Structure and Properties of Bimetallic Colloids Formed in Polystyrene-*block*-Poly-4-vinylpyridine Micelles: Catalytic Behavior in Selective Hydrogenation of Dehydrolinalool

Lyudmila M. Bronstein,^{*,1} Dmitrii M. Chernyshov,[†] Ilya O. Volkov,[†] Marina G. Ezernitskaya,[†] Peter M. Valetsky,[†] Valentina G. Matveeva,[‡] and Esther M. Sulman[‡]

* Chemistry Department, Indiana University, Bloomington, Indiana 47405; †Nesmeyanov Institute of Organoelement Compounds, 28 Vavilov Street, Moscow 117813, Russia; and ‡Tver Technical University, Tver 170000, Russia

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Catalytic properties of palladium and bimetallic (PdAu, PdPt, and PdZn) nanoparticles formed in block copolymer micelles derived from polystyrene-block-poly-4-vinylpyridine (PS-b-P4VP) were studied in dehydrolinalool (DHL) hydrogenation. FTIR spectroscopy on CO adsorption and XPS show that the second metal (Au, Pt, or Zn) acts as a modifier toward Pd, changing both its electronic structure and its surface geometry. In turn, this change provides higher catalytic activity of bimetallic particles formed in PS-b-P4VP micelles compared to Pd micelles, which can be ascribed mainly to an increase in the number of active centers on the particle surface. High selectivity of DHL hydrogenation (99.8% at 100% conversion) was achieved for all the Pd and bimetallic micellar catalysts, by chemical modification of the nanoparticle surface with pyridine units. Kinetic study of DHL hydrogenation, along with computational kinetic models, allowed us to describe a hydrogenation mechanism with these catalysts. © 2000 Academic Press

Key Words: catalysis; hydrogenation; dehydrolinalool; polystyrene-*block*-poly-4-vinylpyridine; block copolymers; micelles; bimetallic colloids.

INTRODUCTION

Nowadays, acceleration of chemical reactions, along with development of highly selective and robust catalysts, remain one of the most vigorously discussed topics in scientific literature. This strongly stimulates the development of new catalytic systems, which might combine the advantages of both heterogeneous and homogeneous catalysts. Among such systems, polymeric catalysts, i.e., catalysts where metal complexes or metal particles are located in polymeric matrices, were expected to be promising (1, 2). They were actively studied in hydrogenation (3–6) and oxidation (7, 8) of various substrates. Hydrogenation of long-chain acetylene alcohols and unsaturated ketones is of particular interest because hydrogenation products are intermediates in the synthesis of vitamins (A, E, and K) and fragrant substances (linalool) (9). Synthesis of linalool (3,7- dimethyloctadiene-1,6-ol-3, LN) can be carried out by selective hydrogenation of dehydrolinalool (3,7-dimethyloctaen-6-yne-1-ol-3, DHL). If hydrogenation goes on non selectively, dihydrolinalool (3,7-dimethyloctaen-6-ol-3, DiHL) forms as well (Scheme 1).



Traditionally, DHL hydrogenation is carried out using a Lindlar catalyst (Pd/CaCO3 modified with Pb acetate and quinoline), which provides selectivity of 95% at 100% conversion (10). However, the use of these modifiers leads to the pollution of end products and has an unfavorable impact on the environment. Another trend in triple-bond hydrogenation was the use of polymer Pd-containing catalysts, which gave higher selectivity (up to 98% in the DHL hydrogenation) and stability without any modification (11, 12); however, the activity of such catalysts was not sufficiently high. Recently, we developed new colloidal catalysts formed in block copolymer micelles derived from the polystyrene-block-poly-4-vinylpyridine (PSb-P4VP) block copolymer (13, 14). In selective solvents (toluene, and THF) these block copolymers form micelles with the P4VP cores, which serve as nanoreactors for metal nanoparticle formation. In our preceding paper (5) we described the hydrogenation of DHL with Pd colloids stabilized in PS-b-P4VP micelles. A crucial feature of colloidal catalysts formed in block copolymer micelles is a polymeric



¹ To whom correspondence should be addressed. Fax: (812) 855-8300. E-mail: lybronst@indiana.edu.

environment in the micelle cores (15, 16). The P4VP micelle cores not only control the nanoparticle size and size distribution (13, 14, 17, 18) but also provide a modification of the nanoparticle surface due to pyridine units. Moreover, this kind of modification is fairly permanent, unlike the low molecular modifiers mentioned above. This stability of modification, which governs the stability of catalytic properties and high selectivity, was discussed in our preceding papers (5, 19). Pd colloids formed in PS-b-P4VP micelles were found to be promising catalysts for hydrogenation of long-chain acetylene alcohols combining high selectivity, stability, and satisfying activity. Nevertheless, an increase in catalytic activity is always desirable. Incorporation of a second metal into metal colloids often modifies their properties, increasing activity of the catalysts (20-22). This can be caused by a change in the electronic structure of the main metal (for one, Pd or Pt), by a change in the morphology of the particle, or by some other changes (23-25). Recently, we described the higher activity of bimetallic PdAu colloids in hydrogenation of cyclohexene and cyclohexadiene (14). In the present paper we report the synthesis and properties of PdAu, PdPt, and PdZn bimetallic colloids synthesized at a molar ratio of 4/1 in PS-b-P4VP micelles and their catalytic behavior in DHL hydrogenation. Because the amount of Pd in all the bimetallic nanoparticles is much higher than that of the second metal, Pd mainly determines the catalytic properties.

METHODS

Materials

Diblock copolymer polystyrene-*block*-poly-4-vinylpyridine (PS-*b*-P4VP), $M_n = 19,400$, $M_w = 22,500$, and X_{4-vp} (relative 4-VP content) = 0.340, was prepared via living anionic polymerization (Max Plank Institute of Colloids and Interfaces, Potsdam/Golm, Germany) according to a synthetic procedure described elsewhere (26, 27). HAuCl₄ · $3H_2O$, Pd(CH₃COO)₂, Zn(CH₃COO)₂, K[Pt(C₂H₄)Cl₃] · H_2O (Zeise salt), LiB(C₂H₅)₃H (SH, 1M solution of LiB(C₂H₅)₃H in THF)) were obtained from Aldrich and used as received. Toluene (Aldrich) was twice distilled under KOH. Petroleum either (Fluka) was distilled under metallic sodium in the Ar counterflow. Other solvents were used without additional purification.

Preparation of Catalysts

Synthesis of block copolymer micelles containing monoand bimetallic nanoparticles was carried out by the method described elsewhere (13, 14). For this, PS-*b*-P4VP samples were dissolved in toluene at a concentration of 10 g/L under stirring (for 1 h). The metal compounds were added to the polymer solutions under air to avoid partial reduction of Pd^{2+} by 4-vinylpyridine units (14) and stirred for 24 h at room temperature (molar ratio N/Pd = 3/1, Pd/Au = 4/1, Pd/Pt = 4/1, and Pd/Zn = 4/1). For bimetallic systems, the addition of both salts was carried out simultaneously. After 24 h of stirring, the resulting metal-containing polymer solution was filtered from the unreacted metal compounds or insoluble by-products of the reaction (KCl in the case of Zeise salt) through a Millipore 0.45- μ m PTEF filter. Reduction of Pd or bimetallic samples was performed in a two-neck flask equipped with a stopcock, a rubber septum, and a Teflon stir bar. The reducing agent (SH) was used in fivefold molar excess. In all the cases reduction was carried out under argon after a standard degassing procedure (14). Airless transfer of solutions was achieved with the Hamilton syringe technique. To isolate metal-colloidcontaining block copolymers for further examination, block copolymer solutions were precipitated with degassed petroleum ether and isolated under Ar. Resulting solids were dried for 24 h in vacuo (0.5 mbar). Colloid-containing block copolymers were easily redispersable in all the solvents that are good for polystyrene (THF and toluene). To avoid oxidation, metal-containing block copolymer samples were stored under Ar. Metal contents in the end polymers were determined by X-ray fluorescence analysis as described elsewhere (28) (see Table 1).

Measurements

FTIR spectra of CO adsorbed on colloidal catalysts were recorded with a Nicolet FTIR spectrometer in the spectral region of 2500–1500 cm⁻¹ with a resolution of 1 cm⁻¹. Typically, a preparation of samples for the FTIR examination was performed as follows. A freshly synthesized solution of metal colloids in block copolymer micelles was concentrated to 15–20 wt% solid content using an Amicon ultrafiltration device. The given solution was degassed under vacuum of 1 mbar and exposed to a slow carbon monoxide bubbling. Saturation of colloidal solutions with CO continued for 2 h at room temperature and then FTIR spectra were recorded.

TABLE 1

Elemental Analysis Data for Mono- and Bimetallic-Colloid-Containing Block Copolymers

Polymer sample	Metal compound used	Metal content wt%	Molar ratio obtained Pd : Mt
PS- <i>b</i> -P4VP/Pd	Pd(CH ₃ COO) ₂	Pd: 6.73	1
PS- <i>b</i> -P4VP/PdAu	Pd(CH ₃ COO) ₂ HAuCl ₄ · 3H ₂ O	Pd: 5.89 Au: 3.01	3.62/1
PS-b-P4VP/PdPt	$\begin{array}{l} Pd(CH_{3}COO)_{2} \\ K[Pt(C_{2}H_{4})Cl_{3}] \cdot H_{2}O \end{array}$	Pd: 5.61 Pd: 2.68	3.86/1
PS- <i>b</i> -P4VP/PdZn	Pd(CH ₃ COO) ₂ Zn(CH ₃ COO) ₂	Pd: 6.16 Zn: 1.03	3.67/1

X-ray photoelectron spectroscopy (XPS) was carried out with a two-chamber XSAM-800 spectrometer (Kratos, UK). For photoelectron excitation, the characteristic Mg*K* α radiation was used; the power (hv = 1253.6 eV) of the X-ray gun did not exceed 75 W (15 kV, 5 mA). The spectra were recorded at a pressure of 10⁻⁹ Torr.

Wide-angle X-ray scattering (WAXS) measurements were performed on a Rigaku D/max-RC X-ray diffractometer operating at 12-kV Cu $K\alpha$ radiation. Because of weak diffraction signals, spectra were recorded with an angle resolution of 0.1°. Estimation of the average crystallite size (or zones of the coherent scattering) was performed using the Debye–Scherer formula.

Samples for transmission electron microscopy (TEM) were prepared by evaporation of 10^{-4} mol/L THF solutions under air. Electron micrographs of the samples were obtained with a Zeiss 912 Omega electron microscope. UV spectra were recorded with a Beckman DU-530 spectrophotometer.

DHL Hydrogenation

Reactor and analysis. The catalytic reactions were carried out in a glass batch isothermal reactor installed in a shaker (maximum 960 shakings min) and connected to a gasometric burette. The reactor was equipped with two inlets: for catalyst, solvent, and substrate loading and for hydrogen feeding. Before the substrate was charged into the reactor, the catalyst was pretreated with H₂ for 60 min at 90°C. DHL concentration (C_0), catalyst amount (C_c), and hydrogenation temperature (t_h) have been varied. The experiments were carried out at atmospheric pressure.

Analysis of the reaction mixture was carried out by gas chromatography (GC) using a CHROM-5 chromatograph with FID and glass column 3 m/3 mm. The column has been filled with solid-phase Chromaton N (0.16-0.20 mm) saturated with 20 M carbowax (10% of liquid phase to support weight).

RESULTS AND DISCUSSION

1. Physicochemical Characterization of Monoand Bimetallic Colloids Formed in Block Copolymer Micelles

The choice of second metal or metal modifier for Pd was based on its electronic properties. Au and Pt have higher electronegativity than Pd, so they can be acceptors of electrons from Pd (Table 2). In contrast, Zn, whose electronegativity is very low, is rather a donor to Pd, so its influence should be the opposite.

Another feature of the synthesized bimetallics derives from the method of preparation. As mentioned in Methods, two metal compounds were incorporated into block copolymer micelles and their reduction occurred simultaneously. The structure of the particle formed strongly de-

TABLE 2

Electronic Properties of Metals Studied

Metal	Electro- negativity (30)	Ionization potential (eV) (31)	Standard potential (V) (32)
Pd	2.20	8.33	$+0.915^{a}$
Au	2.54	9.22	$+1.002^{a} +1.348^{b}$
Pt	2.28	9.0	$+0.749^{a}$
Zn	1.65	9.391	-0.77^{b}

^{*a*} Aqueous medium.

^b Nonaqueous medium.

pends on the ability of the metal to be reduced in the particular environment. Traditionally, this ability is characterized by the ionization potential (Table 2) (14, 23). Comparing Pd, Pt, and Au, one can assume that reduction of Pt and Au compounds proceeds faster than reduction of Pd compounds, providing core-shell structures for PdAu and PdPt bimetallics (23-25). On the other hand, Zn, which cannot be reduced easily, has a high ionization potential (Table 2). This means that the ionization potential value should not be used in the estimation of the ability of metal ions to be reduced. Among known parameters, the ability of metal ions to accept electrons and to be reduced can be characterized most closely by standard (or formal) potentials (Table 2), which, however, strongly depend on the reaction medium (aqueous or nonaqueous, presence of ligands) and conditions of examination (29-31). From the data presented in Table 2 one can see that $AuCl_4^-$ (in any media) can be reduced easier than Pd²⁺ (from Pd acetate), which can govern the possibility of core(Au)-shell(Pd) structure. In contrast, the values of standard potentials for Pd and Pt do not assume this kind of structure. The negative value for Zn^{2+} (from Zn acetate) shows rather the inability of zinc ions to be reduced by common reducing agents (for one, superhydride). So from these facts one can propose that the coreshell structure is possible solely for the PdAu pair, though the polymeric environment can change the ability of ions to be reduced.

As known, FTIR study of carbon monoxide adsorbed on colloidal particles can give useful information about structural peculiarities and active sites of metallic systems (2). Some investigations in this area have shown that there are correlations between the size of colloidal particles and their crystallinity and the relative occupancies of CO molecules in terminal (2040–2060 cm⁻¹) or in bridging (1920–1940 cm⁻¹) positions (32–34). According to Ref. (32), small and probably amorphous metal particles exhibit presumably linear (terminal) CO adsorption. In contrast, an increase of metal particle size gives rise to the fraction of bridging CO molecules (34). In the case of bimetallic particles, adsorbed carbon monoxide is also regarded as a useful infrared probe of surface composition (35). Relying on this



FIG. 1. FTIR spectra of CO adsorption on Pd (a) and bimetallic PdAu (b), PdPt (c), and PdZn (d) colloids formed in the PS-b-P4VP micelles.

information, we studied CO adsorption on monometallic Pd and bimetallic PdAu, PdPt, and PdZn colloids formed in the PS-b-P4VP micellar solutions (Fig. 1). One can see that all the samples except PdAu show both terminal and bridging CO adsorption. Moreover, PdPt and PdZn colloids display two bands in the region of terminal absorption, while Pd and PdAu samples exhibit only one band in this region. The latter should indicate linear CO molecules adsorbed on the Pd surface (32-34). The band at 2058 cm⁻¹ (Fig. 1c) can be ascribed to the terminal CO adsorption on Pt (36), while a band at 1994 $\rm cm^{-1}$ is due to linear CO adsorption on Zn. The lack of the second terminal band for CO adsorption for PdAu (at 2112 cm^{-1} (37)) shows that there are no Au atoms on the particle surface. Then, we can surmise that, for PdAu bimetallics, the core-shell structure does form, while PdPt and PdZn colloids form cluster-in-cluster structures. This demonstrates the difference in the formation of bimetallic particles in block copolymer micelle cores, which are closer to a solid state, and in poly(N-vinyl-2-pyrrolidone)

solutions (23–25), where PdPt colloids prepared by simultaneous reduction of Pd and Pt compounds had core-shell structures.

As mentioned above, the presence of bridging CO adsorption might be an indication of larger and crystalline particles. According to our earlier publication (14), the mean crystallite size of Pd colloids formed in the PS-*b*-P4VP micelles, estimated from WAXS, was 1.8 ± 0.2 nm. This value was in agreement with TEM data (14). However, along with this kind of particles, the overall structure contained a large number of isotropic scatterers, which should be small amorphous clusters. A TEM micrograph of PdPt colloids is presented in Fig. 2. One can see that the micelle cores contain small nanoparticles, whose mean diameter does not exceed 2 nm.

Typical $\theta/2\theta$ diffractograms of PdAu (a) and PdPt(b) bimetallic colloids stabilized in the PS-*b*-P4VP micelles (recorded after subtraction of the background) are presented in Fig. 3. One can see very broadened Bragg



FIG. 2. TEM image of PdPt colloids formed in the PS-b-P4VP micelles.



FIG. 3. WAXS diffractograms of the PdAu (a) and PdPt (b) samples.

reflections at positions typical for Pd crystallites. The average size of the crystallites derived from Bragg peaks does not exceed 1.5–2 nm for both samples. No Bragg peaks related to Au, Pt, or PdO were detected. Similar results were obtained for PdZn colloids. Thus, the presence or absence of bridging CO groups in the FTIR spectra of bimetallic particles formed in the PS-*b*-P4VP micelles cannot indicate the difference in particle size or particle crystallinity. We assign the difference in the CO adsorption to different surface properties of bimetallic colloids: for PdAu colloids only one kind of active center exists (only linear adsorption), while for Pd, PdPt, and PdZn colloids, at least two types of active center are located on the particle surfaces. Probably this difference is caused by the different (core–shell) structures of PdAu colloids.

To probe the influence of the modifying metals (Au, Pt, and Zn) on the Pd particle surface, XPS was employed. The XPS data are presented in Figs. 4 and 5 and Table 3. One can see that monometallic Pd colloids formed in the PS-*b*-P4VP



FIG. 4. The Mg $K\alpha$ induced X-ray photoelectron spectra of monometallic Pd (run 1) and bimetallic PdZn (run 2), PdAu (run 3), and PdPt (run 4) colloids formed in the PS-*b*-P4VP micelles.

micelles core have a binding energy of 335.1 eV, which is characteristic of zerovalent Pd, so the experimental conditions during superhydride reduction do not allow even surface oxidation of nanoparticles (38). On the other hand, XPS spectra of bimetallic colloids show two components in the $Pd3d_{5/2}$ region. One might speculate that the presence of a second metal having electron acceptor properties (Pt and Au) might provide easier oxidation of the particle surface, even in conditions (see Methods) where reduction is carried out in an inert atmosphere. Moreover, this consider-

TABLE 3

Compound	E Pd 3 <i>d</i> _{5/2}	E Au 4 <i>f</i> _{7/2}	$\mathrm{E}\mathrm{Zn}2p_{3/2}$	E Pt 4 <i>f</i> _{7/2}
Pd ⁰	335.7	_	_	_
Pd(CH ₃ COO) ₂	339	_	_	_
PS-b-P4VP/Pd	335.1	_	_	_
Au ⁰	_	83.8	_	_
AuCl	_	84.5	_	_
KAuCl ₄	_	87.9	_	_
PS-b-P4VP/PdAu	338.7	84.5	_	_
Zn ⁰	_	_	1021.6	_
Zn(CH ₃ COO) ₂	_	_	1022.5	_
PS-b-P4VP/PdZn	335.5	_	1022.1	_
Pt ⁰	_	_	_	71.3
$K[Pt(C_2H_4)Cl_3]$	_	_	_	73.6
K ₂ PtCl ₆	_	_	_	75.6
PS-b-P4VP/PdPt	338.2	—	—	73.4

ation fits the acceptor ability of the metal: in the PdAu samples the Pd(II) species strongly prevail, while in the PdPt species (Pt is a weaker acceptor compared to Au), the fraction of Pd(0) is rather noticeable. On the other hand, the presence of a high fraction of the Pd(II) species in the PdZn colloids (Fig. 4) does not fit the suggested idea of easier oxidation in the presence of an acceptor because Zn is a donor toward Pd. To clarify the phenomenon, a series of XPS spectra were recorded immediately after preparation and after 12 h of standing in the camera of the spectrometer. Figure 5 shows the spectra recorded for each bimetallic system. As can be seen, the spectrum of PdAu bimetallics remains unchanged (Fig. 5a), for PdPt, the fraction of Pd(0) noticeably increases (Fig. 5b), and for PdZn, nearly all Pd(II) is converted to Pd(0) (Fig. 5c). Obviously, the changes that occurred in the camera of the spectrometer (in a vacuum of 10^{-9} Torr) should not be discussed in terms of "oxidationreduction." The X-ray diffraction data for monometallic Pd nanoparticles (Fig. 3) characteristic of Pd(0) show that high binding energy values can be attributed to charging of the nanoparticles in a nonconductive polymer environment, which shows an oxidation state higher than the one present in a real sample (38). After treatment of PdAu colloids with H₂ at 90°C for 1 h (typical pretreatment of the catalyst before DHL hydrogenation), the X-ray diffractogram does not change, while in the XPS spectrum of this sample the Pd(0) species prevail. This can be attributed to a change in the nanoparticle charging after hydrogen pretreatment: when the environment changes (hydrogen is adsorbed onto



FIG. 5. The Mg $K\alpha$ induced X-ray photoelectron spectra of bimetallic PdAu (a), PdPt (b), and PdZn (c) colloids recorded immediately after sample preparation (run 1) and after 12 h standing in the vacuum camera of spectrometer (run 2).

the Pd nanoparticle surface), the charge on the nanoparticles can change. Thus, for this particular polymeric environment, XPS data on bimetallic nanoparticles could not be considered as a reliable source of structural information because of artifact charging. On the other hand, because this charging does not occur for Pd nanoparticles, but is rather pronounced for bimetallic ones, this confirms the influence of a modifying metal on the electronic structure of bimetallic colloids.

2. Study of Catalytic Properties of Mono- and Bimetallic Colloidal Micellar Catalysts

2.1. Dependence of selectivity of catalysts on reaction conditions. To find the conditions providing the highest selectivity of colloidal catalysts in DHL hydrogenation, several parameters were varied: temperature, stirring rate, ratio of substrate, and catalyst amounts. These parameters influence both the selectivity and activity of catalysts. Table 4 shows the variation of reaction conditions and selectivity value for the PdAu catalyst as an example. For all the catalysts studied the highest selectivity (99.8% at 100% conversion) was obtained at 90°C, at 480 shakings per minute (with diffusion limitations (19)), at an initial DHL concentration $C_{\rm o}$ of 0.44 mol/L, and with a catalyst amount $C_{\rm c}$ of 2.3 imes 10^{-5} mol of Pd/L). Toluene was chosen as the reaction medium to provide the same environment of colloids in the micelle cores, which existed during synthesis of metal colloids (13, 14) and the most favorable conditions for micelle core availability for the substrate.

2.2. Kinetics of DHL hydrogenation. To find regularities of selective DHL hydrogenation with mono- and bimetallic colloids formed in block copolymer micelles, we studied the kinetics of the reaction. All experiments were carried out in toluene with a stirring rate of 960 shakings/min (without diffusion limitations) at 90°C and varying concentrations of substrate and catalyst in the range of 0.22–0.88 mol/L (C_0) and (1.01×10^{-5})–(4.08×10^{-5}) mol of Pd/L (C_c), respectively.

As a criterion allowing evaluation of the dependence of DHL conversion on time at various C_0 and C_c values, the ratio $q = C_0/C_c$ (mol/mol) was used. The analysis of the primary experimental data, presented in Fig. 6, shows that the higher the C_0/C_c ratio, the higher the hydrogenation time, which is typical for most catalytic reactions. As a result of experimental data processing, the 50% DHL conversion time ($\tau_{0.5}$) has been determined. The value of $\tau_{0.5}$ was found to depend on the ratio (C_0/C_c)ⁿ,

$$\tau_{0.5} \sim (C_{\rm o}/C_{\rm c})^n, \qquad [1]$$

where *n* is the formal parameter characterizing the slope of the ln $\tau_{0.5}$ dependence on ln $C_{\rm o}/C_{\rm c}$. In the case of the PdAu catalyst, n = 2, and for other catalysts, n = 1. These different values will be interpreted in terms of different mechanisms (see below).

GC analysis of all the samples obtained after DHL hydrogenation with mono- and bimetallic micellar catalysts showed mainly LN formation, though further saturation of the double bond to the single one yielding DiHL is also possible (Scheme 1). Other products have not been detected in the reaction mixture. Thus, the following reaction route can be suggested,

$$DHL \xrightarrow{k_1}_{+H_2} LN \xrightarrow{k_2}_{+H_2} DiHL,$$

TABLE 4

Run	Catalyst amount $C_{\rm c} imes 10^5$ (mol of Pd/L)	DHL concentration C _o (mol/L)	Temperature t _h (°C)	Shaking per minute	Hydrogenation time (s)	Selectivity (%)
1	2.30	0.44	90	480	1140	99.8
2	1.15	0.44	90	480	1320	98.7
3	4.45	0.44	90	480	780	98.5
4	2.30	0.66	90	480	1260	98.4
5	2.30	0.33	90	480	840	98.6
6	2.30	0.44	70	480	1680	98.2
7	2.30	0.44	80	480	1500	99.0
8	2.30	0.44	95	480	900	98.7
9	2.30	0.44	90	360	1380	99.0
10	2.30	0.44	90	600	840	97.6

Selectivity of DHL Hydrogenation with PS-b-P4VP/PdAu Depending on Reaction Conditions^a

^a In toluene.

where k_1 and k_2 are the hydrogenation rate constants. Because DHL hydrogenation here is characterized by high selectivity and the DiHL amount in the reaction mixture is negligible, $k_1 \gg k_2$, the second stage can be neglected in the computation.

The linear dependence of $\ln \tau_{0.5}$ on $\ln(C_0/C_c)$ allows us to introduce an independent variable, relative time Θ ,

$$\Theta = \tau / (C_0 / C_c)^n, \qquad [2]$$

where τ is the current reaction time.

To discuss the experimental data obtained at various values of the substrate/catalyst ratio C_o/C_c , we used relative concentrations of substrate (DHL) and product (LN),

$$x_i = C_i / C_0, [3]$$

where i = 1, 2 for DHL and LN, respectively, and C_i is the current substrate or product concentration. In so doing, the experimental data, presented in Fig. 6, have been brought together into a family of curves (Fig. 7) in the $x_2-\Theta$ coordinates. Thus, a mathematical description of the



FIG. 6. Dependence of DHL conversion on reaction time with Pd (a) and bimetallic PdAu (b), PdZn (c), and PdPt (d) catalysts for different substrate/catalysts ratios ($q = C_0/C_c$ mol of DHL/mol of Pd) at t_h 90° and 960 shakings/min.

experimental data can be represented as a system of differential equations,

$$\frac{dx_1}{d\Theta} = -W_1$$

$$\frac{dx_2}{d\Theta} = W_2,$$
[4]

where W_i is the reaction rate at initial concentration of the substrate $C_o = 1$ mol/L and concentration of the catalyst $C_c = 1$ mol/L.

Different mathematical methods are known (39, 40) for the description of the reaction kinetics. In the present paper the integral method (41) has been used to estimate kinetic model parameters. The cubic spline serves as interpolating function in this method. The integral efficiency function formulated has been minimized by the combined gradient method of Levenberg–Marquardt (42, 43). The kinetic equations obtained describing the kinetics of DHL hydrogenation correspond to the form of Langmuir– Hinshelwood equations (44).

For the computation of the kinetic model parameters, the following initial conditions have been defined: $\Theta = 0$, $x_1 = 1$, and $x_2 = 0$. In a first approximation, for W_1 explicit

form assignment, the linear model has been assumed,

$$W_1 = k x_1, [5]$$

where *k* is the kinetic parameter.

In this model the absence of adsorption (or coordination) interactions in the catalytic system has been presumed. To check this hypothesis as well as other models of DHL hydrogenation, the inverse problem has been solved using an explicit integral method (45).

According to the results of the inverse problem solving, for all the catalysts, the kinetic models have been chosen (Table 5) that describe well the hydrogenation kinetics (Fig. 7).

The models obtained are a formal description of the DHL hydrogenation kinetics with mono- and bimetallic colloidal catalysts. One can see that for the Pd catalyst the model equation is the same kind as that for PdPt and PdZn colloidal catalysts, but the coordination (adsorption) parameter Q is very small, so the second component in the denominator can be omitted. Thus, for the Pd catalyst, the rate of hydrogenation does not depend on the current substrate concentration, while for bimetallic catalysts complex dependence of the hydrogenation rate on substrate



FIG. 7. Dependence of DHL conversion on relative time with Pd (a) and bimetallic PdAu (b), PdZn (c), and PdPt (d) catalysts. For conditions see Fig. 6.

TABLE 5

Catalytic system	Model	$k \text{ (mol/mol)}^n \text{s}^{-1}$	Q^a	$\sigma imes 10^{2 b}$
PS- <i>b</i> -P4VP/Pd	W = k	$(2.08\pm0.02)\times10^{-2}$	_	1.65
PS-b-P4VP/PdAu	$W = \frac{kx_1}{(x_1 + Qx_2)^2}$	0.14	$\boldsymbol{0.140 \pm 0.009}$	2.07
PS-b-P4VP/PdZn	$W = \frac{\frac{kx_1}{kx_1}}{\frac{kx_1}{x_1 + Qx_2}}$	$(3.75\pm0.08) imes10^{-2}$	$(1.3\pm 0.1) imes 10^{-2}$	2.72
PS-b-P4VP/PdPt	$W = \frac{kx_1}{x_1 + Qx_2}$	$(5.8\pm0.1) imes10^{-2}$	$(5.2\pm 0.2) imes 10^{-2}$	2.57

Kinetics Models for DHL Hydrogenation with Mono- and Bimetallic Colloids Formed in Block Copolymer Micelles

^a Q is the coordination parameter, taking into account the coordination of the product and the substrate with catalyst.

 ${}^{b}\sigma$ is the mean square deviation of computation curves from the experimental data.

concentration is demonstrated. Moreover, for bimetallic catalysts, in the equation of the model the denominatorcontaining coordination (adsorption) parameter is introduced, which shows a more pronounced impact of the coordination (adsorption) processes on DHL hydrogenation compared to the monometallic one. Among all the catalysts, PdAu appears different: its model equations contain a squared term in the denominator.

To calculate the parameters in the Arrhenius equation, the temperature of DHL hydrogenation was varied from 50 to 95°C. Statistical analysis performed by the method described elsewhere (46) showed that within experimental error the coordination parameter Q can be considered constant and not dependent on the temperature. From the experimental results the Arrhenius dependence was drawn in the coordinates $\ln k - 1/T$ and frequency factor k_0 of the Arrhenius equation (which characterizes the amount of effective collisions or the amount of active centers (47)) and apparent activation energy *E* were calculated:

$$k = k_0 e^{-E/RT}.$$
 [6]

The data obtained are presented in Table 6. For all the bimetallic catalysts one can see the significant increase of active center amount. For PdPt and PdZn colloidal catalysts this can be explained by an increase of defects in bimetallic particles (24). However, particular attention should be drawn to the PdAu catalyst, which k_0 increases by several or-

TABLE 6

Parameters of Arrhenius Equation and TOF for Monoand Bimetallic Colloidal Catalysts

Catalyst	Activation energy (kJ/mol)	Frequency factor	Turnover frequency ^a (s ⁻¹)
PS- <i>b</i> -P4VP/Pd	23	66	18.5
PS-b-P4VP/PdAu	55	10 ⁷	36.9
PS-b-P4VP/PdZn	26	356	34.4
PS-b-P4VP/PdPt	26	659	49.2

^{*a*} Experimental conditions: t_h 90°C, toluene, volume of reaction mixture $V=30\times10^{-3}$ L, $C_0=0.44$ mol/L, $C_c=2.3\times10^{-5}$ mol of Pd/L, 960 shakings/min.

ders of magnitude. At the same time, the activation energy *E* increases approximately by a factor of 2 compared to that of other catalysts. It can be speculated that this difference is determined by the peculiar structure of PdAu colloids.

An increase of the activation energy for PdAu is in agreement with two facts: Au being a strong acceptor toward Pd and being located in the core of the particle (which is confirmed by CO adsorption) pulls electron density from Pd. The low electron density of these bimetallic colloids provides the favorable conditions for hydrogenation of double bonds as described in (23, 24), but at the same time for triple-bond hydrogenation, the high electron density on the catalyst surface is preferable (48). Then, low electron density increases the energy barrier of reaction. On the other hand, at the same nanoparticle size for bimetallic core-shell particles, nearly all the Pd atoms can be located on the surface of bimetallic particles (23, 24), while for Pd colloids, a fraction of Pd atoms is in the center of the particle. Thus, an increase of the number of active centers for PdAu colloids (compared to Pd nanoparticles) can be explained both by defects on the particle surface generated by the formation of core-shell structures and by the fact that all Pd atoms are on the surface and available for the substrate.

As discussed above, for the PdPt catalyst, CO adsorption was observed both for Pd and Pt species, confirming the cluster-in-cluster structure. The activation energy for this catalyst is similar to the Pd one, so an increase of catalytic activity can be ascribed to an increase of defects in bimetallic colloids (23–25). For the PdZn system, according to CO adsorption, we surmise the presence on the surface of both Pd atoms and Zn ions; the latter should not be reduced in the reaction conditions, which is confirmed by XPS data.

The turnover frequency (TOF) values (Table 6) for mono- and bimetallic colloidal catalysts show that, for bimetallics, the catalytic activity is higher than that for the Pd ones, which can be explained by modifying the influence of gold, platinum, and zinc. It is known that the addition of a second metal can change the electronic properties of catalyst (ligand effect) (49–53). As discussed in (54), this change can influence the energy of metal–hydrogen and metal– substrate bonds and the amount of hydrogen adsorbed. The addition of a modifying metal to a basic component can also change the surface geometry (ensemble effect) (51, 55–60). Thus, a combination of all these factors determines the change of catalytic activity of bimetallic catalysts, which is reflected in TOF values. Moreover, according to the kinetic results, DHL hydrogenation with mono- and bimetallic catalysts occurs by different mechanisms. This should be caused by the modifying influence of the second metal as well.

3. Hypothesis on Mechanism of the Selective DHL Hydrogenation

From the above results, we can propose a hypothesis on the mechanism for DHL hydrogenation with Pd and bimetallic catalysts and compare it with the computed kinetic models presented in Table 5.

3.1. Catalysts PS-b-P4VP/Pd, PS-b-P4VP/PdZn, and PSb-P4VP/PdPt. Presumably, hydrogen is activated on one kind of reactive center, which we call "metallic" (Z), and then diffuses along the surface to substrate molecules (S) adsorbed on other centers called "organometallic" (Z). Organometallic centers might be formed due to coordination of metal with polymer ligands (in the P4VP micelle core). For traditional heterogeneous catalysts, organometallic centers are formed due to coordination of metal with a substrate, solvent, or support or can be synthesized purposely (61). These two kinds of active centers should exist on each single colloidal particle. Their presence is confirmed by FTIR data on CO adsorption: existence of terminal and bridging CO.

Let us assume that in the reaction system there are intermediates SZ formed due to associative adsorption of DHL on organometallic active centers. The coordination of a substrate can be envisioned as



As this takes place, we propose that adsorption and desorption are fast and are in equilibrium,

$$S + Z' \stackrel{K_1}{\leftrightarrow} SZ', \tag{7}$$

where K_1 is the equilibrium constant.

Hydrogen is dissociatively adsorbed and activated with formation of atomic hydrogen on metallic active centers Z, which is in agreement with published data (40). Again, we assume that sorption–desorption occurs fast and these stages are in equilibrium,

$$\mathbf{H}_2 + 2Z \stackrel{K_n}{\leftrightarrow} \mathbf{H}_2 Z_2, \qquad \qquad [8]$$

$$H_2Z_2 \stackrel{K_m}{\leftrightarrow} 2HZ,$$
 [9]

where K_n and K_m are the equilibrium constants.

Because DHL hydrogenation is practically irreversible in the conditions used, the surface reaction between the coordinated substrate and hydrogen with the formation of LN (P) should be irreversible as well,

$$SZ' + 2HZ \xrightarrow{k_S} PZ' + 2Z,$$
 [10]

where *P* is the product (LN) and k_s is the rate constant of the surface reaction.

Let us assume that stages of adsorption and desorption of the product are fast as well and in dynamic equilibrium,

$$PZ' \stackrel{K_2}{\leftrightarrow} P + Z', \tag{11}$$

where K_2 is the equilibrium constant.

Then, the equation of the chemical reaction rate taking into account sorption-desorption of DHL and LN on organometallic centers and of hydrogen on metallic centers is given by

$$W = k_{\rm s} [SZ'] [HZ]^2.$$
 [12]

According to the assumption of fast equilibrium for stages [7]–[9], we get

$$[SZ'] = K_1 C_1 Z' \quad C_1 = [S],$$
[13]

$$[HZ]^2 = K_n [H_2 Z_2], [14]$$

$$[H_2 Z_2] = K_m [H_2] Z^2,$$
 [15]

$$[HZ]^2 = K_n K_m [H_2] Z^2, [16]$$

$$[PZ'] = K_2 C_2 Z' \quad C_2[P].$$
[17]

Then, we use a mass balance equation for surface compounds,

$$Z' + [SZ'] + [PZ'] = Z'_0,$$

$$Z^2 + [H_2Z_2] = Z_0,$$
[18]

where Z and Z are the occupied organometallic and metallic active centers and Z'_0 and Z_0 are the total numbers of active centers of both types; the latter values are proportional to the catalyst amount.

Assuming that $1 \ll (K_1C_1 + K_2C_2)$, then

$$Z'_0 = Z' + K_1 C_1 Z' + K_2 C_2 Z' = Z' (1 + K_1 C_1 + K_2 C_2)$$

= Z'(K_1 C_1 + K_2 C_2). [19]

As follows from above, similarly to the metal surface (40),

$$Z' = \frac{Z'_0}{(K_1 C_1 + K_2 C_2)},$$
[20]

$$Z_0 = Z^2 + [H_2 Z_2] = Z^2 (1 + K_n K_m [H_2]), \qquad [21]$$

$$Z^{2} = \frac{Z_{0}}{(1 + K_{n}K_{m}[H_{2}])}.$$
 [22]

Taking into consideration the equations [13]–[19] and [20]–[22], the rate of chemical reaction can be figured as

$$W = k_{s}K_{1}C_{1}Z'K_{n}K_{m}[H_{2}]Z^{2},$$

$$W = \frac{k_{s}K_{1}K_{n}K_{m}C_{1}Z'_{0}[H_{2}]Z_{0}}{(K_{1}C_{1} + K_{2}C_{2})(1 + K_{m}K_{n}[H_{2}])}$$

$$= \frac{kC_{1}C_{k}}{(K_{1}C_{1} + K_{2}C_{2})}.$$
[24]

One can see that the equation obtained is a Langmuir– Hinshelwood equation (44) and it coincides with the equation for the model (Table 5) when $x_1 = C_1$ and $x_2 = C_2$:

$$k = \frac{k_{\rm S} K_1 K_n K_m [{\rm H}_2] Z_0}{(1 + K_n K_m [{\rm H}_2])},$$
[25]

$$Q = \frac{K_2}{K_1}.$$
 [26]

The coincidence of the kinetic equation obtained with the equation of the model allows us to assume the correctness of our hypothesis and shows the physical meaning of the parameters of the model, where k is the kinetic parameter taking into account hydrogen adsorption on the catalyst and Q is the adsorption parameter equal to the ratio of adsorption constants of the product and substrate, respectively.

3.2. Catalyst PS-b-P4VP/PdAu. As discussed above, the PdAu catalyst differs from others and has presumably a core-shell structure. Similar to Pd colloids, PdAu bimetallic nanoparticles have only Pd atoms on the surface; however, judging by FTIR adsorption, on CO, the surface structure for a bimetallic catalyst is quite different. Here, we can assume the existence of active centers of only one type and probably competitive coordination of the substrate and hydrogen on these centers. The surface reactions of sorption–desorption for the substrate and hydrogen can be figured as

$$S + Z \stackrel{K_1}{\leftrightarrow} SZ,$$
 [27]

$$\mathbf{H}_2 + 2Z \stackrel{\kappa_n}{\leftrightarrow} \mathbf{H}_2 Z_2, \qquad [28]$$

$$H_2Z_2 \stackrel{K_m}{\leftrightarrow} 2HZ,$$
 [29]

where K_1 , K_m , and K_m are equilibrium constants.

For irreversible DHL hydrogenation, the surface reaction between the coordinated substrate and hydrogen with a formation of LN (P) is irreversible as well,

$$SZ + 2HZ \xrightarrow{\kappa_{S}} PZ + Z,$$
 [30]

where k_s is the rate constant of the surface reaction, followed by the desorption of the product:

$$PZ \stackrel{\kappa_2}{\leftrightarrow} P + Z'.$$
 [31]

Using all approaches discussed above, we obtain the following equation for the rate of the chemical reaction,

$$W = k_{s}[SZ][H_{2}Z] = k_{s}K_{1}[S]Z^{2}K_{n}[H_{2}],$$

$$Z_{0} = Z + K_{1}C_{1}Z + K_{2}C_{2}Z + ZK_{n}[H_{2}]$$

$$= Z(1 + K_{1}C_{1} + K_{2}C_{2} + K_{n}[H_{2}])$$

$$= Z(K_{1}C_{1} + K_{2}C_{2}),$$
[32]

because K_1C_1 and $K_2C_2 \gg K_n[H_2]$ and 1,

$$Z = \frac{Z_0}{(K_1 C_1 + K_2 C_2)},$$
[33]

$$W = \frac{k_{\rm s} K_1 C_1 K_n [\rm H_2] Z_0^2}{(K_1 C_1 + K_2 C_2)^2},$$
[34]

$$W = k_{s}[SZ'][H_{2}Z'] = \frac{k_{s}K_{1}K_{n}C_{1}(Z_{0})^{2}[H_{2}]}{(K_{1}C_{1} + K_{2}C_{2})^{2}}$$
$$= \frac{kC_{1}C_{k}^{2}}{(K_{1}C_{1} + K_{2}C_{2})^{2}}.$$
[35]

The equation above fits the equation of the model (Table 5) at

$$x_1 = C_1; \quad x_2 = C_2,$$
 [36]

$$k = k_{\rm s} K_1 K_n [\rm H_2], \qquad [37]$$

$$Q = \frac{K_2}{K_1}.$$
 [38]

In the kinetic equation [35], similarly to the model equation presented in Table 5, there is an inverse square dependence of the reaction rate on the concentration of adsorbed substrate and product. This coincidence confirms the correctness of our hypothesis. We surmise that the surface of the PdAu colloid is poor in electron density due to the Au core influence and that it attracts pyridine units more strongly from the P4VP micelle core and thus provides a denser packing of the modifying ligands. This packing yields a more uniform particle surface with only one kind of active center.

SUMMARY

Monometallic (Pd) and bimetallic (PdAu, PdPt, and PdZn) colloids formed in the PS-*b*-P4VP block copolymer micelles were studied in DHL hydrogenation. FTIR spectra of CO adsorbed onto PdPt and PdZn nanoparticles demonstrate two bands for CO terminal adsorption and also a band for the bridging one, while the spectrum of the PdAu sample shows only one band for terminal adsorption. This testifies to the presence of only Pd atoms on the PdAu nanoparticle surface and the existence of only one type of active center. The PdPt and PdZn bimetallics display both Pd and Pt(or Zn) atoms on the particle surface and the presence of two types of active centers on Pd. Due to the influence of the modifying metal, the catalytic activities of bimetallic catalysts are higher than that for the Pd one. For all the catalysts, the optimal conditions were found, providing high selectivity of hydrogenation (up to 99.8%), which is mainly determined by the modifying influence of pyridine groups in the P4VP cores. The study of the kinetics of DHL hydrogenation with these new catalysts allowed us to suggest a hypothesis for a hydrogenation mechanism, which fits computational kinetic models well.

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