

A Catalyst

Technical Field

The present invention generally relates to a catalyst and a method of preparing the same. The present invention also relates to a process of nitrating aromatic compounds. The
5 present invention further relates to a method of synthesizing 4-nitrophenol.

Background Art

Due to their wide use in synthesis of pharmaceutical and dyes among other chemicals, 4-aminophenol has attracted much attention in the past few decades. The most adopted synthetic route to access 4-aminophenol comprises nitration and subsequent reduction of
10 phenol. However, the critical challenges of low yield, low selectivity, high material cost or the generation of hazardous waste in the nitration of phenol hinder the mass production of 4-aminophenol.

Conventional methods of nitrating phenol comprise the use of concentrated nitric acid and sulfuric acid. The hazardous concentrated acids constitute to high operational difficulties.
15 In addition, they have to be used in a large excess, which lead to acid wastes which is not environmental friendly. Further, high costs are associated with the neutralization of the acid waste or maintenance of corroded reactors.

Another method of nitrating phenol comprises the use of a catalyst. This requires a sodium salt but still has unsatisfactory yield and selectivity when 4-nitrophenol is a desired
20 product.

Accordingly, there is a need for a catalyst for a nitrating reaction that ameliorates one or more disadvantages mentioned above.

Summary

In one aspect, there is provided a catalyst comprising a magnetic core, a linker and a shell
25 material.

Advantageously, the catalyst may catalyse a conversion from phenol to 4-nitrophenol with a high yield. This is due to the absence of side products, which is because the shell material does not allow 2-nitrophenol formation. Therefore, the catalyst can be deemed as being selective for the formation of 4-nitrophenol and not selective for 2-nitrophenol or 3-nitrophenol. Therefore,
30 2-nitrophenol or 3-nitrophenol is not formed.

In another aspect, there is provided a method of preparing a catalyst, comprising the steps of:

- (a) synthesizing a magnetic core;
- (b) adding an acidic group to one end of a linker to form a shell material; and

(c) linking the other end of the linker in the shell material of step (b) with the magnetic core of step (a) to form the catalyst.

In another aspect, there is provided a process of linking a nitro group to an aromatic group, comprising the step of mixing the catalyst as described herein, an aromatic compound and a
5 nitric acid in a solvent.

In another aspect, there is provided a method of synthesizing 4-aminophenol, comprising the steps of:

- (a) mixing the catalyst of as described herein, phenol and nitric acid in a solvent to form a mixture;
- 10 (b) isolating 4-nitrophenol from the mixture of step (a) to obtain a solution; and
- (c) reducing the solution of step (b) to obtain 4-aminophenol.

Definitions

The following words and terms used herein shall have the meaning indicated:

As used herein, the term "alkyl" includes within its meaning straight chain or branched
15 chain saturated aliphatic groups having from 6 to 30 carbon atoms.

As used herein, the term "phase" includes within its meaning metal oxides of a magnetic nanoparticle.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word
20 "substantially" may be omitted from the definition of the invention.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

The term "about" as used herein typically means +/- 5 % of the stated value, more typically
25 +/- 4 % of the stated value, more typically +/- 3 % of the stated value, more typically, +/- 2 % of the stated value, even more typically +/- 1 % of the stated value, and even more typically +/- 0.5 % of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that the description in range format is merely for convenience and
30 brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from
35 2 to 4, from 2 to 6, from 3 to 6 etc., as well as individual numbers within that range, for example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Certain embodiments may also be described broadly and generically herein. Each of the narrower species and subgeneric groupings falling within the generic disclosure also form part of the disclosure. This includes the generic description of the embodiments with a proviso or negative limitation removing any subject matter from the genus, regardless of whether or not the excised material is specifically recited herein.

Detailed Disclosure of Embodiments

Exemplary, non-limiting embodiments of a catalyst comprising a magnetic core, a linker and a shell material will now be disclosed.

Advantageously, the catalyst may catalyse a conversion from phenol to 4-nitrophenol with a high yield. This is due to the absence of side products, which in turn is because the shell material does not allow 2-nitrophenol formation.

The magnetic core may be any magnetic material. The magnetic core may comprise a metal or a metal oxide selected from the group consisting of iron, nickel, cobalt, samarium, an alloy thereof, an oxide thereof, and a combination thereof. The magnetic core may be iron, iron oxide, nickel, nickel oxide, cobalt, cobalt oxide, samarium, samarium oxide, an alloy of at least two of iron, nickel, cobalt and samarium (or an oxide of such alloy) or a combination of the foregoing. Where the magnetic core comprises an alloy, the alloy may be samarium cobalt (such as SmCo_5) where the molar ratio of samarium to cobalt in the alloy is about 1:5 to about 2:17, about 1:5 to about 2:13 or about 2:13 to about 2:17.

In the magnetic core, the iron element and the oxygen element may have a molar ratio in the range of about 1:1 to 1:2.5, about 1:1.5 to about 1:2.5, about 1:2 to about 1:2.5, about 1:1 to 1:2 or about 1:1 to about 1:1.5.

Advantageously, the magnetic core may allow for isolation of the catalyst with a magnet. This may reduce operational difficulty for the use of catalyst and increase the catalyst's recyclability.

The magnetic core may be spherical.

The magnetic core may further comprise a silica coating.

The silica coating may have a thickness of about 1 nm to about 10 nm, about 1 nm to about 5 nm or about 5 nm to about 10 nm. The silica coating may encapsulate the surface of the magnetic core such that about 98% to 100% of the surface is encapsulated or covered by the silica coating (forming a protective layer on the magnetic core).

Advantageously, the silica coating may provide stability to the magnetic core in the presence of acid, therefore, the magnetic core is protected from degradation when used under acidic conditions.

The linker may be derived from a diol, a diamine, a di-acid or a di-thiol.

Where the linker is derived from a diol, the diol is covalently bonded by a hydroxyl moiety to the magnetic core at one end of the diol forming an ether bond with the magnetic core and the diol is covalently bonded by a hydroxyl moiety at the other end of the diol to acidic functional group thus forming an ester bond with the shell material. The linker can thus be deemed as a

dioxyalkylene group, wherein the dioxyalkylene group is an alkylene group having oxy groups at both ends of the alkylene group.

The magnetic core may be covalently bonded to the hydroxyl of the diol to form an ether.

The ether may be a silyl ether.

- 5 The diol may be an alkyl diol. The alkyl may be straight chain or branched chain saturated aliphatic groups having from 6 to 30 carbon atoms.

Non-limiting examples of the alkyl diol include 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol or combinations thereof.

The diol may be 1,10-decanediol.

- 10 Advantageously, the 1,10-decanediol may lead to high compatibility between the magnetic core and the shell material, as well as less leaching of components from the catalyst in use and its cost.

- The shell material may comprise acidic moieties or acidic functional groups. The acidic moieties or acidic functional groups may be derived from sulfonic acid, toluenesulfonic acid, 15 sulfinic acid, phosphoric acid, phosphonic acid or combinations thereof.

The acidic moieties or acidic functional groups may be covalently bonded to the hydroxyl of the diol to form an ester. Therefore, the linker together with the acid moieties or acidic functional groups may be deemed as having an ester group. Non-limiting examples of the ester include sulphate, phosphate or combinations thereof.

- 20 The catalyst may have a diameter in the range of about 20 nm to about 100 nm, about 40 nm to about 100 nm, about 60 nm to about 100 nm, about 80 nm to about 100 nm, about 20 nm to about 80 nm, about 20 nm to about 60 nm or about 20 nm to about 40 nm.

Advantageously, the catalyst having the low diameters may have a high catalytic efficiency due to the high area to volume ratio.

- 25 Further advantageously, the catalyst having the diameters as described herein may be easily filtered or separated from liquid.

Exemplary, non-limiting embodiments of a method of preparing a catalyst will now be disclosed.

The method may comprise the steps of:

- 30 (a) synthesizing a magnetic core;
 (b) adding an acidic group to one end of a linker to form a shell material; and
 (c) linking the other end of the linker in the shell material of step (b) with the magnetic core of step (a) to form the catalyst.

The synthesizing step (a) may comprise reacting magnetic nanoparticles with a silylating agent.

- 35 The silylating agent may be tetraethyl orthosilicate (TEOS).

The synthesizing step (a) may further comprise the step of reacting a metal salt with a base in water to form the magnetic nanoparticles.

Non-limiting examples of the metal salt include FeCl₂, FeBr₂, Fe₂SO₄, FeCl₃, FeBr₃, Fe₃(SO₄)₂, Fe(NO₃)₃, NiCl₂, NiBr₂, NiSO₄, Ni(NO₃)₂, CoCl₂, CoBr₂, CoSO₄, Co(NO₃)₂, CoCl₃, CoBr₃, SmCl₂, SmI₂, SmCl₃, SmI₃ or combinations thereof.

Non-limiting examples of the base include NaOH, KOH, LiOH or combinations thereof.

The adding step (b) may comprise mixing the linker and an acid in a first solvent.

In the adding step (b), the linker may be a diol, a diamine, a di-acid or a di-thiol.

Where the linker is the diol, the diol may be an alkyl diol. The alkyl may be straight chain saturated aliphatic groups having from 6 to 30 carbon atoms.

Non-limiting examples of the alkyl diol include 1,6-hexanediol, 1,7-heptanediol, 1,8-octanediol, 1,9-nonanediol, 1,10-decanediol or combinations thereof.

The diol may be 1,10-decanediol.

In the adding step (b), the acid may comprise an acidic moiety or an acidic functional group and a leaving moiety.

The acidic moiety or acidic functional group may be derived from sulfonic acid, toluenesulfonic acid, sulfinic acid, phosphoric acid, phosphonic acid or combinations thereof.

The leaving moiety may drop or be cleaved from the acid in the adding step (b). Non-limiting examples of the leaving moiety include fluoro, chloro, bromo, iodo, methanesulfonyl, trifluoromethanesulfonyl, toluenesulfonyl or combinations thereof.

In the adding step (b), the first solvent may dissolve the linker and the acid without reacting with the linker or the acid. Non-limiting examples of the first solvent include dichloromethane.

In the adding step (b), the linker may be dissolved in the first solvent at a concentration in the range of about 0.01 M to about 10 M, about 0.1 M to about 10 M, about 1 M to about 10 M, about 0.01 M to about 1 M or about 0.01 M to about 0.1 M.

In the adding step (b), the acid may be dissolved in the first solvent at a concentration in the range of about 0.05 M to about 7 M, about 0.5 M to about 7 M, about 5 M to about 7 M, about 0.05 M to about 5 M or about 0.05 M to about 0.5 M.

The adding step (b) may be undertaken at room temperature.

The adding step (b) may be undertaken for a duration in the range of 20 minutes to 300 minutes, about 50 minutes to about 300 minutes, about 100 minutes to about 300 minutes, about 200 minutes to about 300 minutes, about 20 minutes to about 200 minutes, about 20 minutes to about 100 minutes or about 20 minutes to about 50 minutes.

The linking step (c) may comprise mixing the magnetic core of step (a) and the shell material of step (b) in a second solvent.

In the linking step (c), the second solvent may disperse the magnetic core of step (a) or dissolve the shell material of step (b). Non-limiting examples of the second solvent include ethanol, water or combinations thereof.

5 In the linking step (c), the magnetic core of step (a) may be dispersed in the second solvent at a concentration in the range of about 0.02 M to about 3 M, about 0.2 M to about 3 M, about 2 M to about 3 M, about 0.02 M to about 2 M or about 0.02 M to about 0.2 M.

In the linking step (c), the shell material of step (b) may be dissolved in the second solvent at a concentration in the range of about 0.01 M to about 5 M, about 0.1 M to about 5 M, about 1 M to about 5 M, about 0.01 M to about 1 M or about 0.01 M to about 0.1 M.

10 The linking step (c) may be undertaken at a temperature in the range of about 25 °C to about 35 °C, about 25 °C to about 30 °C or about 30 °C to about 35 °C.

The linking step (c) may be undertaken for a duration in the range of about 20 minutes to about 300 minutes, about 50 minutes to about 300 minutes, about 100 minutes to about 300 minutes, about 200 minutes to about 300 minutes, about 20 minutes to about 200 minutes, about 20 minutes to about 100 minutes or about 20 minutes to about 50 minutes.

The linker may form an ester bond with the acid in the adding step (b) and an ether bond with silica coating on the magnetic core in the linking step (c). The ester bond may be derived from a hydroxyl moiety at one end of the linker and the acidic moiety of the acid. The ether bond may be derived from a hydroxyl moiety at another end of the linker and the magnetic core.

20 Exemplary, non-limiting embodiments of a process of linking a nitro group to an aromatic group will now be disclosed.

The process may comprise the step of mixing the catalyst as described herein, an aromatic compound and nitric acid in a solvent.

25 Advantageously, the process uses nitric acid as a source of the nitro group. This may reduce the need of cost and simplify operation by avoiding post-treatments required when a salt of nitric acid is used as the source of the nitro group.

Further advantageously, the process may be performed at a temperature in the range of about 30 °C to about 40 °C. This may improve the yield of the process.

30 Still further advantageously, the recyclability of the catalyst may be improved when the reaction is performed at a temperature in the range of about 30 °C to about 40 °C. At this temperature, the catalyst may be reused for more than 20 cycles without a significant decrease in its performance.

The aromatic compound may comprise the aromatic group covalently bonded with a hydrogen atom.

35 The process may replace the hydrogen atom with a nitro group, thus forming a C-N covalent bond between the aromatic group and the nitro group.

The aromatic group may be phenyl or a 4-substituted phenyl. Non-limiting examples of the aromatic group include phenyl, 4-hydroxyphenyl, 4-methylphenyl, 4-aminophenyl, 4-

carboxyphenyl, 2-methyl-4-hydroxyphenyl, 3-methyl-4-hydroxyphenyl or combinations thereof.

Advantageously, the process has a yield of about 95 to 99% of a product by exclusively linking the nitro group to the aryl or the 1-substituted phenol. Other aromatic groups may be excluded from the process even if they are present, which is due to the low temperature of reaction.

Further advantageously, the process has a high operational simplicity by eliminating the need for complex isolation or purification of the product from impurities. This is due to the high yield of the product.

The solvent may disperse the catalyst and dissolve the aromatic compound and the nitric acid. Non-limiting examples of the solvent include water.

Advantageously, the use of water may keep the reaction at a temperature in the range of about 30 °C to about 40 °C, thus improving the efficiency of the process.

Further advantageously, the use of water is non-hazardous and water is cheaply available.

In the process, the catalyst may be dispersed in the solvent at a concentration in the range of about 0.01 M to about 4.5 M, about 0.1 M to about 4.5 M, about 1 M to about 4.5 M, about 2 M to about 4.5 M, about 0.01 M to about 2 M, about 0.01 M to about 1 M or about 0.01 M to about 0.1 M.

In the process, the aromatic compound may be dissolved in the solvent at a concentration in the range of about 0.05 M to about 10 M, about 0.5 M to about 10 M, about 5 M to about 10 M, about 0.05 M to about 5 M or about 0.05 M to about 0.5 M.

In the process, the nitric acid may be dissolved in the solvent at a concentration in the range of about 0.1 M to about 5.25 M, about 1 M to about 5.25 M, about 2 M to about 5.25 M, about 0.1 M to about 2 M or about 0.1 M to about 1 M.

In the process, the mixing step may be undertaken at a temperature in the range of about 30 °C to about 40 °C, about 35 °C to about 40 °C or about 30 °C to about 35 °C.

In the process, the mixing step may be undertaken for a duration in the range of about 20 minutes to about 300 minutes, about 50 minutes to about 300 minutes, about 100 minutes to about 300 minutes, about 200 minutes to about 300 minutes, about 20 minutes to about 200 minutes, about 20 minutes to about 100 minutes or about 20 minutes to about 50 minutes.

This process may be used to selectively form 4-nitrophenol. In this process, 2-nitrophenol or 3-nitrophenol is not formed.

Exemplary, non-limiting embodiments of a method of synthesizing 4-aminophenol will now be disclosed.

The method may comprise the steps of:

- (a) mixing the catalyst as described herein, phenol and nitric acid in a solvent to form a mixture;
- (b) isolating 4-nitrophenol from the mixture of step (a) to obtain a solution; and
- (c) reducing the solution of step (b) to obtain 4-aminophenol.

Advantageously, the process uses nitric acid for the mixing step (a). This may reduce the need of cost and simplify operation by avoiding post-treatments required when a salt of nitric acid or concentrated nitric acid is used.

- 5 Further advantageously, the process has a yield of about 95 % of the 4-aminophenol by suppressing the formation of 2-aminophenol or 3-aminophenol. Therefore, 2-aminophenol or 3-aminophenol is not formed in this process.

Still further advantageously, the process has a high operational simplicity by eliminating the need for complex isolation or purification of the 4-aminophenol from impurities such as 2-aminophenol or 3-aminophenol.

- 10 In the mixing step (a), the solvent may disperse the catalyst or dissolve the phenol and the nitric acid. Non-limiting examples of the mixing solvent include water.

- In the mixing step (a), the catalyst may be dispersed in the solvent at a concentration in the range of about 0.05 weight % to about 20 weight %, about 0.5 weight % to about 20 weight %, about 5 weight % to about 20 weight %, about 10 weight % to about 20 weight %, about 0.05 weight % to about 10 weight %, about 0.05 weight % to about 5 weight % or about 0.05 weight % to about 0.5 weight % based on the weight of phenol.
- 15

In the mixing step (a), the phenol may be dissolved in the solvent at a concentration in the range of about 0.01 M to about 5.25 M, about 0.1 M to about 5.25 M, about 1 M to about 5.25 M, about 0.01 M to about 1 M or about 0.01 M to about 0.1 M.

- 20 In the mixing step (a), the nitric acid may be dissolved in the solvent at a concentration in the range of about 0.01 M to about 5.25 M, about 0.1 M to about 5.25 M, about 1 M to about 5.25 M, about 0.01 M to about 1 M or about 0.01 M to about 0.1 M.

The mixing step (a) may be undertaken at a temperature in the range of about 30 °C to about 40 °C, about 35 °C to about 40 °C or about 30 °C to about 35 °C.

- 25 The mixing step (a) may be undertaken for a duration in the range of about 10 minutes to about 300 minutes, about 50 minutes to about 300 minutes, about 100 minutes to about 300 minutes, about 200 minutes to about 300 minutes, about 10 minutes to about 200 minutes, about 10 minutes to about 100 minutes or about 10 minutes to about 50 minutes.

- Advantageously, the short duration of the mixing step (a) may save time needed for the synthesis of 4-nitrophenol.
- 30

The isolating step (b) may comprise extracting 4-nitrophenol from the mixture of step (a) with an extracting solvent.

The extracting solvent may dissolve the 4-nitrophenol better than the mixing solvent of the mixing step (a) and be immiscible with the mixing solvent of the mixing step (a).

- 35 Non-limiting examples of the extraction solvent include ethyl acetate, methyl acetate, ethyl formate, methyl formate, 1,1-dichloromethane, 1,1,1-trichloromethane, 1,1-dichloroethane, 1,2-dichloroethane, benzene, toluene or combinations thereof.

The extracting solvent of the isolating step (b) and the solvent of the mixing step (a) may have a volume ratio in the range of about 0.9:1 to about 1.2:1, about 1:1 to about 1.2:1, about 1.1:1 to about 1.2:1, about 0.9:1 to about 1.1:1 or about 0.9:1 to about 1:1.

5 The method may further comprise a step of collecting the catalyst of the mixing step (a) with a magnet after the mixing step (a).

Advantageously, the collected catalyst may be reused for more than 20 cycles at little cost.

The magnet may be an electromagnet or a permanent magnet.

The method may further comprise, after the isolating step (b) but before the reducing step (c), a step of replacing the extraction solvent of the isolating step (b) with a reduction solvent.

10 Non-limiting examples of the reduction solvent include ethanol, methanol, propanol, butanol, ether, toluene, dichloromethane, chloroform or combinations thereof.

The replacing step may comprise evaporating the extracting solvent of the isolating step (b) and then adding the reduction solvent.

15 The reduction solvent added and the extraction solvent of the isolating step (b) may have a volume ratio in the range of about 1:100 to about 18:100, about 6:100 to about 18:100, about 12:100 to about 18:100, about 1:100 to about 12:100 or about 1:100 to about 6:100.

The reducing step (c) may comprise adding a reducing catalyst to the solution of the isolating step (b) and passing a flow of hydrogen through the solution.

20 In the reducing step (c), the reducing catalyst may be a solid that is not dissolved in the solution of the isolating step (b). Non-limiting examples of the reducing catalyst include Ruthenium, gadolinium or combinations thereof.

25 In the reducing step (c), the reducing catalyst may be added at a concentration of about 1 weight % to about 5 weight %, about 2 weight % to about 5 weight %, about 3 weight % to about 5 weight %, about 4 weight % to about 5 weight %, about 1 weight % to about 4 weight %, about 1 weight % to about 3 weight % or about 1 weight % to about 2 weight % based on the weight of 4-nitrophenol.

30 In the reducing step (c), the flow of hydrogen may have a flow rate of about 0.2 litre per minute to about 15 litre per minute, about 2 litre per minute to about 15 litre per minute, about 5 litre per minute to about 15 litre per minute, about 10 litre per minute to about 15 litre per minute, about 0.2 litre per minute to about 10 litre per minute, about 0.2 litre per minute to about 5 litre per minute or about 0.2 litre per minute to about 2 litre per minute.

The reducing step may be undertaken at a temperature in the range of about 25 °C to about 35 °C, about 30 °C to about 35 °C or about 25 °C to about 30 °C.

35 The reducing step (c) may be undertaken for a duration in the range of about 12 minutes to about 40 minutes, about 20 minutes to about 40 minutes, about 30 minutes to about 40 minutes, about 12 minutes to about 30 minutes or about 12 minutes to about 20 minutes.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serves to explain the principles of the disclosed embodiment. It is to be understood, however, that the drawings are designed for purposes of illustration only, and not as a definition of the limits of the invention.

Fig. 1

[Fig. 1] shows an infrared (IR) spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2$. The absorption at about 3455 cm^{-1} confirms presence of OH group and at about 1096 cm^{-1} is due to Si-O stretching.

Fig. 2

[Fig. 2] shows an IR spectrum of $\text{Fe}_3\text{O}_4@\text{SiO}_2@2\text{-hydroxydecyl hydrogen sulphate}$. A peak at $\sim 3437\text{ cm}^{-1}$ confirms the presence of $-\text{OH}$ and could be from $-\text{SO}_3\text{H}$ group.

Fig. 3

[Fig. 3] shows nuclear magnetic resonance (NMR) spectra of (A) 2-hydroxydecyl hydrogen sulphate synthesized by the method as described herein and (B) 4-nitrophenol isolated by the method as described herein. Chemical shift of peaks are shown on the top of the spectra and the integration of the peaks are shown below the peaks.

Examples

Non-limiting examples of the invention and a comparative example will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Example 1 – Synthesis of Fe_3O_4 -Magnetic nano-particle

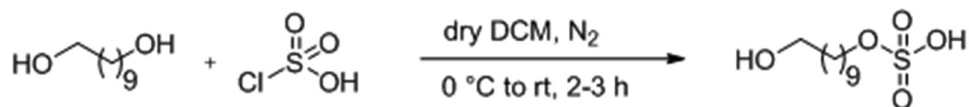
Magnetite nano-particle (Fe_3O_4) was synthesized by co-precipitation of ferric chloride and ferrous chloride using NaOH solution in nitrogen atmosphere. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (50 g, 0.185 mol purchased from Sigma-Aldrich) and FeCl_2 (11.47g, 0.091 mol purchased from Sigma-Aldrich) were dissolved in a liter of distilled water from inhouse production using MILLIPORE water filtration system. Co-precipitation was carried out by addition of 32 g of NaOH (purchased from Sigma Aldrich) in 200 ml solution under N_2 atmosphere with vigorous stirring (at 500 rpm). The reaction mixture was stirred at a temperature of $50\text{ }^\circ\text{C}$ for 6 hours, pH was ~ 12 . Then the solution was allowed to cool down to room temperature. The formed black precipitate was filtered (by normal filtration) and washed with distilled water and dried at $50\text{ }^\circ\text{C}$ overnight. The synthesized material was confirmed by XRD studies and showed that pure phase of Fe_3O_4 phase was formed.

Example 2 – Synthesis of $\text{Fe}_3\text{O}_4@\text{SiO}_2$

Fe_3O_4 nanoparticles (5 g) were dispersed by stirring in a mixture of ethanol (purchased from Sigma-Aldrich) and deionized water (obtained via MILLIPORE water filtration system) (100

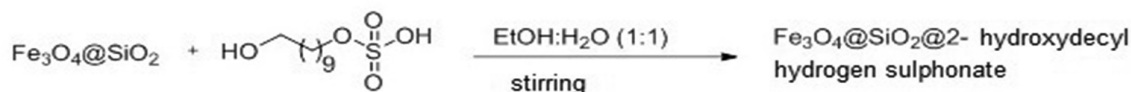
mL, 1:10 volume ratio). Then, tetraethyl orthosilicate (TEOS, 2 mL, purchased from Sigma Aldrich) was added dropwise and the stirring was continued for 2 hours at 60 °C. The resulted product was magnetically separated, washed repeatedly with deionized water and ethanol, and then dried in air for 4 hours. The synthesized powder was characterized by IR spectra analysis (Fig. 1). Absorption at $\sim 3455\text{ cm}^{-1}$ confirms presence of OH group and at $\sim 1096\text{ cm}^{-1}$ is due to Si-O stretching.

Example 3 – Synthesis of 2-hydroxydecyl hydrogen sulphonate



1,10-Decanediol (50 g, 0.28 mol purchased from Sigma Aldrich) was dissolved in dry dichloromethane (DCM, 200 mL, purchased from Sigma Aldrich) in a 500-mL round bottom flask. The solution thus prepared was stirred for one hour, followed by drop-wise addition of chlorosulfonic acid (35.9 gm 0.31 M, purchased from Sigma Aldrich) at 0 °C under nitrogen atmosphere. The reaction mixture was then warmed up to room temperature and stirred for another one hour. After removal of DCM via evaporation, a product was obtained as a 2-hydroxydecyl hydrogen sulphonate shell material.

Example 4 – Synthesis of Fe₃O₄@SiO₂@2-hydroxydecyl hydrogen sulphonate



Fe₃O₄@SiO₂ (0.25 g) were dispersed in water/ethanol solution (25 mL, 1:1 by volume) by stirring at room temperature for 15 to 20 minutes. Then, 2-hydroxydecyl hydrogen sulphonate (0.25 g) in 5 mL ethanol was added, after that reaction was stirred for 3 hours. After that core-shell catalyst of Fe₃O₄@SiO₂@2-hydroxydecyl hydrogen sulphonate were separated by external magnet, washed with ethanol (100 mL) three times and dried under vacuum at 50 °C for 2 hours. The synthesized powder was characterized by IR spectra analysis (Fig. 2).

Example 5 – Synthesis of 4-nitrophenol

Phenol (94 g, purchased from Sigma Aldrich) was added slowly to 100 mL of water containing equal molar of nitric acid (60 weight %, purchased from Sigma Aldrich). The mixture temperature was maintained at a temperature in the range of about 30 °C to about 40 °C under constant stirring throughout the reaction. The above prepared catalyst Fe₃O₄@SiO₂@2-hydroxydecyl hydrogen sulphonate (9.4 g) was added to the reaction mixture. The reaction progress was monitored using thin layer chromatography (TLC). After completion of reaction, the catalyst was separated using a magnet and the formed 4-nitrophenol was separated using vacuum distillation followed by Nuclear Magnetic Resonance (NMR) characterization (Fig. 3).

Industrial Applicability

The catalyst may be used to synthesize intermediates for pharmaceuticals such as paracetamol. The catalyst may be used to synthesize dyes used for textiles, hair, fur, feathers or wood stains. The catalyst may be used to synthesize reducing agents for photographic developing. The catalyst may be used in chemical industry where nitration is required.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A catalyst comprising a magnetic core, a linker and a shell material.
2. The catalyst of claim 1, wherein the linker is derived from a diol, a diamine, a di-acid or a di-thiol.
3. The catalyst of claim 2, wherein the diol is a C₆₋₃₀ alkyl diol of chain length.
4. The catalyst of claim 2 or 3, wherein the diol is 1,10-decanediol.
5. The catalyst of any one of claims 1 to 4, wherein the magnetic core comprises a metal or a metal oxide selected from the group consisting of iron, nickel, cobalt, samarium, an alloy thereof, an oxide thereof, and a combination thereof.
6. The catalyst of any one of claims 1 to 5, wherein the shell material comprises acidic moieties or acidic functional groups.
7. The catalyst of any one of claims 1 to 6, wherein the catalyst has a diameter in the range of 20 nm to 100 nm.
8. A method of preparing a catalyst, comprising the steps of:
 - (a) synthesizing a magnetic core;
 - (b) adding an acidic group to one end of a linker to form a shell material; and
 - (c) linking the other end of the linker in the shell material of step (b) with the magnetic core of step (a) to form the catalyst.
9. The method of claim 8, wherein the synthesizing step (a) comprises reacting magnetic nanoparticles with a silylating agent.
10. The method of claim 8 or 9, wherein the adding step (b) comprises mixing the linker and an acid in a first solvent.
11. The method of any one of claims 8 to 10, wherein the linking step (c) comprises mixing the magnetic core of step (a) and the shell material of step (b) in a second solvent.
12. A process of linking a nitro group to an aromatic group, comprising the step of mixing the catalyst of any one of claims 1 to 7, an aromatic compound and a nitric acid in a solvent.
13. The process of claim 12, wherein the aromatic compound comprises the aromatic group covalently bonded with a hydrogen atom.

14. The process of claim 13, wherein the aromatic group is phenol or a 4-substituted phenyl.
15. A method of synthesizing 4-aminophenol, comprising the steps of:
- (a) mixing the catalyst of any one of claims 1 to 7, phenol and nitric acid in a solvent to form a mixture;
 - (b) producing 4-nitrophenol from the mixture of step (a) to obtain a solution; and
 - (c) reducing the solution of step (b) to obtain 4-aminophenol.
16. The method of claim 15, wherein the isolating step (b) comprises extracting 4-nitrophenol from the mixture of step (a) with an extracting solvent.
17. The method of claim 15 or 16, further comprising a step of collecting the catalyst of the mixing step (a) with a magnet after the mixing step (a).
18. The method of any one of claims 15 to 17, further comprising, after the isolating step (b) but before the reducing step (c), a step of replacing the extracting solvent of the isolating step (b) with a reduction solvent.
19. The method of claim 18, wherein the replacing step comprises evaporating the extracting solvent of the isolating step (b) and then adding the reduction solvent.
20. The method of any one of claims 15 to 19, wherein the reducing step (c) comprises adding a reducing catalyst to the solution of the isolating step (b) and passing a flow of hydrogen through the solution.