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CHEMISTRY

Polymerization of Acetylene in Aqueous $PdCl_2$–CuCl Solutions: Novel Catalytically Active Palladium–Copper-Containing Carbon Materials

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Catalysis by transition metal complexes plays an important and increasing role in fine organic synthesis [1, 2] and chemical technology [3]. Homogeneous catalysis by metal complexes is fast progressing [4]. In recent years, there is an increasing trend to combine the advantages of homogeneous and heterogeneous catalysis by immobilization of transition metal compounds on active surfaces [5]. Carbon supports are of particular interest among such surfaces [6]. As a rule, catalysts are prepared by impregnation of the supports with transition metal compounds showing catalytic activity followed by their modification through thermal or chemical treatment [7] or by the grafting of metal complexes to functional polymers [8].

In this paper, we briefly discuss a new concept for the synthesis of catalysts, nano- and microreactors that are carbon materials incorporating transition metal compounds. The concept is that the carbon material is formed in a solution of transition metal compounds through the polymerization of low-molecular-weight precursors (acetylene, vinylacetylene, divinylacetylene, diacetylene, their oligomers and functional derivatives, for example, diacetylene alcohols, acids, amines, and heterocycles with acetylene substituents). Taking into account the high propensity of acetylene and diacetylene compounds to undergo polymerization, especially in the presence of transition metal compounds, one can expect their transformation into carbon materials incorporating polymerization catalysts in resulting macrochains, globules, and nanometer and submicron spheres.

This approach opens an opportunity for the tailor-made synthesis of nano- and microreactors as nanoclusters of catalytically active metals or their compounds encapsulated into a carbon material (polyconjugated polymers with electron conductivity). The hydrogen content in these composites can be controlled owing to the capacity of acetylene compounds for oxidative polycondensation to eliminate hydrogen and owing to oxidative aromatization. In this paper, we consider the efficacy of this approach using the simplest example of redox polymerization of acetylene in aqueous $PdCl_2$–CuCl solutions. The use of these transition metal salts is determined by the tremendous upgrowth of catalysis by palladium compounds [9] and by the fact that copper compounds are well-known catalysts of oligomerization and polymerization of acetylene and its oxidative polycondensation (vinylacetylene; divinylacetylene; "one-dimensional carbon," Sladkov's carbyne [10]).

Under these conditions, one can expect the formation of both polyvinylene **1** (acetylene polymerization via the triple bond):

$$n\mathrm{HC{\equiv}CH} \xrightarrow[\mathrm{H_2O}]{\mathrm{PdCl_2/CuCl/O_2\ (H_2O_2)}} \underset{\mathbf{1}}{\text{-}\!\!\left[\mathrm{CH{=}CH}\right]_n\!\!\text{-}}, \qquad (1)$$

and polyethynylene **2** (the oxidative polycondensation of acetylene):

$$n\mathrm{HC{\equiv}CH} \xrightarrow[\mathrm{H_2O}]{\mathrm{PdCl_2/CuCl/O_2\ (H_2O_2)}} \underset{\mathbf{2}}{\text{-}\!\!\left[\mathrm{C{\equiv}C}\right]_n\!\!\text{-}} + \mathrm{H_2O}. \qquad (2)$$

Furthermore, expected reactions are the cyclooligomerization of acetylene to yield, for example cyclooctatetraene, and trimerization of oligomers

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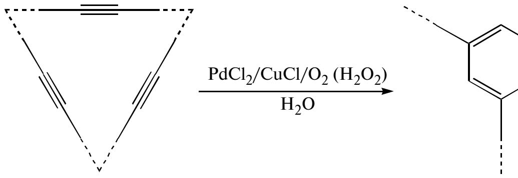
Table 1. Composition of acetylene polymerization products obtained in aqueous $PdCl_2$–CuCl solutions

Sample	Yield, %[a]	Composition, %					
		C[b]	H[b]	Cl[b]	Ash[b]	Pd[c]	Cu[c]
1[d]	81	26.3	1.3	9.4	61.3	6.4 (±0.5)	56.8 (±5.8)
2[e]	72	50.3	3.6	4.7	19.3	34.2 (±0.7)	1.0 (±0.1)
3[f]	67	54.2	4.1	13.6	17.5	29.6 (±2.3)	1.5 (±0.2)
4[g]	81	55.2	3.1	11.7	18.5	24.2 (±3.7)	3.7 (±0.4)
5[h]	91	55.5	3.8	3.3	11.2	13.3 (±2.9)	13.5 (±0.6)

Note: Reaction conditions: 100 mL of H_2O, 0.12% of $PdCl_2$, and 2.4% of CuCl, 20–25°C, acetylene passage rate is 20–30 mL/min. [a] Per $PdCl_2$ incorporated in the composite. [b] Elemental analysis data. [c] Data of atomic emission analysis. [d] Reaction time is 18 h. [e] Ammonium chloride (2.2 g) and 5 mL of 36% HCl were added to the reaction mixture, reaction time was 48 h, the composite was additionally washed with aqueous ammonia solution. The composite contained 4% of nitrogen in addition to the noted elements. [f] Reaction was carried out in 100 mL of 36% aqueous solution of hydrogen peroxide in the presence of 2.2 g NH_4Cl and 5 mL of 36% HCl, reaction time was 12 h. [g] Ammonium chloride (2.2 g) and 5 mL of 36% HCl were added to the reaction mixture, reaction time was 12 h. [h] Ammonium chloride (2.2 g) and 5 mL of 36% HCl were added to the reaction mixture, reaction time was 12 h, the composite was additionally washed with aqueous ammonia solution. The composite contained 8% of nitrogen in addition to the noted elements.

containing triple bonds to form compounds with cage or crosslinked structures:



3 (3)

The resulting polyconjugated blocks containing double (**1**) and triple bonds (**2**) and benzene rings (**3**) show a reduced ionization potential (low-energy HOMOs) and enhanced electron affinity (low-energy LUMOs) and, hence, should be apt to complexation with transition metal compounds.

Thus, the formation of the coordination sphere composed of a polyconjugated chain of a carbon polymer around the transition metal cation is probable in the course of polymerization.

The results of our experiments confirm the above assumptions. The polymerization of acetylene was carried out in air in diluted aqueous $PdCl_2$–CuCl solutions at ambient temperature and atmospheric pressure. In certain experiments, NH_4Cl and/or HCl were added to the salt solution. Atmospheric oxygen or hydrogen peroxide was used as the oxidizing agent. After 5–10 min of acetylene passage, the solution became rich black, which indicates the formation of a sol of a polymeric complex composed of polyacetylene, polydiacetylene, and palladium and copper compounds. The sol was gradually transformed into highly dispersed suspension (sol–gel transition). The resulting composites (dark brown light electrifiable powders) were analyzed. Their composition was determined by elemental analysis and atomic emission spectrometry (Table 1).

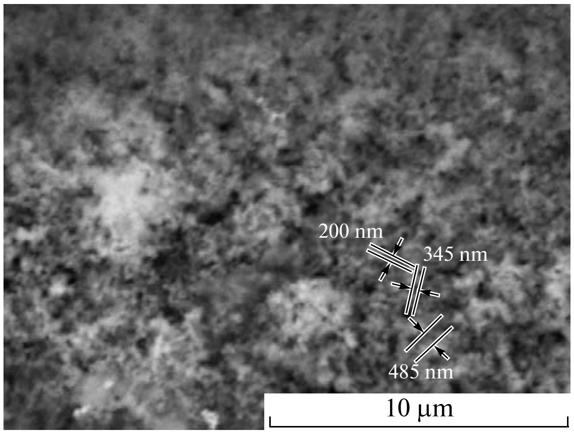
The composites were also studied by X-ray diffraction analysis and ESR spectroscopy (Table 2).

Elemental analysis and atomic emission spectrometry showed that the composites contained $PdCl_2$, copper chlorides, Pd(0), and, in some cases, Cu(0) (sample **1**) in different ratios depending on polymerization conditions. It is important that the main portion of palladium binds to the resulting polymer (the yield of the composite is 67–91% as calculated for palladium) (Table 1), the ratio is one palladium atom per 8–10 vinylene (ethynylene) units. The presence of up to 11% of Pd(0) (sample **3**) and up to 18% of Cu(0) (sample **1**) follows from the fact that the equivalent content of chlorine in the samples is much lower than the content of the metals.

The X-ray diffraction pattern of sample **1** shows narrow lines of paratacamite $Cu_2Cl(OH)_3$ [11]. The line with the interplanar spacing $d = 2.115$ Å, according to [12], refers to skaergaardite (PdCu) whose most intense line has $d = 2.122$ Å, the weak shoulder with $d = 2.093$ Å seems to refer to copper metal. The intense line of Pd(0) ($d = 2.2458$ Å) is likely to be overlapped with the nearby line of paratacamite ($d = 2.265$ Å), and the Pd(0) lines of lower intensity may not be detected on account of its low concentration.

Table 2. ESR characteristics of the composites

Sample	$N \times 10^{-19}$, spin/g	*g* factor	ΔH, G	Asymmetry parameter A/B
1	0.28	2.0041	6.3	Not determined
2	0.49	2.0044	7.0	0.79
4	5.30	2.0010	4.6	0.83
5	0.87	2.0012	7.1	Not determined



A micrograph of sample **2**.

The X-ray diffraction patterns of samples **2**–**5** show three significantly broadened lines (half-width is ~6° 2θ) which indicates the ultradisperse state of the composites (nanosystems). The interplanar spacing of lines with maxima at $d = 6.3$, 2.93, and 2.21 Å according to the data of [13, 14] refer to compounds $Pd(NH_3)_4PdCl_4$ and $Pd(NH_3)_2Cl_2$. The profile of experimental diffraction reflections is an envelope covering the lines (from three to seven) of the noted compounds; therefore it is difficult to assess the parameters of coherent scattering.

The relative content of carbon and hydrogen in the polymers indicates that, along with polyvinylene fragments **1**, they contain up to 4–5% (samples **1**–**3**) of polyethynylene blocks **2** (hydrogen-free). Thus, this confirms that the oxidative polycondensation of acetylene (equation (2)) also proceeds along with its polymerization at the triple bond (equation (1)).

The polyconjugated (polyvinylene–polyethynylene) structure of the polymers is confirmed by their characteristic paramagnetism (Table 2).

The ESR spectra of the composites show singlets common for polyconjugated polymers. They differ from narrow symmetrical lines typical for polyacetylenes [15] and show marked asymmetry and a larger width between maximal slope points. The spectra also show wide signals of different intensity related to Cu(II). The lack of correlation between the copper concentration and the intensity of Cu(II) signals confirms that copper in the composites is present preferably in nonmagnetic forms (Cu(0) or Cu(I)).

As for the morphology of the polymers (figure), they are nanometer and submicron spheres of 200–1000 nm in size where metallic components seem to be distributed over the surface as molecular complexes. The radius of the polymeric spheres and the extent of their dimensional homogeneity are dependent on polymerization conditions.

The catalytic activity of the composites was tested by the examples of important cross-coupling reactions (Sonogashira, Heck, and Suzuki reactions) and the oxidative coupling of acetylenes.

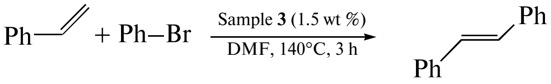
Under Sonogashira reaction conditions, sample **2** catalyses mainly the cross-coupling of phenylacetylene with iodobenzene (the yield of diphenylacetylene (**4**) is 31%)[1]:

$$\text{Ph}{-}{\equiv}{-}\text{H} + \text{Ph}{-}\text{I} \xrightarrow[\text{Et}_3\text{N, 90–93°C, 3 h}]{\text{Sample } \mathbf{2} \text{ (6.6 wt \%)}} \underset{\mathbf{4}}{\text{Ph}{-}{\equiv}{-}\text{Ph}}\,.$$

Sample **1** under the same conditions selectively catalyses the oxidative dimerization of phenylacetylene (the yield of diphenyldiacetylene (**5**) is 94%)[1]:

$$\text{Ph}{-}{\equiv}{-}\text{H} + \text{Ph}{-}\text{I} \xrightarrow[\text{Et}_3\text{N, 90–93°C, 3 h}]{\text{Sample } \mathbf{1} \text{ (6.7 wt \%)}} \underset{\mathbf{5}}{\text{Ph}{-}{\equiv}{-}{\equiv}{-}\text{Ph}}$$

The catalytic activity of composite **3** in the Heck reaction,[1]



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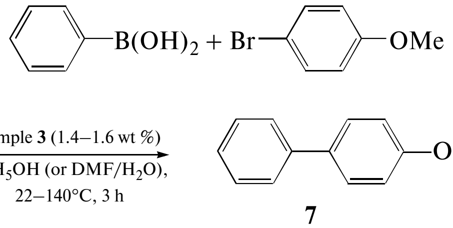
and Suzuki reaction was studied in comparison with couplings in the presence of $PdCl_2$ and 4% Pd/C (Table 3).



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Sample **3** catalyzes the Heck reaction between bromobenzene and styrene with efficacy virtually the same as 4% Pd/C or $PdCl_2$ and gives close yields of *trans*-stilbene **6** (Table 3, runs 1–3).

At the same time, sample **3** proved to be a more active catalyst in the Suzuki reaction than 4% Pd/C: the yield of the product of cross-coupling with *p*-bromoanisole was ~23%, whereas 4% Pd/C even with more reactive bromobenzene afforded about 5% yield. At the same time, sample **3** in the same reaction was found to be less active than $PdCl_2$. However, its activity at 140°C is close to that of $PdCl_2$ (Table 3, runs 8, 9). In the presence of 4% Pd/C, comparable yields were obtained only for more reactive bromobenzene (Table 3, run 10).

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[1] The concentration of samples is given toward the initial reagents.

Table 3. Heck and Suzuki reaction conditions

Run	Bromoarene (5 mmol)	Catalyst (wt %)[a]	Solvent (5 mL)	Yield of product, %
		Heck reaction[b]		
1	PhBr	Sample **3** (1.5)	DMF	16.0
2	PhBr	$PdCl_2$ (0.8)	"	16.0
3	PhBr	4% Pd/C (10.4)	"	16.3
		Suzuki reaction		
4[c]	*n*-BrC_6H_4OMe	Sample **3** (1.6)	Ethanol	22.9
5[c]	*n*-BrC_6H_4OMe	$PdCl_2$ (0.8)	"	66.3
6[c]	*n*-BrC_6H_4OMe	Pd/C (10.7), 4%	"	–
7[c]	PhBr	Pd/C (11.5), 4%	"	5.3
8[d]	*n*-BrC_6H_4OMe	Sample **3** (1.4)	DMF-H_2O	66.7
9[d]	*n*-BrC_6H_4OMe	$PdCl_2$ (0.7)	"	67.6
10[d]	PhBr	4% Pd/C (9.9)	"	70.1

Note: [a] Toward the initial reagents. [b] Styrene (5 mmol), NaOAc (6.5 mmol), 140°C, 3 h. [c] Phenylboronic acid (5 mmol), NaOH (6 mmol), 22°C, 3 h. [d] Phenylboronic acid (5 mmol), NaOAc (6.5 mmol), DMF–H_2O, 4 : 1 (5 mL), 140°C, 3 h.

EXPERIMENTAL

X-ray diffraction analysis was performed on a D8 Advance diffractometer with CuK_α radiation. Atomic emission analysis was carried out on a DFS-458 diffraction spectrograph with an MAES multichannel analyzer of emission spectra (VMK–Optoelektronika, Russia) using the method of complete evaporation of a sample from a channel of the graphite electrode in the direct current arc. ESR spectra were recorded on a Bruker ELEXSYS E 580 spectrometer. The concentration of paramagnetic centers was calculated with the use of diphenylpicrylhydrazyl standard. The micrographs of powders were obtained with a Hitachi TM-1000 scanning electron microscope. The powders were applied to a carbon support. The survey was carried out under reduced vacuum conditions (1.5×10^{-1} mm Hg).

Polymerization of acetylene in aqueous solutions (typical example). A mixture of 2.35 g (23.6 mmol) of CuCl, 2.24 g (42.0 mmol) of NH_4Cl, 0.123 g (0.7 mmol) of $PdCl_2$, and 100 mL of water was placed in a wide glass beaker and 5 mL of 36% HCl was added. Acetylene was passed through the solution at ambient temperature at a rate of 20–30 mL/min for 42 h, a black suspension formed in the solution, the suspension was allowed to stand for 12 h and filtered, the precipitate was washed with water (200 mL), alcohol (30 mL), and diethyl ether (30 mL). The precipitate was dried in vacuum (1 mmHg) for 12 h to give 0.41 g (81% based upon taken $PdCl_2$) of a dark-brown highly dispersed powder (Table 1, sample **4**).

Thus, we have demonstrated experimentally for the first time the possibility to obtain catalytically active palladium- and copper-containing carbon nanometer and submicron spheres by the polymerization of acetylene in aqueous $PdCl_2$–CuCl solutions.

The obtained composites catalyze synthetically important cross-coupling reactions (Sonogashira, Heck, Suzuki) and the oxidative dimerization of acetylenes. Change in polymerization conditions provides a possibility to vary within a wide range the morphology and filling of carbon matrix with palladium and copper in different valence states and hence to manage the catalytic activity of the composites. The results illustrate the new concept for the synthesis of catalysts applied on carbon matrix. The concept is based on the formation of carbon material from low-molecular-weight precursors, for example, acetylene or its derivatives, in the presence of compounds of catalytically active metals.

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