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Preparation, characterisation and catalytic hydrogenation properties of palladium supported on C_{60}

Rongqing Yu,[a] Qiping Liu,[a] Kuang-Lee Tan,[b] Guo-Qin Xu,[a]* Siu Choon Ng,[a] Hardy S. O. Chan[a] and T. S. Andy Hor[a]*

Departments of Chemistry[a] and Physics[b], Faculty of Science, National University of Singapore, Kent Ridge, Singapore 119260

A C_{60}-supported Pd catalyst has been prepared by reaction between C_{60} and $Pd(OAc)_2(PPh_3)_2$ in toluene, to give the complex $C_{60}[Pd(OAc)_2(PPh_3)]_3$, followed by H_2 treatment at 523 K for 4 h. Catalytic quantities (1 mol%) promote hydrogenation of diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene to give 100% conversion to 1,2-diphenylethane, phenylethane, cyclohexane and hexane within 18, 13, 21 and 12 min, respectively. Hydrogenation of the same substrates under similar conditions using Pd on activated charcoal (10%) as catalyst gives similar yields but at a longer time (20, 18, 27 and 15 min, respectively). Both the Pd-C_{60} catalyst and its precursor were characterised by thermogravimetry (TG), FTIR, mass spectrometry (MS), powder XRD, X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM).

Since the discovery and subsequent large-scale production of C_{60} as a new allotrope of carbon, there has been great activity in the development of the science and technology of this new material.[1–7] In line with our on-going work on the synthesis and catalytic applications of organometallic complexes[8] and C_{60}-doped polymeric materials,[9] we are especially interested in the development of metallobuckminsterfullerenes, $(ML_x)_nC_{60}$, and their catalytic applications. In recent years, there has been increasing interest in this area of research.[10–14] The technological significance of catalytic hydrogenation and the established hydrogenation ability of many organometallic complexes in catalytic quantities prompted us to focus our investigations in this direction. Palladium on activated carbon in the form of charcoal is an established hydrogenation catalyst and is one of the current catalysts-of-choice.[15] Its multitude of applications in organic synthesis, materials science and industrial operations reflects its scientific and technological significance. The use of this heterogeneous catalyst, however, has several notable problems: (1) the preparative procedure usually involves heterogeneous deposition, such as ion exchange or impregnation, whereby the conformity and uniformity of the dispersion are critical as they affect the catalyst performance; (2) commercial samples are commonly available in the form of 1–10% Pd on charcoal. There is little room for regio- or chemioselectivity except by changing the concentration of Pd on the support; (3) despite the wide uses of Pd on charcoal, the catalytic mechanism in many cases is still poorly understood. This is traced to the difficulty in the study of surface structure and behaviour of impregnated Pd solids in solution. In an attempt to overcome these problems, we chose to study the molecular interaction of palladium complexes on C_{60}, where we can afford a leverage of control on the nature of the catalyst used. This molecular control is facilitated by adjusting the nature and number of the ligands on the metal, or the number of metal fragments on the spherical buckyball. It is somewhat surprising that the catalytic use of Pd complexes on C_{60} as a molecular model for Pd on charcoal is ill developed in the current literature.[12] Here, we report some of our initial findings and establish a means of hydrogenation of a Pd-C_{60} complex to give a catalyst which shows comparable, or better hydrogenation activity than conventional Pd on charcoal catalysts.

Experimental

Preparation of palladium-C_{60} catalyst (**2**) and its precursor, $C_{60}[Pd(OAc)_2(PPh_3)]_3$ (**1**) was as follows: $Pd(OAc)_2$ ($OAc^- = CH_3CO_2^-$) (0.033 g, 0.15 mmol) was dissolved in toluene (15 ml) and triphenylphosphine (PPh_3) (0.0786 g, 0.3 mmol) was added under a nitrogen atmosphere. After 30 min, a toluene solution (35 ml) of C_{60} (0.036 g, 0.05 mmol) was added to the resultant yellow solution. Upon stirring, the mixture darkened and a black precipitate formed. This precipitate was isolated by filtration and washed with toluene (2 × 15 ml). The resulting black product (**1**) was dried *in vacuo* for 5 h. **1** was then reduced under a dynamic flow (20 $cm^3\ min^{-1}$) of H_2 gas while the temperature was raised from 298 to 523 K at 3 K min^{-1} and then held at 523 K for 4 h. The gas flow was then changed to helium and the catalyst **2** was obtained after cooling the sample.

Microanalysis, FTIR, MS and TG were used to characterise **1** and **2**. Powder XRD was measured with a Philips 1700 diffractometer with Cu-Kα radiation. XPS analysis for the Pd state in **1** and **2** was carried out on a VG ESCALAB MKII spectrometer using an Mg-Kα X-ray source (1253.6 eV, 120 W) at a constant analyser. TEM observation was made on a JEOL-100 CX II transmission electron microscope at 100 keV accelerating voltage. A conventional carbon-supported palladium catalyst (Pd/C) with 10% Pd content was obtained from Aldrich Chemical Inc.

Catalytic hydrogenation over the Pd-C_{60} catalyst and Pd/C was carried out in methanol under 1 atm H_2 at room temperature (rt). Four substrates were investigated: diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene. In a typical reaction, Pd in the form of **2** or commercial Pd/C (0.01 mmol) was mixed with the substrate (1 mmol) in methanol (15 ml) under a H_2 atmosphere. Conversion was monitored by gas chromatographic (GC) analysis using a Hewlett-Packard 5890 GC equipped with a flame ionisation detector and methyl silicone capillary column.

Results and Discussion

A catalyst precursor **1** was synthesised as a near-black powder from $Pd(OAc)_2(PPh_3)_2$, generated *in situ* from $Pd(OAc)_2$ and PPh_3 (1 : 2),[16] and C_{60} in toluene. Microanalysis of $C_{60}[Pd(OAc)_2(PPh_3)]_3$ gives: C, 69.06; H, 2.69; Pd, 15.40; P, 4.11%. Calc. for $C_{126}H_{63}P_3O_{12}Pd_3$: C, 69.38; H, 2.89; Pd, 14.65; P, 4.26%. Its insolubility in all common organic solvents precludes the growth of suitable crystals for X-ray single-crystal diffraction analysis. It was characterised by FTIR, MS, TG, XRD, TEM and XPS.

$Pd(OAc)_2(PPh_3)_2$ is an established pre-catalyst in many C–C coupling reactions, especially the Heck-type reactions.[17] Its ability to undergo spontaneous decomposition to a Pd^0 phosphine complex enables it to be used as a convenient catalyst precursor.[18,19] This complex is hence not isolated upon formation. Its reaction with C_{60} is rapid and not sensitive to the stoichiometry; use of molar ratios 1 : 1, 2 : 1, 3 : 1 and 5 : 1 for $Pd(OAc)_2(PPh_3)_2 : C_{60}$ lead to the same product. These reactions suggest that **1** is in a thermodynamically stable form.

The IR spectrum of **1** shows, besides the usual absorption peaks of coordinated acetate and PPh_3, some C_{60} absorptions characterising metal-coordinated C_{60}. The absorption peaks of its FTIR spectrum (KBr) are at 486(s), 524(vs), 565(w), 578(w), 692(s), 726(s), 1182(m), 1424(m), 1650(m, br) cm^{-1}. The doublet pattern of a weak band at *ca.* 576 cm^{-1} is indicative of a lower symmetry of the C_{60} moiety upon metal attachment.[20] The mass spectrum confirms the presence of the ligands, *viz.* PPh_3 and $CH_3CO_2^-$, and their oxidised and thermal fragments, such as $OPPh_3$, $OPPh_2$, Ph and CO_2. The TG profile also indicates the release of the ligands below 573 K and the C_{60} fragment at a higher temperature.

Although the molecular structure of **1** cannot be ascertained, based on the above data, there is strong evidence that it contains a palladium fragment bearing labile acetate and phosphine ligands anchoring onto a spherical C_{60} ball. The elimination of one phosphine from $Pd(OAc)_2(PPh_3)_2$ in the formation of **1** is consistent with its replacement by an electron-donating ethylene-type group at the 6 : 6 ring fusion of C_{60}.[21,22] This would maintain a 16-electron d^8-Pd^{II} complex. It is interesting to note the thermodynamic stability of a 3 : 1 Pd : C_{60} complex. Similar observations have been found in a similar *exo*-complex, $\{C_{60}[Ru(C_5Me_5)(CH_3CN)_2]_3\}^{3+}3X^-$,[3] and a metallofullerene solid, $C_{60}Pd_3$.[23]

Although complex **1** is catalytically active for the hydrogenation of diphenylacetylene, the level of activity (17% yield at rt after 3 h) is unsatisfactory. This is explained by the saturation of the Pd^{II} sphere. Treatment with H_2 by heating the complex under a dynamic gas flow of H_2 at a temperature of 523 K activates the catalyst by introducing coordination unsaturation by ligand elimination with simultaneous reduction by providing active hydrogenated sites. The catalyst, **2**, thus formed was similarly analysed by FTIR, XRD, TEM and XPS.

The IR spectrum of **2** shows the characteristic coordinated C_{60} absorptions, but those of the co-ligands are significantly diminished. The peaks are found at 487(s), 516(vs), 692(vs), 740(vs), 1093(m), 1182(m), 1433(s) cm^{-1}. Powder XRD reveals that both **1** and **2** are poorly crystalline, in contrast to the pristine crystallinity of C_{60}. The diffraction patterns of **1** and **2** are similar and contain broad peaks. One notable difference between **1** and **2** is an additional diffraction peak in the latter at $2\theta \approx 40°$, which could be assigned to the (111) plane of metallic Pd clusters[24] supported on the C_{60}. The broadness of this peak signifies the small particle size of the clusters. This conclusion is supported by the TEM studies which indicate that **1** is a uniform amorphous powder and that **2** contains black particles of metallic palladium dispersed on the C_{60} supporting surface (see Fig. 1). These Pd clusters are 5–15 nm in diameter and are not found in the TEM of the precursor **1**. This is understandable, since **1** resembles more a molecular complex of Pd^{II}. Further support for this arises from the XPS data shown in Fig. 2. Complex **1** gives a pair of peaks with the binding energy (E_b) of the $Pd3d_{5/2}$ state at 338.1 eV and a spin–orbit splitting of the $3d_{5/2}$ and $3d_{3/2}$ states of 5.3 eV. The spectrum of **2** gives a broad band which can be curve-fitted into two pairs of peaks with E_b at 335.5 and 337.0 eV of $Pd3d_{5/2}$ (in a 7 : 3 ratio) with a spin–orbit splitting of *ca.* 5.3 eV. These peaks correspond to the presence of both Pd^0 metallic state and a higher oxidation state intermediate between 0 and +2. The higher E_b found in **1** is consistent with the higher oxidation state of Pd (*i.e.* +2) in **1**. The dominant peak of **2**, with a lower E_b, is indicative of metallic Pd clusters on the C_{60} support. As fullerenes are known to be electron deficient,[25] it is reasonable to suggest

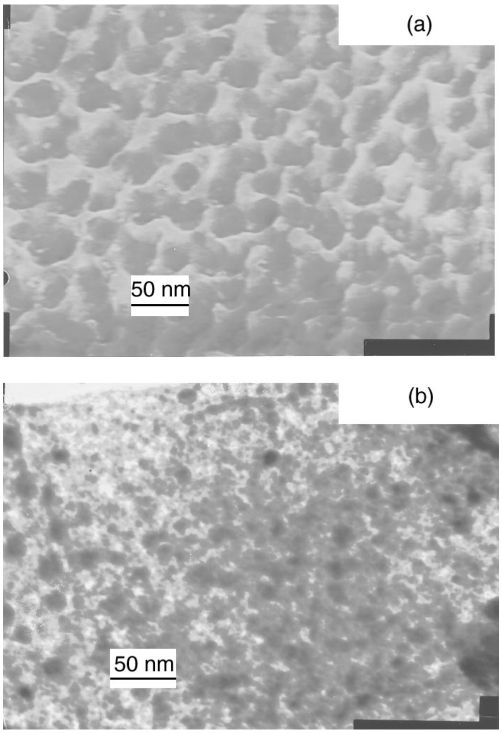

Fig. 1 TEMs of (a) the precursor, $C_{60}[Pd(OAc)_2(PPh_3)]_3$, **1**, showing its molecular aggregation, and (b) the catalyst, **2**, showing the Pd clusters formed during treatment with hydrogen

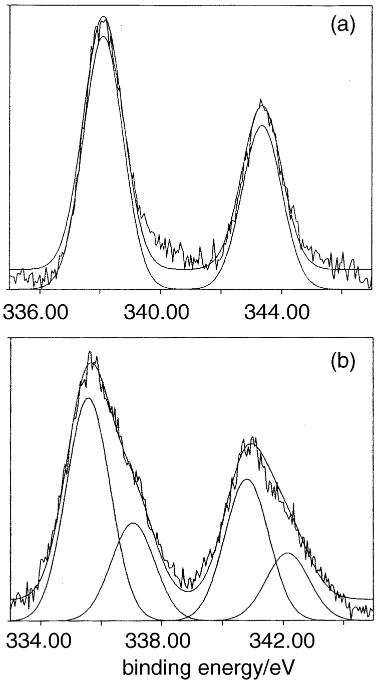

Fig. 2 XP spectra with computer-fitted peak of Pd 3d core level for (a) the precursor, $C_{60}[Pd(OAc)_2(PPh_3)]_3$, **1** and (b) the catalyst, **2**

Table 1 Catalytic hydrogenation of alkynes and alkenes at rt in methanol

substrate	catalyst	product	yield (%)	time/ min
diphenylacetylene	Pd-C_{60}	1,2-diphenylethane	100	18
	Pd/C	1,2-diphenylethane	100	20
phenylacetylene	Pd-C_{60}	phenylethane	100	13
	Pd/C	phenylethane	100	18
cyclohexene	Pd-C_{60}	cyclohexane	100	21
	Pd/C	cyclohexane	100	27
hex-1-ene	Pd-C_{60}	hexane	100	12
	Pd/C	hexane	100	15

that some interaction exists between Pd clusters and the C_{60} support, whereby electron donation from the metal fragment to C_{60} is achieved. The observed higher oxidation state in **2** with higher E_b can be attributed to this interaction. Similar behaviour has been observed in Pd dispersed on fullerene soot.[26]

A series of experiments was carried out for the hydrogenation of diphenylacetylene, phenylacetylene, cyclohexene and hex-1-ene under 1 atm of H_2 in methanol, catalysed by 1 mol% of **2** at rt. Two typical reaction profiles are depicted in Fig. 3 and the final results are listed in Table 1. All four substrates indicate complete conversion (100% yields) within 13 to 21 min. For comparison, a commercial sample of 10% Pd/C catalyst was also studied in these systems under the same conditions. The results, which are summarised in Table 1, showed a similar conversion but at a slightly longer time (15 to 27 min). This suggests that our Pd-C_{60} composite is an efficient hydrogenation catalyst which may be applied to other stubborn substrates. Catalyst **2** can also be recycled by reactivation with H_2. Although the detailed catalytic mechanism is presently unknown, it is reasonable to propose that the spherical nature of C_{60} provides an effective surface support for a number of metal fragments, at which the active catalytic sites are found. In addition, the good dispersion of Pd on C_{60} and the interaction between Pd clusters and the C_{60} support probably contribute to the high hydrogenation activities in these systems.

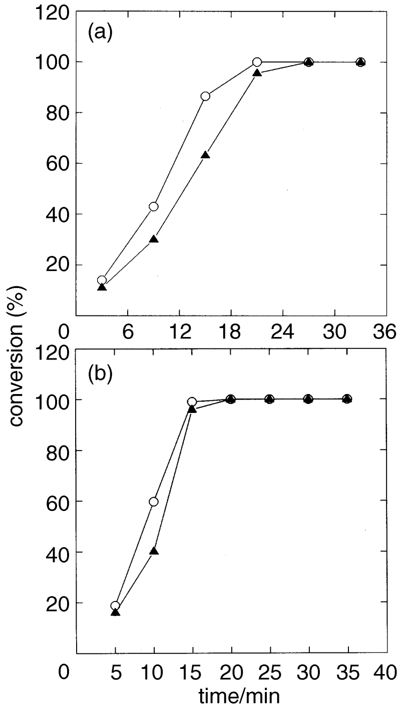

Fig. 3 Hydrogenation of substrates: (a) cyclohexene and (b) diphenylacetylene over the catalyst, **2** (○) and Pd/C (▲) in methanol under a H_2 atmosphere at rt

This study serves as a model for our future study of the interaction of other metallic fragments with the spherical π-electron system of C_{60}. A study of catalytic dehalogenation of polyhalogenated aromatic hydrocarbons (PHAHs) using these metallofullerene catalysts is in progress.

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