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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 $Fe_3O_4@SiO_2\sim$MPS grafted by poly(*N*-vinyl-2-pyrrolidone) (PVP). The solid magnetic support was prepared by anchoring 3-methacryloxypropyltrimethoxysilane (MPS) onto the $Fe_3O_4@SiO_2$ 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)/$Fe_3O_4@SiO_2\sim$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 $AuCl_3$. Moreover, the supported catalyst is easy to recover and can be used in four cycles without apparent loss of activity.

Halogenation of aromatic compounds with *N*-halosuccinimides (NXS, X = Cl, Br, and I) is an important process in organic synthesis,[1] as their products have been widely employed as the substrates in various important organic reactions such as Suzuki coupling, Heck reactions, and Sonogashira reactions.[2–4] 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 ($FeCl_3$, $BF_3–H_2O$, H_2SO_4, etc.) as catalyst, and the reaction conditions are generally harsh.[5–9] In view of those deficiencies, Wang and co-workers[10] recently developed a mild efficient method for the bromination of arenes by using $AuCl_3$ as catalyst. In Wang's procedure, only a tiny amount of (0.1–1 mol %) $AuCl_3$ 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_{Ar}–M bond through direct metallation of a C_{Ar}–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,[11–14] 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.[15–23] 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_3O_4–polymer nanocomposites have demonstrated great promise for immobilization of metal catalysts, due to their multifunctional properties including special magnetic behavior, chemical durability, and stability.[24] Due to the considerable stabilization of poly(*N*-vinyl-2-pyrrolidone) (PVP) for Au,[25,26] Hidehiro Sakurai and co-workers examined the catalytic activity and recyclability of Au supported on Fe_3O_4/PVP for the oxidation of alcohols and obtained excellent results.[27] However, the dosage of Au had to be excessive to some extent because the interaction between Fe_3O_4 and PVP is not strong enough. Herein, we wish to report a facile alternative synthesis of a heterogeneous gold catalyst supported on $Fe_3O_4@SiO_2\sim$MPS grafted by PVP. We applied the newly prepared Au/$Fe_3O_4@SiO_2\sim$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/$Fe_3O_4@SiO_2\sim$PVP catalyst was outlined in Scheme 1. Magnetic Fe_3O_4 nanoparticles were obtained by coprecipitation of $FeCl_2$ and $FeCl_3$ in an aqueous solution at 85 °C.[28] TEM image (Fig. 1a) shows that the obtained Fe_3O_4 nanoparticles are in slight aggregation, with the size between 8–12 nm. Stirring the Fe_3O_4 nanoparticles with *n*-ethyl silicate (TEOS) 24 h at room temperature resulted in formation of $Fe_3O_4@SiO_2$. As shown in

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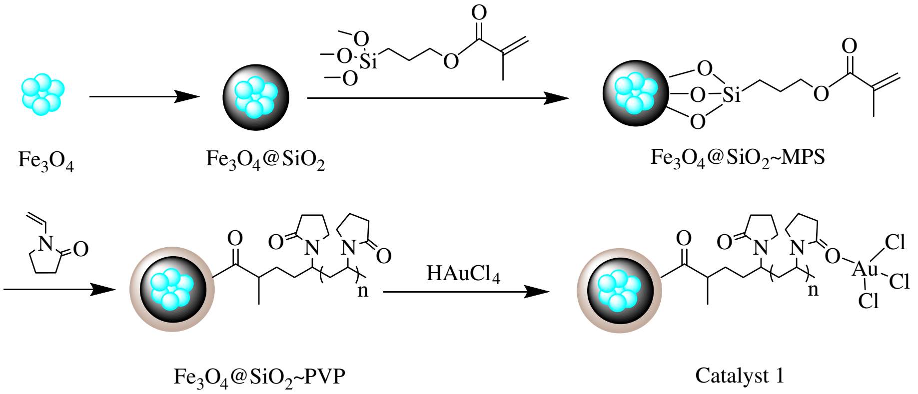

Scheme 1. Synthesis of Au/Fe_3O_4@SiO_2~PVP catalyst.

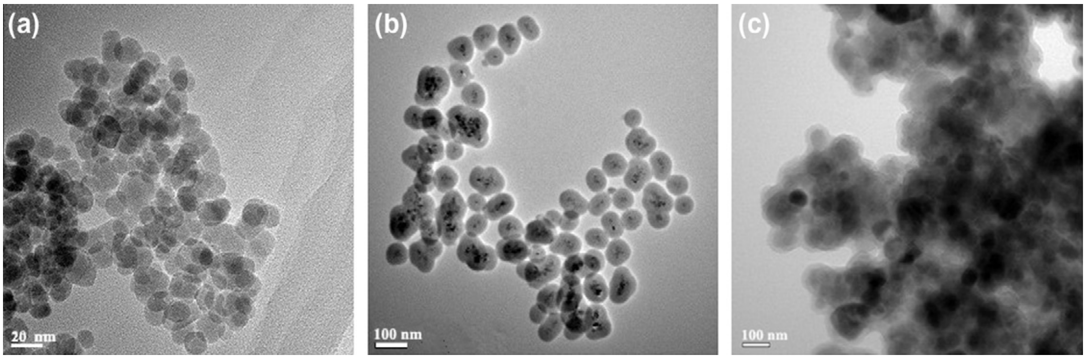

Figure 1. TEM image of (a) Fe_3O_4 in ethanol; (b) Fe_3O_4@SiO_2 in ethanol;; (c) Fe_3O_4@SiO_2~PVP nanoparticles in 1,2-dichloro ethane.

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_3O_4 nanoparticles were coated with SiO_2.[29] 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_3O_4@SiO_2~PVP nanocomposite via radical polymerization with MPS in Fe_3O_4@SiO_2~MPS. The TEM image of Fe_3O_4@SiO_2~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_3O_4@SiO_2~PVP shows strong absorptions at 1646 cm^{-1} and 1700 cm^{-1}, 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^{-1} of MPS disappears in Fe_3O_4@SiO_2~PVP. These results demonstrated that NVP unit was introduced onto the magnetic nanocomposite by polymerization.[30] Vibrating sample magnetometry (VSM) (see Supplementary data Fig. S2) reveals that the resulted Fe_3O_4, Fe_3O_4@SiO_2, and Fe_3O_4@SiO_2~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_3O_4@SiO_2 (a), Fe_3O_4@SiO_2~MPS (b); and Fe_3O_4@SiO_2~PVP (c) (see Supplementary data Fig. S3). The weight loss of 1.5 wt % for Fe_3O_4@SiO_2~MPS and the weight loss of 4.5 wt % for Fe_3O_4@SiO_2~PVP in the range of 250–800 °C suggested that the Fe_3O_4@SiO_2~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_3O_4@SiO_2~PVP). Finally, the Fe_3O_4@SiO_2~PVP was added to the aqueous solution of $HAuCl_4$, and the mixture was stirred for 12 h at room temperature. Thus formed Au/Fe_3O_4@SiO_2~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 electron-rich 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 $AuCl_3$ catalyst.[8] We believe that catalytic mechanism of catalyst **1** is the same as $AuCl_3$. This hypothesis is verified by the kinetic isotopic effect (KIE) experiment through intermolecular competitive bromination of benzene and benzene-d_6. The $k_H/k_{D(inter)}$ value was determined to be 1.60, very close to the value of 1.66 reported with $AuCl_3$ as catalyst[8] (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_3O_4@SiO_2:PVP (catalyst **2**). The support in catalyst **2** was prepared by simply blending PVP and Fe_3O_4@SiO_2~MPS under 60 °C for 24 h.[28] Au(III) was then loaded on Fe_3O_4@SiO_2:PVP via similar procedure as in the preparation of