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Metal Supported on Dendronized Magnetic Nanoparticles: Highly Selective Hydroformylation Catalysts

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Abstract: A method for homogenizing heterogeneous catalyst is described. The method is based on growing polyaminoamido (PAMAM) dendrons on silica-coated magnetic nanoparticles. After the dendronizing process, the silica-coated magnetic nanoparticles are more stable and more soluble in organic solvents. The dendronized particles are phosphonated, complexed with $[Rh(COD)Cl]_2$, and applied in catalytic hydroformylation reactions. These new catalysts are proven to be highly selective and reactive.

Introduction

During the past two decades, a great deal of attention has been paid to developing methods for heterogenizing homogeneous catalysts in order to combine the advantages of both homogeneous and heterogeneous catalysis.[1] Among these methods, the binding of catalysts to organic polymer solids[2] or inorganic solids[3] is widely used. Although the heterogenized catalysts can be recycled and easily separated from the reaction mixtures, they are significantly less reactive and selective than their homogeneous counterparts. For this reason, there is a need to find new methods and strategies in order to overcome these limitations.

Dendrimers, a class of macromolecules with special properties and functions, have been utilized for several applications[4] including homogeneous catalysis.[5] Interestingly, in many cases, the soluble dendritic catalysts were found to be more efficient or selective than the traditional analogues of metal complexes. In recent years, dendrimers immobilized on silica or polymers have been investigated intensively by our group[6] and others[7−10] and applied to several catalytic organic transformations. These new catalytic materials are sometimes highly efficient in terms of reactivity and selectivity and are easily recyclable.

Magnetic nanoparticles that can be magnetized in the presence of an external magnet have been studied extensively for various biological applications such as magnetic resonance imaging,[11] drug delivery,[12] biomolecular sensors,[13] bioseparation,[14] and

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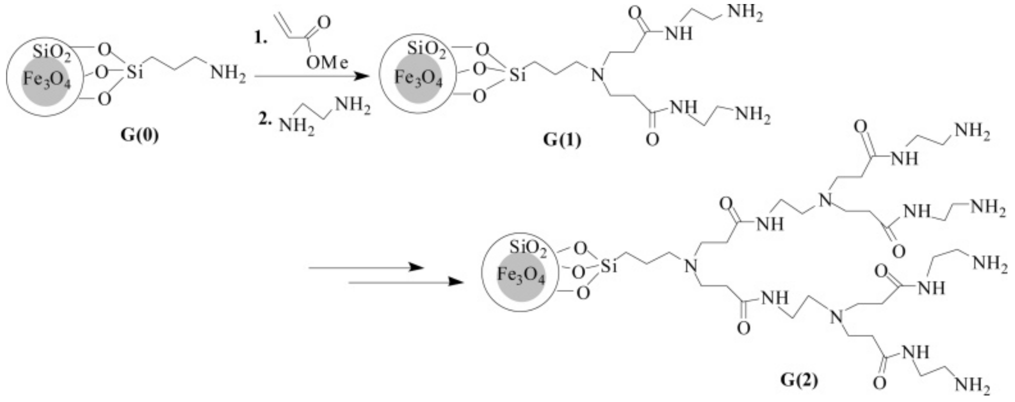
Scheme 1. Dendronizing Process of the Silica-Coated Magnetic Nanoparticles



magneto-thermal therapy.[15] Recent reports show that magnetic nanoparticles are efficient supports for catalysts and can facilitate their separation from the reaction media after magnetization with a permanent magnetic field.[16−19]

We now describe a method based on combining the features of magnetic nanoparticles and dendrimers. The objective of this novel strategy is to homogenize heterogeneous catalysts as follows: use magnetic nanoparticles to minimize the support for the immobilization of the catalyst, while at the same time keeping it easily separable. Second, by using dendrimers on a support, one can enhance the solubility of the support in an organic solvent. The dendrimerization process can produce organic arms on the support enhancing its compatibility with the medium, and the surrounding linked metallic complexes can behave as real homogeneous catalysts. We demonstrate this by growing a polyaminoamido (PAMAM) dendron on nanomagnetite, Fe_3O_4, coated by a silica shell.

Results and Discussion

The magnetite nanoparticles of 8−12 nm were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution at 85 °C using the method described by Massart.[20] Our initial attempts to grow PAMAM dendrimers directly on the magnetic nanoparticles failed, due to coagulation of the particles and solubility problems in organic media. These problems could be solved by coating the magnetic nanoparticles with silica. The process of the coating was performed by suspending the magnetic particles in 2-propanol after coating with poly(vinylpyrrolidone) (PVP) and mixing with tetraethoxysilane to start creating a silica shell under basic conditions via a sol−gel process.[21] TEM analysis (see Supporting Information) confirms the structure of the core−shell of the obtained particles, and thus the core contains the nanomagnetite. The average size of the coated particles is 50−60 nm. In addition, the particles before and after coating with silica were analyzed by X-ray powder diffraction. While the XRD pattern of the bare magnetic particle shows characteristic peak positions and relative intensity, the XRD pattern of the coated nanoparticles has the same characteristic peaks with an additional broad peak between $2\theta = 15$ and $2\theta = 30$ which is attributed to the amorphous silica shell (see Supporting Information). Silanation of these silica-coated particles with (3-aminopropyl)triethoxysilane under reflux in toluene for 24 h gave 0.25−0.27 mmol/g of amino groups (determined by back-titration). PAMAM dendrons, up to generation three, were constructed on the particles containing amino groups as initiators by two subsequent steps for each generation: Michael-type addition of methyl acrylate to produce the amino propionate ester and amidation of the resulting ester groups with ethylenediamine (see Scheme 1). During the advance in the dendronizing process, it was noticed that the solubility of the magnetic nanoparticles in organic solvents is enhanced, and they become more stable for a prolonged time in organic media.

The growth of the PAMAM dendrons was followed by infrared spectroscopy and thermal gravimetric analysis. The IR spectra G(0)−G(3) are shown in Figure 1. In the spectra of half generations there is a well-defined absorption at 1738 cm^{-1} attributed to CO stretching of the ester groups. Amidation affords the full-generations with the disappearance of the absorption at 1738 cm^{-1} in the spectrum of G(1), but G(2) and G(3) show a small amount of ester groups. An absorption at 1668 cm^{-1} is due to CO stretching of a secondary amide. This absorption also appeared in the spectra of G(0) due to PVP molecules that are encapsulated between the magnetite core and the shell of silica.

TGA analysis (Figure 2) shows that there was an increase in the organic content when the growth of the PAMAM dendrons was increased to higher generations. The silica coated magnetite contained 6.4% of organic material which belongs to the PVP adsorbed on the magnetite nanoparticles. The organic content

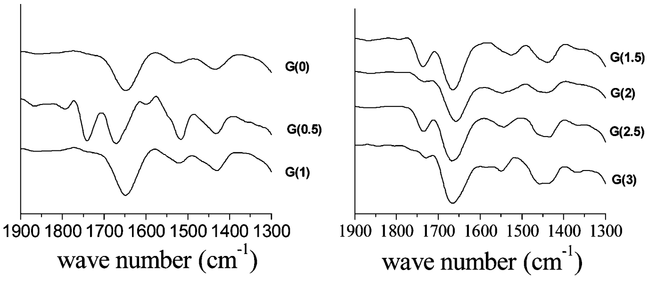


Figure 1. FT-IR spectra of silica-coated nanomagnetite supported PAMAM dendrons.

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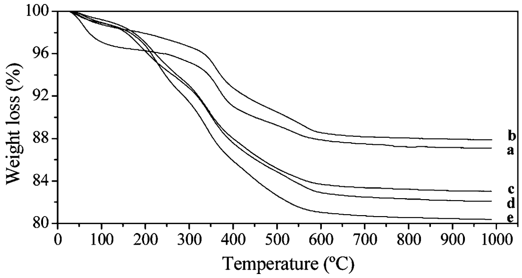
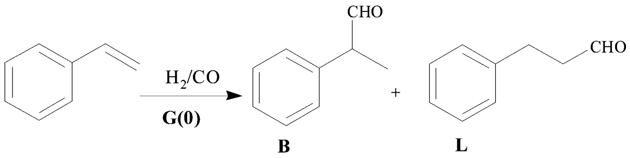


Figure 2. Weight loss as measured by TGA for silica-coated nanomagnetite-supported PAMAM dendrons. (a) After coating with silica; (b) after silanation; (c) G(1), (d) G(2); and (e) G(3).

Table 1. Hydroformylation of Styrene by a Rhodium-Complexed G(0) Dendron Supported on Silica-Coated Magnetite Nanoparticles[a]



entry	solvent	temp (°C)	time (h)	conversion[b] (%)	selectivity B:L ratio[c]
1	CH_2Cl_2	rt	24	50	76:1
2	CH_2Cl_2	rt	48	100	70:1
3	CH_2Cl_2	40	24	>99	45:1
4	CH_2Cl_2	50	16	100	42:1
5	toluene	50	16	100	38:1
6	benzene	50	16	95	35:1
7	THF	50	16	54	83:1
8	THF	50	24	90	32:1
9	CH_3CN	50	24	58	46:1
10	ether	50	24	84	25:1

[a] 1 mmol of styrene, 10 mL of solvent, 1000 psi of 1:1 H_2:CO, 50 mg of catalyst. [b] Determined by ^{1}H NMR and GC. [c] Determined by ^{1}H NMR.

Table 2. Hydroformylation of Various Substrates by Rhodium-Complexed Dendrons Supported on Silica-Coated Magnetite Nanoparticle[a]

entry	substrate	generation	conversion[b] (%)	selectivity[c] B:L ratio
1	4-vinylanisole	G (0)	100	35:1
2	vinyl benzoate	G (0)	30	100:0
3	1-octene	G (0)	100	1:2.2
4	styrene	G (1)	100	44:1
5	styrene	G (2)	100	43:1
6	styrene	G (3)	100	40:1
7	4-methylstyrene	G (1)	>99	45:1
8	4-vinylanisole	G (1)	>99	44:1
9	4-flourostyrene	G (1)	100	42:1
10	4-chlorostyrene	G (1)	100	48:1
11	4-vinylbenzoic acid	G (1)	100	>99:1
12	2-bromostyrene	G (1)	52	65:1
13	2-vinylnaphthalene	G (1)	100	53:1
14	vinyl acetate	G (1)	40	42:1
15	4-vinylbiphenyl	G (1)	>99	47:1
16	9-vinylanthracene	G (1)	5	100:0

[a] 1 mmol of the substrate, 10 mL of dichloromethane, 50 °C, 1000 psi of 1:1 H_2:CO, 50 mg of catalyst, 16 h. [b] Determined by ^{1}H NMR and GC. [c] Determined by ^{1}H NMR.

for the G(0), G(1), G(2), and G(3) steps was 7.3%, 13.3%, 14.1%, and 16.6%, respectively (for more details see Supporting Information).

The dendrons on silica-coated nanomagnetite were phosphonated by reaction of the terminal amino groups with diphenylphosphinomethanol prepared in situ from diphenylphosphine with paraformaldehyde.[6] ICP analysis showed that the content of phosphorus in G(0), G(1), G(2), and G(3) was 0.2, 0.16, 0.189, and 0.19 mmol/g, respectively. Although the amino groups increased with the increase of the growth of the dendrons, the phosphorus content was almost the same. We attribute the incomplete phosphination reaction to steric effects resulting from the growth of the dendrons to higher generations. The phosphonated dendrons were complexed by mixing at room temperature with $[Rh(cod)Cl]_2$ in dry and degassed toluene for 5 h. The resultant complexes were tested in hydroformylation reactions using a 1:1 mixture of carbon monoxide and hydrogen pressurized to 1000 psi. The optimization of the reaction was carried out using styrene as the model substrate and the rhodium-complexed G(0) complex as the catalyst, and the results are shown in Table 1. The reaction could be performed at room temperature, but it was slow and needed 48 h for completion (Table 1, entries 1 and 2). Nevertheless, the reaction was highly regioselective for the branched aldehyde. Increases in temperature decrease the regioselectivity of the reaction and increase the reactivity of the catalyst (Table 1, entries 2−4), but this decrease is not considered as significant and the reaction was still highly selective to the branched aldehyde, even at 50 °C. The solvent plays an important role in the reactivity and selectivity of the catalyst; e.g., polar solvents negatively affect the reaction resulting in reduction in reactivity and selectivity (Table 1, entries 7−10), and nonpolar solvents are very efficient media for the same reaction (Table 1, entries 4−6). The highest reactivity and selectivity could be achieved by using dichloromethane as the solvent. This solvent polarity effect was observed even using toluene or benzene. Benzene is slightly more polar than toluene and could decrease the conversion of the reaction and the yield of the desired branched product (Table 1, entry 6).

The hydroformylation of various substrates with G(0)−G(3) catalysts were carried out at 50 °C with a 1:1 mixture of carbon monoxide and hydrogen under a total pressure of 1000 psi. The results are shown in Table 2. For the hydroformylation of styrene, the generation 1 catalyst was found to be the most efficient (Table 2, entry 2), although the other catalysts were still considered selective and reactive. In contrast to previous studies[6l] in which there was a significant decrease observed in activity and selectivity going to higher generations, the present catalyst systems, at higher generations, essentially retained their reactivity or selectivity. Apparently there is no significant electronic effect for the hydroformylation reaction as shown by results for the reactivity and selectivity of styrenes substituted with electron-donating or -withdrawing groups (Table 2, entries 7−10). In the case of 4-vinylbenzoic acid (Table 2, entry 11) the branched isomer was formed almost exclusively. The hydroformylation of 2-bromostyrene was slow but highly regioselective for the branched aldehyde (Table 2, entry 12), and we believe that the decrease in reactivity in this case may be due to steric effects. The substrates 4-vinylbiphenyl and 2-vinylnaphthalene undergo hydroformylation efficiently, in terms of both reactivity and regioselectivity (Table 2, entries 13 and 15). In addition the lowest reactivity was observed for the hydroformylation of 9-vinylanthracene (Table 2, entry 16). Vinyl acetate and vinyl benzoate also gave the isomeric aldehydes at low conversion (Table 2, entries 14 and 2), but the selectivity toward the branched products was still high.

Table 3. Recycling of the Rhodium-Complexed Dendrons Supported on Silica-Coated Magnetite Nanoparticles for the Hydroformylation of Styrene[a]

run	generation	conversion[b] (%)	selectivity[c] B:L ratio
1	G (0)	>99	45:1
2	G (0)	>99	41:1
3	G (0)	97	47:1
4	G (0)	98	45:1
5	G (0)	69	43:1
1	G (1)	100	48:1
2	G (1)	100	48:1
3	G (1)	>99	45:1
4	G (1)	98	47:1
5	G (1)	98	42:1

[a] 1 mmol of styrene, 10 mL of dichloromethane, 1000 psi of 1:1 H_2:CO, 40 °C, 50 mg of catalyst, 20 h. [b] Determined by ^1H NMR and GC. [c] Determined by ^1H NMR.

In comparison with previous studies,[6h,k,l] the new catalysts are much more reactive and selective**.** Unfortunately, our catalyst is not selective for the hydroformylation of linear aliphatic olefins, e.g., 1-octene produces isomeric aldehydes in a ratio of 2.2:1 L:B.

Importantly, G(0) and G(1) catalysts can be recycled under the same pressure, and at 40 °C, for up to five runs without significant loss in activity or selectivity. In the fifth run the G(0) catalyst was far less reactive (see Table 3). The recycling was very simple, and thus after each run the catalyst was separated magnetically, washed with dichloromethane, and after flushing with nitrogen, used for the next run. After the reactions were complete, the solution was reddish-brown in color, and after magnetic separation, the solution became very clear.

Summary

In conclusion, PAMAM dendrons were grown for the first time on silica-coated magnetic nanoparticles, for up to three generations. After phosphination of the heterogenized dendron with various generations, it was complexed with rhodium and used as the catalyst for hydroformylation reactions. The reactivity and selectivity of the catalyst were very high. In addition, the new dendronized magnetic nanoparticles were applied to catalytic processes, but we believe they will find application in many other domains.

Experimental Section

Nanomagnetite particles of 8−12 nm were prepared according to Massart's method.[20] Coating of the nanoparticles with PVP was achieved following the procedure of Lee and co-workers.[22]

Large-Scale Coating of the Magnetite Nanoparticles with Silica. A solution of 1 g of PVP-coated magnetite nanoparticles was suspended in 2 L of 2-propanol containing 50 mL of concentrated ammonia (28%). The solution was divided into three portions, and each was sonicated for 1 h. After combining the solutions, 5 mL (22.4 mmol) of tetraethoxysilane (TEOS) in 100 mL of 2-propanol were added dropwise, over a 3-h period, to the magnetite solution using a mechanical stirrer. The stirring was continued for another 3 h, and then the silica-coated nanoparticles were separated magnetically after decantation of the solution and washed three times with TDW. The final product (2 g) was obtained after drying at room temperature, under a vacuum of 0.2 mmHg, for 24 h.

Silanation of the Silica-Coated Magnetite Nanoparticles. 10 g of dry silica-coated magnetite powder were suspended in 200 mL of dry toluene. After sonication for 35 min, a solution of 2.5 mL (10.68 mmol) of (3-aminopropyl) triethoxysilane was added under mechanical stirring. The solution was heated at 105 °C for 20 h. The particles were separated by an external magnet after cooling to room temperature, washed 3 times with dry methanol, and dried under vacuum for 24 h. 0.25−0.27 mmol/g of amino groups was found (as determined by back-titration).

General Procedure for the Preparation of PAMAM Dendrons on the Silica-Coated Magnetite Nanoparticles. 8 g of silanated particles were suspended in 120 mL of dry methanol, and after sonication for 35 min, 10 mL (111 mmol) of methyl acrylate were added and the mixture was heated at 50 °C for 5 days. After cooling to room temperature, the particles were separated magnetically, washed 3 times with dry methanol, and dried under a vacuum for 24 h to give G(0.5). The dried material was then suspended again in 120 mL of methanol and sonicated for 35 min. After the addition of 17.2 mL (257 mmol) of ethylenediamine dropwise at room temperature, the solution was heated at 50 °C for 5 days. The magnetic material was magnetically separated, washed 3 times with dry methanol, and dried under a vacuum to give G(1). The second and third generations were prepared following the same manner, using a 50-fold excess of methyl acrylate and a 125-fold excess of methylenediamine with respect to the amount of amino groups.

General Procedure for the Phosphination of PAMAM Dendrons on the Silica-Coated Magnetite Nanoparticles. 10 g (53.7 mmol) of diphenylphosphine were added to 1.7 g (54 mmol) of paraformaldehyde in 50 mL of dry and degassed methanol. The solution was heated for 1 h under N_2 at 65 °C. After the solution was cooled to room temperature, 2 g of the silanated silica-coated magnetite nanoparticles were added and the mixture was heated at reflux for 3 days. The resulting phosphinated particles were magnetically separated and washed 4 times with degassed methanol and dried under vacuum for 24 h.

General Procedure for the Complexation of Phosphinated PAMAM Dendrons on the Silica-Coated Magnetite Nanoparticles. 2 g of the phosphinated particles containing 0.4 mmol of phosphorus and 0.1 g (0.2 mmol) of $[Rh(cod)Cl]_2$were added to 40 mL of dry and degassed toluene. The mixture was stirred for 5 h, and the particles were magnetically separated, washed 3 times with dry toluene, and dried under a vacuum for 24 h.

General Procedure for the Hydroformylation reaction. 50 mg of the catalyst, which was homogenized in 10 mL of dichloromethane by sonication for 10 min, and 1 mmol of appropriate substrate were placed in a 45 mL glass-lined autoclave. After sealing, the autoclave was purged 3 times with carbon monoxide and pressurized to 1000 psi with a 1:1 of mixture of carbon monoxide and hydrogen. The autoclave was placed in an oil bath preset to the desired temperature. After the appropriate reaction time, the autoclave was cooled to room temperature and the gases were released. The catalyst was separated magnetically, and the solution was concentrated by evaporation of the solvent. The catalyst was washed with dichloromethane, flushed with a nitrogen stream, and used for subsequent cycles.

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Supporting Information Available: DTA-TG curves for the dendronized magnetic nanoparticles, XRD patterns, and TEM-images for the silica-coated magnetic nanoparticles. This material is available free of charge via the Internet at http://pubs.acs.org.

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