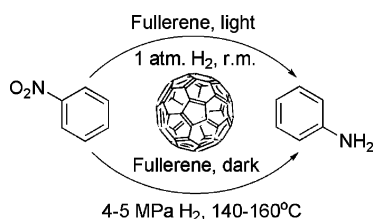# A Nonmetal Catalyst for Molecular Hydrogen Activation with Comparable Catalytic Hydrogenation Capability to Noble Metal Catalyst

Baojun Li and Zheng Xu*

State Key Laboratory of Coordination Chemistry and Nanjing National Laboratory of Microstructure, Department of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, PR China

Received August 5, 2009; E-mail: zhengxu@netra.nju.edu.cn

Molecular hydrogen not only is a bright future fuel but also is widely used today in fundamental chemical transformations. For example, all crude oil is treated with H_2 and 10^8 tons of ammonia fertilizer is produced annually via catalytic hydrogenation. Any small improvement of the performance and cost of the catalysts would help to cut the cost of these important processes. But such improvements are hard to achieve because the H_2 is held together in a strong marriage. It can be split apart only by using a transition metal in most of the catalytic systems known.[1] Although a few of nontransition metal catalysts for hydrogenation reactions have been reported such as KOtBu[2,3] and organocatalyst,[4,5] such systems require serious reaction conditions or do not employ H_2 directly but a surrogate as the stoichiometric source of hydrogen. The only nonmetallic systems reported to split apart H_2 under mild experimental conditions are phosphine-borane species,[6–10] a stable digermyne,[11] and selected carbenes.[12,13] The key issue for developing nonmetal hydrogenation systems is to search out an effective system that reacts cleanly with H_2, but few are known.

Here we demonstrate that fullerene[14] can activate molecular hydrogen and is a novel nonmetal hydrogenation catalyst. The hydrogenation of aromatic nitro compounds to amino aromatics is achieved on this catalyst with high yield and selectivity under 1 atmospheric pressure of H_2 and light irradiation at room temperature. More interestingly, there exists a cooperation effect between C_{60} and C_{60}^-. At $C_{60}:C_{60}^- = 2:1$, ~100% conversion and ~100% selectivity are achieved under conditions of 120–160 °C and 4–5 MPa of H_2 pressure without light irradiation. The catalytic performance is comparable with that of the noble metal catalyst. Also, it exclusively catalyzes the reduction of a nitro group without the need to add metal salts and avoids the accumulation of the corresponding hydroxylamine and the formation of azoxy and azo compounds and is a highly selective and environmentally friendly catalyst. These findings foreshadow a new catalytic system available for applications both in academic laboratories and in industry, allowing stoichiometric reductions mediated by Fe or Na_2S to be performed in a catalytic fashion and greatly reducing subsequent waste production. Moreover, the catalyst developed here could replace expensive precious metal catalysts, therefore offering the potential benefit of lowering cost and diminishing the environmental impact from heavy-metal pollutants.

Table 1. Hydrogenation of Nitrobenzene to Aniline under Light Irradiation with Various Fullerene Catalysts at Room Temperature[a]

entry	catalyst	light radiation	t, h	conv. %	select. %
1	absence	UV	1.0	0	~
2	C_{60}	absence	4.0	0	~
3	C_{60}^-	absence	1.0	0	~
4	C_{60}	UV	1.0	82.6	78.9
5	C_{60}	UV	4.0	100	92.4
6	C_{60}^-	UV	4.0	98.2	72.5
7	C_{70}	UV	4.0	89.9	92.9
8	C_{70}^-	UV	4.0	84.0	87.6
9	C_{60}	visible	4.0	39.1	74.8

[a] Reaction conditions: 1.0 g of substrate, 0.036 g of catalyst, and 250 mL of THF solvent under 1 atmospheric pressure of H_2 and light irradiation (300 W high pressure Hg lamp or 350 W Xe lamp) in a cylinder quartz reactor.

The control experiments showed that the H_2 molecule cannot react with nitrobenzene to form aniline in the absence of light irradiation or C_{60} catalyst (Table 1, entries 1–3). In a typical reaction, 0.036 g of C_{60} and 1.0 g of nitrobenzene were added in a quartz reactor containing 250 mL of tetrahydrofuran (THF) with stirring and bubbled with N_2 and H_2 in succession to remove air and to saturate the reactor with H_2 respectively, and the high-pressure-mercury lamp was turned on and illuminated for 1 h with bubbled H_2; the reacted solution was then filtered to separate the solid C_{60} catalyst. The filtrate was analyzed by GC–MS. The results show that the main product is aniline with 21.1% azoxybenzene and azobenzene. The yield of aniline is 78.9% with 82.6% conversion of nitrobenzene (Table 1, entry 4). Prolonging the time to 4 h gives aniline in 92.4% yield with ~100% conversion of nitrobenzene and the yield of azoxybenzene and azobenzene further decreases to 7.6%. The results showed that the C_{70} molecule as well as C_{70} and C_{60} anions also can catalyze the hydrogenation of nitrobenzene with similar conversion and selectivity under the same conditions as in the case of C_{60} catalyst (Table 1, entries 6–8). The conversion and selectivity are 98.2% and 72.5% for C_{60}^- catalyst; 89.9% and 92.9% for C_{70} catalyst, and 84.0% and 87.6% for C_{70}^- catalyst. MALDI TOF MS data show that the fullerene catalyst after reaction still is fullerene itself without fullerene hydride, which rules out the possibility of fullerene hydride as an active hydrogen intermediate (Figure S4). The experiments under visible light irradiation were conducted. The result (Table 1, entry 9) indicates that it also works, but the efficiency is less than that of UV irradiation; a possible reason is that there is insufficient overlap between the emission spectra of the Xe lamp and the absorption of one C_{60}. Various C_{60} produced by different companies exhibit a similar catalytic performance with ~96% conversion and ~88% selectivity under UV irradiation and ~94% conversion and ~73% selectivity under dark. The detailed

results are listed in Tables S1 and S2. Recently, the catalysis of a trace amount of metal contaminates in the coupling reactions has been reported.[15] To rule out the possibility of catalysis by a trace amount of metal contaminates in the fullerene, the metal contaminates in fullerene were determined by an inductively coupled plasma (ICP) emission spectrometer. A trace amount (ppm) of Co, Cr, Cu, Fe, and Ag was found in C_{60} samples, others are below the detecting limit (Table S3). The control experiments of catalytic hydrogenation of nitrobenzene by various metal ions alone (absence of fullerenes) and by the blank solution of preparation C_{60}^- (that is, absence of C_{60}, see SI for details) were completed, and the results showed that no aniline could be detected and the influence of a trace amount of metal contaminates on the catalytic hydrogenation of nitrobenzene may be neglected (see SI).
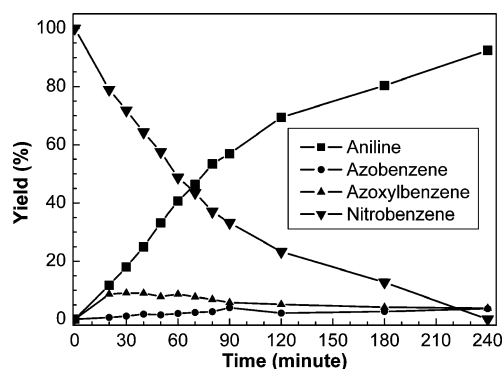

Figure 1. Catalytic hydrogenation of nitrobenzene on C_{60} catalyst under light irradiation. Reaction conditions: 1.0 g of substrate, 0.036 g of catalyst, and 250 mL of THF solvent under 1 atmospheric pressure of H_2 and room temperature.

To determine if the azoxybenzene and azobenzene are intermediates of the consecutive reactions, we carried out hydrogenation of nitrobenzene on the C_{60} catalyst in a batch reactor by following the reaction with time. The plots of reaction products against time are depicted in Figure 1. In the case of C_{70} or the C_{70} anion as a catalyst, similar curves were obtained (Figures S9, S10). These results show that the yields of azoxybenzene and azobenzene are quite low and are almost constant within 240 min, which are out of accordance with the character of the consecutive reactions. It seems that azoxybenzene and azobenzene were not an intermediate in the reaction sequence nitrobenzene→nitrosobenzene→azoxybenene→azobenzene→aniline[16] but rather products from a side reaction. The hydrogenation of nitrobenzene is more like to occur mainly through the direct route, that is, nitrobenzene→nitrosobenzene→phenyl hydroxylamine→aniline.[16] The exact mechanism is unknown; a further study is underway.

Fullerene is excellent in hydrogenation not only for nitrobenzene but also for aromatic nitro compounds such as 4-nitrobenzonitrile, 4-nitroacetophenone, and 4-chloronitrobenzene. The plots of products vs time are shown in Figures 2, S7, and S8, respectively. From Figure 2, we can see that the hydrogenation reaction proceeds very rapidly, and ∼100% conversion of nitrobenzonitrile with ∼100% selectivity was achieved within only 1 h. There is no bis(cyano)azoxybenzene in the reaction products after reacting for 1 h.

Based on these results, we might conjecture that electronically excited C_{60} or C_{70}, H_2, and nitrobenzene form a synergistic exciplex, which makes the H_2 molecule active and achieves transfer of hydrogen atoms to the nitro group to form aniline. Unfortunately,
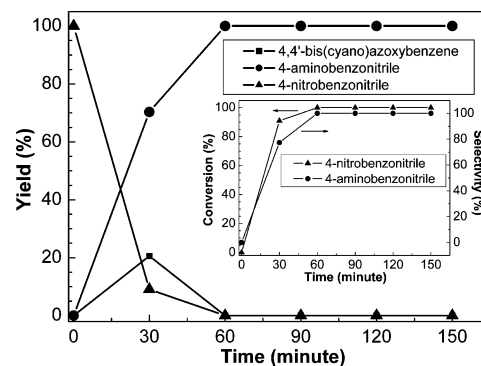

Figure 2. Catalytic hydrogenation of 4-nitrobenzonitrile on C_{60} catalyst under light irradiation. Reaction conditions: 1.0 g of substrate, 0.036 g of catalyst, and 250 mL of THF solvent under 1 atmospheric pressure of H_2 and room temperature.

the reactivity of the electronically excited state of C_{60} and C_{70} is all but unknown. Further studies including kinetic and theory calculation are underway.

Table 2. Hydrogenation of Nitrobenzene to Aniline with Various C_{60} Catalysts under Dark Condition[a]

entry	catalyst	H_2, MPa	T, °C	conv. %	select. %
1	C_{60}	5.0	140	3.8	87.8
2	C_{60}^-	absence	140	0	∼
3	C_{60}^-	2.0	100	21.4	46.4
4	C_{60}^-	3.0	100	45.0	40.4
5	C_{60}^-	3.0	120	92.4	74.1[b]
6	C_{60}^-	3.0	140	96.0	70.9
7	C_{60}^-	3.0	140	71.2[c]	61.1
8	C_{60}^-	5.0	140	99.7	73.2
9	C_{60}^-	5.0	160	>99.9	88.9
10	C_{60}/C_{60}^- (1:1)	5.0	140	99.9	91.3
11	C_{60}/C_{60}^- (2:1)	5.0	140	99.8	99.0
12	C_{60}/C_{60}^- (2:1)	5.0	160	>99.9	>99.9
13	C_{60}^{2-}	5.0	140	45.5	27.4
14	C_{70}^-	5.0	140	37.3	84.7

[a] Reaction conditions: 1.0 g of substrate, 0.036 g of catalyst, and 40 mL of THF solvent for 4.0 h; the different components in the product are listed in Table 3. [b] Azoxybenzene as main product. [c] Reaction conditions: 4.0 g of substrate, 0.036 g of catalyst, and 40 mL of THF solvent for 12 h.

Although catalytic hydrogenation of aromatic nitro compounds cannot occur without light irradiation at ambient conditions, it takes place well under forcing conditions of 120−160 °C and 4−5 MPa of H_2 pressure (Table 2). In this case, the catalytic performance of the C_{60} anion is better than that of neutral C_{60}. The reason for that is inclear; it seems that the solubility of C_{60} anion in THF is better than that of neutral C_{60}, and the charge on the C_{60} anion is of benefit to the formation of a synergistic complex. The experimental results exhibit that conversion of nitrobenzene increases with increasing H_2 pressure or reaction temperature (Table 2, entries 3−9). At the optimum conditions (160 °C, 5 MPa of H_2), 99.9% conversion of nitrobenzene with 88.9% selectivity of aniline are achieved (Table 2, entry 9). The results show that the catalytic performance of the C_{60}^- catalyst has no remarkable degradation after increasing the amount of substrate and prolonging the reaction time by 4 and 3 times respectively (Table 2, entry 7), which is equivalent to that of the catalyst after reuse ∼4 times. It is interesting that there was a cooperative effect between the C_{60} anion and neutral C_{60} (Table 2, entries 10−12). At the optimum ratio of C_{60}/C_{60}^- (= 2:1), the selectivity of aniline significantly increases from 73.2% (C_{60}^- alone,

140 °C) to 99% (C_{60}:C_{60}^- = 2:1, 140 °C) and to ~100% (C_{60}:C_{60}^- = 2:1, 160 °C), while the conversion of nitrobenzene is maintained at ~100%. It is an excellent nonmetal hydrogenation catalyst for hydrogenation of aromatic nitro compounds, and the catalytic performance is comparable to that of the noble metal counterpart, which has never been reported before.

Table 3. Product Distribution of Hydrogenation Reactions Listed in Table 2

entry in Table 2	nitro-	azoxy-	azo-	aniline
1 (C_{60}, 5 MPa of H_2, 140 °C)	96.2	0.5	0	3.4
3 (C_{60}^-, 2 MPa of H_2, 100 °C)	78.7	11.5	0	9.8
4 (C_{60}^-, 3 MPa of H_2, 100 °C)	55.0	26.1	0.7	18.2
5 (C_{60}^-, 3 MPa of H_2, 120 °C)	7.6	68.5	7.5	16.4
6 (C_{60}^-, 3 MPa of H_2, 140 °C)	4.1	0	27.9	68.0
8 (C_{60}^-, 5 MPa of H_2, 140 °C)	0.3	5.0	21.7	73.2

The distribution of different products of hydrogenation reactions is listed in Table 3. The catalytic activity of the neutral C_{60} solid is quite poor and the conversion of nitrobenzene and selectivity of aniline are only 3.8% and 87.8% respectively with 0.5% azoxybenzene (Table 3, entry 1), whereas the catalytic performance of the C_{60} anion is quite good with the conversion and selectivity at 99.7% and 73.2% respectively; the byproducts are azobenzene (21.7%) and azoxybenzene (5%)(Table 3, entry 8). As the reaction temperature and H_2 pressure increase, the conversion of nitrobenzene increases and the product compositions change significantly. For example, the yield of azoxybenzene increases remarkably from 11.5% to 26.1% with increasing H_2 pressure from 2 to 3 MPa (Table 3, entry 4) and further increases to 68.5% with increasing reaction temperature to 120 °C (Table 3, entry 5). Upon further increase in temperature to 140 °C, aniline becomes a main product with 68.0% yield (Table 3, entry 6). It seems that increasing the reaction temperature and H_2 pressure is of benefit to the formation of aniline and azobenzene.

Table 4. Hydrogenation of Various Substrates with C_{60} and C_{60}^- Catalyst[a]

entry	substrate	catalyst	product	conv. %	select. %
1	azobenzene	C_{60}^-	aniline	34.6	100
2	azoxybenzene	C_{60}^-	azobenzene	82.7	91.6
3	azobenzene	C_{60}	aniline	2.9	100
4	azoxybenzene	C_{60}	azobenzene	3.4	80.2

[a] Reaction conditions: 0.5 g of substrate, 0.036 g of catalyst, 40 mL of THF solvent, under 5.0 MPa of H_2 and 140 °C for 4 h.

To gain insight into the reaction mechanism, the catalytic hydrogenations of azoxybenzene and azobenzene were studied (Table 4). We can see clearly that their conversion is quite low under the same conditions as those for hydrogenation of nitrobenzene. If they are the intermediates of the reaction sequence, their conversion and the yield of aniline should be similar with those for the hydrogenation of nitrobenzene. It seems that the hydrogenation reaction under dark conditions occurs mainly through a direct route but also condensation route.[16]

In summary, the results reported here show that neutral fullerene, the fullerene anion, and their combination are excellent nonmetal hydrogenation catalysts for aromatic nitro compounds to amino aromatics with high conversion and selectivity under UV irradiation

and 1 atmospheric pressure of H_2 at room temperature. There was a cooperative effect between C_{60} and C_{60}^- and at an optimum ratio (2:1); ~100% conversion and ~100% selectivity are achieved under dark conditions at 5 MPa of H_2 and 160 °C. The results are comparable with those of the noble metal catalyst, which are being reported for the first time. The reaction mechanism might involve a synergistic exciplex (under light irradiation) or an active complex (under dark conditions). We anticipate our discovery to be a starting point for more effective all carbon molecular-based nonmetal catalyst systems for molecular hydrogen activation and will promote the development of electronically excited state reactions and novel molecular H_2 activation and storage systems. The exact mechanism is not clearly understood at this moment, and a further study is underway.

Supporting Information Available: Experimental details and analytical results of fullerene catalysts. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For general reviews on the hydrogenation, see: (a) Chen, B.; Dingerdissen, U.; Krauter, J. G. E.; Lansink Rotgerink, H. G. J.; Möbus, K.; Ostgard, D. J.; Panster, P.; Riermeier, T. H.; Seebald, S.; Tacke, T.; Trauthwein, H. Appl. Catal., A **2005**, 280, 17–46. (b) Mäki-Arvela, P.; Hájek, J.; Salmi, T.; Murzin, D. Y. Appl. Catal., A **2005**, 292, 1–49.
(2) (a) Walling, C.; Bollyky, L. J. Am. Chem. Soc. **1961**, 83, 2968–2969. (b) Walling, C.; Bollyky, L. J. Am. Chem. Soc. **1964**, 86, 3750–3752.
(3) Berkessel, A.; Schubert, T. J. S.; Mller, T. N. J. Am. Chem. Soc. **2002**, 124, 8693–8698.
(4) Barbe, G.; Charette, A. B. J. Am. Chem. Soc. **2008**, 130, 18–19.
(5) Magnus, R.; Antonchick, A. P.; Theissmann, T. Angew. Chem., Int. Ed. **2006**, 45, 3683–3686.
(6) (a) Welch, G. C.; San Juan, R. R.; Masuda, J. D.; Stephan, D. W. Science **2006**, 314, 1124–1126. (b) Stephan, D. W. Dalton Trans. **2009**, 3129–3136.
(7) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. Dalton Trans. **2007**, 3407–3414. (b) Spies, P.; Erker, G.; Kehr, G.; Bergander, K.; Fröhlich, R.; Grimme, S.; Stephan, D. W. Chem. Commun. **2007**, 5072–5074.
(8) (a) Welch, G. C.; Stephan, D. W. J. Am. Chem. Soc. **2007**, 129, 1880–1881. (b) Geier, S. J.; Gilbert, T. M.; Stephan, D. W. J. Am. Chem. Soc. **2008**, 130, 16232–16233. (c) Kenward, A. L.; Piers, W. E. Angew. Chem., Int. Ed. **2008**, 47, 38–41. (d) Holschumacher, D.; Bannenberg, T.; Hrib, C. G.; Jones, P. G.; Tamm, M. Angew. Chem., Int. Ed. **2008**, 47, 7428–7432. (e) Chase, P. A.; Stephan, D. W. Angew. Chem., Int. Ed. **2008**, 47, 7433–7437.
(9) (a) Ullrich, M.; Lough, A. J.; Stephan, D. W. J. Am. Chem. Soc. **2009**, 131, 52–53. (b) Geier, S. J.; Stephan, D. W. J. Am. Chem. Soc. **2009**, 131, 3476–3477. (c) Ramos, A.; Lough, A. J.; Stephan, D. W. Chem. Commun. **2009**, 1118–1120.
(10) (a) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Angew. Chem., Int. Ed. **2007**, 46, 8050–8053. (b) Chase, P. A.; Jurca, T.; Stephan, D. W. Chem. Commun. **2008**, 1701–1703. (c) Rokob, T. A.; Hamza, A.; Stirling, A.; Pápai, I. J. Am. Chem. Soc. **2009**, 131, 2029–2036.
(11) (a) Spikes, G. H.; Fettinger, J. C.; Power, P. J. Am. Chem. Soc. **2005**, 127, 12232–12233. (b) Peng, Y.; Brynda, M.; Ellis, B. D.; Fettinger, J. C.; Rivard, E.; Power, P. P. Chem. Commun. **2008**, 6042–6044.
(12) Ko1tting, C.; Sander, W. J. Am. Chem. Soc. **1999**, 121, 8891–8897.
(13) Frey, G. D.; Lavallo, V.; Donnadieu, B.; Schoeller, W. W.; Bertrand, G. Science **2007**, 316, 439–441.
(14) (a) Wu, M.; Wei, X.; Qi, L.; Xu, Z. Tetrahedron Lett. **1996**, 37, 7409–7412. (b) Wei, X.; Wu, M.; Qi, L.; Xu, Z. J. Chem. Soc., Perkin Trans. 2 **1997**, 1389–1393.
(15) (a) Arvela, R. K.; Leadbeater, N. E.; Sangi, M. S.; Williams, V. A.; Granados, P.; Singer, R. D. J. Org. Chem. **2005**, 70, 168–168. (b) Buchwald, S. L.; Bolm, C. Angew. Chem., Int. Ed. **2009**, 48, 5586–5587.
(16) Corma, A.; Concepción, P.; Serna, P. Angew. Chem., Int. Ed. **2007**, 46, 7266–7269.

JA9061097