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A Highly Active Nano-Palladium Catalyst for the Preparation of Aromatic Azos under Mild Conditions

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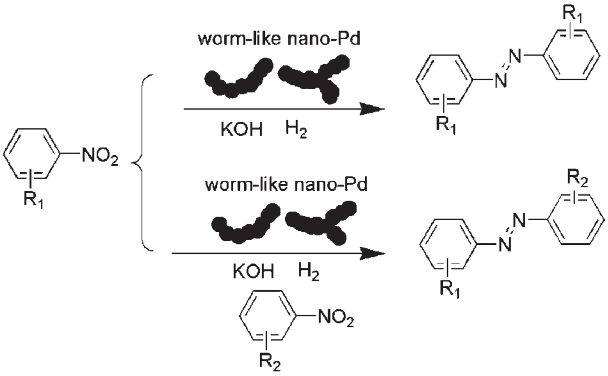
ABSTRACT



A worm-like Pd nanocatalyst has been prepared and used in the preparation of azo compounds from nitroaromatics under mild reaction conditions. This highly dispersible nano-Pd catalyst shows high activity toward the synthesis of both symmetric aromatic azo compounds and a range of asymmetric aromatic azo compounds.

Aromatic azo (**AAzo**) compounds are key raw materials and are widely used in the synthesis of organic dyes, food additives, indicators, and drugs.[1] The industrial production of **AAzo** entails the coupling of diazonium salts with electron-rich aromatic compounds.[2] This process requires stoichiometric amounts of nitrite salts to form the diazonium salt and generates significant amounts of inorganic waste. Therefore, a sustainable and industrially applicable process for highly selective **AAzo** formation is of fundamental and practical interest. In the past, many efforts have been made to use the catalytic oxidation of amines[3] in **AAzo** synthesis; however, these approaches always require environmentally unfriendly transition metals such as lead catalysts. Recently, Merino[4] reviews various synthetic methods on AAzo compounds. Jiao's group[5] demonstrated a novel approach to the synthesis of **AAzo** compounds from the corresponding amines under mild conditions (60 °C and 1 atm O_2) using CuBr and pyridine as a homogeneous catalyst. Corma and García[6] reported a novel catalytic route applying a Au/TiO_2 catalyst for the oxidation of amines at 5 atm of initial oxygen pressure. Furthermore, they found the Au/TiO_2 catalyst could act as a hydrogenation catalyst for the formation of the amines at 9 atm of hydrogen. The **AAzo**

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[3] (a) Baumgarten, H. E.; Staklis, A.; Miller, E. M. *J. Org. Chem.* **1965**, *30*, 1203. (b) Wenkert, K.; Wickberg, B. *J. Am. Chem. Soc.* **1962**, *84*, 4914. (c) Werkurt, E.; Angell, E. C. *Synth. Commun.* **1988**, *18*, 1331.

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[5] Zhang, C.; Jiao, N. *Angew. Chem., Int. Ed.* **2010**, *49*, 6174.

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compounds in these reactions were thus obtained from the corresponding nitroaromatics through a two-step, one-pot reaction. The nitroaromatic compound was reduced to aniline and then oxidized to form the **AAzo**. In this process, the **AAzo** is formed as an unstable intermediate from the hydrogenation of a nitroaromatic compound and is then quickly reduced to an amine. To isolate this unstable intermediate, transition metals[7] or a complicated reductive system[8] have been used to obtain the **AAzo** from the corresponding nitroaromatic compound.

Numerous studies have been devoted to the properties which affect the catalytic activity and selectivity of nanocatalysts. The shape of the nanomaterials has been studied most widely and many groups have reported that nanowires or multipots have much higher catalytic activity than nanoparticles.[9] Palladium has long been one of the most useful catalysts in hydrogenation and coupling reactions, and many efforts have been put into developing novel Pd based nanomaterials with higher catalytic activity.[10] Herein, we have synthesized a worm-like Pd nanomaterial and used it as the catalyst for the preparation of **AAzo** compounds from nitroaromatics under mild reaction conditions.

The worm-like Pd catalyst was prepared following a reported methodology with minor modifications.[9d,11] Pd(CH_3COO)$_2$, *n*-hexadecyl trimethyl ammonium bromide, and 1-dodecylamine were dissolved in toluene. Reduction was then performed by the dropwise addition of a freshly prepared $NaBH_4$ solution followed by stirring for 1 h at rt. The worm-like Pd was isolated by precipitation with ethanol and centrifuging at 8000 rpm for 10 min. Figure 1 A and B show the transmission electron microscopy (TEM) images of this worm-like Pdcatalyst. The diameter of the Pd catalyst was about 3.5 nm with a narrow size distribution. Selected area electron diffraction (SAED) indicates the worm-like Pd has a face-centered cubic (FCC) phase (Figure 1C) which is confirmed by powder X-ray diffraction (Figure S1). Figure 1D shows the high-resolution TEM image of the worm-like Pd and the lattice fringe with an interplanar spacing of 0.23 nm, assigned to the (111) plane of FCC Pd. The X-ray photoelectron spectrum of the catalyst at the palladium 3d level indicated that most of the palladium was present in the reduced form (Figure S2).

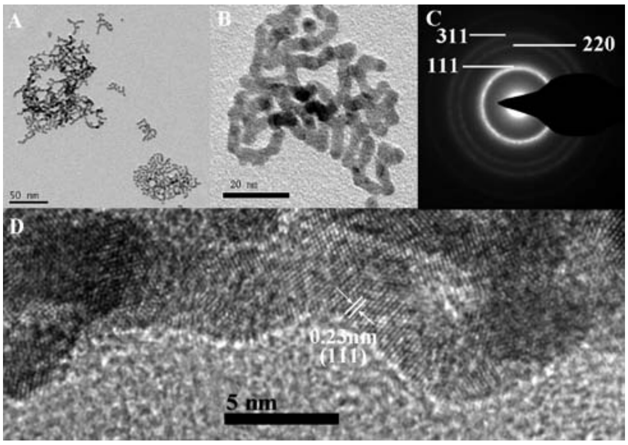
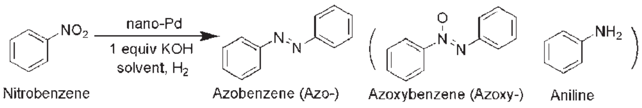


Figure 1. (A, B) TEM, (C) SAED, and (D) high resolution TEM images of the worm-like Pd.

Table 1. Azobenzene Formation from Nitrobenzene in Different Solvents[a]



entry	solvent	temp (°C)	conv (%)[b]	selectivity (%)[b] Azo-	Azoxy-	aniline
1	*o*-xylene	120	92.8	24.4	58.8	8.3
2	*m*-xylene	120	100	80.0	1.4	18.6
3[c]	***p*-xylene**	**120**	**100**	**87.4**	**0**	**12.6**
4	toluene	100	100	33.4	56.0	10.6
5	*n*-heptane	100	99	52.6	40.6	3.5
6	dioxane	100	32.6	9.9	78.7	5.3
7	ethanol	80	>99	27.9	67.1	4.8
8	2-propanol	80	>99	2.2	77.7	18.9
9	acetonitrile	80	40.4	4.0	61.9	24.3
10	H_2O	80	86.5	1.2	83.7	15.1

[a] All reactions were carried out with 1 mg of nano-Pd catalyst, 1 mmol of nitrobenzene, 1 equiv of KOH, and 2 mL of solvent at the appropriate temperature for 24 h under 1 atm of hydrogen. [b] GC yield. [c] 7 h. All reactions were exposed to air at 120 °C for 2 h.

To demonstrate the high catalytic activity of this Pd nanocatalyst in the preparation of **AAzo** compounds, nitrobenzene was selected as the substrate for the optimization of conditions. Table 1 shows the reduction and coupling of nitrobenzene to form azobenzene (**Azo-**) and azoxybenzene (**Azoxy-**). Comparison of 10 commonly

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[7] (a) Srinivasa, G. R.; Abiraj, K.; Gowda, D. C. *Synth. Commun.* **2003**, *33*, 4221. (b) Ohe, K.; Uemura, S.; Sugita, N.; Masuda, H.; Taga, T. *J. Org. Chem.* **1989**, *54*, 4169. (c) Srinivasa, G. R.; Abiraj, K.; Channe Gowda, D. *Tetrahedron Lett.* **2003**, *44*, 5835.

[8] (a) Sakai, N.; Fujii, K.; Nabeshima, S.; Ikeda, R.; Konakahara, T. *Chem. Commun.* **2010**, *46*, 3173. (b) Zhu, H.; Ke, X.; Yang, X.; Sarina, S.; Liu, H. *Angew. Chem., Int. Ed.* **2010**, *49*, 9657.

[9] (a) Hu, B.; Ding, K.; Wu, T.; Zhou, X.; Fan, H.; Jiang, T.; Wang, Q.; Han, B. *Chem. Commun.* **2010**, *46*, 8552. (b) Qin, G. W.; Pei, W.; Ma, X.; Xu, X.; Ren, Y.; Sun, W.; Zuo, L. *J. Phys. Chem. C* **2010**, *114*, 6909. (c) Hong, H.; Hu, L.; Li, M.; Zheng, J.; Sun, X.; Lu, X.; Cao, X.; Lu, J.; Gu, H. *Chem.—Eur. J.* **2011**, *17*, 8726. (d) Hu, L.; Shi, L.; Hong, H.; Li, M.; Bao, Q.; Tang, J.; Ge, J.; Lu, J.; Cao, X.; Gu, H. *Chem. Commun.* **2010**, *46*, 8591. (e) Li, M.; Hu, L.; Cao, X.; Hong, H.; Lu, J.; Gu, H. *Chem.—Eur. J.* **2011**, *17*, 2763.

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[11] Yang, J.; Sargent, E. H.; Kelley, S. O.; Ying, J. Y. *Nat. Mater.* **2009**, *8*, 683.

used solvents showed *p*-xylene to be the best solvent for the formation of **Azo-** (87.4% yield, Table 1, entry 3). Nonpolar solvents like xylene, toluene, and heptane also encourage **Azo-** formation (Table 1, entries 1−2 and 4−5). **Azoxy-** can be reduced to **Azo-** by prolonging the reaction time in these solvents (Table S1, entries 1−4). The polar solvents encourage **Azoxy-** formation (Table 1, entries 6−10) and hinder further reduction to **Azo-** (Table S1, entries 5−9).

Table 2. Azobenzene Formation from Nitrobenzene Using Different Bases[a]

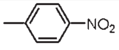
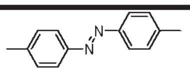
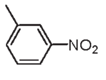
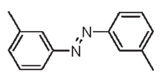
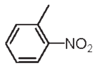
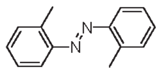
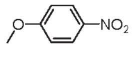
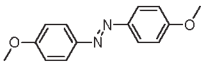
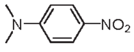
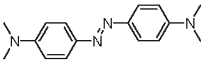
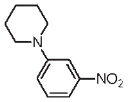
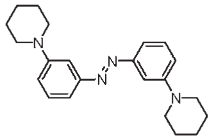
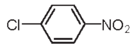
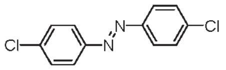
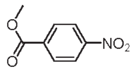
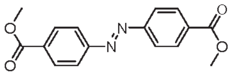
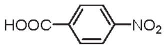
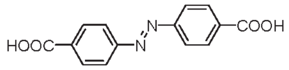
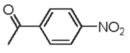
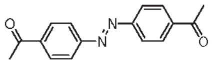
entry	base (equiv)	temp (h)	conv (%)[b]	selectivity (%)[b] Azo-	Azoxy-	aniline
1	none	24	100	0	0	92.4
2	NaOH (1)	24	100	64.2	28.8	7.0
3	$(CH_3)_3CONa$ (1)	24	100	28.6	60.6	10.2
4	K_2CO_3 (1)	24	47.3	3.6	39.8	56.6
5	$(C_2H_5)_3N$ (1)	24	22.4	0	0	>99
6	KOH (0.25)	18	100	74.1	0	21.7
7	KOH (0.5)	13	100	80.1	0	8.8
8	**KOH (1)**	**7**	**100**	**87.4**	**0**	**12.6**
9	KOH (2)	6	100	85.8	0	14.2
10	KOH (2)	3	100	76.8	0	20.5
11	KOH (4)	1.5	100	75.4	0	22.2

[a] All reactions were carried out with 1 mg of nano-Pd catalyst, 1 mmol of nitrobenzene, base, and 2 mL of *p*-xylene at 120 °C for the appropriate time under 1 atm of hydrogen. [b] GC yield. All reactions were exposed to air at 120 °C for 2 h.

Further investigation into the reaction parameters revealed that the catalytic activity and selectivity were sensitive to the base employed in this reaction. Table 2 shows the results of this reaction with and without a base. Without a base, aniline was the main product and no **Azo-** was detected by GC (Table 2, entry 1). Five different bases were used to investigate the selectivity of this reaction. KOH was the most effective for the formation of azobenzene (Table 2, entries 2−5, 8). Further optimization revealed that superior yields (87.4%) of **Azo-** were achieved when 1 equiv of KOH was used for 6 h at 120 °C (Table 2, entry 8). When an excess of KOH was used, the azobenzene was obtained faster, but with less selectivity (Table 2, entries 9−11). Decreasing the amount of KOH to 0.5 or 0.25 equiv resulted in **Azo-** only being observed after longer reaction times (24 h) (Table 2, entries 6 and 7).

Having optimized the catalytic system and reaction conditions for the formation of azobenzene from nitrobenzene, other nitroaromatic compounds were investigated as substrates. Three nitrotoluenes were investigated with *p*-nitrotoluene giving the highest yield and *o*-nitrotoluene requiring a higher initial hydrogen pressure to obtain the corresponding **AAzo** (4 atm) (Table 3, entries 1−3). Electron-rich nitroaromatic compounds gave the corresponding **AAzo** in good to excellent yields (66−83%) in these conditions (Table 3, entries 4−6). The electron-poor nitroaromatic compounds also formed the corresponding **AAzo** compounds in useful yields (Table 3, entries 7−10). Furthermore, asymmetrical **AAzo** were successfully synthesized with good yields while using two different substituted nitrobenzenes as reactants (Table 4, entries 1−3).

Table 3. Aromatic Azos Formation from Different Nitro-Compounds[a]

entry	substrate	product	time (h)	yield (%)[b]
1			12	83.1
2			12	78.7
3[c]			12	70.1
4			24	82.4
5			24	65.9
6			24	74.8
7			24	24.2
8[d]			5	60.7
9[e]			8	38.1
10[c]			12	15.7

[a] All reactions were carried out with 1 mg of nano-Pd catalyst, 1 mmol of nitroaromatic, 1 mmol of KOH, and 2 mL of *p*-xylene at 120 °C for 24 h under 1 atm of hydrogen. [b] Isolated yield. [c] 4 atm of H_2. [d] 4 atm of H_2, 40 °C, $CHCl_3$ as the solvent. [e] 80 °C, water as the solvent. All reactions were exposed to air at 120 °C for 2 h.

The transformation from nitrobenzene to azobenzene was investigated over the time of the reaction based on GC yields (Figure 2). The amount of azoxybenzene was increased to a maximum at 1.5 h with the nitrobenzene being quickly consumed in the reaction. As the reaction proceeded, more azoxybenzene was reduced to azobenzene, with the quantity of aniline remaining the same. Using this catalyst system, excellent yields of azobenzene can be achieved in 7 h.

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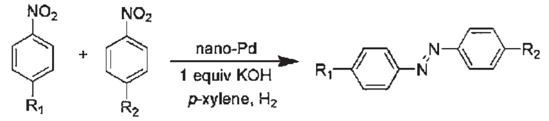
Table 4. Formation of Asymmetric Azobenzenes from an Equimolar Mixture of Nitroaromatics[a]



entry	R_1	R_2	time (h)	yield (%)[b]
1	$COCH_3$	H	24	55.3
2	CH_3	OCH_3	36	42.4
3	COOH	H	36	70.1

[a] All reactions were carried out with 1 mg of nano-Pd catalyst, 0.5 mmol of nitroaromatics, 1 mmol of KOH, and 2 mL of *p*-xylene at 120 °C for the appropriate time under 1 atm of hydrogen. [b] Isolated yield. All reactions were exposed to air at 120 °C for 2 h.

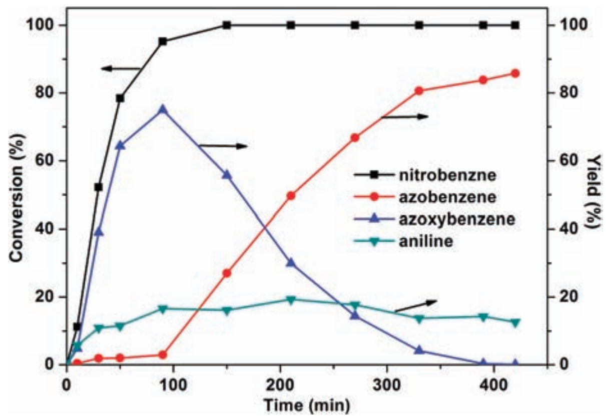
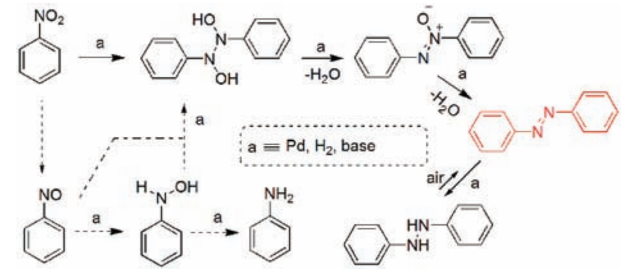


Figure 2. Time−conversion plot for nitrobenzene hydrogenation using nano-Pd as the catalyst.

The proposed mechanism for the azobenzene formation from nitrobenzene is shown in Scheme 1. Hydrogen is first adsorbed on the surface of nano-Pd and nitrobenzene is reduced to nitrosobenzene, which in turn is quickly converted to *N*-hydroxybenzenamine. The *N*-hydroxybenzenamine can be further reduced to aniline under acidic or neutral conditions and acts as a sink toward **AAzo** formation. However, when KOH is added, the *N*-hydroxybenzenamine primarily couples to nitrosobenzene to form *N*,*N*′-dihydroxy-diphenylhydrazine.[12] This dihydroxy intermediate is then dehydrated to give azoxybenzene. It is possible to interrupt the reaction at this point if azoxybenzene is the desired product. Azoxybenzene can also be further reduced to azobenzene and then hydrazobenzene. This product spontaneously oxidizes to azobenzene in air. As a result, azobenzene is the only observed coupling product via GC analysis. In addition, a serial experiment detailing the transformations of azoxybenzene, azobenzene, and hydroazobenzene was performed. Hydrogenation of azoxybenzene can form azobenzene in high yield (Table S3, entry A) which is then reduced to form hydrazobenzene by extending the reaction time (Table S3, entries B). Hydrazobenzene can be quantitatively converted back to azobenzene while heating in air for 2 h at 120 °C. Even in the absence of the Pd catalyst, hydrazobenzene was converted to azobenzene in a yield of 94.7% in 12 h at 120 °C. The oxidization of azobenzene to azoxybenzene was found to be less facile (Table S3, entry C). Overall, azobenzene is the major product from these transformations.

Scheme 1. Proposed Mechanism for the Hydrogenation of Nitrobenzene



In conclusion, we have developed a novel worm-like Pd nanomaterial which shows high catalytic activity toward the formation of **AAzo** directly from the corresponding nitroaromatic compounds. The reaction is simple and efficient and does not need harmful transition metals which makes this **AAzo** preparation much easier and more environmentally friendly. Further study of this catalytic system for wider application is under investigation in our laboratory.

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Supporting Information Available. Experimental procedures and full spectroscopic data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.