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COMMUNICATION

Efficient, Green, and Magnetically-recoverable Triazole Ligand-stabilized Au and Pd Nanoparticle Catalysts†

Received 00th January 20xx,
Accepted 00th January 20xx

Song Su^{ab}, Guozong Yue^a, Deshun Huang^a, Guiying Yang^{ab}, Xinchun Lai^{ab} and Pengxiang Zhao^{*a}

DOI: 10.1039/x0xx00000x

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Triazole ligands with carboxylic acid at one termini and polyethylene oxide (PEO) at the other termini are synthesized via “click” chemistry and subsequently attached onto the Fe₃O₄ surface by ligand-exchange reactions. Then the small-sized Au or Pd nanoparticles are encapsulated into this nanocomposite by their mild coordination with triazole, yielding the efficient, green and magnetically-recoverable nano catalysts.

Nanocatalysts are alternatives to conventional catalysts, due to their enhancements in catalytic activity, selectivity and stability.¹ The nanogold and related noble metals represent the central field of nanocatalysis, in particular, since Haruta’s breakthrough discovery of gold nanoparticle (AuNP)-catalyzed low-temperature oxidation of CO². Up to now, a series of organic reactions including multiple carbon-carbon bonds addition,³ oxidation,⁴ carbon-carbon coupling,⁵ and hydrogenation⁶ that are efficiently catalyzed by these metal NPs have been reported. For the metal NP catalysts, the property of capping ligand is considered as the key role for their catalytic activity. The metal NPs with strongly bonded capping ligands e.g. Au-S bonds have less active sites at the metal surface, and as a result lose their activity. Thus, weakly bonded ligands to the metal NP surface are crucial to overcome the catalytic limitations.⁷ Among all weakly-bonded ligands, the neutral and mild 1,2,3-triazole (trz) ligands that are produced via “click” chemistry⁸ are most attractive for us owing to their biocompatibility and stability toward both oxidizing and reducing agents.⁹ In addition, this ligand is also geared to the needs of environmental friendly and green chemistry, and may open up a new route to develop catalytic materials. Generally, the trz ligand associates with AuNP or PdNP surface through one pair of electrons on the sp²-hybridized nitrogen atoms to form the trz-AuNP or trz-PdNP catalyst.^{9,10} Indeed, recent works have confirmed that these catalysts are very efficient for a number of organic reactions and could even catalyze C-C coupling

using parts per million (ppm) catalyst amounts in water or ethanol/water solution.¹¹ However, due to their good dispersity either in organic or aqueous solution this ppm-level catalyst could not be efficiently recovered by filtration or centrifugation methods. Hence, it is still challenging to determine the balance between the high catalytic activity and the recyclability for these trz-catalysts. Indeed, one of the most logical solutions is to introduce the Fe₃O₄ NPs supports that are already extensively used for the easy recovery of nanocatalysts. Since the Fe₃O₄ NP-supported trz-AuNP or -PdNP catalyst should be simply and efficiently isolated from reaction mixtures with an external magnetic field.¹²⁻¹⁵ Therefore, in this present work, we report our attempts in designing and preparing this novel catalyst.

As shown in Scheme 1, the monodispersed, oleic-acid stabilized Fe₃O₄NP **1** with an average size of 7 nm (see Figure 1a) was prepared by Sun’s method.¹⁶ The heterobifunctional trz ligand **2** that contains the carboxylic acid in one termini and polyethylene oxide (PEO) fragment in the other termini was synthesized via “click” chemistry (see ESI†). It is worth noting that the carboxylic acid in ligand **2** could strongly coordinate the Fe₃O₄ surface. Thus, through the ligand exchange reaction, the Fe₃O₄NP **1** with ligand **2** yielded the Fe₃O₄NP **3**, and the excess ligand and salts were removed by dialysis. The core size of Fe₃O₄NP **3** (Figure 1b) was the same as that of Fe₃O₄ NP **1**, which indicated the non-aggregation during the ligand-exchange process. This may be attributed to the presence of the PEO tail that prevented the agglomeration of Fe₃O₄NP. Moreover, the PEO chain also brought solubility in aqueous media and biocompatibility, which is favorable for green catalysis. The Fe₃O₄NP **1** and Fe₃O₄NP **3** were also characterized by the UV-Vis spectra (see ESI†). It is worth noting that the Fe₃O₄NP **1** have no absorption, which was according to the report by Sun’s group.¹⁶ Otherwise, the new absorption of Fe₃O₄NP **3** at 256 nm belongs to the triazole and aromatic ring in ligand **2**. Besides, to better understand this system, a series of parameters of Fe₃O₄NP **3** were calculated by experiments or theory. The surface area of Fe₃O₄NP core was 154 nm², followed with the equation: $A = 4\pi R^2$ (A : surface area, R : radius, 3.5 nm in figure 1b), and the footprint of ligand **2** was 0.193 nm² according to the simulation (details see ESI

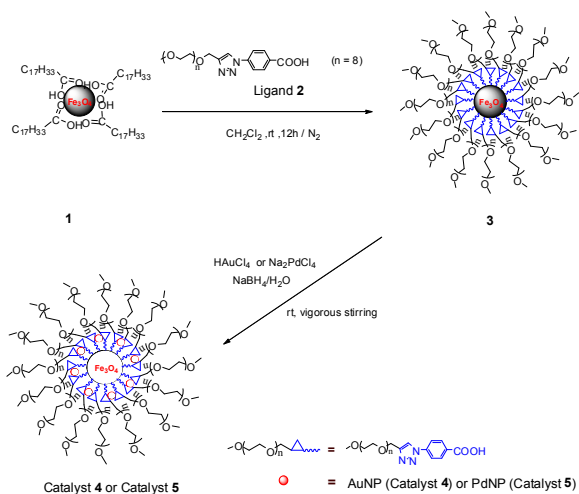
^a Nano Chemistry Group, Science and Technology on Surface Physics and Chemistry Laboratory, P.O. Box 718-35, Mianyang 621907, Sichuan, China.

^b College of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang, Sichuan 621010, China.

* Pengxiang zhao, Email: zhaopx@spc-lab.org

† Electronic Supplementary Information (ESI) available: The details of Materials and methods, experimental conditions, fully characterizations. See DOI: 10.1039/x0xx00000x

†). Therefore, about 800 trz ligands were attached on each Fe_3O_4 NP **3** surface.



Scheme 1. Synthetic route of Fe_3O_4 -supported Trz-AuNP (and Trz-PdNP) catalyst.

At last, $\text{HAu}^{\text{III}}\text{Cl}_4$ (0.16 mg) or $\text{Na}_2\text{Pd}^{\text{II}}\text{Cl}_4$ (0.44 mg) was reduced to Au^0 or Pd^0 by dropwise addition of NaBH_4 in the presence of Fe_3O_4 NP **3**, and produced the supported trz-AuNP catalyst **4** (Au: 0.7 wt%) or trz-PdNP catalyst **5** (Pd: 1.4 wt%). To our best knowledge and the HAADF-STEM image (Figure 1c and Figure S3 in SI), the AuNPs (yellow rings) in catalysts **4** were entrapped into the PEO chain and attached onto the surface of the Fe_3O_4 NP (blue rings) via trz-Au bonds. It is obvious that the average size of the AuNPs in Figure 1c was smaller than 2 nm, and no plasmon absorbance was observed in the UV-vis. spectrum (Figure 1d). All elements that included in catalyst **4** could be illustrated in EDX analysis (Figure 1e), however, other elements e.g. Cu and Si were from the grid that used for TEM. Similarly, the trz-PdNP catalyst **5** also had a quantum-related size (see ESI†).

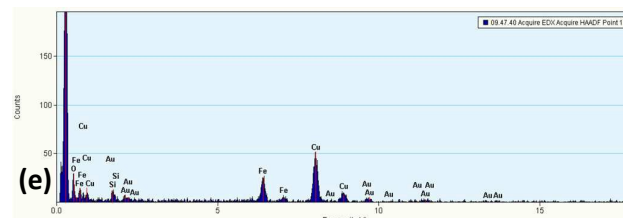
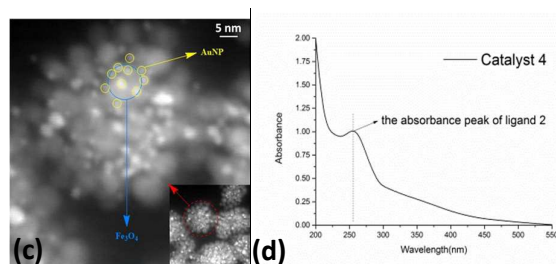
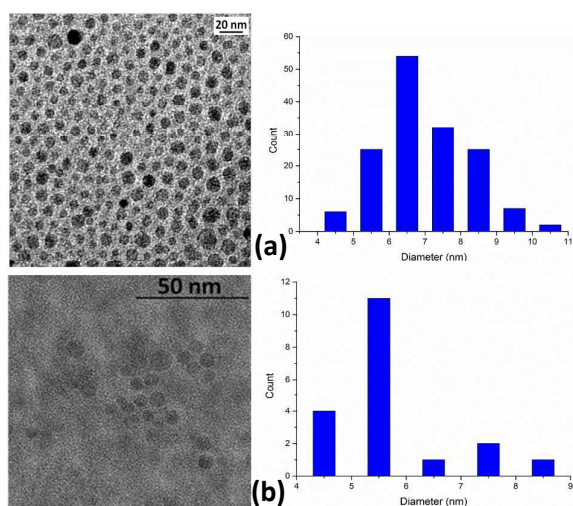
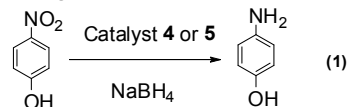
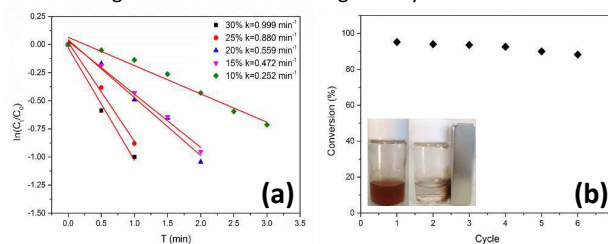


Figure 1. TEM images and size distribution of (a) Fe_3O_4 NP **1** and (b) Fe_3O_4 NP **3**, HAADF-STEM image (c) and UV-vis. spectrum (d) of catalyst **4**, and the EDX analysis of (e) catalyst **4**.

Reduction of 4-nitrophenol (4-NP) was an example to test the catalytic efficacy and recyclability of catalyst **4** and **5** [Eq. (1)] because the product, 4-aminophenol (4-AP), found broad applications including photographic developer of black and white films, corrosion inhibitor, dyeing agent, precursor for the manufacture of drugs.



In this study, an aqueous solution (2.5 mL) containing 4-NP (0.375×10^{-3} mmol) and NaBH_4 (0.12 mmol) was first mixed in a 3 mL standard quartz cuvette, followed by addition of the catalyst. Then, the intensity of the absorbance peak of 4-nitrophenolate ions at 400 nm rapidly decreased, while the appearance and increase of the absorbance peak at 300 nm confirmed the formation of 4-AP (see ESI†). The catalytic activity for different amounts of catalysts **4** and **5** was demonstrated in Figure 2. The apparent rate constant k was directly obtained from the curve of $\ln(C_t/C_0)$ vs. time by linear fit. It is worth noting that even with the lowest amount catalyst, i.e. 10% of catalyst **4** ($k = 0.252 \text{ min}^{-1}$) and 3% of catalyst **5** ($k = 0.461 \text{ min}^{-1}$), the catalytic activity was comparable for recent trz-stabilized NP catalysts.¹⁷ However, it should be pointed out that the catalysts **4** (Figure 2b) and **5** (Figure 2d) could be easily recycled with an external magnetic field without losing activity for at least 6 times.



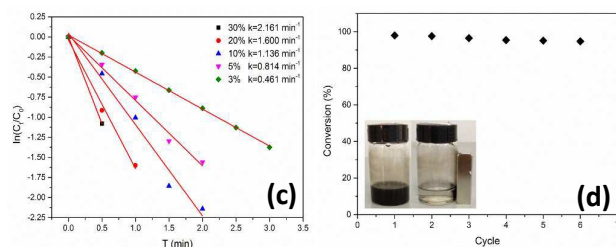
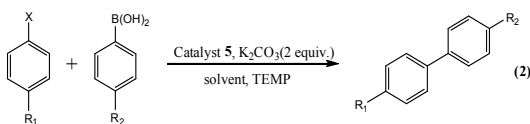


Figure 2. Plot of $\ln(c/c_0)$ vs. reaction time during the reduction of 4-NP catalyzed by catalyst 4 (a) with recycling (b), and catalyst 5 (c) with recycling (d) at 20 °C.

However, to better evaluate the catalytic activity of our PdNP catalyst, the Suzuki-Miyaura C-C coupling that represents a typical example for Pd catalysis^{18,19} was investigated. The reactions were conducted in THF/H₂O(1/1) or EtOH/H₂O (1/1), with two boronic acids and iodoarenes (or bromoarenes) [Eq. (2)], and all the data were gathered in Table 1. The solvent effect of this reaction was examined (from entry 1 to entry 4), and the results indicated that the presence of the green and environment friendly solvent EtOH/H₂O improved the catalytic activity of catalyst 5. In addition, concerning the reaction of iodobenzene with boronic acids and their derivatives with electron-donating groups, the Suzuki-Miyaura reaction worked very well even with a quite small quantity of catalyst 5, down to 10ppm, with 84% (entry 8) and 82%(entry 5) yields, respectively. Furthermore, the low amounts of catalyst 5 also exhibited favorable catalytic activity even with the more difficult reaction, the coupling between bromobenzene and boronic acids.

Table 1. Summary of the Suzuki coupling reaction of aryl halide p -R₁C₆H₄X with arylboronic acid p -R₂C₆H₄B(OH)₂



X	R ₁	R ₂	Entry	Solvent (1:1)	Catalyst (mol%)	Time (h)	Yield (%) ^d
I	H	OMe	1 ^a	THF/H ₂ O	0.1	6	70
			2 ^a	THF/H ₂ O	0.01	12	68
			3 ^b	EtOH/H ₂ O	0.01	50	67
			4 ^c	EtOH/H ₂ O	0.01	13	86
			5 ^c	EtOH/H ₂ O	0.001	96	82
			6 ^c	EtOH/H ₂ O	0.0001	96	40
H	H	H	7 ^c	EtOH/H ₂ O	0.01	16	96
			8 ^c	EtOH/H ₂ O	0.001	96	84
			9 ^c	EtOH/H ₂ O	0.0001	96	28
Br	Me	OMe	10 ^c	EtOH/H ₂ O	0.01	23	75
			11 ^c	EtOH/H ₂ O	0.001	32	59
			12 ^c	EtOH/H ₂ O	0.0001	96	30

^aEach reaction is conducted with 0.5 mmol aryl halide p -R₁C₆H₄X, 0.65 mmol of arylboronic acid p -R₂C₆H₄B(OH)₂, 1mmol of K₂CO₃ in THF/H₂O 1 ml/1 ml at 66 °C.

^bEach reaction is conducted with 0.5 mmol aryl halide p -R₁C₆H₄X, 0.65 mmol of arylboronic acid p -R₂C₆H₄B(OH)₂, 1mmol of K₂CO₃ in EtOH/H₂O 1 ml/1 ml at 25 °C.

^cStandard conditions, but at 70 °C instead of 25 °C.

^dIsolated yield (%)

Indeed, the remarkable catalytic activity of catalyst 5 could be attributed to the following three reasons: (i) the size effect. The catalyst 5 with small-sized PdNPs, and due to the quantum-related effect and abundance of active sites on their surface, these NPs always exhibit better reactivity than that of larger-sized NPs;²⁰ (ii) the presence of a strong electronegative group in trz ligands: the electron-withdraw group benzoic acid in the trz termini may decrease the electron density on the trz unit through inductive effects, and consequently lead to weaker bonding between trz and the PdNP. The weaker bonding allowed enough active sites of the PdNP surface to be exposed to the substrates, and finally provide high catalytic activity; (iii) the PEO at the periphery of Fe₃O₄NPs could be considered as a nanoreactor that encapsulated substrates inside and consequently accelerate the reaction. Finally, the advantages of recovering and reusing catalyst 5 should not escape our attention. It is well known that recycling of low amounts PdNPs is very difficult to carry out, and it is rarely reported. In our case, however, the catalyst 5 could be easily recovered using an external magnet even down to 100ppm level. Although the irreversible aggregation of PdNPs at such a low amount were unavoidable during the recycling procedure, the catalyst 5 still kept its activity even at least for 4 times recycling (see table 2).

Table 2 Recycling results of entry 7 with catalyst 5 (0.01mol%).

Run	1st	2nd	3rd	4th	5th	6th
Yield (%)	96	95	86	76	67	63

Finally, to evaluate the efficiency of the catalyst 5 in low catalyst concentration, we compared our results with those of Pd-based catalysts reported in recent years. As shown in Table 3. our catalyst 5 achieved the two highest yield with least amounts.

Table 3 Catalytic performance of different Pd-based catalysts in the coupling reaction of iodobenzene and phenylboronic acid in recent years

Catalyst [mol%]	Temp. (°C)	Solvent	Yield (%)	Ref.
Pd-Glucose [1]	100	iPrOH	73	21
Fe ₃ O ₄ /SiO ₂ /HPG-OPPh ₂ -Pd [0.76]	25	DMF/H ₂ O	90	22
Cell-OPPh ₂ -Pd [0.5]	78	EtOH	85	23
Pd-NPs@Chitosan [0.1]	70	TBAB	98	24
Mag-IL-Pd [0.025]	60	H ₂ O	95	25
HT-Pd(0) [2]	100	H ₂ O	92	26
Pd/UIO-66-NH ₂ [0.25]	60	DMF/H ₂ O	92	27
CB[6]-Pd NPs [0.05]	40	EtOH/H ₂ O	92	28

CeIMcPd ⁰ -1 [0.5]	78	EtOH	91	29
NHC-Pd/GO-ILn [0.02]	60	EtOH/H ₂ O	42	30
trz-PdNP catalyst 5 [0.01]	70	EtOH/H ₂ O	96	This work

Conclusions

In conclusion, the magnetic Fe₃O₄NP-supported trz-AuNP and trz-PdNP catalysts are prepared by a facile route. These catalysts exhibit excellent activities towards 4-nitrophenol reduction and Suzuki coupling reactions. In particular, the Fe₃O₄NP-supported trz-PdNPs even catalyzed the Suzuki coupling with amounts down to 10 ppm. In addition, the catalyst at 100ppm level could be simply recovered using an external magnet. It is believed that these remarkable results should pave the way for improving the trz-AuNP and other related noble metal catalysis.

Acknowledgements

Financial supports from the China Academy of Engineering Physics (Item NO. 2013B0302047), and the funding from Science and Technology on Surface Physics and Chemistry Laboratory (TP201302-1) are gratefully acknowledged.

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