Letter

Magnetic nanoparticles as a catalyst vehicle for simple and easy recycling†

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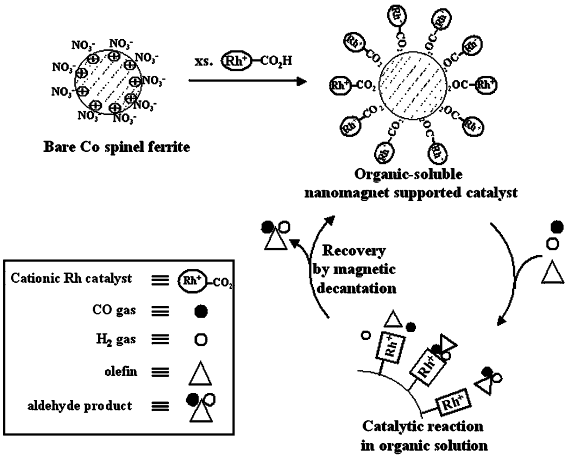
The surface of magnetic ferrite nanoparticles ($CoFe_2O_4$) was coated with a Rh-based cationic complex, [Rh(cod)(η^6-benzoic acid)]BF_4, to make them homogeneously dispersable and thermodynamically stable without an excess amount of surface capping molecules in normal organic solvents. Since magnetic nanoparticles themselves have strong magnetic properties and could be considered as a nanometer-sized solid support for the surface-anchored Rh-based catalyst, the ferrite nanoparticle-supported Rh catalyst showed very effective catalytic activity toward the hydroformylation reaction of olefins and could be easily recovered from the reaction mixture by magnetic decantation to be used for subsequent reactions.

Immobilization of homogeneous catalysts on various support materials such as organic polymers and inorganic silica and other metal oxides has been investigated for many years to recover and recycle catalysts, especially when expensive and/or toxic heavy metal complexes are employed.[1] However, immobilization of homogeneous catalysts usually decreases the catalytic activity (or efficiency) due to the problem of diffusion of reactants to the surface-anchored catalysts. In order to increase the active surface area, porous support materials such as zeolite and porous silica have been employed and have shown some promising results.[2,3] Another way to increase the surface area is, of course, to utilize smaller sized support materials with the same total volume. When the size of the support materials is decreased to the nanometer scale, the surface area will increase dramatically and the nanometer-sized supports will even be dispersible in solution, forming an emulsion. However, in this extreme case of immobilized systems, the same problems of isolation and recycling of homogeneous catalysts will also be encountered. If nanometer-sized support materials have another characteristic property, such as ferromagnetism, which allows them to be dispersed or aggregated by controlling the conditions (such as applying an external magnetic field in the case of ferromagnetic materials), it seems possible to separate and easily recycle immobilized catalysts on the nanometer-sized supports. In this communication, we propose a new utilization of magnetic nanoparticles as a catalyst support by modifying the surface of ferrite nanoparticles ($CoFe_2O_4$) with an active Rh-based cationic catalyst, [Rh(cod)-(η^6-benzoic acid)]BF_4, to make them homogeneously dispersed and very stable in normal organic solvents without an excess amount of surface capping molecules, and most importantly easily isolated and recycled (Scheme 1).



Scheme 1 Schematic illustration of the synthesis of organic-soluble magnetic nanoparticles and the recycling of the nanomagnet-supported catalyst by magnetic decantation.

Water-soluble Co-ferrite particles were prepared by a slight modification of the known co-precipitation method,[4] which involves ionic sites on the surface leading to electrostatic repulsion between magnetic nanoparticles. The chemical composition of bare (water-soluble) Co-ferrite nanoparticles was determined by both inductively coupled plasma-atomic emission spectroscopy (ICP-AES, SHIMADZU/ICPS-1000IV) analysis and electron probe micro analysis (EPMA, WDS mode, JEOL/JXA-8900R), giving reproducibly the composition in the form of $(CoFe_2O_4)_{core}(Fe_{0.19}O_x)_{shell}$. Such a non-stoichiometric deviation from the nominal composition of typical spinel ferrites (*i.e.*, MFe_2O_4) might originate from the contribution of a stable amorphous ferric hydroxide [*i.e.*, FeO(OH)] layer existing at the surface of the magnetic nanoparticles as suggested recently by Sousa *et al.*[5]

The powder XRD (Philips/PW 3710) data of the synthesized nanoparticles exhibit the typical diffraction pattern of the spinel structure, confirming the core structure of the magnetic Co-ferrite nanoparticle. The magnetic properties of the Co-ferrite nanoparticles were determined with a vibrating sample magnetometer (VSM; Lake Shore Model 7304) and a value of $M_{s,\ 293\ K} \approx 60$ emu g^{-1} was obtained.

In order to check the idea of utilizing magnetic nanoparticles as a catalyst support, the known Rh-based hydroformylation catalyst system was selected.[6] The cationic rhodium complex having a carboxylic acid functional group was prepared, which could be attached onto the magnetic Co-ferrite nanoparticle as suggested in the literature; carboxylic acid is a suitable binding group for the surface of ferrite nanoparticles.[7] [Rh(cod)(η^6-benzoic acid)]BF_4 (cod = cyclooctadiene, compound **1**) was

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† Electronic supplementary information (ESI) available: XRD and FT-IR data, as well as the detailed experimental conditions for the catalytic hydroformylation reactions. See http://www.rsc.org/suppdata/nj/b2/b209391j/.

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easily prepared in high isolated yield by treating an ethanolic solution of $[Rh(cod)Cl]_2$ with 2 equiv. of benzoic acid and $AgBF_4$; this method is slightly modified from the known synthetic method for $\{[Rh(cod)(\eta^6\text{-arene})]BF_4\}$ in order to introduce the carboxylic acid site.[6] Compound **1** is soluble in acetone, DMF, and methylene chloride, but insoluble in hexane and diethyl ether. Organic-soluble $[Rh(cod)(\eta^6\text{-benzoic acid})]BF_4$ coated Co-ferrite nanoparticles were easily obtained by using a modified surface-capping reaction.

From the electron microscopic analyses of the organic-soluble Co-ferrite magnetic nanoparticles derivatized with the Rh complex, it was confirmed that well separated nanoparticles with a size distribution ranging from 8 to 20 nm were homogeneously dispersed over the entire area (Fig. 1). The selected area electron diffraction (SAED) pattern of the sample revealed that the core spinel structure of the Co-ferrite nanoparticle was not altered during the surface modification process. The chemical composition of the Rh-catalyst-capped magnetic nanoparticle (nanomagnet-supported catalyst, **2**) was established by ICP-AES and EPMA (WDS mode), independently, to be $(CoFe_2O_4)_{core}(Fe_{0.19}O_x)_{shell}\text{–}\{[Rh(cod)(\eta^6\text{-benzoic acid})]BF_4\}_{0.013}$.

The nanomagnet-supported catalyst (**2**) showed excellent catalytic activity with a good regioselectivity toward the hydroformylation reaction of 4-vinylanisole, which is comparable to that of its homogeneous counterpart (*i.e.*, compound **1**), as presented in Table 1. Although the catalytic activity of **2** is one-third that of its homogeneous counterpart, probably due to steric and diffusion rate differences (entries 1–5 *vs.* entry 6), this relative activity of **2** seems to be extraordinarily high based on the general trend of decreasing activity in immobilized catalysts [*e.g.*, inorganic-supported, biphasic (water–organic phase), and organic polymer-supported catalysts].[8–10] The high catalytic activity of **2**, even though the actual catalyst molecules are immobilized on the support, can be largely attributed to the size effect of the ferrite nanoparticle support, which provides a very large effective surface for the catalytic reactions. Therefore, the present nanomagnet-supported catalyst **2** can be regarded as a "quasi-homogeneous" catalyst: it has a very large effective surface for the catalytic reactions that are comparable to those of the homogeneous molecular catalyst. Furthermore, the most profitable feature of **2** lies in its unique recycling process, where catalyst recovery can be achieved by simple magnetic decantation after applying a magnetic field on the surface of the reaction vessel. Nanomagnet-supported catalyst **2** can also be recovered with the solubility control method by adding a large amount of a poor solvent such as alcohol to the reaction mixture followed by ultra-centrifugation, if preferred. The recovered nanomagnet-supported catalyst (**2**) could be completely re-dispersed in methylene chloride solvent again and could be reused without any further unusual treatment. Reaction results from consecutive usages (5 times) of catalyst **2** did not show any differences in catalytic activities (entries 2–5 in Table 1).

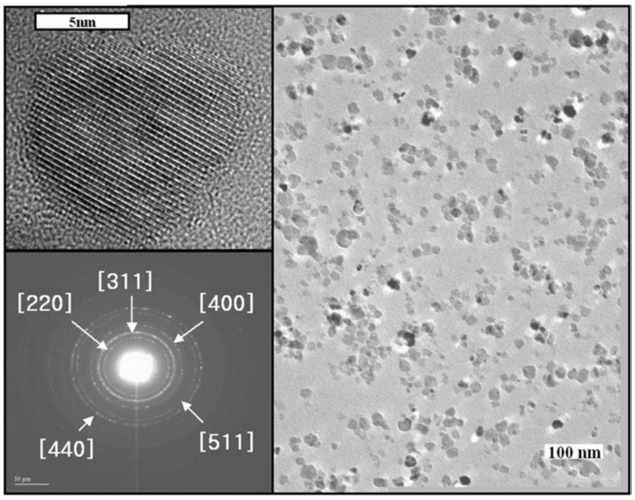
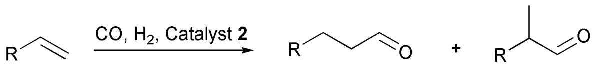


Fig. 1 TEM micrograph of $(CoFe_2O_4)_{core}(Fe_{0.19}O_x)_{shell}\text{–}\{[Rh(cod)(\eta^6\text{-benzoic acid})]BF_4\}_{0.013}$. The insets are the electron diffraction pattern at the selected area (below left) and the micrograph at high resolution (above left).

Table 1 Hydroformylation of 4-vinylanisole by the nanomagnet-supported catalyst **2** ($R = C_6H_5OCH_3$)



Entry	Time/h	l/b[a]	Yield (%)[b]
1	3	9/91	> 99
2 (reused)	3	10/90	> 99
3 (reused)	3	10/90	> 99
4 (reused)	3	9/91	> 99
5 (reused)	3	10/90	> 99
6[c]	1	10/90	> 99

[a] Structural ratio of aldehyde products was measured by ^{1}H-NMR spectroscopy (b: 9.26 ppm, l: 9.78 ppm); b stands for the branched form and l for the linear form. [b] Determined by ^{1}H-NMR spectroscopy and gas chromatography. [c] Homogeneous reaction with compound **1**.

In summary, an organic-soluble, processible and very stable magnetic nanoparticle was successfully synthesized by deliberately choosing an ionic organometallic compound as a surface-stabilizing molecule. The novel stability of this magnetic nanoparticle in organic solution is most likely to be due to the ionic repulsive forces between the surface-anchored ionic organometallic compounds, which can overcome the magnetic dipolar interaction that leads to aggregation of magnetic ferrite particles. The prepared organic-soluble magnetic nanoparticle could be used as an immobilized homogeneous catalyst, and the unique properties of the nanosized magnetic support revealed several novel features. An excellent catalytic activity, comparable to that of the homogeneous catalyst, could be obtained and the simple and efficient recycling of the catalyst by magnetic decantation was clearly demonstrated. This finding is expected to be very important in connection with the processing of magnetic nanoparticles with various hybridizing materials, such as polymeric and inorganic matrices, and suggests that it is also very attractive for application as a new support material for precious organometallic catalysts.

Experimental

The mixed solution of bare Co-ferrite nanoparticles and an excess amount of compound **1** in DMF was stirred for 2 h at room temperature. The product was precipitated from the mixture by adding a large amount of chloroform and hexane (DMF:chloroform:hexane = 1:3:3) and was collected by centrifugation. After the collected crude solid product had been washed several times with a mixed solution of chloroform and hexane ($v/v = 1{:}1$), the product was re-dispersed in acetone and any insoluble materials were removed by centrifugation. From the clear supernatant, a dark brown powdery product was obtained after evaporating the solvent. It showed excellent solubility in various organic solvents such as CH_2Cl_2, THF, acetone, and DMF with long-term stability (more than a few months). The successful modification of the surface of Co-ferrite nanoparticles with Rh complex was confirmed by FT-IR spectroscopy. The XRD and FT-IR data along with the detailed conditions of the catalytic hydroformylation reactions are given in the electronic supplementary information (ESI).

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