Preparation of Noble-Metal Colloids in Block Copolymer Micelles and Their Catalytic Properties in Hydrogenation

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Monometallic and bimetallic colloids were prepared in micelles of the block copolymer polystyrene-*b*-poly-4-vinylpyridine in toluene and analyzed by electron microscopy and various techniques of X-ray analysis. These metal colloids were studied in hydrogenation of cyclohexene, 1,3-cyclooctadiene, and 1,3-cyclohexadiene. A strong influence of the synthetic pathway to the colloids and the type of reducing agent on the catalytic activity of the colloids was found. The lowest activity was observed for $N_2H_4 \cdot H_2O$ reduction which is related to a morphology where only a small number of noble-metal colloids is embedded in the micelle core. The highest activity was obtained for the super-hydride reduction where the data suggest the existence of many metal clusters per micelle. The bimetallic Au/Pd colloids with metal ratios 1/5, 1/4, and 1/3 show the highest activity in hydrogenation of cyclohexene to cyclohexane. The Pd monometallic and Au/Pd bimetallic colloids are also rather selective catalysts (both in the homogeneous and a heterogeneous modification), as shown by the hydrogenation of 1,3-cyclooctadiene and 1,3-cyclohexadiene to the corresponding cycloalkenes.

Introduction

In recent years, the interest in the synthesis and properties of colloidal metal particles and metal clusters has constantly grown because of their unique properties, and great expectations develop for the application of metal colloids as catalysts, ferrofluids, and semiconductors.[1−3] For the noble-metal colloids, the interest mainly focuses on catalytic applications.[3] The advantages of colloidally dispersed noble metals are advantages of colloidal particles in general: they have huge surfaces, and they exhibit unique activities and spectroscopic features due to the size quantization of most electronic properties.

Formation of metal colloids is however still far from being sufficiently well handled, and two main problems remain in the synthesis of metal colloids. On one hand, it is still a desired goal to control the growth of metal particles in terms of particle size, particle size distribution, and structure of the particles, since these quantities influence the material properties. On the other hand, stabilization of the colloids is also far from being ideal, and quantities such as durability in catalytic reactions are directly related to more efficient particle stabilization.

Consequently, a variety of methods for the preparation and stabilization of metal colloids exists, the advantages and disadvantages of which were discussed in detail elsewhere.[4] One very promising strategy was recently developed by some research teams, including us, dealing with a formation of metal particles in block copolymers.[4−16] Semiconductor nanoparticles (CdS, PbS) in ionomer block copolymer micelles were synthesized and characterized in the group of Eisenberg.[13,14] An elegant preparation of nanoparticles in segregated blocks of copolymers in solid was described by Schrock and Cohen and co-workers in refs 6−8. The formation of gold colloids in thin films of block copolymers under the electron beam was thoroughly studied by Möller's group.[11,12] At the same time we have elaborated the synthesis of noble-metal nanoparticles in block copolymer micelles derived from polystyrene−poly(4-vinylpyridine) (PS-*b*-P4VP) in selective solvents.[4,5] Here, the

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micellar cores can be considered as a nanoreactor for metal colloid formation. By using gold colloids as a model, it was found that the particle size depends on the micelle size and the molar ratio Au:N, but it is mainly controlled by the type of the reducing agent applied. In all cases, the stability of the formed colloids turned out to be very high, which is directly related to the stability of the block copolymer micelles. This stability was provided by the location of metal colloids in micelle cores. Mayer and Mark[15,16] developed the preparation of noble-metal colloids in the corona of some block copolymer micelles with PS cores and have studied their activity in hydrogenation.

In this paper we focus on the relation between inner structure of Pd colloids synthesized in block copolymer micelles and their catalytic behavior in the hydrogenation of some substrates. In addition, we will present for the first time the use of block copolymer "nanoreactors" for preparation of bimetallic colloids and on the dependence of the catalytic properties on the type of doping metal and conditions of catalyst preparation.

Experimental Section

The synthesis of PS-*b*-P4VP block copolymers via anionic polymerization and their characterization by NMR, GPC, and dynamic light scattering (DHL) were performed as described in ref 17. For the preparation of metal colloids, two different PS-*b*-P4VP block copolymers were chosen: PS-1,2, which has $M_n = 127\,400$; $M_w = 149\,000$; $U = 1.17$; and a relative 4-VP content of $X_{4-vp} = 0.216$; and PS-3,4, which is characterized by $M_n = 19\,400$; $M_w = 22\,500$; $U = 1.16$; $X_{4-vp} = 0.340$. PS-1,2 forms big, strongly segregated micelles with a hydrodynamic radius r_h(DLS) = 77 nm, while PS-3,4 shows a weakly segregated, smaller micellar structure with r_h(DLS) = 32 nm.

$HAuCl_4{\cdot}3H_2O$, Na_2PdCl_4, $Pd(CH_3COO)_2$, Pd/C (1% of Pd), and the different solvents were obtained from Aldrich and were used as received. Cyclohexene (99%), 1,3-cyclohexadiene (97%), and 1,3-cyclooctadiene (95%, Aldrich) were freshly distilled prior to use. $[Rh(CO)_2Cl]_2$ was prepared by the method described in ref 18. $K[Pt(C_2H_4)Cl_3]{\cdot}H_2O$ was synthesized according to ref 19.

Preparation of Metal Colloids in Block Copolymer Micelles. Block copolymer micelles containing Pd, Pt, Rh, and Au colloids were synthesized by the method described in our earlier publication.[5] Solutions of PS-*b*-P4VP were prepared in a spectral grade toluene. Metalation of micelles was performed under argon by mixing of the block copolymer solutions in toluene with metal salts. The samples were prepared in a two-neck flask containing stopcock, rubber septum, and a Teflon stir bar. Oxygen removal was achieved by a three-time degassing procedure and storage under argon. Airless transfer of solution was achieved by Hamilton syringe techniques. Handling with degassed samples during reduction provides the stability of metal colloids under air. For the preparation of bimetallic systems, the two metal salts were added to the PS-*b*-P4VP solution simultaneously. The introduction of Pd and the mixture of Pd and Pt salts inside the micelles were performed under air.

The reducing agents $N_2H_4{\cdot}H_2O$, $C_6H_5NHNH_2$, $NaBH_4$ (0.5 M in 2-methoxyethyl ether), $(C_2H_5)_3SiH$, and super-hydride (SH, 1 M solution of $LiB(C_2H_5)_3H$ in THF) obtained from Aldrich were used in a 3−5-fold excess in the case of hydrazines, $NaBH_4$ and $(C_2H_5)_3SiH$ and in a 1.3−2.6-fold excess for SH. In all cases reduction was carried out under argon after a degassing procedure.[5] For $(C_2H_5)_3SiH$ the reduction of the initial solution before hydrogenation was carried out at 80 °C for 5.5 h.

Preparation of Metal-Containing Block Copolymers Supported on Al_2O_3. Al_2O_3 was dried at 320 °C for 2.5 h; after cooling, the micellar solutions of block copolymer stabilized nanoparticles in toluene were added. The resulting mixture was stirred for 2−3 days at room temperature. The Al_2O_3 was filtered, washed with petroleum ether (five times) and dried in vacuum over P_2O_5 for 2 days. The remainder of the solution was colored because the block copolymer solution was taken in excess to provide the maximum saturation of the support.

Hydrogenation of Unsaturated Compounds. The hydrogenation of cyclohexene, 1,3-cyclooctadiene, and 1,3-cyclohexadiene was carried out at 30 °C. The molar ratios of catalyst/substrate were chosen for the cyclohexene reduction to be 1:250 and 1:500. In the case of 1,3-cyclohexadiene reduction, the molar ratio was varied from 1:500 to 1:10 000. The stirring speed was kept at 800 rpm; some experiments were done with stirring speed 1200 rpm.

(a) Homogeneous Hydrogenation. An amount of 1×10^{-5} mol of metal salt in the block copolymer micelles diluted with a total of 7 mL toluene was added to a three-neck glass flask sealed with a Normag overpressure valve (1.10 atm maximum pressure) and equipped with a silicone rubber septum and a Teflon stir bar. Oxygen removal was achieved by three-time degassing procedure in freezing/thawing cycles and filling with argon at the end. Then the reducing agent was added, the flask was evacuated while frozen, then refilled with 1.10 atm of hydrogen. An additional 2 L glass flask with inlet and outlet was maintained between the reaction flask and hydrogen line to keep a sufficient volume of H_2. The solution was kept under hydrogen at 30 °C for 3 h in the reactor as a pretreating of the catalysts, before the substrate was injected. In the case of cyclohexene, a sample was taken 30 min after the addition of the substrate, filtered, and analyzed by GC. For selective hydrogenation of 1,3-cyclooctadiene and 1,3-cyclohexadiene and in one case of cyclohexene hydrogenation, 10 samples were taken at equal time intervals after the addition of the substrate with a syringe equipped with a filter. The selectivity was derived from the product distribution based on the gas chromatography of the samples; the results are given in the Table 4.

(b) Heterogeneous Hydrogenation. The powder of Pd/Al_2O_3 containing 1×10^{-5} mol of Pd dispersed in 7 mL of toluene was added in the reactor described above. The following procedure was similar to the homogeneous hydrogenation, except that the catalyst is already active and does not require the reduction.

To check the stability of heterogeneous catalysts (PS-3,4-Pd/Al_2O_3, PS-3,4-Pd/Au(4/1)/Al_2O_3, and Pd/C), three series of experiments were done including six runs each. For the first run in each sequence the amount of all reagents was increased by five times to provide a required amounts for subsequent experiments. To judge the course of hydrogenation for catalysts PS-3,4-Pd/Al_2O_3 and PS-3,4-Pd/Au(4/1)/Al_2O_3, seven samples were taken at in 10 min intervals after the addition of the substrate with a syringe equipped with a filter. Then the hydrogenation catalyst was filtered, washed with toluene and petroleum ether, dried in a vacuum desiccator, and used for the next run.

The chromatographic analysis was carried out on a Biochrom-1 gas chromatograph using a flame ionization detector and a 54 m length capillary glass column filled with the liquid-phase XE-60. The experimental error was 1.5%.

Sample Characterization. Samples for transmission electron microscopy were prepared by evaporation of 10^{-4} mol/L toluene solutions under air. A drop of solution was placed on an electron microscope copper sample grid. After drying, electron micrographs of the sample were prepared with a Zeiss 912 Omega electron microscope. A magnification of 125 000 was used. Particle sizes were determined by processing from the photographs.

Wide-angle X-ray scattering (WAXS) measurements were performed with Nonius PDS120 powder diffractometer in transmission geometry.

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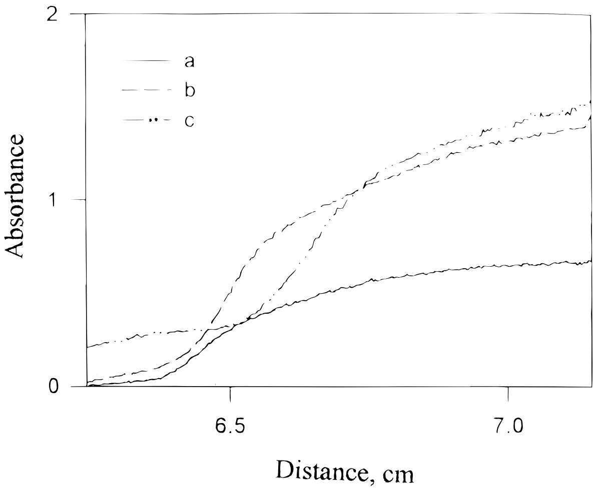

Figure 1. Sedimentation of PS-3,4-Pd(II) micellar solutions (toluene, 4 g/L) in ultracentrifuge with a rate of 10 000 *U*/min (UV detection: $\lambda = 400$ nm) for samples Pd:N equal to (a) 1:5, (b) 1:3, and (c) 1:2.

Results and Discussion

Preparation of Metal Colloids. The preparation of metal colloids was carried out in the inert atmosphere after three freeze/pump/thaw cycles in vacuum. Contrary to the other salts, the storage of micellular dissolved $Pd(CH_3COO)_2$ solution in inert atmosphere at room temperature is accompanied by slow formation of some minor amount of black precipitate (in a day). This is probably due to the reduction of Pd^{2+} by the vinylpyridine units of PS-*b*-P4VP. Decreasing to lower temperatures slows this process. The simultaneous introduction of Pd and Pt salts induces even faster self-reduction of Pd (without reducing agent), within 5 h. This can be explained by a catalytic assist of the Pt complex, which facilitates the electron transfer. To suppress the reduction of Pd in PS-*b*-P4VP solutions, the introduction of Pd salt was carried out under air. The presence of oxygen prevents the reduction of $Pd(CH_3COO)_2$ and provides the stability of solutions for many weeks, even for Pd−Pt samples. For the mixture of Pd and Au salts, the micellar block copolymer solutions are very stable for a long time both in air and in argon.

Because the $Pd(CH_3COO)_2$ is soluble in toluene, it can be present both inside and outside micelles. To check whether the soluble Pd salt is consumed by the micelle core, ultracentrifugation was employed. Since the block copolymer/metal salt hybrid solution exhibits a yellow color, the simple sedimentation run where the optical absorption is measured at 400 nm permits us to judge the location of the salt. Ultracentrifugation was performed for three solutions with molar ratios Pd/4VP: 1/2, 1/3, 1/5. Already in 4 h complete uptake of the salt by micelles was achieved if the molar ratio Pd/4VP did not exceed 1/3 (Figure 1).

Our earlier papers[4,5] on Au colloids showed that the nature of the reducing agent can control the rate of metal particle formation and determines the overall morphology of colloids. On the other hand, it involves the production of side products which are able to interact with the surface of colloid particles and influence the catalytic properties.

These considerations can partly be transferred to the formation of Pd colloids. It was found that hydrazine hydrate causes very slow reduction of Pd. Although it is known that Rh salts can form complexes with hydrazine and Pd compounds can give similar ammoniates,[20] we finally did not observe any indications for a stable hydrazine complex with $Pd(CH_3COO)_2$. If these complexes formed (the color of solution changed for some hours from yellow to brown and then black) as intermediates, they were reduced by the excess of hydrazine hydrate. On the other hand, addition of phenylhydrazine leads only to complex formation: no reduction and no colloid formation were obtained.

In the case of fast reducing agents (SH, $NaBH_4$), the solutions change their color from yellow to black practically immediately after adding the reducing agent, an evidence for Pd colloid formation.

Electron microscopy gives a first indication of the structure of the resulting Pd colloids. Figure 2a depicts the morphology of the Pd colloids in the block copolymer micelles as synthesized by reduction with hydrazine. We observe groups of 3−8 Pd colloids in each micelle core, which are visible as shadows in the background pattern. This is related a changed dynamics of the nucleation-and-growth processes of Pd as compared to Au, and the so-called “cherry morphology” (one particle per micelle) has changed to a related architecture being characterized by a small number of well-defined colloids per micelle.

This has to be compared with the product of $NaBH_4$ reduction (Figure 2b). A much higher number of smaller Pd colloids is obtained, in coexistence with some remainder of Pd atoms contrasting the micellar background. According to X-ray photoelectron spectroscopy (XPS) for this sample $E_bPd\ 3d_{5/2} = 335.15$ eV, which exactly matches that of Pd(0). The $NaBH_4$ reduction results obviously in more complicated architectures, but both morphologies are colloidally stable for months and can be redispersed after precipitation without complications.

Wide-angle X-ray scattering complements these observations; the resulting diffractograms including a line width analysis are compared in Figure 3. The diffractogram of the hydrazine-reduced sample is perfectly described by a superposition of an amorphous halo coming from the polymeric stabilizers and a cubic packing of Pd atoms into the colloids where a quantitative fit of the line width results in a crystallite size of 3.3 ± 0.2 nm, which is just slightly smaller than the averaged colloid size as determined from electron microscopy. The $NaBH_4$ product is more complicated to analyze. Although the structure definitely contains crystalline components, as seen by the cubic peaks, it also contains scattering components which cannot be interpreted (as indicated by question marks in Figure 3b). In addition, a rather strong scattering background (dashed line) is obtained, thus underlining the presence of a larger number of isotropic scatterers, i.e., small Pd clusters or isolated atoms. A quantitative fit of the crystallite size reveals 1.8 ± 0.2 nm, which again corresponds to the values taken from the EM pictures.

In any case, reduction with $NaBH_4$ results in smaller particles and a much less defined colloid organization as compared to the hydrazine reduction.

Influence of the Reducing Agent Type on Activity of Catalysts in Hydrogenation. In a previous paper, it was already shown[5] that Pd colloids stabilized

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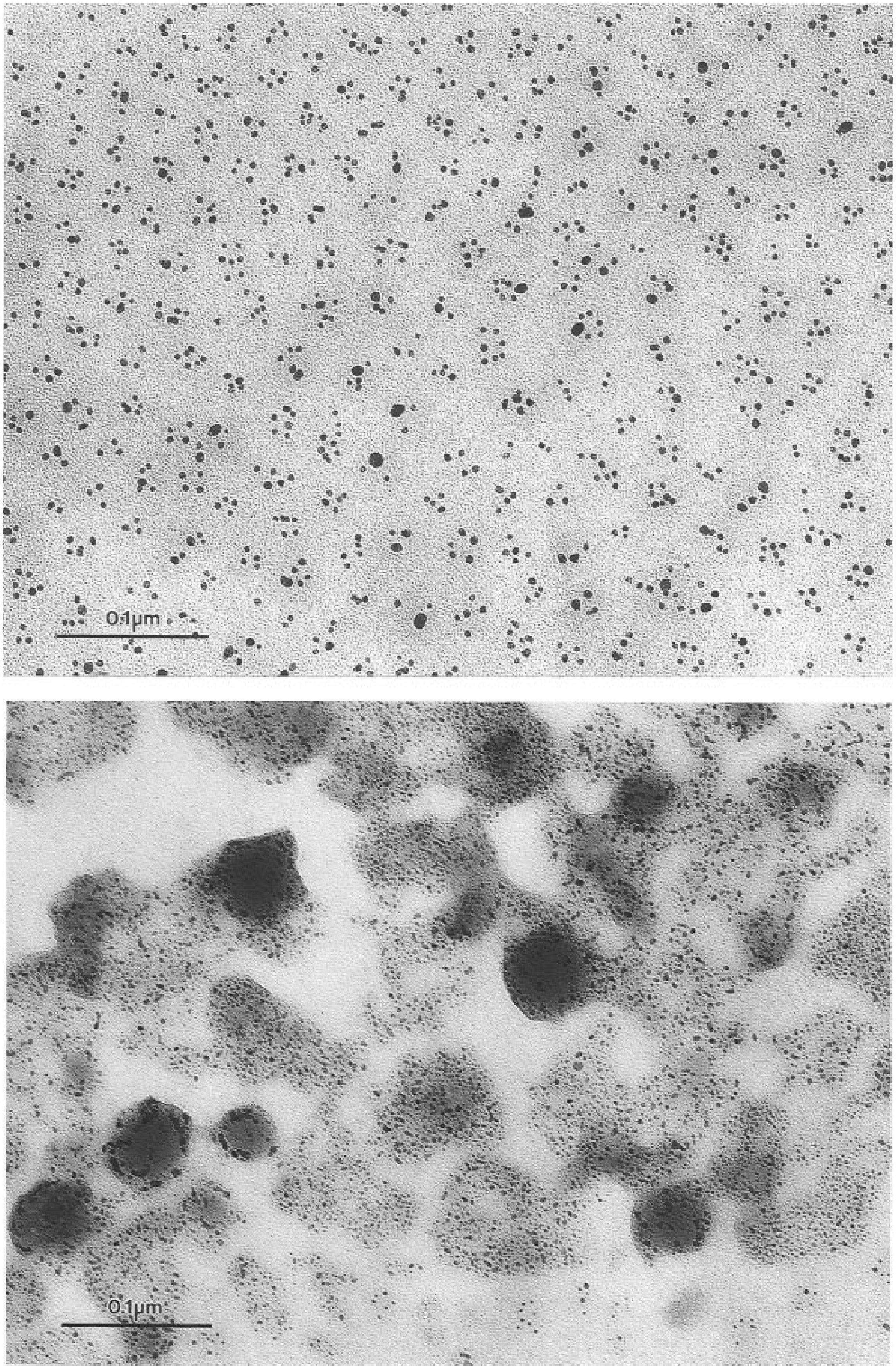

Figure 2. Electron micrographs of Pd colloids synthesized in PS-*b*-P4VP block copolymers (PS-3,4) via reduction with hydrazine (a, top) and $NaBH_4$ (b, bottom).

by block copolymer micelles derived from Na_2PdCl_4 and $Pd(CH_3COO)_2$ and reduced by SH display nearly the same catalytic activity as commercial, optimized catalysts. This reactivity also does not depend on the micellar environment: strongly segregated large micelles (PS-1,2) formed by high molecular weight block copolymers or weakly segregated small micelles (PS-3,4) as a matrix both support the Pd colloids in a similar fashion. In the present work, we investigate the dependence of the catalytic activity on the metal type,

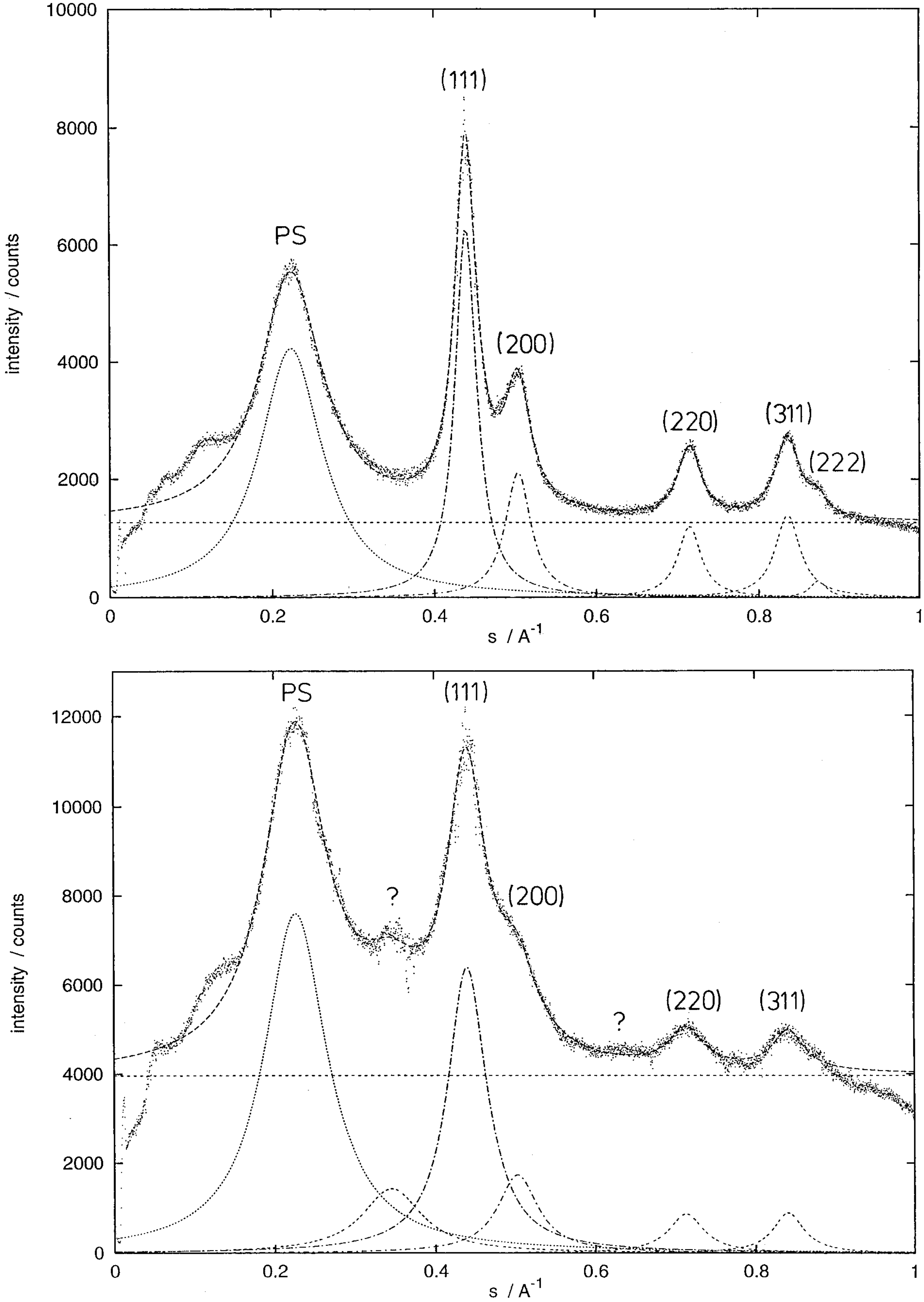

Figure 3. WAXS diffractograms of the Pd-colloids synthesized in PS-*b*-P4VP block copolymers (PS-3,4) via reduction with hydrazine (a, top) and $NaBH_4$ (b, bottom). The curves are quantitatively described by a superposition of a scattering background (dashed line), the scattering due to the stabilizing polymer (dotted line, PS), and five peaks due to the cubic packing of Pd into the clusters (dotted–dashed). The line width of these peaks reveals a measure for the crystallite size given in the text. In Figure 2b, additional scattering contributions are obtained (question marks) which are not interpreted.

on the presence of a second metal in micelle core, on the metal inner structure which, in turn, depends on the type of reducing agent, and on some other parameters. As a control, the commercial catalyst, Pd on activated carbon (Aldrich), was used in all catalytic reactions.

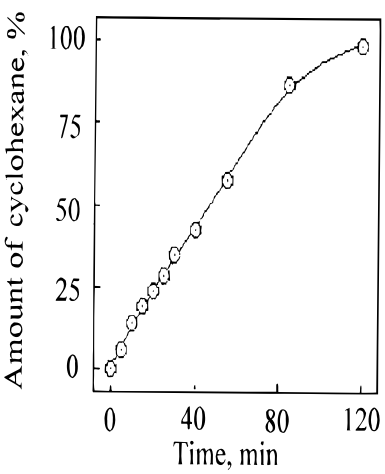

Figure 4. Dependence of the amount of cyclohexane on time in hydrogenation of cyclohexene with PS-3,4-Pd.

The dependence of cyclohexane formation on time in the hydrogenation of cyclohexene with homogeneous Pd catalyst derived from PS-3,4 and $Pd(CH_3COO)_2$ (Pd:N = 1:3) and reduced by SH is presented in Figure 4. One can see that this dependence is practically linear up to the 75% of conversion, an evidence of pseudo-zero-order in cyclohexene hydrogenation. The experimental data show also the lack of an induction period in hydrogenation. Similar behavior was observed for other metal colloids supported by block copolymer micelles. This permitted us to compare the catalytic activity of metal colloids simply by the production of cyclohexane after 30 min of hydrogenation. To make certain that we measure the intrinsic catalytic activity of metal colloids and that the concentration of all reactants (including dissolved hydrogen) stays constant during reaction, we have examined the catalytic activity for both homogeneous and heterogeneous Pd catalysts derived from PS-3,4 and $Pd(CH_3COO)_2$ (Pd:N = 1:3) and reduced by SH at two stirring speeds: 800 and 1200 rpm. The yields of cyclohexane after 30 min of hydrogenation were 32.7 and 33.0%, correspondingly, which shows no diffusion limitations at the chosen agitation rate. Another experiment, halving catalyst amount (molar ratio substrate:catalyst = 1:500), reduced the cyclohexane yield to 16.1%, which is half the yield. This is an additional proof of constant concentration of all reactants and catalyst during hydrogenation that allows comparison of various colloids.

The influence of the type of reducing agent on the activities of Pd colloids derived from PS-3,4 and $Pd(CH_3COO)_2$ in the hydrogenation of cyclohexene to cyclohexane is presented in Table 1.

We note that the activity of the palladium acetate species in PS-3,4 micelles is very low. In ref 21 it was discussed that the $P4VP-PdCl_2$ complex can be reduced by H_2, and active polymer catalysts are obtained. In this context, the very low activity of the PS-3,4/ $Pd(CH_3COO)_2$ is rather surprising and can be explained only by a strong passivation of the metal salt by 4-VP units in the micellar cores.

All other systems behave according to our expectations which relate the activity to the colloid size, i.e., the smaller the colloid size, the higher the reactivity. Table 1 shows that reduction by hydrazine hydrate and phenylhydrazine results in the formation of practically inactive colloids, while reduction by $NaBH_4$ and superhydride results in active Pd nanoparticles which exhibit a conversion of 28.3−32.7%. Reduction by $(C_2H_5)_3SiH$ produces an intermediate result.

Table 1. Influence of Reducing Agent Type on Conversion of Cyclohexene into Cyclohexane for Pd Colloids Derived from PS-3,4 and $Pd(CH_3COO)_2$

reducing agent	cyclohexane, %
without reducing agent	4.2
superhydride	32.7
$NaBH_4$	28.3
$N_2H_4{\cdot}H_2O$	1.0
phenylhydrazine	0.2
$(C_2H_5)_3SiH$	10.8
superhydride (large excess)[a]	26.7
superhydride (deposited on Al_2O_3)	45.5
Pd on activated carbon (Aldrich, 1 wt % Pd)	40.0

[a] The excess of superhydride is calculated to modify all the vinylpyridine units and to reduce all the Pd atoms.

The Pd colloids stabilized in block copolymer micelles were also deposited on Al_2O_3 to prepare a more processable and stable heterogeneous catalyst for hydrogenation. This procedure is very successful and not only yields a catalyst with a longer lifetime but also increases the activity of the catalyst to 45.5% (Table 1). It is proposed that the increase of catalytic activity can be explained by the influence of an electron transfer to the support (Al_2O_3), which is already described for other systems.[22] The activity of this catalyst (and also the dependence of cyclohexane formation on time in the hydrogenation of cyclohexene with PS-3,4-Pd/Al_2O_3) stays practically unaffected after five cycles in hydrogenation, which underlines the good stabilization of the block copolymer protected Pd colloids on the support surface, while the commercial Pd/C catalyst displays the loss of activity already in third run.

Influence of the Metal Type on Catalytic Activity in Hydrogenation. As shown in the literature,[23−26] the formation of a bimetallic mixture should increase the activity of the Pd in such colloids in hydrogenation. In the case of stable block copolymer micelles, we have a special advantage because we are able to introduce in the micelle core practically any metal which is able to interact with 4VP units. Such a reaction mixture is constrained to each nanometer-size reaction vessel and cannot separate; consequently, alloy particles or at least a mixture of colloidal particles in very close proximity of each other are obtained. In this paper we report on bimetallic colloids based on of Pd/Pt and Pd/Au in the PS-*b*-P4VP micelles. The activities of these colloids in cyclohexene hydrogenation as compared to four different pure noble metal colloids are presented in Table 2.

The activity of Pd catalyst prepared by the reduction of $Pd(CH_3COO)_2$ by SH in block copolymer micelles as a reference state is 32.7%. On the other hand, monometallic Au colloids prepared from $HAuCl_4{\cdot}3H_2O$ by the same method have no activity. This is expected since Au colloids are known to be catalytically inactive. However, the coexistence of Au and Pd in mixed colloids obtained by the simultaneous reduction of $Pd(CH_3COO)_2$ and $HAuCl_4{\cdot}3H_2O$ (Au/Pd = 1/4) increases the catalytic activity by no less than a factor of 2.

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Table 2. Catalytic Activity of Mono- and Bimetallic Colloids in the Hydrogenation of Cyclohexene

catalyst	cyclohexane, %
PS-3,4; $[Rh(CO)_2Cl]_2$	26.4
PS-3,4; $Pd(CH_3COO)_2$	32.7
PS-3,4; $K[Pt(C_2H_4)Cl_3]$	60.7
PS-3,4; $HAuCl_4 \cdot 3H_2O$	0.0
PS-3,4; $Pd(CH_3COO)_2$, $K[Pt(C_2H_4)Cl_3]$ (Pd:Pt = 4:1)	55.5
PS-3,4; $Pd(CH_3COO)_2$, $HAuCl_4 \cdot 3H_2O$ (Pd:Au = 4:1)	65.7
Pd on activated carbon (Aldrich, 1 wt % Pd)	40.0

According to ref 24 the corresponding simple mixture of both Au and Pd monometallic colloids did not produce such high activities as the bimetallic colloids prepared by the simultaneous reduction. In the same paper, Toshima et al. described the structure of Au/Pd bimetallic colloid and their catalytic activity for the selective partial hydrogenation of 1,3-cyclooctadiene to cyclooctene depending on their composition. It was found that in the Au/Pd (1/4) bimetallic cluster the Au atoms form the core, whereas the Pd atoms are located on the surface of the cluster particles. Because Pd has a lower ionization potential (8.33 eV) than Au (9.22 eV),[27] the reduction of the Au ions proceeds more easily than the reduction of the Pd ions, and it is reasonable that Au nucleates first and forms the core. The difference in the ionization potentials and the different height of the electronic band levels of the colloidal metals in combination with the core-shell structure provides an uneven distribution of electrons: the Pd in the surface layer becomes poorer in electron density than the Au core. This might explain the increased activity of the Au/Pd (1:4) bimetallic clusters, since the substrate having a double bond favors an electron-deficient surface. For the structure of the Au/Pd(1/1) bimetallic colloid, a cluster-in-cluster model was suggested, in which a couple of Au particles form a cluster, and the Pd atoms connect the Au subparticles.[24]

Because of this proposed dependence of the inner structure of bimetallic colloids on the composition, we have also varied the relative composition of Au/Pd, leaving all other parameters constant. These data are shown in Table 3. It is seen that the variation of molar ratio Au/Pd within the limits 1/5, 1/4, 1/3 has almost no influence on the catalytic activity of the bimetallic colloids. Within this composition range, it is assumed that the core/shell structure is preserved, which is preferable for olefin hydrogenation. A further increase of the Pd or Au content beyond this range results in the drop of activity. In this context, we follow Toshima, who explains the decreased activity with a less "perfect" electron density distribution, related to the bimetallic colloids Au/Pd = 1/6 and Au/Pd = 1/2.

For the use of $NaAuCl_4$ instead of $HAuCl_4 \cdot 3H_2O$ the activity of bimetallic Au/Pd = 1/4 catalyst drops from 65.7% to 58.0% (the experimental error is about 1.5%). We speculatively attribute this phenomenon to a different binding mechanism which occurs via the protonation of the vinylpyridine units of the block copolymers in the case of $HAuCl_4 \cdot 3H_2O$, as compared to complex formation in the other case.[4] This decreases the interaction of the pyridine units with the metal particles in the micelle core and, as a consequence, increases the catalytic activity (pyridine is known to deactivate catalysts).

Table 3. Catalytic Activity of Pd–Au Bimetallic Particles with Different Ratios of Pd:Au in the Hydrogenation of Cyclohexene[a]

ratio Au/Pd, mol	cyclohexane, %
1/6	55.5
1/5	71.3
1/4	65.7
1/3	68.7
1/2	39.4
1/5 (deposited on Al_2O_3)	72.5
Pd on activated carbon (Aldrich, 1 wt % Pd)	40.0

[a] The initial polymer is PS-3,4; salts: $Pd(CH_3COO)_2$ and $HAuCl_4 \cdot 3H_2O$; reducing agent is superhydride.

For Au/Pd bimetallic colloids we find that the catalytic activity also depends on the type of reducing agent, similarly to the monometallic Pd colloids. The reduction by $NaBH_4$ results in a slight decrease of activity that can be explained by the formation of borides as the secondary product along with the metal colloids which again slightly deactivate the catalyst.[28] At a ratio of Au/Pd = 1/4, the activity of the catalyst reduced with $NaBH_4$ diminishes to 57.8%.

In the literature, a similar synergistic increase of catalytic activity by metal mixing is described for bimetallic Pd/Pt clusters,[23] and it can be explained in a similar fashion by a preferable reduction of Pt (the ionization potential is 8.96 eV) as compared to Pd, and a subsequent electron transfer from a Pd shell to the Pt core. Our experiments shown in Table 2 however reveal that we cannot reproduce this effect in our system: there is no synergistic increase of activity of the Pd/Pt bimetallic colloids as compared to the monometallic ones. The bimetallic particles are clearly more active than the pure Pd colloids but less active than the pure Pt particles, which are a very good catalyst for hydrogenation, too. To our opinion, due to the smaller difference in ionization potential it is not straightforward to assume a core/shell structure for these particles, too; they might be also build up in a more random fashion. A further discussion requires a more detailed analysis of the inner structure of the Pd/Pt colloids by EXAFS, which is planned but is currently not available to us.

Closing these series, we have also tried to support the bimetallic Au/Pd colloids prepared in block copolymer micelles by deposition on activated Al_2O_3. Similar to the Pd colloids, the deposition increases the activity (Table 3). The resulting optimized product shows an activity value that competes very well with commercial Pd/C catalyst but exhibits a lifetime at least twice as long: contrary to the commercial system, our Al_2O_3-supported material shows within the range of our experiments (six runs) no loss of activity and no change in the dependence of cyclohexane yield on time. This

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Table 4. Activity of Pd- and Au/Pd Colloids in Selective Hydrogenation of 1,3-Cyclohexadiene in Cyclohexene

catalyst	reducing agent	ratio substrate/ catalyst (mol)	τ, min	1,3-cyclohexadiene conversion, %	selectivity, %			rate[a] (mol of cyclohexene/min g atom of metal)
					cyclohexene	cyclohexane	benzene	
PS-1,2; Na_2PdCl_4	superhydride	500:1	10	100.0	71.3	0.1	28.6	40
PS-3,4; $Pd(CH_3COO)_2$	superhydride	750:1	5	100.0	58.5	0.0	41.5	90
PS-3,4; $Pd(CH_3COO)_2$	$NaBH_4$	10,000:1	5	100.0	65.9	0.0	34.1	1230
PS-3,4; $Pd(CH_3COO)_2$	no reduction	500:1	25	100.0	60.1	5.4	34.5	10
PS-3,4; $Pd(CH_3COO)_2$ (deposited on Al_2O_3)	superhydride	10 000:1	12	85.5	50.0	2.0	33.5	420
PS-3,4; $Pd(CH_3COO)_2$, $HAuCl_4\cdot 3H_2O$ (deposited on Al_2O_3) Au/Pd = 1:5	superhydride	5 000:1	9	94.8	82.2	1.1	11.5	350
Pd on activated carbon (Aldrich, 1 wt % Pd)	–	5 000:1	7	100.0	54.7	0.7	44.6	390

[a] Rate is calculated for cyclohexene yield per minute and per g atom of metal as a total for both hydrogenation and disproportionation.

strongly supports the concept of block-copolymer stabilizers acting as a preserving the nanoenvironment.[4]

Catalytic Activity of Mono- and Bimetallic Colloids in the Selective Hydrogenation of 1,3-Cyclooctadiene and 1,3-Cyclohexadiene. The monometallic Pd colloids protected by block-copolymer micelles were also examined with respect to their selectivity in the hydrogenation of 1,3-cyclooctadiene to cyclooctene (ratio substrate/catalyst = 500/1). It was found that selectivity of the Pd colloids prepared from PS-1,2 and Na_2PdCl_4 (Pd/N = 1/9) in toluene, reduced by superhydride, was nearly 100%: no cyclooctane could be detected. At the same time, the commercial Pd/C (1 wt % Pd) leads to a value of only 97.3%. In the product, both remainders of 1,3-cyclooctadiene as well as cyclooctane were detected. This underlines the general observation that protected and stabilized catalysts are more selective catalysts as compared to modified Pd on activated carbon. Such a difference in selectivity becomes especially important for substrates such as long-chain acetylene alcohols C_{10}, C_{15}, and C_{20} which are intermediate products in the preparation of vitamins and fragrances. In this case the selectivity of hydrogenation about 100% provides the high quality of end products and helps solve a number of environmental problems. That is why the elaboration of approaches to highly selective catalytic systems is technologically relevant.

To enable a more definitive rating of the different catalysts, we switched to 1,3-cyclohexadiene, which is a more difficult substrate for the study of selective hydrogenation. Here, unlike 1,3-cyclooctadiene, the hydrogenation is accompanied with the disproportionation of 1,3-cyclohexadiene to cyclohexene and benzene as a side reaction. Table 4 shows these data on selective hydrogenation of 1,3-cyclohexadiene on metal colloids prepared in block copolymer micelles. The ratio substrate/catalyst was chosen from the viewpoint of the best selectivity achieved for each catalyst.

Table 4 shows that all systems are catalysts both for hydrogenation of 1,3-cyclohexadiene and its disproportionation. The rates of these two competitive reactions are however very different for the various catalysts. Obviously, for hydrogenation one molecule of 1,3-cyclohexadiene and one H_2 molecule should coordinate with Pd catalyst, while for disproportionation, two 1,3-cyclohexadiene molecules must be activated simultaneously. We expect the difference in catalytic response to be determined by properties both of colloids and of the block copolymer micelles (or support).

This is nicely seen by comparing the Pd colloids derived from Na_2PdCl_4 and $Pd(CH_3COO)_2$ after reduction by SH. Whereas in cyclohexene hydrogenation nearly the same activity,[4] independently on the type of block copolymer micelles is obtained, their behavior differs in selective hydrogenation of 1,3-cyclohexadiene. The colloids prepared from Na_2PdCl_4 in PS-1,2 micelles are less active but more selective than colloids formed from $Pd(CH_3COO)_2$ and PS-3,4. For the latter catalyst, also the disproportionation goes much faster than 1,3-cyclohexadiene hydrogenation. The deposition of Pd colloids prepared from $Pd(CH_3COO)_2$ and PS-3,4 on Al_2O_3 leads again to a significant increase of activity, but the selectivity in hydrogenation is low and not improved.

It should be noted that the use of $NaBH_4$ as the reducing agent instead of SH results in a more than significant growth of the activity nearly by a factor of 14, contrary to the hydrogenation experiments with cyclohexene; the rate of 1,3-cyclohexadiene disproportionation is however increased in a similar fashion and also high (34.5% of benzene and 65.9% of cyclohexene). No definitive explanation for this very interesting behavior can be given, since the only difference lies to our knowledge in the existence of borides, which are formed as a coproduct in the course of the $NaBH_4$ reduction and remain in the final catalyst.

The cross-control, application of $Pd(CH_3COO)_2$ into PS-3,4 micelles as a nonreduced salt, shows activity neither in cyclohexene nor in cyclohexadiene hydrogenation. We can therefore conclude that all observed effects are really caused by the colloid morphology, and the supporting shell of block copolymers and the emerging coproducts.

Similar to the cyclohexene hydrogenation, the best catalyst in selective hydrogenation of 1,3-cyclohexadiene seemed to be the bimetallic Au/Pd catalyst prepared from the mixture of Au and Pd salts, reduced by SH and deposited on Al_2O_3. It is seen from Table 4 that 82.2% of cyclohexene are formed simultaneously with 11.5% of benzene and 1.1% of cyclohexane, leaving 5.2% of the initial diene. At the same time this catalyst displays a high activity and selectivity, and it is a very promising starting point for further progress in catalyst design for selective hydrogenation reactions.

Conclusion

Noble-metal colloids prepared in the micelles of amphiphilic block copolymers show a strong catalytic activity in hydrogenation reactions, which was found to depend strongly on a number of parameters which are closely related both to colloid morphology and to the chemical surrounding of the colloids.

These are directly controlled by the type of reducing agent being applied during colloid synthesis. The strength of reducing agent determines the rate of nucleation and growth of the colloids inside the micelle core, and consequently, a number of different architectures can be tailor-made. With electron microscopy and X-ray scattering, two different morphologies with a different number of noble-metal clusters per micelle core and a different quality of the formed colloids were identified, which describe the catalysts used throughout this paper. The second effect is given by the chemistry of the reducing agent, since its residues or reaction products after reduction of the metal colloids might remain in the micelle core and can influence the catalytic properties very strongly.

In addition, the reactivity of the catalysts is also adjusted by the inner structure of the noble-metal colloids: an added secondary metal, its type, and the colloid composition are other ways to influence the activity and selectivity of the catalyst. Also support on active materials such as activated Al_2O_3 illustrates this type of control.

A number of our colloids compete well with the activity of the commercial catalysts but show at the same time a higher stability as well as a higher selectivity. Considering these facts, the further development of similarly complex structured noble metal colloids seems to be very promising.

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