Facile Synthesis of Iron-Titanate Nanocomposite as a Sustainable Material for Selective Amination of Substituted Nitro-Arenes

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Abstract: The fabrication of durable and low-cost nanostructured materials remains important in chemical, biologic and medicinal applications. Particularly, iron-based nanomaterials are of central importance due to the ‘noble’ features of iron such as its high abundance, low cost and non-toxicity. Herein we report a simple sol–gel method for the synthesis of novel iron–titanium nanocomposite-based material (Fe₉TiO₁₅@TiO₂). In order to prepare this material, we made a polymeric gel using ferrocene, titanium isopropoxide and THF precursors. The calcination of this gel in air at 500 °C produced Fe-Ti bimetallic nanoparticles-based composite and nano-TiO₂ as support. Noteworthy, our methodology provides an excellent control over composition, size and shape of the resulting nanoparticles. The resulted Fe-based material provides a sustainable catalyst for selective synthesis of anilines, which are key intermediates for the synthesis of several chemicals, dyes and materials, via reduction of structurally diverse and functionalized nitroarenes.

Keywords: iron titanate; sustainable catalysis; nanocomposites; nitroarenes; anilines; hydrogenation

1. Introduction

Among nanomaterials, synthesis of non-noble metal based nanostructures is crucial to mitigate the cost associated with the valued applications such as heterogeneous catalysis, biologic applications and many more [1,2]. Preparation of stable iron-based nanocomposite materials remains a foremost challenge for the advancement of chemical processes in academia, research in industrial processes and drug discovery [3–10]. Remarkably, more abundance, lesser price, environment friendly nature and less toxicity of iron make it an ideal element for many valuable applications. The high surface-to-volume ratio, low dimensionality, controllable particle size and morphology during synthetic processes, make them potential candidates for use in heterogeneous catalysis. Another key feature of iron nanoparticles as catalyst is magnetism of these materials, which allows effortless separation by an external magnet. Separation of catalyst by a magnet saves tedious and overwhelming processes of filtration and subsequently allowing the catalyst to be reused for multiple cycles [11]. Iron oxide nanoparticles appear in different morphologies depending upon the synthesis method and precursor salt being used. Hydrothermally stable iron oxide nanomaterials inherit water-tolerant property which make them desirable to be used for aqueous phase catalytic processes [12].

Considering the variable properties of iron nanoparticles, they have been employed in numerous applications ranging from nanocatalysis to biomedicine. In order to avoid agglomeration and volume
changes in iron oxide nanoparticles, support materials like activated carbon, silica, alumina and magnesium oxide have been incorporated for various organic transformations [13]. Iron based nanocatalysts have been widely known to serve the purpose in synthesis of hydrocarbons, not only by hydrogenation reaction of CO which is employed in Fischer-Tropsch process, but also through hydrogenation of CO2 to prepare light olefins [14]. Ferrite nanocatalysts have been reported to be used in the treatment of waste water by oxidation process, allowing purification of water along with regeneration of adsorbed support surface [15]. Supported iron oxide nanoparticles as heterogeneous catalysts have been extensively investigated in a large number of processes such as acid-catalyzed reactions, C–C and C–O cross coupling reactions, oxidation and hydrogenation reactions [12]. Iron nanostructures have also been reported as anode materials for efficient and eco-friendly Li-ion batteries[11]. Jagadeesh [16] et al. reported Fe3O4 support on nitrogen-doped graphene as a catalyst being explored for the synthesis of aromatic and aliphatic nitriles by employing NH3 and O2 as reactants, followed by catalytic hydrogenation of nitroarenes [17]. Cerium-doped iron titanate (FeCexTi1-xO powder X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR). Figure 1 shows the XRD patterns of Fe9TiO15@TiO2 and TiO2 (anatase) and Fe3O4 (hematite). Fe9TiO15@TiO2 is identified by JCPDS File no. 054–1267, with major peaks at 2θ = 33.16 (1 0 4), 35.64 (1 1 0), 54.08 (1 1 6), 62.44 (2 1 4) and 64.01° (3 0 0). Pure α-hematite prepared (by the calcination of ferrocene gel 500 °C, 4 h without Ti precursor) was identified by sharp reflection peaks in XRD. Similarly, pure anatase TiO2 was obtained when only titanium isopropoxide gel was calcined (500 °C, 4 h). Broadening of XRD peaks in Fe9TiO15 is the evidence of successful doping of Ti4+ within the crystal lattice [21,22]. Here, TiO2 is generated in situ and acts as the self-scarifying support for iron-titania nanoparticles. TiO2 produced is entirely in anatase phase, conclusively identified by major peaks at 2θ = 25.28° (1 0 1) and 48.05° (2 0 0) (JCPDS File no. 21–1272). The crystallite sizes by for Fe9TiO15 were estimated from XRD peaks by Debye–Scherrer method and were found to be in the range 11–18 nm.

Next, we performed SEM and TEM analysis to elucidate the size and distribution of nanoparticles, as well as the structure of Fe9TiO15@TiO2. The SEM micrographs in Figure S1 show greatly porous nanostructures; EDX elemental mapping revealed that Fe and Ti metals were homogeneously dispersed and present in the each other’s vicinity (Figure 2). TEM images at 100 nm resolution showed particles sizes between 10–36 nm, which suggests that nanoparticles were constituted of 1–2 crystallites (Figure S2). Next, HRTEM images (Figure 3) showed that the nanoparticles were highly crystalline in nature and TiO2 could be differentiated from Fe9TiO15 nanoparticles by measuring the inter planar distance from fringes as shown in Figure 3. The Fe9TiO15 particles possessed an interplanar distance
of 0.241 nm between well-defined fringes, while TiO₂ nanoparticles showed a 0.341-nm intra-fringe distance [22].

![XRD patterns of Fe₉TiO₁₅@TiO₂ nanocomposites.](image)

**Figure 1.** XRD patterns of Fe₉TiO₁₅@TiO₂ nanocomposites.

![Elemental mapping and EDS spectrum of Fe₉TiO₁₅.TiO₂.](image)

**Figure 2.** (a) Elemental mapping and (b) EDS spectrum of Fe₉TiO₁₅.TiO₂.
The XPS spectral analysis was performed to determine the elemental composition and oxidation states of iron and titanium (Figure 4). Peak fitting clearly showed the presence of both Fe(III) and Fe(II) species. A well resolved peak doublet at 710 eV (2p$_{3/2}$) and 723.9 eV (2p$_{1/2}$) represents Fe(II), while shoulder peaks due to presence of Fe(III) 2p peaks can be observed at 714.2 eV (2p$_{3/2}$) and 726.9 eV (2p$_{1/2}$) (Figure 4a) [23]. A predominant presence of Fe (II) may be due to the beam damage and electron gun used to compensate charging which can reduce Fe(III) to Fe(II) [24]. Ti (2p) XPS spectra (Figure 4b) shows that Ti(IV) specie present in titanium oxide. Typical sharp peaks of Ti(2p)$_{1/2}$ and Ti(2p)$_{3/2}$ are at 458.6 eV and 464.3 eV, respectively. The peak separation of 5.7 eV is assigned to titanium oxide. A satellite peak at 472.0 eV is also a feature of Ti (IV) in TiO$_2$ [21,23]. In addition, O(1s) XPS spectra shows the presence of two types of O atoms (Figure 4c); one at 530.0 eV and other 531.1 eV [21,23]. Both species lie in the typical metal oxide regions. Depending on the relative concentrations, first peak at 530.0 eV can be assigned to oxygen present in titanium oxide support and second peak at 531.1 eV can be assigned to oxygen atoms present in Fe$_9$TiO$_{15}$.

Further, EPR spectral analysis was performed (Figure 5) and found that the g-factor of Fe$_9$TiO$_{15}$@TiO$_2$ composite was found to be 2.19585. This is a normal value of Fe–complex systems and it is expected to be a bit higher than the free electron (2.002319) as it is correlated with the observed high oxidation state of the Fe species (+3). The broadness of signal is related to the presence of a Fe(II) atom present in the Fe$_9$TiO$_{15}$ [25,26]. All of these characterizations confirmed the formation of Fe$_9$TiO$_{15}$ bimetallic nanocomposite particles supported on in situ generated nano-TiO$_2$ support.
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Figure 4. XPS spectra of Fe (2p) (A), Ti (2p) and (B) O (1s) (C) present in Fe9TiO15@TiO2.

Figure 5. Electron paramagnetic resonance (EPR) spectra of Fe9TiO15@TiO2.

2.2. Catalytic Applications of Fe9TiO15@TiO2 for Selective Reduction of Nitroarenes to Anilines

Anilines represent central intermediates and key precursors for the synthesis of life science molecules, dyes, materials and petrochemical derivatives [27–33]. Generally, anilines have been prepared by the catalytic reduction or hydrogenation of nitroarenes [34,35]. Despite number of catalysts have been developed for this reaction [32,36–43], still the development of novel and selective nanocatalysts, especially based on iron is interesting. Here, we demonstrated the application of our prepared composite nanomaterial (Fe9TiO15@TiO2) for the reduction of nitrobenzene as the model substrate using hydrazine hydrate as reducing agent. Hydrazine hydrate is an abundantly available inexpensive reagent and produces only water as a byproduct in reduction reactions [44]. It is commonly used as a reducing agent and hydrogen storage material, as well as a reagent in organic synthesis [44]. The reduction of nitrobenzene with Fe9TiO15@TiO2 underwent complete conversion and produced aniline in high yields (Table 1; entry 1). Along with this material, we also tested newly prepared Fe2O3 and TiO2 and found that these materials were not active. This clearly indicates that both the Fe or Ti particles alone are not active (Table 1, entries 2 and 3). However, bimetallic nanoparticles of Fe and Ti metals supported on nano-TiO2 exhibits superior catalytic activity. As expected, the unpyrolyzed polymeric gel and catalyst under homogeneous conditions were also not active (Table 1; entries 4,5).

Table 1. Reduction of nitrobenzene: activity of catalysts.

| Entry | Catalyst        | Conversion (%) | Yield (%) |
|-------|-----------------|----------------|-----------|
| a 1   | Fe9TiO15@TiO2   | >99            | 99        |
| a 2   | Fe2O3          | <2             | <1        |
| a 3   | TiO2           | <2             | <1        |
| a 4   | Polymeric gel   |                |           |
| b 5   | Ferrocene + Titanium isopropoxide | <2 | <1 |

Reaction conditions: a 0.5-mmol nitroarene, 2.5-mmol hydrazine hydrate, 5 mg catalyst, 2 mL tetrahydrofuran (THF), 20, 100 °C. Yields were determined using n-hexadecane as standard. b Same as a with 0.02-mmol ferrocene and 0.03-mmol titanium isopropoxide. Fe2O3 was prepared using ferrocene. TiO2 was prepared using titanium isopropoxide.
2.2. Catalytic Applications of Fe\textsubscript{9}TiO\textsubscript{15}@TiO\textsubscript{2} for Selective Reduction of Nitroarenes to Anilines

Anilines represent central intermediates and key precursors for the synthesis of life science molecules, dyes, materials and petrochemical derivatives [27–33]. Generally, anilines have been prepared by the catalytic reduction or hydrogenation of nitroarenes [34,35]. Despite number of catalysts have been developed for this reaction [32,36–43], still the development of novel and selective nanocatalysts, especially based on iron is interesting. Here, we demonstrated the application of our prepared composite nanomaterial (Fe\textsubscript{9}TiO\textsubscript{15}@TiO\textsubscript{2}) for the reduction of nitrobenzene as the model substrate using hydrazine hydrate as reducing agent. Hydrazine hydrate is an abundantly available inexpensive reagent and produces only water as a byproduct in reduction reactions [44]. It is commonly used as a reducing agent and hydrogen storage material, as well as a reagent in organic synthesis [44]. The reduction of nitrobenzene with Fe\textsubscript{9}TiO\textsubscript{15}@TiO\textsubscript{2} underwent complete conversion and produced aniline in high yields (Table 1; entry 1). Along with this material, we also tested newly prepared Fe\textsubscript{2}O\textsubscript{3} and TiO\textsubscript{2} and found that these materials were not active. This clearly indicates that both the Fe or Ti particles alone are not active (Table 1, entries 2 and 3). However, bimetallic nanoparticles of Fe and Ti metals supported on nano-TiO\textsubscript{2} exhibits superior catalytic activity. As expected, the unpyrolyzed polymeric gel and catalyst under homogeneous conditions were also not active (Table 1; entries 4,5).

![Reduction of nitrobenzene](image)

**Table 1. Reduction of nitrobenzene: activity of catalysts.**

| Entry | Catalyst                      | Conversion (%) | Yield (%) |
|-------|-------------------------------|----------------|-----------|
| a 1   | Fe\textsubscript{9}TiO\textsubscript{15}@TiO\textsubscript{2} | >99            | 99        |
| a 2   | Fe\textsubscript{2}O\textsubscript{3} | <2             | <1        |
| a 3   | TiO\textsubscript{2}        | <2             | <1        |
| a 4   | Polymeric gel                 |                |           |
| b 5   | Ferrocene + Titanium isopropoxide | <2            | <1        |

*Reaction conditions:* a 0.5 mmol nitroarene, 2.5 mmol hydrazine hydrate, 5 mg catalyst, 2 mL tetrahydrofuran (THF), 20, 100 °C. Yields were determined using n-hexadecane as standard. b Same as a with 0.02 mmol ferrocene and 0.03 mmol titanium isopropoxide. Fe\textsubscript{2}O\textsubscript{3} was prepared using ferrocene. TiO\textsubscript{2} was prepared using titanium isopropoxide.

After having found the excellent activity of the Fe\textsubscript{9}TiO\textsubscript{15}@TiO\textsubscript{2} material, we demonstrated its general applicability for the reduction of nitro compounds. As shown in Schemes 1 and 2, structurally diverse and functionalized nitroarenes and heterocycles underwent highly selective reduction and produced corresponding aromatic and heterocyclic primary amines in good to excellent yields.

All the tested simple and substituted nitroarenes yielded respective anilines in up to 99% yields (Scheme 1; products 1–8). Interestingly, nitrophenol was reduced to aminophenol (88% yield; product 9), which is an important intermediate for the preparation of various dyes and pharmaceuticals; for example, paracetamol. Moreover, the presence of nitro-substituted phenols poses a major threat to vital human organs including kidneys, liver and central nervous system. Such nitrophenols are soluble in aqueous media and are not naturally degradable. In this regard, the present method offers suitable solution for the conversion of hazardous nitro phenol containing molecules to amino phenols [45]. Next, different halogenated anilines were obtained without being significant dehalogenation (Scheme 1; products 10–13). Importantly, iodo–nitrobenzene, which is more sensitive, is reduced to iodo–aniline without de-iiodination (Scheme 1; product 10).

For demonstrating chemo-selectivity of our catalyst system, we tested various functionalized nitroarenes. Remarkably, the nitro was selectively reduced in presence of other reducible groups such as ether, thioether, ester, nitrile, amide and sulfonamide. Subsequently, we carried out the synthesis of amino-heterocycles (Scheme 2), which serve as important intermediates and starting materials for...
Recycling and reusability of a given catalyst is an important aspect and crucial for the various life science molecule as well as natural products. Here again, this Fe-based catalyst was highly active and selective for the reduction of nitro-heterocycles to amino-heterocycles in up to 97%.

![Diagram showing Fe₉TiO₁₅@TiO₂ nanocatalysts for the reduction of nitrobenzene to aniline.](image)

**Scheme 1.** Fe₉TiO₁₅@TiO₂ nanocomposite catalyzed reduction of structurally diverse and functionalized nitroarenes to anilines. 

**Scheme 2.** Selective reduction of heterocyclic nitro compounds to amino-heterocycles using Fe₉TiO₁₅@TiO₂ nanocatalysts.

Finally, we performed recycling of Fe₉TiO₁₅@TiO₂ catalyst for the reduction of nitrobenzene (Figure 6). Recycling and reusability of a given catalyst is an important aspect and crucial for the

various life science molecule as well as natural products. Here again, this Fe-based catalyst was highly active and selective for the reduction of nitro-heterocycles to amino-heterocycles in up to 97%.
advancement of cost-effective of chemical processes. Indeed, our catalyst was highly stable and reused up to 4 times without significant loss of activity and selectivity.

![Graph](Image)

**Figure 6.** Recycling of Fe$_{9}$TiO$_{15}$@TiO$_{2}$ catalysts for the reduction of nitrobenzene to aniline. Reaction conditions: 5-mmol nitrobenzene, hydrazine hydrate, 50 mg catalyst (4 mol% Fe), 20 mL THF, 15 h, 100 °C, yields were determined by GC using n-hexadecane as standard.

3. Experimental Section

3.1. Materials and Methods

Ferrocene, titanium isopropoxide, triflic acid (TFC) and tetrahydrofuran (THF), nitro compounds and anilines were obtained from Sigma-Aldrich (Shanghai, China) and used without any purification. The XRD patterns were recorded using a Smart Lab X-ray diffractometer (Rigaku, Akishima-shi, Tokyo, Japan) using Cu-Kα X-rays radiations (λ = 0.15406 nm). X-ray photoelectron spectroscopy (XPS) was carried out with ESCALAB 250Xi, Thermo Scientific Waltham, MA USA instrument. The adventitious carbon peak appeared at binding energy of 284.8 eV was used as a reference. The surface morphology (SEM) and energy dispersive X-ray (EDS), analysis were carried out by field emission scanning electron microscope (FESEM-Tescan Lyra-3, (Kohoutovice, Czech Republic) equipped with focused ion beam (FIB) and EDS, detector. TEM analysis were performed using scanning transmission electron microscope (FEI Tecnai F-20, Graz, Austria) coupled with a Fischione HAADF detector.

Electron paramagnetic resonance (EPR) spectra were recorded in X-band at 273 K on an Adani SPINSCAN X-band electron paramagnetic resonance (Minsk, Belarus) spectrometer equipped with Cavity Q factor and MW power measurement with a magnetic field modulation capability of 10 kHz–250 kHz. The data were measured at microwave frequency = 9.48 GHz; modulation amplitude = 8 G; modulation frequency = 100 kHz [46]. GC Conversion and yields were determined by GC-FID, HP6890 with FID detector, column HP530 m × 250 mm × 0.25 μm. NMR data were recorded on a Bruker ARX 300 and Bruker ARX 400 spectrometers. All catalytic reactions have been performed in pressure tubes purchased from Sigma-Aldrich. Pyrolysis and calcination was carried out in a Thermo Scientific Thermolyne industrial benchtop muffle furnace (Model 120 °C SSP) fitted with a has a B1 single-setpoint digital controller with ramp and dwell and 2.2 L heating area capacity, with a temperature range of 100–1200 °C.

3.2. Procedure for Preparation of Fe$_9$TiO$_{15}$@TiO$_2$ Nanocomposite

In order to prepare Fe-Ti-based nanocomposites, first we mixed ferrocene and titanium isopropoxide in THF, then and initiated THF polymerization with the addition of few drops of TFC (Scheme 3 as reported recently by our research group [47,48]. In a 50-mL round bottomed flask, ferrocene (0.00537 M, 1 g) and titanium isopropoxide (0.0075 M, 2.13 g) were dissolved in 25 mL THF at room temperature. Then, a few drops of TFC were added for the polymerization of THF. Slow polymerization of THF was allowed to occur overnight with constant stirring at room temperature. After the formation of the polymeric gel, the entire reaction products were transferred to a crucible and
placed in furnace. Calcination was performed by raising the temperature to 500 °C at a rate of 4 °C per minute, then held for 2 h. After pyrolysis, the catalytic material was cooled to room temperature and stored in glass vials. ICP elemental analysis shows 22.8% of Fe and 25.6% of Ti, while EDX shows 24.2% of Fe and 26.2% of Ti. Elemental analysis results and EDX elemental mapping also shows similar results. Fe₉TiO₁₅ was prepared by using 9:1 molar ratios of the precursors (0.00537 M of ferrocene and 0.000596 M of titanium isopropoxide), TiO₂ (anatase) and Fe₂O₃ (hematite) were prepared under the similar conditions by using only titanium isopropoxide and ferrocene precursors, respectively.

**Scheme 3.** Synthesis of Fe-Ti nanocomposite material.

### 3.3. Procedure for Catalytic Reduction of Nitroarenes to Anilines

The procedure described earlier was followed [42]. The oven dried 25 mL ACE pressure autoclave vessel fitted with magnetic stir bar was charged with 0.5-mmol nitroarene in 2 mL THF. Then, 5 mg of Fe₉TiO₁₅@TiO₂ catalyst and 2.5-mmol hydrazine hydrate was added. Oxygen was removed from the reaction mixture by passing argon for 5 min. The pressure autoclave was then placed in the preheated aluminum block (100 °C) and left for 15–18 h at 100 °C. The autoclave tube was then removed from aluminum block and allowed to cool at room temperature. After autoclave was cooled down the cap was removed, and 100 μL hexadecane as internal standard was added. The catalyst was separated from the reaction mixture and GC-MS analysis of products was carried out. The corresponding aniline was purified by column chromatography (silica; n-hexane-ethyl acetate mixture), dried over anhydrous Na₂SO₄, solvent was removed in vacuum and NMR analysis of the product was carried out.

For recycling of the catalyst, a 5-mmol scale of reaction was carried out in a 50-mL pressure tube. After each run, the catalyst was washed with THF and ethyl acetate. The washed catalyst was in oven at 50 °C and reused for next run without any further purification.

### 4. Conclusions

New Fe-Ti-based nanocomposite materials (Fe₉TiO₁₅@TiO₂) were synthesized using simple sol-gel and calcination methodology. The generation of Fe-Ti polymeric gel using ferrocene, titanium isopropoxide and THF induced by triflic acid and subsequent calcination of this gel produced Fe₉TiO₁₅ bimetallic nanoparticles supported on nano-TiO₂. This new nanocomposite material revealed magnificent catalytic activity and selectivity for the production of functionalized and structurally diverse anilines from corresponding nitroarenes. The applicability, chemo-selectivity and recycling of this Fe-based nanomaterial was well-demonstrated.

**Supplementary Materials:** The following are available online at http://www.mdpi.com/2073-4344/10/8/871/s1, Representative ¹H- and ¹³C-NMR Spectra of Amines synthesized from nitroarenes are available as S1.

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