

### Preliminary communication

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## HETEROGENEOUS CATALYTIC HYDROGENATION OF ALKENES AND ALKYNES IN THE PRESENCE OF COORDINATION POLYMERS OF PALLADIUM(0;II) AND PLATINUM(0;II)

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### Summary

Coordination polymer matrices of palladium(0;II) and platinum(0;II) with 4,4'-diisocyanobiphenyl linkages, constitute a new class of effective heterogeneous hydrogenation catalysts for alkenes and alkynes.

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Heterogeneous catalytic hydrogenation of alkenes and alkynes comprises a wide variety of synthetically useful reactions [1], some of which are of industrial importance. Active metal dispersions are often used as heterogeneous catalysts for such reactions [2]. Special emphasis in the past decade has been placed on the development of immobilized catalysts on solid supports (e.g., organic polymers, inorganic oxides, etc.) [3]. Polymer-bound catalysts are in general less reactive than the active metal dispersions, and therefore, their synthetic applications appear to be limited in scope. In an attempt to develop new and effective catalyst systems, the hydrogenation of certain alkenes and alkynes has been examined in the presence of heterogeneous catalysts consisting of coordination polymers of palladium(0;II) and platinum(0;II), and the results are described below.

The reaction of  $\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\eta^5\text{-C}_5\text{H}_5)$  and  $\text{Pt}(1,5\text{-cyclooctadiene})_2$  with the polymerizing ligand 4,4'-diisocyanobiphenyl [4] in toluene at ambient temperature gave totally insoluble brown to rust colored polycrystalline precipitates of the approximate compositions  $[\text{M}(\text{C}_{14}\text{H}_8\text{N}_2)_x]_n$  (1:  $\text{M} = \text{Pd}$ ,  $x = 1.82 \pm 0.12$ ; 2: ( $\text{M} = \text{Pt}$ ,  $x = 1.25 \pm 0.2$ ). Similar reactions between 4,4'-diisocyanobiphenyl and  $\text{MCl}_2(1,5\text{-cyclooctadiene})$  ( $\text{M} = \text{Pd}$  and  $\text{Pt}$ ) in  $\text{CH}_2\text{Cl}_2$  gave the insoluble yellow

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TABLE 1

INITIAL RATES AND SELECTIVITIES DURING THE HETEROGENEOUS CATALYTIC HYDROGENATION OF CERTAIN ALKENES AND ALKYNES IN THE PRESENCE OF THE NEW ZERO-VALENT MATRICES 1 (M = Pd) AND 2 (M = Pt)

Substrate	Catalyst	Initial rates (mmol min) <sup>-1</sup> [mmol-metal] <sup>-1</sup> <sup>a</sup>			
		Consumption	Hydrogenation	Isomerization	Selectivity (%)
1-Octene	1; M = Pd	56	25	31	45 <sup>b</sup>
1-Hexene	1; M = Pd	46	14	32	30 <sup>b</sup>
1-Hexene	Pd (10%)/carbon	48	18	30	37 <sup>b</sup>
1-Hexene	PdO	19	6	13	32 <sup>b</sup>
1-Hexene	2; M = Pt	15	11	4	73 <sup>b</sup>
<i>trans</i> -2-Hexene	1; M = Pd	16	8	8	50 <sup>b</sup>
Cyclohexene	1; M = Pd	5	5	—	—
	2; M = Pt	5	5	—	—
Cyclooctene	1; M = Pd	4	4	—	—
Styrene	1; M = Pd	4	4	—	—
	2; M = Pt	4	4	—	—
1,5-Cyclooctadiene	1; M = Pd	4	3(ene)	1 <sup>c</sup>	93 <sup>d</sup>
			<0.1(ane)		
1,5-Cyclooctadiene	2; M = Pt	0.52	0.41(ene)	—	84 <sup>d</sup>
			0.11(ane)		
1-Hexyne	1; M = Pd	2.7	2.7(ene)	<sup>e</sup>	76 <sup>d</sup>
			<0.01(ane)		
Phenylacetylene	1; M = Pd	0.71	0.63(ene)	—	84 <sup>d</sup>
			0.08(ane)		
Phenylacetylene	2; M = Pt	0.14	0.11(ene)	—	77 <sup>d</sup>
			0.03(ane)		

<sup>a</sup> Conditions: 0.017–0.019 mmol-metal; 15 ml methanol solution of the substrate (0.2–0.3 M); 25°C; 2 atm H<sub>2</sub>; catalyst prehydrogenated (~15 h). <sup>b</sup> [Rate of hydrogenation/rate of consumption] × 100.

<sup>c</sup> Small amounts of 1,4-cyclooctadiene are initially formed; this isomer disappears rather fast from the reaction mixture. <sup>d</sup> Calculated on the basis of ene-ane composition at half reaction point with respect to hydrogen consumption. <sup>e</sup> Isomerization of 1-hexene, the initial product in this reaction, becomes meaningful only close to the half reaction point.

low polymers [MCl<sub>2</sub>(C<sub>14</sub>H<sub>8</sub>N<sub>2</sub>)]<sub>n</sub> of palladium(II) (3) and platinum(II) (4). Water adsorbed by polymers 1–4 when handled in air can be removed under vacuum. The new coordination polymer matrices were characterized by elemental and thermal gravimetric analyses and power X-ray diffraction, and from their infrared, diffuse reflectance, and X-ray photoelectron spectra. The structures of 1 and 2 appear to consist of [M(4,4'-diisocyanobiphenyl)]<sub>n</sub> networks which are cross-linked by bridging 4,4'-diisocyanobiphenyl ligands. Comparison between the *x* terms in 1 and 2 suggests fewer cross-linking ligands in the latter matrix. The structural features of 3 and 4 are consistent with the polymerization of the bi-valent metals, mainly through terminally coordinated diisocyanide linkages.

The heterogeneous catalytic activity of the prehydrogenated zero-valent matrices 1 and 2 during the hydrogenation (2 atm. H<sub>2</sub>; 25°C; CH<sub>3</sub>OH) of certain alkenes and alkynes, was evaluated with respect to initial rates and selectivities (Table 1). High rates, comparable with those obtained with the commercial catalyst Pd(10%)/carbon, were observed in the presence of 1 (M = Pd) for the terminal aliphatic alkenes 1-octene and 1-hexene. Hydrogenation of hexene is slower in the presence of 2 (M = Pt) than of 1 (M = Pd), but there is significantly greater selectivity. The rates in the presence of 1 (M = Pd) decrease in the order 1-hexene (terminal) > *trans*-2-hexene (internal) > cyclohexene (cyclic).

Comparable rates were observed for 1 (M = Pd) and 2 (M = Pt) as catalysts in hydrogenation of cyclohexene, cyclooctene and styrene. The semihydrogenation of 1,5-cyclooctadiene, a non-conjugated diene, to cyclooctene in the presence of 1 (M = Pd) or 2 (M = Pt), proceeds with a selectivity of 93 and 94%, respectively. A somewhat lower selectivity, in the range of 76–84%, was observed for semihydrogenation of the terminal acetylenes, 1-hexyne (1, M = Pd) and phenylacetylene (1, M = Pd; 2, M = Pt). The rates and selectivities in the semihydrogenation reactions appear to be lower for 2 (M = Pt) than for 1 (M = Pd).

The new zero-valent catalysts 1 and 2 reported herein are readily prepared and stored. These catalysts undergo neither leaching out nor degradation to metallic particles under the mild conditions utilized in the catalysis. Moreover, catalysts may be recycled without any apparent loss in their catalytic activity. In most instances, the performance of the new zero-valence matrices in terms of initial rates and selectivities (Table 1) appears to be superior to that obtained with various polymer-bound complexes [5–7], as well as metal/graphite catalysts [8]. The high and durable catalytic activity under mild conditions, achieved with a low catalyst-substrate molar ratio (0.5%), are points relevant to possible synthetic organic applications.

In comparison with the zero-valent matrices 1 (M = Pd) and 2 (M = Pt), the catalytic hydrogenation of alkenes and alkynes in the presence of the bi-valent polymers 3 (M = Pd) and 4 (M = Pt) is quite slow. Nevertheless, these bi-valent matrices bring about the stereoselective semihydrogenation of certain internal alkynes. For instance, the semihydrogenation of 2-octyne with 3 (M = Pd) proceeds with an initial rate of  $0.5 \text{ mmol min}^{-1} [\text{mmol-Pd}]^{-1}$  to give *cis*-2-octene, with stereoselectivity of 95%. A similar reaction with 4 (M = Pt) involves an initial rate of  $0.4 \text{ mmol min}^{-1} [\text{mmol-Pt}]^{-1}$  and stereoselectivity of ~89%. In contrast to the results with bi-valent matrices, the catalytic hydrogenation of 2-octyne in the presence of 1 (M = Pd) proceeds via the *trans*-2-octene (major) and *cis*-2-octene (minor) isomers to *n*-octane which is formed with an initial rate of  $0.45 \text{ mmol min}^{-1} [\text{mmol-Pd}]^{-1}$ . The stereoselectivity observed with the new bi-valent matrices 3 and 4 appears to approach the range of performance of some of the best stereospecific semihydrogenation catalyst systems reported to date [8–12]. The advantages presented by 3 and 4 relate to ease of their preparation and their stability under normal storage conditions.

The development of the new palladium(0;II) and platinum(0;II) 4,4'-diisocyanobiphenyl matrices 1–4 exemplify the potential of coordination polymers in catalysis.

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