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Catalytic Hydrogenation of Olefins and Acetylenes over $C_{60}Pd_n$

Hideo NAGASHIMA, * Akihito NAKAOKA, Syuji TAJIMA, Yahachi SAITO,† and Kenji ITOH
Department of Materials Science, Toyohashi University of Technology, Toyohashi, Aichi 441
†Department of Electrical and Electronic Engineering, Mie University, Tsu, Mie 514

Organopalladium polymers of buckminsterfullerene, $C_{60}Pd_n$, catalyze hydrogenation of olefins and acetylenes at room temperature under a hydrogen atmosphere. The catalytic activity is mainly dependent on the ratio of C_{60} to Pd in the polymers. Partial hydrogenation of acetylenes is achieved by adding benzylamine as the cocatalyst.

Explosive studies on Buckminsterfullerene (C_{60}) and other spherical carbon clusters have provided us a number of fascinating physical properties and chemical reactivities of these new aromatic molecules.[1,2] In our previous paper, we reported a preparative route to organopalladium polymers, $C_{60}Pd_n$, as the first organometallic polymer of fullerenes, and referred to their catalysis toward heterogeneous hydrogenation of diphenylacetylene to 1,2-diphenylethane.[3] In this paper, we describe that the catalytic activity of $C_{60}Pd_n$ is dependent on the preparative route of the polymer, and successful hydrogenation of olefins and partial hydrogenation of acetylenes can be achieved with certain composition of $C_{60}Pd_n$.

Two methods were so far established to synthesize various composition of $C_{60}Pd_n$ as shown in Eqs. 1 - 2.[3] The reaction of C_{60} and $Pd_2(dba)_3{\cdot}CHCl_3$ [dba = dibenzylideneacetone] can control the composition of C_{60} to Pd in the polymer by changing the charged ratios of C_{60} to the palladium precursor (Eq. 1). $C_{60}Pd_n$, where n = 1 - 7, were synthesized by this method. An alternative synthetic method for $C_{60}Pd_n$, where n = 2 - 3, is thermal disproportionation of $C_{60}Pd_n$ (n = 1 - 2) as shown in Eq. 2. On heating in refluxing toluene, palladium content in $C_{60}Pd_n$ became close to 2.5 - 2.7 and C_{60} was regenerated. Similar thermal disproportionation did not occur with $C_{60}Pd_n$ ($n > 3$). In contrast, we have now discovered that C_{60} reacted with $C_{60}Pd_n$ ($n > 3$) in boiling toluene to lower the palladium content as shown in eq. 3. In a typical example, a mixture of $C_{60}Pd_{3.37}$ (5 mg, 4.7 μmol) prepared by Method A and C_{60} (11.5 mg, 16 μmol) was heated in toluene under reflux for 5 h to give $C_{60}Pd_{2.84}$ (4.5 mg) and recovery of C_{60} (10 mg). Substantial change of the palladium contents was not observed with $C_{60}Pd_n$ ($n < 3$) under the same conditions.

$$C_{60} + (n/2)Pd_2(dba)_3{\cdot}CHCl_3 \longrightarrow C_{60}Pd_n\ [n = 1 - 7] \quad \text{(Method A)} \qquad (1)$$

$$C_{60}Pd_n\ (n < 3) \longrightarrow C_{60}Pd_n\ [n = \text{ca. } 3] + C_{60} \quad \text{(Method B)} \qquad (2)$$

$$C_{60}Pd_n\ (n > 3) + C_{60} \longrightarrow C_{60}Pd_n\ [n = \text{ca. } 3] \quad \text{(Method C)} \qquad (3)$$

Table 1. Preparation of $C_{60}Pd_n$ and Catalytic hydrogenation of diphenylacetylene [a)]

Precursor	Method	Catalyst (mg)[b)]	$t_{1/2}$
$Pd_2(dba)_3 \cdot CHCl_3 + C_{60}$ (0.5 : 1)	A	$C_{60}Pd_{1.44}$	No reaction
$Pd_2(dba)_3 \cdot CHCl_3 + C_{60}$ (1.5 : 1)	A	$C_{60}Pd_{2.58}$	No reaction
$Pd_2(dba)_3 \cdot CHCl_3 + C_{60}$ (2.5 : 1)	A	$C_{60}Pd_{3.37}$	45 min
$Pd_2(dba)_3 \cdot CHCl_3 + C_{60}$ (5 : 1)	A	$C_{60}Pd_{6.99}$	13 min
$C_{60}Pd_{1.44}$	B	$C_{60}Pd_{2.46}$	No reaction
$C_{60}Pd_{2.58}$	B	$C_{60}Pd_{2.71}$	No reaction
$C_{60}Pd_{3.37}$	C	$C_{60}Pd_{2.78}$	330 min
$C_{60}Pd_{6.99}$	C	$C_{60}Pd_{4.23}$	20 min

a) Diphenylacetylene (1 mmol) was stirred in cyclohexane (10 ml) at room temperature under a hydrogen atmosphere. Amount of palladium in the catalyst is 1 mol% to diphenylacetylene.

b) The ratios of palladium and C_{60} in $C_{60}Pd_n$ were determined by the Elemental Analysis and EPMA.

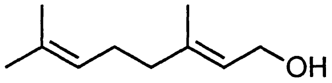
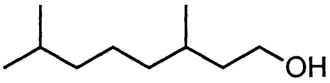
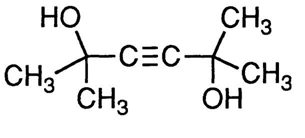
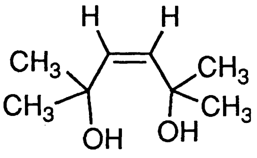
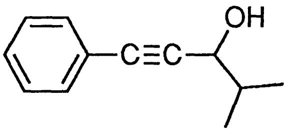
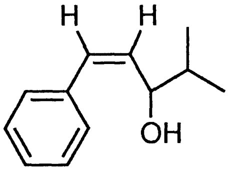
Hydrogenation over $C_{60}Pd_n$ was carried out in cyclohexane under a hydrogen atmosphere at room temperature. In Table I is summarized the catalytic activity as half-lives of the reaction with $C_{60}Pd_n$ prepared by the above three methods. The rate of the reaction was mainly dependent on the C_{60}/Pd ratio in the catalyst. Higher ratio of Pd to C_{60} in $C_{60}Pd_n$ resulted in the increase of the reaction rate in the case of $n > 3$. In contrast, $C_{60}Pd_n$ ($n < 3$) prepared by Method A or Method B was totally inactive. The catalytic activity of $C_{60}Pd_{2.78}$ or $C_{60}Pd_{4.23}$ prepared by Method C was lower than their precursors, $C_{60}Pd_{3.37}$ or $C_{60}Pd_{6.99}$, respectively.

We have pointed out in our previous paper, there would be two types of palladium atoms in $C_{60}Pd_n$; one is a binder of C_{60}, another is surface palladium atoms active for the catalytic hydrogenation.[3,4)] The above results showed that the surface palladium atoms would exist in $C_{60}Pd_n$ ($n > 3$), but do not in $C_{60}Pd_n$ ($n < 3$). The reaction of C_{60} with up to 1.5 molar excess of $Pd_2(dba)_3 \cdot CHCl_3$ gave $C_{60}Pd_n$, in which all of the palladium atoms act as the binder of C_{60}. In increasing the ratio of the palladium precursor to C_{60} over 1.5, the surface palladium atoms are produced. Thermal disproportionation shown in Eq. 2 from $C_{60}Pd_n$ ($n < 3$) does not produce the surface palladium atoms. In contrast, the reaction of $C_{60}Pd_n$ ($n > 3$) with C_{60} shown in Eq. 3, which lowered the catalytic activity, suggests that a part of the surface palladium atoms reacted with C_{60}, giving rise to the conversion to the binder of C_{60}.

Catalytic hydrogenation of olefins over $C_{60}Pd_n$ ($n = 4.61$) also proceeded at room temperature under a hydrogen atmosphere. Ketones, esters, and aromatic rings were not hydrogenated under the conditions. The results are summarized in Table 2.

Interest in the hydrogenation of acetylenes is a possibility of partial hydrogenation of acetylenes to cis-olefins. A time-conversion plot of the hydrogenation of diphenylacetylene over $C_{60}Pd_n$ revealed the existence of cis-stilbene as an intermediate, suggesting the substantial rate

Table 2. Hydrogenation of olefins and acetylenes over $C_{60}Pd_n$ [a)]

Substrate	Method	Time	Product	Yield/%
diphenylacetylene	I	70min	1,2-Diphenylethane	91
	II	6 h	cis-stilbene	$77^{b)}$ (95 : 0 : 5)
cyclooctene	I	3 h	cyclooctane	98(GC)
methylcyclohexene	I	160 min	methylcyclohexane	98(GC)
	I	24 h		83
$PhCH=CHCH_2OAc$	I	45 min	$PhCH_2CH_2CH_2OAc$	87
$PhCH=CHCO_2Me$	I	2 h	$PhCH_2CH_2CO_2Me$	95
$PhCH=CHCOMe$	I	80 min	$PhCH_2CH_2COMe$	80
	II	6 h		$80^{b)}$ (96 : 4 : 0)
	II	6 h		$76^{b)}$ (95 : 5 : 0)

a) Typical procedures; Method I. A mixture of $C_{60}Pd_{5.05}$ (1 mg, 4×10^{-3}mmol) and substrate (4.8×10^{-2} mmol) was stirred in cyclohexane (3 ml) under a hydrogen atmosphere. Method II. A mixture of $C_{60}Pd_{4.61}$ (3 mg, 1.15×10^{-2} mmol) and benzylamine (1.15 mmol) was stirred overnight under a hydrogen atmosphere. Then, a substrate (1.45 mmol) was added and the mixture was stirred for 6 h under a hydrogen atmosphere. It was confirmed that no substantial difference of the catalytic activity was observed between $C_{60}Pd_{4.61}$ and $C_{60}Pd_{5.05}$. b) Figures in parenthesis were the ratios among cis-olefin, trans-olefin, and alkane, respectively, determined by ^1H NMR.

difference between the hydrogenation of diphenylacetylene to cis-stilbene and that of cis-stilbene to 1,2-diphenylethane. After screening of solvents and several cocatalyst, we found that the partial hydogenation to cis-stilbene was achieved by the addition of amines in methanol. In Table II are shown three examples of partial hydrogenation of internal acetylenes over $C_{60}Pd_n$ (n = 5.05) in the presence of benzylamine.

Spherical carbon clusters (fullerenes) are large aromatic molecules having extensively delocalized π-electrons on their surface. Because of their spherical structure, the shape of π-orbitals is close to sp^3 rather than sp^2. Catalysis of $C_{60}Pd_n$ is an interesting entry to understand the interaction of these characteristic π-orbitals on C_{60} with metallic species from synthetic organic chemistry. The above results suggest that features of $C_{60}Pd_n$ as the hydrogenation catalysts resemble the Lindler catalyst[6,7] or palladium on graphite[8] rather than Pd / C. In fact, the addition of benzylamine to Pd /C (5%) retarded the rates of hydrogenation of diphenylacetylene; however, hydrogenation to form 1,2-diphenylethane was seriously competed with the selective hydrogenation to stilbene. Selectivity of cis-stilbene formation is comparable or sometimes more excellent than the conventional catalysts.[6-8] These results suggest that the nature of C_{60} as a metal support is of interest in comparison with charcoal and graphite. Mechanistic studies and development of new catalysis are actively in progress.

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