γ-Al_2O_3	7.9±2.1	0.15	–	0.85
Pt-1/α-Al_2O_3	1.5±0.3	0.67	–	0.33
Pt-1/γ-Al_2O_3	1.5±0.3	0.68	0.32	–
Pt-1/(Ac)/α-Al_2O_3	1.2±0.3	0.67	–	0.33
Pt-1/(Ac)/γ-Al_2O_3	1.5±0.5	0.32	–	0.68

[a] Since the Pt 4*f* and Al 2*p* lines overlap, the low content of platinum in the absence of the 'shell' effect of active component distribution over the grain, typical of samples on γ-Al_2O_3, decreases the accuracy of the state ratio determination for this sample.

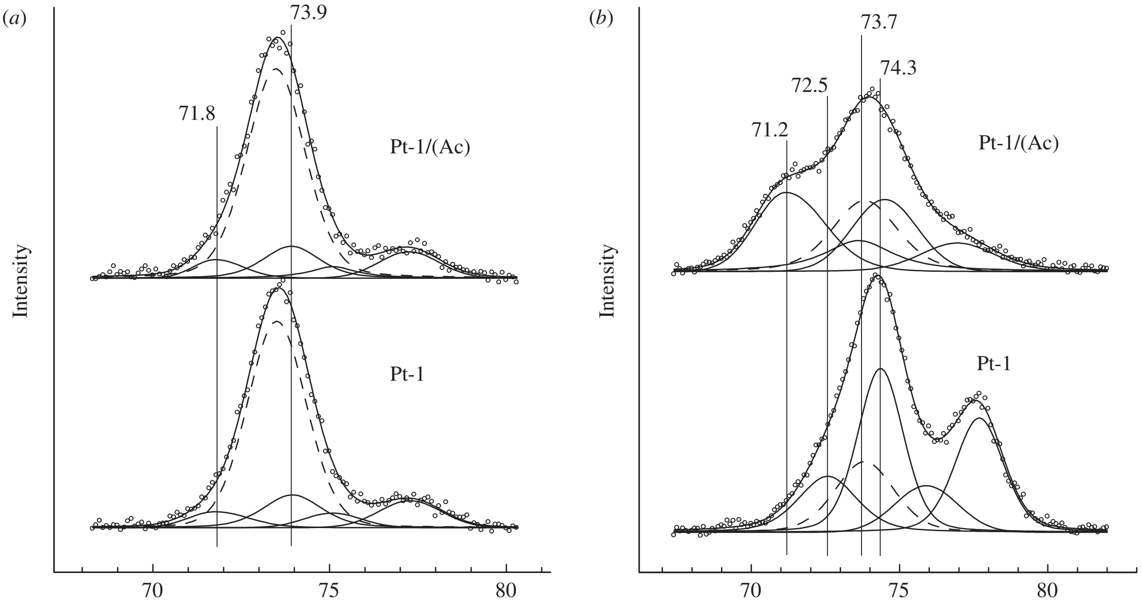

Figure 2 XPS spectra of Pt 4*f* (solid lines) + Al 2*p* (dashed lines) region of Pt-1 on (*a*) α-Al_2O_3 and (*b*) γ-Al_2O_3 after air calcination at 400 °C.

the composition of the impregnating solution. While interacting with the support surface, the polynuclear species originally formed in the solution as it is prepared get compact. The XPS data show that during calcination the supported particles sinter, which is corroborated by the SAXS data. Thus, the final particle size in the prepared catalyst is determined by the composition of the impregnating solution as well as by the sample calcination temperature, and it weakly depends on the nature of alumina.

The final chemical state of the active component and, consequently, its interaction with the support are determined by the conditions of the catalyst calcination and by the support nature, particularly, by the support susceptibility to the pre-treatments. Under calcination in the presence of oxygen, alumina is capable of stabilizing the ionic states of platinum in the small particles as well as possibly existing at the periphery of the large particles. The XPS data allow us to suppose that glacial acetic acid passivates the surface of γ-Al_2O_3 most likely by blocking the Lewis centers and serves as an interlayer that prevents the direct interaction of the precursor with the active centers on the support surface. A similar treatment of α-Al_2O_3 does not lead to the adsorption of the acidic residues on the surface of the inert modification of alumina; consequently, it does not have any effect over this support and, as a result, over the catalyst based on it. The obtained data give ground to the following arrangement of the used supports according to their ability to stabilize the ionic states of platinum: (Ac)/γ-Al_2O_3– α-Al_2O_3–γ-Al_2O_3. Thus, the features of the interaction of the active component with the support surface given by both the type of alumina and the support pre-treatment have a great influence on the active component oxidation/reduction and can affect the catalytic behavior of the systems and the sample thermal stability under the reaction conditions. The mobility of the chemical composition of γ-Al_2O_3 makes it possible to control the platinum support interaction in the course of catalyst preparation.

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