Synthesis and study of palladium colloids and related catalysts

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Abstract

Colloidal palladium particles were prepared by reduction with hydrogen of H_2PdCl_4 in a mixture of H_2O, trioctylamine (TOA), and cyclohexane. According to ^{14}N NMR, [35]Cl NMR and EXAFS data, the reduction of Pd was found to proceed under an auto-catalyzed regime via $(HTOA)_2[PdCl_4]$ complex formation. After complete reduction of Pd(II) (1 mol H_2 consumed per 1 Pd atom), H_2 consumption abruptly changed to 0.7 H_2 mol per 1 Pd atom. Unusually large amounts of H_2 adsorbed per Pd-atom could be due to the formation of palladium hydride by highly dispersed and defected Pd particles. TEM shows that Pd particles in catalysts obtained by metal particles deposition on carbon material Sibunit look like ''hedgehogs'' with needles 100 Å long and 20–40 Å in diameter. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The use of solutions of pre-synthesized metal nanoparticles makes it possible to prepare highly active catalysts and to investigate mechanisms of the catalytic reactions. Modern research methods allow for the process of nanoparticle formation to be studied at the molecular level. For this reason, numerous studies in the field have been recently reported. Nanoparticles are formed upon reduction of salts of the corresponding metals with a number of reductants in the presence of substrates, which stabilize the colloidal particles in the solutions. Surfactants (amines, phosphines [1,2]) or solutions of polymers [3] can be used as the stabilizers. The present work was aimed at studying the process of formation of Pd nanoparticles during reduction of Pd(II) with hydrogen gas in the presence of trioctylamine (TOA). The approach was the same as that we used before [4,5] for studying hydrolysis of Pd(II) in aqueous solutions but using a number of complementary up-to-date physicochemical techniques.

Experimental

Samples were prepared by mixing cyclohexane (c-C_6) in a calculated amount and triocty-

lamine (TOA) with an aqueous H_2PdCl_4 (0.1–0.2 M) solution. The component ratio was varied to study the process of formation of colloidal particles. From the outset, a three-phase mixture (aqueous H_2PdCl_4 solution–TOA–c-C_6) is formed, in which Pd(II) is dissolved in water. As palladium is reduced by hydrogen at room temperature and ambient pressure, a colloid solution of Pd(0) in the organic phase is formed. The process is controlled based on the hydrogen absorption. ^{35}Cl and ^{14}N NMR spectra were recorded using a MSL-400 Bruker spectrometer. EXAFS spectra at the K-side of palladium were recorded by the EXAFS Station of the Siberian Center of Synchrotronic Radiation and processed using the EXCURV92 software.

Three methods were used for synthesizing catalysts:

1. Synthesis of metal colloids followed by transferring the organic solution of them onto a support;
2. Introduction of a support into a mixture of c-C_6 and TOA with the aqueous H_2PdCl_4 solution prior to the reduction;
3. Reduction of the aqueous H_2PdCl_4 solution in the presence of a support.

Carbon material Sibunit ($S = 360$ m^2/g) and SiO_2 ($S = 250$ m^2/g) were used as supports. Catalysts were tested in the reaction of cyclohexene hydrogenation and studied using TEM (a JEM-100 CX microscope) and XRD (a HZG-4C apparatus, CuK_a beams) techniques.

Results and discussion

Processes proceeding in the Pd(II)–TOA–c-C_6–H_2 system can be classified into two groups: (1) interaction of Pd(II) complexes with the solution constituents, and (2) reduction of Pd(II) to metal. The extraction of Pd(II) from the aqueous solution into the organic phase was established to proceed faster by an order of magnitude than the reduction of Pd(II), the process

kinetics being independent of whether the reduction occurred in the H_2O–TOA–c-C_6 medium or in the organic phase comprising extracted Pd(II) compounds separated from the aqueous phase. When stirring the reaction was stopped, practically all palladium transferred from the aqueous phase to the organic one as soon as the hydrogen uptake started. The data obtained allow the statement that majority of colloidal Pd particles were formed upon reduction of Pd(II) compounds in the organic phase.

From the ^{35}Cl NMR data, there is almost zero concentration of unbounded Cl^- ions in both the aqueous phase of the Pd(II) solutions and in the H_2O–TOA–c-C_6 medium. Notice that the quadrupole ^{35}Cl nucleus does not produce a signal at non-symmetrical solvating, i.e., Cl^- ions are not detected in the spectra recorded for a HCl solution in c-C_6. However, the addition of water into such a solution results in the redistribution of Cl^- ions between the organic and aqueous phases that makes it possible to determine the concentration of Cl^- ions from the ^{35}Cl NMR spectra of the aqueous phase. We determined the concentration of Cl^- ions in the solution modeling elimination of one Cl^--ligand of Pd (HCl_{aq}–TOA–c-C_6) to show that the ions were distributed at the ratio of 7:3 between the aqueous and organic phases, and the substitution for Cl^--ligands of the $[PdCl_4]^{2-}$ complex had to result in a remarkable concentration of Cl^- in the aqueous phase.

From the ^{14}N NMR data, no N atom was detected in the internal coordination sphere of palladium but the only peak at c.s. -307.3 ppm was observed corresponding to the nitrogen constituent of TOA molecules in the c-C_6 medium. Again, no EXAFS signal was observed for nitrogen atoms in the first coordination sphere of palladium ($d = 2.1$ Å [6]) and for Pd–Pd distances which would argue the formation of polynuclear complexes. Hence, the organic phase is assumed to comprise palladium in the form of $(HTOA)_2[PdCl_4]$ complex with the ionic bond between the internal and external spheres. Thus, the equation for extraction of
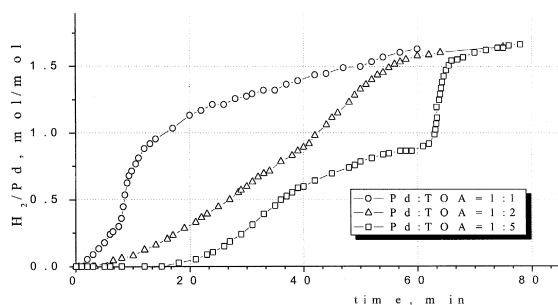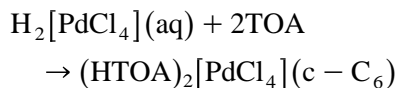
Fig. 1. Kinetic curves for reduction of Pd^{2+} to Pd^0 in the $(H_2[PdCl_4]H_2O)$–TOA–c-C_6 system.

Pd(II) from the aqueous phase to the organic phase can be written as

$$H_2[PdCl_4](aq) + 2TOA$$
$$\rightarrow (HTOA)_2[PdCl_4](c - C_6)$$

Kinetic curves for reduction of Pd^{2+} to Pd^0 in the $(H_2[PdCl_4]H_2O)$–TOA–c-C_6 system are plotted in Fig. 1.

The autocatalytic nature of the reaction is seen from the curves: reduced palladium atoms behave as catalysts for reduction of Pd^{2+}. At the early stage, 1 mol H_2 per palladium atom is absorbed that corresponds to reduction of all Pd^{2+} ions to Pd^0. Then the colloidal palladium particles are saturated with hydrogen in the amount of 0.7 mol H_2 per palladium atom. The curves shown in Fig. 1 were plotted at different TOA:Pd ratios; they demonstrate an increase in the Pd reduction rate with a decrease in the TOA concentration. The reason is that the surface of Pd particles becomes more accessible to reactants and can grow. When the TOA:Pd ratio is low, the processes of Pd(II) reduction and hydrogen absorption by the particles proceed concurrently. Notice that even higher rate of hydrogen absorption is observed for the reduction in the absence of TOA.

Absorption of abnormally high amount of H_2 by palladium metal observed in this case is accounted for by the high dispersion and defectiveness of the generated Pd particles (from the XRD data, the coherent scattering region is not more than 30 Å for the Pd particles). As a result, H atoms can migrate into subsurface layers of the particle crystal structure and be stabilized in octahedral voids of the lattice, which are inaccessible in the case of the bulky metal. Adsorption of H_2 on the Pd particle surface is thought to be another reason for excessive hydrogen absorption.

Low values of the coordination numbers of Pd and high Debay–Waller factors (compared to those of the bulky metal) obtained by EXAFS for nanoparticles (see Table 1) argue a high level of disordering of the crystal lattice of Pd nanoparticles.

The samples are: Pd nanoparticles after reduction (a) and following passing helium through the solution (b), bulky Pd (c).

It is seen from Table 1 that the lattice constants of Pd nanoparticles formed (sample a) are higher for that of bulky palladium. The interatomic distance (2.80 Å) corresponds to that of palladium b-hydride $PdH_{0.7}$ [7]. After helium was substituted for hydrogen (sample b), the lattice constants decrease to those characteristic of the bulky metal (sample c). The sorption of hydrogen by palladium accompanied by variation in the lattice constants is reversible and can be repeated by alternating flowing hydrogen and helium.

Table 1

EXAFS data of the samples of Pd nanoparticles after reduction (a), reduction and following passing helium through the solution (b), bulky Pd (c)

Sample	Interatomic distances, Å	Coordination number	Debay–Waller factor
a	2.80	7.8	0.015
	3.94	3.4	0.025
	4.90	6.9	0.028
	5.65	6.8	0.023
b	2.74	7.7	0.014
	3.83	3.8	0.027
	4.78	4.7	0.019
	5.52	6.8	0.031
c	2.71	12.0	0.010
	3.82	6.0	0.019
	4.71	24.0	0.014
	5.59	12	0.021

From TEM data, Pd particles in catalysts prepared by adsorbing the products of Pd(II) reduction from cyclohexane on Sibunit are needles of ca. 300 Å length and 20–40 Å diameter (Fig. 2). Aggregates formed by intergrowing needle-like particles look like ''hedgehogs''. During the growth of these crystals, TOA molecules are assumed to sorb on edges and planes of primary palladium microcrystals to block them but to leave free two opposite crystal planes where the growth proceeds (due to reduction of dissolved Pd(II) complexes) until the reduction of Pd(II) stops.

If Sibunit or SiO_2 is introduced into the reaction mixture before the reduction starts, dispersed spherical Pd particles of 20–30 Å diameter are formed (Fig. 3). In this case, the growth of metal particles is restricted by both blocking them with TOA molecules and by the porous structure of the support surface. When catalysts are synthesized in the same manner except introduction of TOA into the reaction mixture,
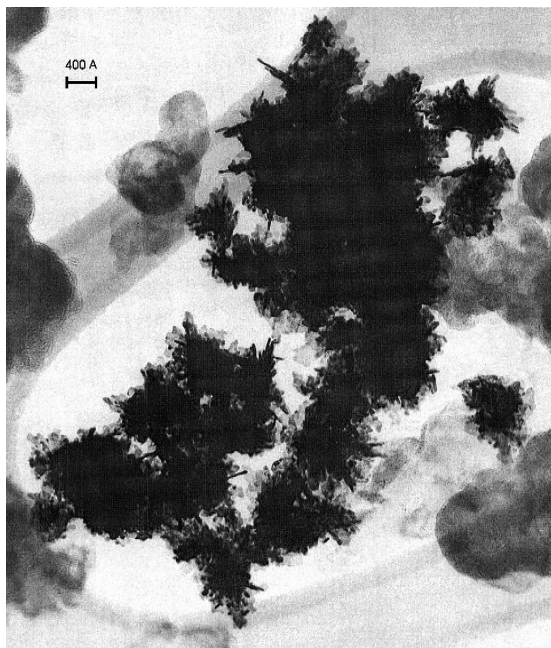

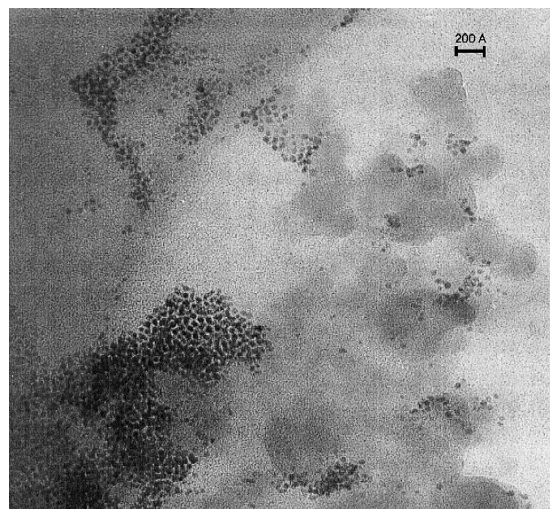Fig. 3. TEM-photo of the products of Pd(II) reduction formed in the presence of SiO_2.

Fig. 2. TEM-photo of the products of Pd(II) reduction adsorbed from cyclohexene by Sibunit.

both dispersed particles with a wide-size distribution (10–15 Å) and facet Pd crystals of 300 Å diameter are formed on the support surface because the crystals grow at uncontrollable high rate. This fact is an evidence of the crucial role of TOA during the formation of Pd nanoparticles.

The catalysts which were synthesized based on the nanoparticles reveal a high activity due to their high dispersion level. Approximately equal activities to hydrogenation of cyclohexene were observed for the catalysts comprising needle-like palladium metal particles and for those with spherical particles (8.51 and 8.93 min^{-1}, respectively). These activities are noticeably higher than that of the catalyst synthesized through reduction of H_2PdCl_4 with hydrogen in the absence of TOA (4.49 min^{-1}).

Conclusions

The method for catalyst preparation based on synthesis of dispersed metal particles in solution allows for the influence of nature of supports on the catalytic properties to be studied due to the

fact that precursors of the active component, pre-synthesized metal particles, can be introduced in the form independent of the support nature into the catalyst.

Acknowledgements

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