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# A new recoverable Au(III) catalyst supported on magnetic polymer nanocomposite for aromatic bromination

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## ABSTRACT

This Letter presents a facile alternative synthesis of a recoverable Au(III) catalyst supported on Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>~MPS grafted by poly(*N*-vinyl-2-pyrrolidone) (PVP). The solid magnetic support was prepared by anchoring 3-methacryloxypropyltrimethoxysilane (MPS) onto the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> surfaces followed by free radical polymerization with *N*-vinyl-2-pyrrolidone. Au(III) was immobilized onto the magnetic support in aqueous media to afford Au(III)/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP (catalyst 1). Catalyst 1 was characterized by FT-IR, TEM, VSM, TGA, XRD, and ICP-AES. The amount of Au in catalyst 1 was measured to be 0.64 wt % by ICP-AES. This newly prepared catalyst can catalyze the aromatic bromination reaction with comparable activity as homogeneous AuCl<sub>3</sub>. Moreover, the supported catalyst is easy to recover and can be used in four cycles without apparent loss of activity.

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Halogenation of aromatic compounds with N-halosuccinimides (NXS, X = Cl, Br, and I) is an important process in organic synthesis,<sup>1</sup> as their products have been widely employed as the substrates in various important organic reactions such as Suzuki coupling, Heck reactions, and Sonogashira reactions.<sup>2-4</sup> Using NXS as the halogenating reagents is advantageous in terms of ease of handling and low toxicity. However, traditional methods for halogenating inactivated aromatic compounds with NXS require large amounts of strong Lewis acids or Brønsted acids (FeCl<sub>3</sub>, BF<sub>3</sub>-H<sub>2</sub>O, H<sub>2</sub>SO<sub>4</sub>, etc.) as catalyst, and the reaction conditions are generally harsh.<sup>5-9</sup> In view of those deficiencies, Wang and co-workers<sup>10</sup> recently developed a mild efficient method for the bromination of arenes by using AuCl<sub>3</sub> as catalyst. In Wang's procedure, only a tiny amount of (0.1-1 mol %) AuCl<sub>3</sub> catalyst is needed, and the reaction proceeds well at lower temperatures (25 or 80 °C). The protocol is based on a hypothetical dual activation mode: Au(III) can form C<sub>Ar</sub>-M bond through direct metallation of a C<sub>Ar</sub>-H bond; it is also capable of activating NBS by complexing the carbonyl group in NBS. Consequently, complexation by Au(III) could greatly enhance the reactivity of both the aromatic ring and NBS.

Although Au-catalyzed transformations have drawn much attention in the last decade,<sup>11–14</sup> the high costs and difficulties in reprocessing are the two major factors that hinder their practical applications in industrial processes. Therefore, many approaches

have been developed to generate heterogeneous gold catalysts to overcome these problems.<sup>15–23</sup> Various kinds of materials with different properties have been selected as candidates for catalyst supports. Among them, the composite materials have properties of both inorganic materials' physicochemical stability and polymers' excellent modifiability. Fe<sub>3</sub>O<sub>4</sub>-polymer nanocomposites have demonstrated great promise for immobilization of metal catalysts, due to their multifunctional properties including special magnetic behavior, chemical durability, and stability.<sup>24</sup> Due to the considerable stabilization of poly(N-vinyl-2-pyrrolidone) (PVP) for Au,<sup>25,26</sup> Hidehiro Sakurai and co-workers examined the catalytic activity and recyclability of Au supported on Fe<sub>3</sub>O<sub>4</sub>/PVP for the oxidation of alcohols and obtained excellent results.<sup>27</sup> However, the dosage of Au had to be excessive to some extent because the interaction between Fe<sub>3</sub>O<sub>4</sub> and PVP is not strong enough. Herein, we wish to report a facile alternative synthesis of a heterogeneous gold catalyst supported on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~MPS grafted by PVP. We applied the newly prepared Au/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP catalyst to the aromatic bromination with NBS as brominating reagent. Our results show that the catalyst demonstrates high catalytic capacity, and can be reused in four runs without apparent decrease of activity.

The synthesis of Au/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP catalyst was outlined in Scheme 1. Magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles were obtained by coprecipitation of FeCl<sub>2</sub> and FeCl<sub>3</sub> in an aqueous solution at 85 °C.<sup>28</sup> TEM image (Fig. 1a) shows that the obtained Fe<sub>3</sub>O<sub>4</sub> nanoparticles are in slight aggregation, with the size between 8–12 nm. Stirring the Fe<sub>3</sub>O<sub>4</sub> nanoparticles with *n*-ethyl silicate (TEOS) 24 h at room temperature resulted in formation of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>. As shown in



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Scheme 1. Synthesis of Au/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP catalyst.



Figure 1. TEM image of (a) Fe<sub>3</sub>O<sub>4</sub> in ethanol; (b) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> in ethanol; (c) Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP nanoparticles in 1,2-dichloro ethane.

Figure 1(b), the diameter of the particles increased to 70–80 nm, and silica coated iron oxide nanoparticles had favorable appearance, namely, all the Fe<sub>3</sub>O<sub>4</sub> nanoparticles were coated with SiO<sub>2</sub>.<sup>29</sup> 3-Methacryloxypropyltrimethoxysilane (MPS) was anchored on  $Fe_3O_4@SiO_2$  in a mixed solvent of ethanol and  $H_2O(v/v:4/1)$  under 40 °C. Then N-vinyl-2-pyrrolidone (NVP) was introduced to form Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP nanocomposite via radical polymerization with MPS in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~MPS. The TEM image of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP (Fig. 1c) reveals that the diameter of magnetic microspheres did not change conspicuously, but adhesion among the particles appeared, probably due to the entanglement between PVP polymer chains. The FT-IR spectrum (see Supplementary data Fig. S1) of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP shows strong absorptions at 1646 cm<sup>-1</sup> and 1700 cm<sup>-1</sup>, which can be attributed to the carbonyl group in PVP and MPS respectively. On the other hand, the C=C bond absorption at 1638 cm<sup>-1</sup> of MPS disappears in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP. These results demonstrated that NVP unit was introduced onto the magnetic nanocomposite by polymerization.<sup>30</sup> Vibrating sample magnetometry (VSM) (see Supplementary data Fig. S2) reveals that the resulted Fe<sub>3</sub>O<sub>4</sub>, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>, and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP exhibited superparamagnetic behavior and the saturated magnetization values were 79.84, 40.60, and 36.75 emu/g, respectively. Thermogravimetric analysis (TGA) was used to measure the weight loss of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> (a), Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> $\sim$ MPS (b); and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> $\sim$ PVP (c) (see Supplementary data Fig. S3). The weight loss of 1.5 wt % for Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~MPS and the weight loss of 4.5 wt % for Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>~PVP in the range of 250-800 °C suggested that the Fe<sub>3</sub>O<sub>4</sub>@ SiO<sub>2</sub>~PVP has been successfully prepared and the weight loss of PVP matched the elementary analysis data 33 mg/g (the content of PVP in Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP). Finally, the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~PVP was added to the aqueous solution of HAuCl<sub>4</sub>, and the mixture was stirred for 12 h at room temperature. Thus formed Au/Fe<sub>3</sub>O<sub>4</sub>  $@SiO_2 \sim PVP$  catalysts (catalyst 1) were separated with the aid of external magnet. The content of Au(III) in catalyst 1 was determined to be 0.64 wt % by ICP-AES.

Following the successful synthesis of catalyst 1, it was applied to the NBS-involved aromatic bromination reaction to examine its catalytic performance. Various substituted arenes were chosen as substrates, and the reaction was carried out on 1.0 mmol scale in a 10 mL sealed vessel. As shown in Table 1, under the indicated reaction conditions, the bromination smoothly occurred, affording the corresponding aryl bromides in good to excellent yields except for nitrobenzene, which was inert to the conditions. For electronrich aromatic compounds (entries 2, 5, 6, and 8), 45 mg catalyst 1 (0.1 mol % Au based on the substrate) was enough to guarantee a clean conversion, and the bromination products were obtained in excellent yields (92-98%) at 25 °C or 30 °C. Substrates incorporating halogen and carbonyl groups (entries 9–11) could also be brominated in good yields, albeit that elevated temperature (60 or 80 °C) and higher catalyst dosage (1 mol % Au) were required. The activity of catalyst 1 was comparable to the corresponding homogeneous AuCl<sub>3</sub> catalyst.<sup>8</sup> We believe that catalytic mechanism of catalyst 1 is the same as AuCl<sub>3</sub>. This hypothesis is verified by the kinetic isotopic effect (KIE) experiment through intermolecular competitive bromination of benzene and benzene- $d_6$ . The  $k_{\rm H}/k_{\rm D(inter)}$  value was determined to be 1.60, very close to the value of 1.66 reported with AuCl<sub>3</sub> as catalyst<sup>8</sup> (see Supplementary data 2.8).

Catalyst **1** was then subject to experiments to test its recyclability. In this regard, comparison was made of catalyst **1** to another immobilized gold catalyst Au/Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>:PVP (catalyst **2**). The support in catalyst **2** was prepared by simply blending PVP and Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>~MPS under 60 °C for 24 h.<sup>28</sup> Au(III) was then loaded on Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>:PVP via similar procedure as in the preparation of

Br

## Table 1

Bromination of aromatic with magnetic nanocomposite-supported Au catalyst<sup>a</sup>

+ NBS $\xrightarrow{\text{Au/Fe}_{3}O_{4}@SiO_{2} \rightarrow PVP}$							
			R	DCE	R		
Entry	Substrate	Product	Cat. (mol % Au)	Temp (°C)	Equiv of NBS (mmol)	Time (h)	Yield <sup>b</sup> (%)
1		Br	1	80	1	11	92
2		Br	0.1	25	1	40	98 (o/p = 1:2) <sup>c</sup>
3		Br	1	25	1	30	91
4		Br	1	60	1	10	97
5		Br	0.1	30	1	24	92
6		Br	0.1	25	1	12	98
7		Br	0.1	80	1	15	95
8	OMe	OMe	0.1	25	1	3	98
9	COOMe		1	80	1	48	83
10		Br	1	60	1	12	97 (o/p = 7:3) <sup>c</sup>
11	3 $1$ $Cl$ $4$ $5$ $6$ $10$	3 4 Br $56$	1	60	1	15	83 (4-Br/5-Br = 4:1) <sup>d</sup>
12	NO <sub>2</sub>	Br	1	80	1	24	No reaction

<sup>a</sup> DCE: 2 mL, substrate: 1.0 mmol, NBS: 1.0 mmol.

<sup>b</sup> Isolated yields.

<sup>c</sup> The proportion was determined by GC–MS.

<sup>d</sup> The proportion was determined by <sup>1</sup>H NMR.

catalyst 1. The bromination of anisole was chosen to make the comparison, and the result was listed in Table 2. As shown in Table 2, catalyst 1 performed much better than catalyst 2. While both catalysts exhibited high catalytic activity in the first run, catalyst **1** can be recycled four times without significant reduction in activity. In contrast, catalyst 2 lost most of its catalytic ability after only two runs. The results revealed that catalyst 1 was much more stable than catalyst 2. The polymerization grafting of PVP to

#### Table 2

Recycling experiment of catalyst 1 and catalyst 2 for anisole bromination<sup>a</sup>



 $^a\,$  Reaction condition: anisole (1.0 mmol), NBS (1.0 mmol), Catalyst (0.1 mol % Au based on anisole), 2 mL. DCE, 25 °C, 3 h.

<sup>b</sup> Isolated yield.



**Figure 2.** (a) Reaction mixture containing catalyst **1**; (b) Magnetic separation after the reaction.

 $Fe_3O_4$ @SiO<sub>2</sub>~MPS is responsible for the strong binding of Au(III) to the solid support.

Besides its high catalytic capacity and stability, a noticeable feature of catalyst **1** is that it can be easily removed by magnetic separation after reaction. As shown in Figure 2, by applying an external magnet to the side wall of sealed vessel, catalyst **1** was concentrated in 20 s. After separation from the reaction mixture, catalyst **1** was recovered simply by washing with ethanol and vacuum drying, and then used for the next run. The gold leaching of catalyst **1** in reaction solution (DCE) and washing solution (10 mL ethanol) was measured by the AAS analysis. It was found that the Au contents were only 0.55 ppm and 0.12 ppm respectively in above solutions. The low leaching amount reflects as well the high stability of catalyst **1**.

In summary, we have prepared a new heterogeneous gold catalyst (catalyst 1) by loading Au(III) onto the magnetic nanocomposite  $Fe_3O_4@SiO_2\sim$ PVP. This catalyst exhibited outstanding catalytic performance comparable to that of AuCl<sub>3</sub> for the aromatic bromination with NBS as the brominating agent. It can be easily separated and recovered from the reaction mixture with an external mag-

netic bar. The supported Au(III) catalyst shows high stability, and allows to be used in four runs without apparent loss of activity. It is hoped that this economical and recoverable immobilized Au(III) catalyst might find applications in organic synthesis.

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## Supplementary data

Supplementary data (experimental details see Supplementary data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2012.12.017.

#### **References and notes**

- (a) Djerassi, C. Chem. Rev. **1948**, 43, 271–317; (b) Goldberg, Y.; Alper, H. J. Org. Chem. **1993**, 58, 3072–3075; (c) Nishina, Y.; Takiami, K. Green Chem. **2012**, 14, 2380–2383; (d) Zhang, R.; Huang, L.; Zhang, Y. F.; Chen, X. R.; Xing, W. H.; Huang, J. Catal. Lett. **2012**, 142, 378–383.
- 2. Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457-2483.
- 3. Cabri, W.; Candiani, I. Acc. Chem. Res. 1995, 28, 2-7.
- 4. Chinchilla, R.; Nájera, C. Chem. Soc. Rev. 2011, 40, 5084-5121.
- 5. Schmid, H. Helv. Chim. Acta 1946, 29, 1144–1151.
- Paul, V.; Sudalai, A.; Daniel, T.; Srinvasan, K. V. Tetrahedron Lett. 1994, 35, 7055– 7056.
- Prakash, G. K. S.; Mathew, T.; Hoole, D.; Esteves, P. M.; Wang, Q.; Rasul, G.; Olah, G. A. J. Am. Chem. Soc. 2004, 126, 15770–15776.
- Rajesh, K.; Somasundaram, M.; Saiganesh, R.; Balasubramanian, K. K. J. Org. Chem. 2007, 72, 5867–5869.
- 9. Tanemura, K.; Suzuki, T.; Nishida, Y.; Satsumabayashi, K.; Horaguchi, T. *Chem. Lett.* **2003**, *32*, 932–933.
- Mo, F. Y.; Yan, M. T.; Qiu, D.; Li, F.; Zhang, Y.; Wang, J. B. Angew. Chem., Int. Ed. 2010, 49, 2028–2032.
- 11. Hashmi, A. S. K. Chem. Rev. 2007, 107, 3180-3211.
- 12. Li, Z. G.; Brouwer, C.; He, C. Chem. Rev. 2008, 108, 3239-3265.
- 13. Corma, A.; Leyva-Pérez, A.; Sabater, M. J. Chem. Rev. 2011, 111, 1657-1712.
- 14. Xiao, J.; Li, X. W. Angew. Chem., Int. Ed. 2011, 50, 7226-7236.
- 15. Schwank, J.; Galvagno, S.; Parravano, G. J. Catal. 1980, 63, 415-424.
- 16. Lin, S.; Vannice, M. A. Catal. Lett. 1991, 10, 47-62.
- 17. Tanielyan, S. K.; Augustine, R. L. Appl. Catal. A **1992**, 85, 73–87.
- Tsunoyama, H.; Ichikuni, N.; Sakurai, H.; Tsukuda, T. J. Am. Chem. Soc. 2009, 131, 7086–7093.
- 19. Cao, W. J.; Yu, B. Adv. Synth. Catal. **2011**, 353, 1903–1907.
- Polshettiwar, V.; Luque, R.; Fihri, A.; Zhu, H. B.; Bouhrara, M.; Basset, J. M. Chem. Rev. 2011, 111, 3036–3075.
- 21. Jin, M. J.; Lee, D. H. Angew. Chem., Int. Ed. 2010, 49, 1119-1122.
- 22. Yi, D. K.; Lee, S. S.; Ying, J. Y. Chem. Mater. 2006, 18, 2459-2461.
- Dálaigh, C. Ó.; Corr, S. A.; Gun'ko, Y.; Connon, S. J. Angew. Chem., Int. Ed. 2007, 46, 4329–4332.
- 24. Amstad, E.; Textor, M.; Reimhult, E. Nanoscale 2011, 3, 2819–2843.
- Tsunoyama, H.; Sakurai, H.; Negishi, Y.; Tsukuda, T. J. Am. Chem. Soc. 2005, 127, 9374–9375.
- 26. Tsunoyama, H.; Tsukuda, T.; Sakurai, H. Chem. Lett. 2007, 36, 212-213.
- Chen, H. W.; Murugadoss, A.; Hor, T. S. A.; Sakurai, H. Molecules 2011, 16, 149– 161.
- 28. Massart, R. IEEE Trans. Magn. 1981, 17, 1247-1248.
- 29. Lu, Y.; Yin, Y. D.; Mayers, B. T.; Xia, Y. N. Nano Lett. 2002, 2, 183-186.
- Zhou, X. S.; Wu, T. B.; Hu, B. J.; Jiang, T.; Han, B. X. J. Mol. Catal. A: Chem. 2009, 306, 143–148.

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