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Short Communication

Magnetic nanoparticles coated by acidic functionalized poly(amidoamine) dendrimer: Effective acidic organocatalyst

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ABSTRACT

A novel magnetic BrØnsted acid catalyst was synthesized based on growing poly(amidoamine) dendrimers on the surface of magnetic nanoparticles. After the dendronizing process, the MNP coated PAMAM was functionalized by chlorosulfuric acid to form an acid catalyst. Because of dendrimer coating of MNPs, catalyst shows good loading level of acidic groups on the surface. Also zwitterion nature of catalyst surface improves the catalytic activity. This new catalyst is proven to be highly effective in the synthesis of α-aminophosphonate compounds in a green way.

1. Introduction

Despite of the lower activity of heterogeneous catalysts than homogenous ones, in the last decade, a lot of efforts have been done to develop novel methods for heterogenizing homogeneous catalysts in order to combine the advantages of both homogeneous and heterogeneous catalysts [1–5]. In order to achieve this matter, homogeneous catalysts were immobilized on the surface of solid supported materials such as mesoporous silica [6–8], polymers [9,10] and magnetic nanoparticles [11,12]. Among the solid support materials, magnetic nanoparticles (MNPs) were more interesting for immobilization of homogeneous catalysts, because their magnetic response causes simple separation of catalyst by using an external magnet. Although MNPs always tend to agglomerate due to their dipole–dipole interaction, it was found that coating of MNPs by polymers could help to prevent their aggregation and improve their chemical stability [13].

However these heterogenized catalysts can be easily separated from the reaction mixtures, but their activity is significantly less than their homogeneous counterparts. The activity of heterogeneous catalysts strongly depended on the loading amount of their immobilized homogenous part. Moreover the short lengths of soluble homogenous part (spacer) on the solid catalyst surface make difficult interaction between substrates and immobilized homogenous catalyst. The problem of low activity could be overcome by using a longer spacer group with the multi catalytic site. For these reasons, there is still a need to find new protocols for synthesis of novel heterogeneous catalysts to overcome these problems. A rationalized choice for solving this problem in the heterogeneous catalysts is immobilization of polymers, especially dendrimers on the solid surface.

Dendrimers, a class of macromolecules with highly branched structure and globular shape, possess unique properties such as high density of active groups, good structural homogeneity, intense internal porosity and good biocompatibility [14]. Among the various types of dendrimers, poly(amidoamine) (PAMAM) dendrimers are particularly interesting because of their globular structure, mimicking the three-dimensional structure of biomacromolecules, and their good biocompatibility [15]. PAMAM dendrimers in the homogenous forms [16–18] or the immobilized heterogeneous forms [19–21] have been used intensively as catalyst in the several catalytic organic transformations. Interestingly, in many cases, the dendritic catalysts were found to be more efficient or selective than the traditional analog catalyst.

Herein, we describe synthesis of a novel magnetic organocatalyst which magnetic Fe_3O_4 nanoparticles were coated by sulfamic acid functionalized PAMAM dendrimer. The synthesized catalyst was used in the synthesis of α-aminophosphonate in the mild reaction condition and excellent yields.

α-Aminophosphonates are an important class of compounds in modern pharmaceutical chemistry [22–24] and their synthesis has received considerable attention because of their structural analogy to α-amino acids. Therefore, a number of methods have been developed for synthesis of α-aminophosphonate family. These methods include Lewis metal acids, such as $FeCl_3$ [25], $LiClO_4$ [26], $InCl_3$ [27], $ZrCl_4$ [28], $SbCl_3$/Al_2O_3 [29], SiO_2@$TaCl_5$ [30] and BrØnsted acids such as Amberlite-IR 120 [31], CF_3CO_2H [32] and sulfamic acid [33]. However, many of these methods have some drawbacks such as using expensive, toxic and

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moisture sensitive catalysts, long reaction times, low yield of products and tedious separation procedures. Therefore, the development of an effective, convenient, and green protocol for synthesis of α-aminophosphonates is still a challenge.

2. Result and discussion

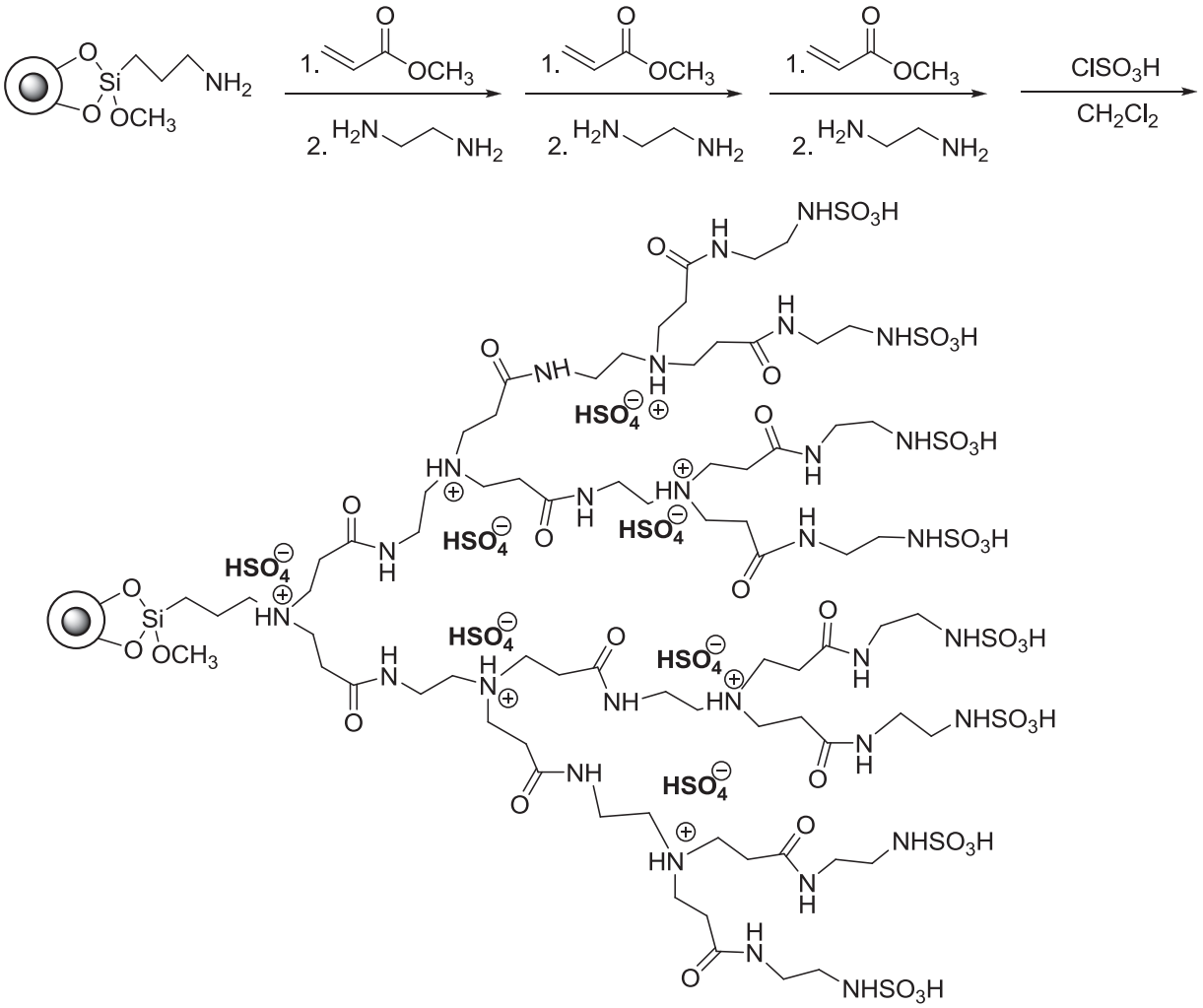
2.1. Synthesis of MNP@DSO3H

The magnetic nanoparticles (MNPs) were synthesized by co-precipitation method in the basic condition. A solution of iron (II) and iron (III) was vigorously stirred (700 rpm) in deionized water under N_2 atmosphere. Then, ammonia solution was dropwise added to the mixture at 70 °C, immediately followed by the addition of NH_3 solution; MNP black precipitate was formed. Silica coating is one of the most ideal methods for protection of MNPs, due to its high chemical and thermal stabilities, large surface areas and good compatibilities [34]. For silica coating procedure, the resulted MNPs were ultrasonically suspended in ethanol/water mixture and pH of solution was adjusted on 10 by adding ammonium solution. Tetraethyl orthosilicate (TEOS) was dropwise added to the solution at 50 °C in the presence of a constant nitrogen flux. The mixture was stirred for 6 h to allow the silica shell to grow on the surface of the nanoparticles.

To growing dendrimer on the surface of MNPs, the surface of nanoparticles should have amine groups for initiation. Amine functionalization of MNP surface was performed by (3-aminopropyl) triethoxysilane under reflux condition in ethanol/water mixture for 24 h.

Propagation of PAMAM dendrimer onto the surface of MNPs, up to the third generation, was prepared using standard methods introduced by Tomalia [35] and co-workers (Scheme 1). The amino groups on the surface of MNPs react with methyl acrylate in a Michael-type addition reaction to form the amino propionate ester. Subsequent amidation of the ester groups with excess amount of ethylenediamine completes the first generation. Repetition of these two reactions forms the next generation of PAMAM dendrimer. Simple magnetic filtration and solvent rinsing served to remove excess reagents.

After preparation of PAMAM (G3) coated MNPs (MNP@PAMAM), an excess amount of chlorosulfuric acid was added to a dispersed dichloromethane solution of MNP@PAMAM for two purposes: (1) conversion of terminal amine groups of PAMAM to sulfamic acid and (2) the neutralization of inner tertiary amine groups in PAMAM dendrimer. The nucleophilic attack of terminal amine groups to $ClSO_3H$ and substitution with chloride will result in sulfamic acid functions. Tertiary inner amine groups initially react with $ClSO_3H$ in an acid–base reaction type. In this step, counterion of neutralized tertiary inner amine groups will be $ClSO_3^-$ or released Cl^-. Although, the excess amount of chlorosulfuric acid



Scheme 1. Synthetic route to catalyst.

will cause chloride anion replacement with $ClSO_3^-$. After washing several times with water, H_2O molecules react with $ClSO_3^-$ anions and convert them to HSO_4^- anions. $AgNO_3$ test shows that there is no chloride ion (<2%) in the final catalyst structure.

2.2. Catalyst activity of MNP@DSO$_3$H

To investigate the catalyst activity of MNP@DSO$_3$H, we choose the synthesis of α-aminophosphonate by three-component reaction of various aldehydes, amines and triethyl phosphite (Fig. 1).

Table 1 shows control experiment and optimization of reaction conditions for synthesis of α-aminophosphonate. Reaction between benzaldehyde, aniline and triethyl phosphite was chosen as model reaction. As seen in Table 1, the reaction does not proceed without any catalyst at room temperature. Using Fe_3O_4@SiO_2 as catalyst at room temperature gave only 18% yield in 2 h. For the activity comparison we used homogenous sulfamic acid and sulfamic acid functionalized MNP and the results are shown in Table 1. When MNP@DSO$_3$H was used in the reaction medium, yield of reaction was increased to 95% in 25 min at room temperature under solvent free condition. Comparison between Entries 4 and 5 shows that the dendrimer coated catalyst is more active than sulfamic acid functionalized MNP. It may correspond to the zwitterion nature of MNP@DSO$_3$H surface. To optimize the catalyst loading in the reaction we reduced the amount of catalyst and it was found that 5 mg of catalyst was enough for 3 mmol scale of reaction. For optimization of reaction solvent, similar condition was performed in various solvents, but solvent free condition gave better yields. As seen in Table 1, in the optimum condition a good turn over frequency (TOF) is obtained.

Subsequently, we investigated the diversity of MNP@DSO$_3$H in the synthesis of α-aminophosphonate. Reaction was performed under the optimized condition with the various aromatic and aliphatic aldehydes and amines and the corresponding α-aminophosphonate products were obtained in good to excellent yields (Table 2). Hindered aldehydes and highly deactivated aldehydes were also reacted under the same condition and obtained good yields.

2.3. Catalyst recycling

The recyclability of the MNP@DSO$_3$H was investigated in the syntheses of α-aminophosphonate by choosing a reaction between benzaldehyde, aniline and triethyl phosphite as modeling reaction at room temperature and solvent free condition. After completion of the reaction, monitored by TLC, catalyst was magnetically separated (Fig. 2) and reused in another reaction vessel under the same condition.

As seen in Fig. 3 even after seven cycles, products were obtained in high yield.

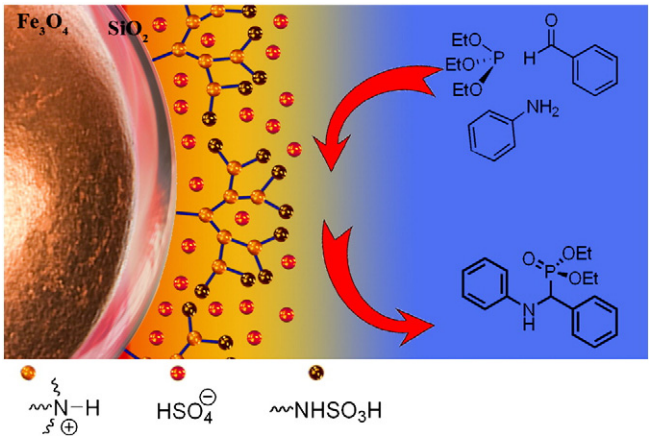


Fig. 1. Synthesis of α-aminophosphonate catalyzed by MNP@DSO$_3$H.

Table 1
Control experiments in synthesis of α-aminophosphonate.[a]

Entry	Catalyst	Amount of catalyst (mg)	Solvent	Time (min)	Yield[b] (%)	TOF (h^{-1})
1	–	–	Neat	3 h	1<	–
2	Fe_3O_4@SiO_2	20	Neat	120	18	–
3	MNP@$(CH_2)_3NHSO_3H$[c]	30	Neat	60	78	50.0
4	MNP@DSO$_3$H[d]	20	Neat	25	95	107.5
5	MNP@DSO$_3$H	10	Neat	25	94	212.8
6	MNP@DSO$_3$H	5	Neat	25	95	430.2
7	MNP@DSO$_3$H[e]	5	Neat	25	91	1236.2
8	MNP@DSO$_3$H[f]	5	Neat	40	79	1117.9
9	MNP@DSO$_3$H[e]	5	CH_2Cl_2	45	90	679.2
10	MNP@DSO$_3$H[e]	5	CH_3CN	45	86	649.0
11	MNP@DSO$_3$H[e]	5	Et_2O	45	57	430.2
12	MNP@DSO$_3$H[e]	5	THF	45	71	535.1
13	MNP@DSO$_3$H[e]	5	Hexane	45	42	316.9
14	Amberlite-IR 120[e]	100	Neat	45	31	4.07
15	H_2SO_4	10	Neat	45	63	8.23
16	NH_2SO_3H	10	Neat	120	87	4.21

[a] Reaction condition: benzaldehyde (1 mmol), aniline (1 mmol) and triethyl phosphite (1.3 mmol) at room temperature.
[b] Isolated yield.
[c] Loading amount of protons is 0.73.
[d] Loading of protons in MNP@ DSO$_3$H was 1.06 mmol/g.
[e] 3 mmol scale.
[f] 5 mmol scale.

3. Conclusion

In conclusion, we have developed green magnetic catalyst for the synthesis of α-aminophosphonate in solvent free condition at room temperature. Because of the ionic surface of MNP@DSO$_3$H, dendrimer coated catalyst shows high catalytic activity. Increasing the catalytic functional groups on the surface of MNPs by generation of PAMAM caused MNP@DSO$_3$H and was used in the low weight percent compared with substrates. Catalyst was recycled and reused for seven times without considerable loss of catalytic activity. Also, easy magnetic separation of the catalyst is an additional suitable aspect of our catalyst.

Table 2
Synthesis of α-aminophosphonate catalyzed by MNP@DSO$_3$H.[a]

Entry	R^1CHO	R^2NH_2	Time (min)	Yield (%)[b]
1	ph-	ph-	25	91
2	4-(OH)ph-	ph-	30	90
3	4-(Cl)ph-	ph-	25	92
4	4-(Me)ph-	ph-	35	89
5	4-(OMe)ph-	ph-	35	88
6	4-(NO_2)ph-	ph-	20	95
7	3-(NO_2)ph-	ph-	20	93
8	2-(NO_2)ph-	ph-	30	88
9	Furfuryl-	ph-	20	92
10	^{iso}butyr-	ph-	35	79
11	Morpholine	ph-	20	92
12	ph-	4-(Br)ph-	25	86
13	ph-	4-(Me)ph-	25	91
14	ph-	4-(NO_2)ph-	40	89
15	ph-	4-(Cl)ph-	30	90
16	ph-	3-(Cl)ph-	30	90
17	ph-	2-(Cl)ph-	35	82
18	ph-	4-(Cl),2-(NO_2)ph-	2 h	N.R.
19	ph-	Cyclohexyl-	25	90
20	4-(Cl)ph-	4-(NO_2)ph-	30	85
21	4-(Cl)ph-	4-(Br)ph-	35	90
22	4-(NO_2)ph-	4-(NO_2)ph-	40	86
23	4-(NO_2)ph-	4-(OMe)ph-	20	94
24	Furfuryl-	4-(Cl)ph-	35	92
25	4-(OMe)ph-	4-(Cl)ph-	30	90

[a] Reaction condition: aldehyde (3 mmol), amine (3 mmol), triethyl phosphite (3.5 mmol) and MNP@DSO$_3$H (5 mg), room temperature, solvent free.
[b] Isolated yield.

Fig. 2. Magnetic separation of catalyst by external magnet.

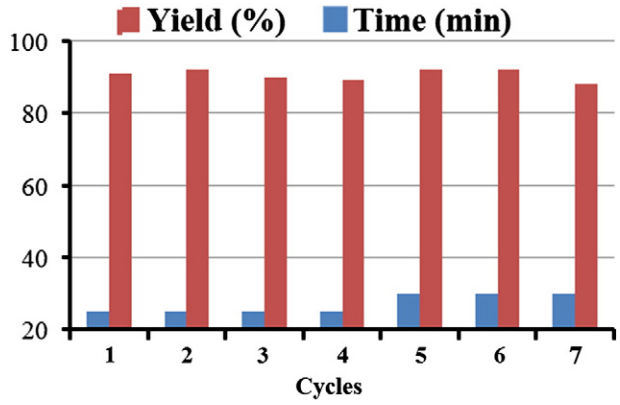


Fig. 3. Catalyst reusability.

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.catcom.2012.08.018.

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