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Short communication

# Selective reduction of nitro-compounds to primary amines by tetrapyridinoporphyrazinato zinc (II) supported on DFNS

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# A R T I C L E I N F O A B S T R A C T Keywords: Nanocatalyst Green chemistry DFNS Zinc Zinc Over seme deter production Zinc Construction Constructio

### 1. Introduction

One-pot synthesis

Dendritic fibrous nanosilica has been recently discovered by Polshettiwar et al. [1-3] and has illustrated exceptional activity in all areas, such as gas adsorption, catalysis, energy storage, solar-energy harvesting, biomedical applications, and sensors. It is called dendritic fibers nanosilica (DFNS) because of its fibrous morphology (thin sheets 3.5 to 5.2 nm thick) [4-7]. Many other names are utilized in the literature to name it, including wrinkled, fibrous, dendritic, nanoflower, lamellar, and dandelion. In this review, to avoid confusion, we use dendritic fibrous nanosilica as the common name for this family of materials.

The uniformity of DFNS was usually due to its dendritic fibrous morphology that was basically attainable from all sides compared to SBA-15 and MCM-41 tubular pores. The enhanced availability increases the loading of active sites like metal oxides, metals, organic molecules, and organometallics on the outer layer of silica without blocking the channels (pores). In addition, it provides more access to generated active sites. By modifying the size of particles (40–1120 nm) as well as the density of fibers (number of fibers into one sphere), the outer layer of DFNS may alter from 450 to 1244 m<sup>2</sup>g<sup>-1</sup> [8]. Unlike the narrow poresize distribution determined in usual silica materials, DFNS has radially directional pores that increase in size from the center of the sphere to its outer layer. DFNS fiber density control can help adjust pore volume and size. Its adjustable pore sizes in the range of 3.7–25 nm let pores be

made to fit specific guest molecules in different sizes. Moreover, its adjustable pore volume in the range of 2.18  $\text{cm}^3\text{g}^{-1}$  facilitates the high loadings of these guests [9,10]. Guests include organometallic complexes, organic molecules, metals, inorganic salts, peptides, metal oxides, enzymes, proteins, carbon, and polymers. The integrated porosity of DFNS and its hierarchical arrangement of pores, including mesopores of different sizes (such as proper values of macr- and microopores), assist the guest molecules to efficiently adsorb and diffuse in the fibrous spheres with minimal restrictions. Moreover, this substance enhances theta availability of active sites and the internal surface. Macropores contribute to the effective initial diffusion/adsorption of guest molecules. DFNS have appropriate mechanical, chemical, hydrothermal, and thermal stability compared to conventional mesoporous materials, which is a concern due to the presence of thin silica walls. Particle size control of DFNS, which is a biocompatible and nontoxic material, facilitates the regulation of the dispersion and realization of the nanospheres.

Amines are advantageous intermediates in the production of colors, medicines, and agricultural chemicals. In addition, they are effortlessly attained by dropping aromatic nitro-compounds [11,13–16]. There are various methods for the reduction of aromatic nitro-compounds, including reductions through hydrogenation with noble metal-based catalysts (Pd [17], Ru [18], Pt [19], etc.), hydrazine hydrate/catalysts (Co,[20] Fe,[21], etc.), methanol/catalysts (Pd[22], Zn,[23], etc.) or

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Scheme 1. The reduction of nitro groups using tmtppa-Zn/DFNS catalysts.

under transfer hydrogenation situations. However, these common techniques require stoichiometric reducing agents, high pressure and temperature, as well as the employment of hazardous reagents (e.g., hydrazine). Notably, a variety of these techniques suffer from the absence of chemo selectivity compared to other functional groups that are usually exist in the substrates like alkene, halide, and nitrile. Moreover, the reduction of nitro-compounds often stops at an intermediate phase and results in the production of hydroxylamine, hydrazines, and azoreans. The excessive significance of the selective reduction of nitro-compounds has made the search for alternative techniques an important goal in organic synthesis.

Here, a 2D closely packed amide polyphthalocyaninezinc (tmtppa-Zn) was synthesized employing a one-step solid-state technique. Catalyst achieved by tmtppa-Zn supported on DFNS (tmtppa-Zn/DFNS) was predicted to be highly active, sustainable, and potentially catalytic for transfer hydrogenation of nitro-compounds to primary amines. A catalytic reaction is an approach for the reduction of nitro groups under mild reaction situations (Scheme 1).

#### 2. Experimental

# 2.1. Materials and methods

High purity chemicals were purchased from Fluka and Merck. Melting points were specified in the open capillaries employing the Electrothermal 9100 apparatus and were not modified. Particle size and structure of nanoparticles were perceived using a Philips CM10 Transmission Electron Microscope (TEM) operating at 100 kV. Field Emission Scanning Electron Microscopy (FE-SEM) images were obtained from a HITACHI S-4160. XPS studies were carried out employing an XR3E2 (VG Microtech) twin anode X-ray source with AlK $\alpha$  = 1486.6 eV. EDX spectroscopy was done deploying a field emission scanning electron microscope (FESEM, JEOL 7600F), equipped with energy dispersed Xray Spectroscopy (Oxford instruments). Powder X-ray Diffraction data were obtained using Bruker D8 Advance model with Cu karadiation. ICP experiments were done employing a VARIAN VISTA-PRO CCD Simultaneous ICP-OES instrument. NMR spectra of <sup>1</sup>H and <sup>13</sup>C were determined with BRUKER DRX-300 AVANCE and BRUKER DRX-400 AVANCE Spectrometers. The surface area, pore-volume, and pore diameter of NPs were specified by N<sub>2</sub> physisorption at -196 °C using Micromeritics ASAP 2000 instrumentand BET method. Determination of the purity of the products and monitoring the reaction were performed by TLC on silica gel (Polygram®SILG/UV 254 pre-coated plates).

# 2.2. The global approach for the creation of DFNS nanoparticles

Urea (1.8 g) and CTAB (3 g) were released in distilled water and mixed for 5 h to dissolve. It was added to a blend of TEOS (7.5 g), pentanol (3.5 mL), and cyclohexane (50 mL) and stirred for 45 min at room temperature. Next, it was refluxed for 4 h at 140  $^{\circ}$ C while stirring in an oil bath. The final product was placed in an oven at 80  $^{\circ}$ C for 20 h. The silica was isolated by centrifugation (45 min, 4000 rpm), washed with acetone as well as distilled water, and vacuum-dried for 20 h. The synthesized DFNS was then calcined at 400  $^{\circ}$ C in the air for 6 h.

# 2.3. The global method for the creation of DFNS/3-Chloropropyl NPs

The DFNS (3.0 g) was added to the solution of NaOH (50 mL, 0.5 M), and refluxed for 3 h to boost hydrophilicity. The generated nanoparticles were washed with H<sub>2</sub>O to neutralize the pH of the deionized H<sub>2</sub>O and then vacuum-dried at 70 °C for 6 h. Next, 3-Chloropropyltrimethoxysilane was supported on the DFNS outer layer to synthesis aminomodified DFNS/3-Chloropropyl. A mixture of activated DFNS (3.0 g) and 3-Chloropropyltrimethoxysilane (6.0 mL) was mixed in 100 mL ethanol at 100 °C for 17 h. Finally, DFNS/3-Chloropropyl was filtered, cleansed twice with deionized water, and dried at 80 °C for 10 h.

# 2.4. Synthesis of tmtppa-Zn complex

For the synthesis of tmtppa-Zn, urea (8 g), 2,3-Pyridinedicarboxylic acid (4 g), ammonium heptamolybdate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O; 25 mg), and Zn(OAc)<sub>2</sub> (2 g) were mixed and a homogenous blend was obtained. The blend was located in a heating mantle and warmed up under a solvent-free situation at 160 °C for 15 h. The achieved rough dark-blue solid was mangled, filtered, and cleansed with EtOH (15 mL), aqueous NaOH blend (0.1 %w/v, 2.5 mL), H<sub>2</sub>O (6 mL), warm diluted aqueous HCl (0.2 %v/v, 7.5 mL), and H<sub>2</sub>O (15 mL). The final product was dried at 70 °C.

# 2.5. The global method for the creation of tmtppa-Zn/DFNS NPs

The 3.0 g of DFNS/3-Chloropropyl was suspended in tmtppa-Zn (3.0 g). Then, tetrahydrofuran (50.0 mL) was released and the blend was mixed at 75 °C for 20 h. Then, tmtppa-Zn/DFNS was added into deionized water. EtOH mixture (5:5 v/v, 80 mL) consisted of 2-chloroacetic acid (3.0 g), and the reaction was done at r.t. for 2.5 h. After isolating the solvent, the resulting mixture was filtered and vacuum-dried at 50 °C.

#### 2.6. The global method for the reduction of Nitro-Compounds

In the first step, Nitro-Compounds (1 mmol) were released in water (10.0 mL) and mixed with 1.0 mmol of  $K_2CO_3$  to give a deep yellow solution. Next, tmtppa-Zn/DFNS (10 mg) and NaBH<sub>4</sub> (2 mmol) were added to the yellow solution. While the solution was decolorizing, the reaction became complete. Reaction progress was analyzed utilizing UV–Vis absorption spectra for the reaction mixture.

*Compound 1a*: colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 3.56 (s, 2H), 6.58–6.77 (m, 3H), 7.09 (t, J = 8 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 115.1, 118.4, 128.9, 146.2.

*Compound 1b*: whrite solid, m.p. = 65–67 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 3.59 (s, 2H), 6.60 (d, J = 8.4 Hz, 2H), 7.11 (d, J = 8.4 Hz, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 116.4, 122.9, 128.9, 145.0.

*Compound 2a*: yellow solid, m.p. = 207–209 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 9.04 (s, 1H), 7.53 (s, 1H), 6.90 (d, J = 8.0 Hz, 2H), 6.49 (d, J = 8.0 Hz, 2H), 4.99 (s, 2H), 4.96 (s, 1H), 4.00 (q, J = 6.8 Hz, 2H), 2.19 (s, 3H), 1.09 (t, J = 6.8 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 170.5, 157.6, 152.9, 152.4, 137.2, 131.9, 118.9, 104.9, 64.3, 58.6, 23.0, 19.4.

*Compound 2c*: yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  (ppm) = 9.10 (s, 1H), 7.05 (t, J = 5.2 Hz, 1H), 6.69 (d, J = 1.2 Hz, 1H), 6.59–6.62 (m, 2H), 5.23 (s, 1H), 4.20–4.24 (m, 2H), 3.96 (s, 2H), 3.79–3.83 (m, 1H), 3.49–3.54 (m, 1H), 2.81–2.86 (m, 1H), 2.64 (s, 3H), 2.44–2.49 (m, 1H), 1.20 (t, J = 4.4 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  (ppm) = 165.1, 151.9, 147.9, 147.4, 145.1, 128.4, 115.4, 113.1, 112.4, 110.9, 99.3, 59.4, 54.1, 41.8, 19.4, 17.9, 13.9.

#### 3. Results and discussion

The impact of tmtppa-Zn/DFNS NPs catalyst on the synthesis of



Scheme 2. Creation of tmtppa-Zn/DFNS nanocatalyst.

quinazoline-2,4(1H,3H)-dione from carbon dioxide, isocyanides, and 2iodoaniline was studied. The tmtppa-Zn functional groups in DFNS (as a dendrimer) could vigorously support the loading of tmtppa-Zn. This was because the interaction between  $CH_2$ —Cl categories of tmtppa-Zn and the internal  $CH_2$ —Cl groups of the dendrimer was the main reason for the loading of tmtppa-Zn in the dendrimer (Scheme 2).

The morphology and form of the DFNS and tmtppa-Zn/DFNS NPs were specified by deploying TEM and FESEM analysis. TEM photo of dendritic filamentary nanosilica nanoparticles revealed a folded and dandelion-like shape with a diameter of around ~320 nm (Fig. 1a). In addition, these centric fibers (with thicknesses around ~17.0 nm) were dispersed radically in all dimensions (Fig. 1b). Excessive development of the corrugated radial shape caused the conical pores to open. As FESEM

and TEM photos show, the sphere was solid and filamentary. Furthermore, hierarchical channels and fibers support the extensive displacement of reactants and boost the accessibility of active sites. The FESEM and TEM photos of tmtppa-Zn/DFNS nanoparticles demonstrate that the morphology of DFNS did not alter after moderation (Fig. 1b and d).

The surface modification of the tmtppa-Zn/DFNS was followed by FT-IR spectroscopy (Fig. 2). The 808, 1109, and 1635 cm<sup>-1</sup> bands in both FT-IR spectra correspond to the tensile state of Si—OH group, Si—O—Si vibrations, and the water absorbed to the solid outer layer (Fig. 2a). The tmtppa-Zn/DFNS spectrum demonstrates two prime sections. A broad peak of about  $3412 \text{ cm}^{-1}$  shows the H—O tensile strength of the hydroxyl groups on the exterior layer. The next peak is around 1671 cm<sup>-1</sup>. The peak at 1678 cm<sup>-1</sup> formed due to the C—N tensile



Fig.1. TEM photos of DFNS NPs (a); and tmtppa-Zn/DFNS NPs (b); FESEM photos of DFNS NPs (c); and tmtppa-Zn/DFNS (d).

vibrations from tmtppa (Fig. 2a). Peaks of 2934 cm<sup>-1</sup> and 3123 cm<sup>-1</sup> appeared because of the elongation of the C—H aliphatic groups, and the C—H aromatic group in the tmtppa-Zn/DFNS NPs (Fig. 2c). A comparison of the three sections of Fig. 2 underlines the creation of a new band at 746 cm<sup>-1</sup>. Even though this peak is placed in the fingerprint zone of the IR spectrum, a new phenomenon was identified after the tmtppa-Zn loading process, while such a peak is not noticed in the pristine DFNS spectrum. This phenomenon can prove the synthesis of tmtppa-Zn molecules into DFNS.

The anatomy of tmtppa-Zn/DFNS NPs was investigated by TGA analysis (Fig. 3). Furthermore, tmtppa-Zn/DFNS NPs illustrated weight reduction at 50 °C and 280 °C, which can be attributed to the water molecules adsorbed on the support. The organic group that functionalized tmtppa-Zn/DFNS NPs showed remarkable weight loss of 21% at 400 °C due to ligand degradation.

We employed XPS to investigate the chemical sections on the tmtppa-Zn/DFNS surface. Fig. 4 depicts a scheme of XPS for the gathered catalyst. Peaks Cl, N, O, C, and Zn are visible and the participation of N 1s additional proves that DFNS were functionalized deploying tmtppa. Moreover, the participation of  $Cl^-$  ions (the tmtppa counter ion) was specified by an edged apex. Peaks Zn illustrated the participation of zinc in the catalyst. Fig. 5 depicts the components of tmtppa-Zn/DFNS NPs

like nitrogen, silicon, oxygen, carbon, chlorine, and zinc. The NPs exterior layer roughness was identified by AFM (atomic force microscopy) analysis. Fig. 6 depicts the topographic scheme. The higher altitude zone, indicated by bright yellowish-white color, was enhanced by decreasing T/W. This specified a boost in the irregularity of the catalyst's exterior bed.

The adsorption–desorption isotherm of N<sub>2</sub> was examined for the analysis of the porosity and particular exterior bed of the products. Table 1 shows the mean pore diameter, the specific exterior layer, and the total pore volume values based on the BJH method. The results of BET confirmed that the active exterior layer of the DFNS and tmtppa-Zn/DFNS were 621 and 409 m<sup>2</sup> g<sup>-1</sup>, respectively. The specific exterior layer decreased after tmtppa-Zn intercalation, the pore volume and average pore radius decreased by utilizing tmtppa-Zn, and tmtppa-Zn became more porous.

The catalytic activity of the different kinds of tmtppa-Zn/DFNS was examined by reducing nitrobenzene on the test bed (refer to Table 2). The effect of time, base, and solvent on the model reaction and the impact of solvents on the reduction of nitrobenzene were investigated (Table 2, rows 1–14). According to the results, no quantity of the desired product was formed in the presence of polar protic solvents (iso-propanol, methanol, and ethanol). Nevertheless, the efficiency of the





Fig. 3. TGA diagram of tmtppa-Zn/DFNS NPs.

product was relatively moderate in the attendance of polar aprotic solvents, such as EtOAc, Toluene, DMF, CHCl<sub>3</sub>, DMSO, and CH<sub>2</sub>Cl<sub>2</sub>. Conventional underwater heating was more effective than the use of organic solvents (Table 2, rows 1). It is widely accepted that bases play a key role in coupling reactions; therefore, we performed the reaction in the attendance of different inorganic and organic bases (Table 2, rows 15–23). The results showed that  $K_2CO_3$  was the most efficient base for the reduction of nitrobenzene. Under ideal circumstances, the reaction progress was monitored by GC to detect the minimum time required in

the attendance of 10 mg of tmtppa-Zn/DFNS NPs. Results showed that the excellent reduction of nitrobenzene could be achieved in 15 h (Table 2, rows 25). Moreover, we investigated the key role of temperature in the reduction of nitrobenzene to aniline in the attendance of tmtppa-Zn/DFNS as a catalyst. The most effective temperature for this reaction was room temperature. The reaction efficiency did not change with increasing temperature, indicating that the catalytic activity was not temperature sensitive. Catalyst loading was another key determining element in the current reaction. The reduction of nitrobenzene had low







Fig. 6. 3D AFM figures of tmtppa-Zn/DFNS.

efficiency in the absence of the catalyst. When 6–8 mg of tmtppa-Zn/ DFNS NPs were added to the reaction, a moderate yield of the reaction was achieved. The best result was obtained in the attendance of 10 mg of tmtppa-Zn/DFNS NPs. Increasing the amount of the catalyst did not cause any improvement in the model reaction. No product was achieved in the nonattendance of the catalyst. Table 1

Anatomical	parameters	of DFNS a	and the	tmtppa-Zn,	/DFNS.
	•				

Catalysts	$S_{BET} (m^2 g^{-1})$	$V_a (cm^3 g^{-1})$	D <sub>BJH</sub> (nm)
DFNS	621	2.7	18
tmtppa-Zn/DFNS	409	1.5	10

#### Table 2

Reduction of nitrobenzene to aniline by tmtppa-Zn/DFNS NPs in different times, and with different solvents and bases.<sup>a</sup>

Entry	Solvent	Base	Time (h)	Catalyst (mg)	Yield (%) <sup>b</sup>
1	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	20	12	89
2	EtOH	K <sub>2</sub> CO <sub>3</sub>	20	12	-
3	MeOH	K <sub>2</sub> CO <sub>3</sub>	20	12	-
4	i-PrOH	K <sub>2</sub> CO <sub>3</sub>	20	12	-
5	Dioxane	K <sub>2</sub> CO <sub>3</sub>	20	12	-
6	solvent-free	K <sub>2</sub> CO <sub>3</sub>	20	12	-
7	n-Hexane	K <sub>2</sub> CO <sub>3</sub>	20	12	-
8	DMSO	K <sub>2</sub> CO <sub>3</sub>	20	12	44
9	EtOAc	K <sub>2</sub> CO <sub>3</sub>	20	12	17
10	DMF	K <sub>2</sub> CO <sub>3</sub>	20	12	61
11	THF	K <sub>2</sub> CO <sub>3</sub>	20	12	19
12	CH <sub>3</sub> CN	K <sub>2</sub> CO <sub>3</sub>	20	12	47
13	$CH_2Cl_2$	K <sub>2</sub> CO <sub>3</sub>	20	12	31
14	CHCl <sub>3</sub>	K <sub>2</sub> CO <sub>3</sub>	20	12	33
15	$H_2O$	_	20	12	-
16	$H_2O$	CsF	20	12	-
17	$H_2O$	Na <sub>2</sub> CO <sub>3</sub>	20	12	59
18	$H_2O$	Et <sub>3</sub> N	20	12	-
19	$H_2O$	NaOAc	20	12	-
20	$H_2O$	KOH	20	12	35
21	$H_2O$	K <sub>3</sub> PO <sub>4</sub>	20	12	64
22	$H_2O$	Cs <sub>2</sub> CO <sub>3</sub>	20	12	71
23	$H_2O$	tBuOK	20	12	-
24	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	18	12	89
25	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	15	12	89
26	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	12	12	81
27	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	10	12	67
28	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	15	10	89
29	$H_2O$	K <sub>2</sub> CO <sub>3</sub>	15	8	80
30	H <sub>2</sub> O	K <sub>2</sub> CO <sub>3</sub>	15	6	68

 $^{\rm a}$  Reaction conditions: nitrobenzene (1 mmol), base (5 mmol), NaBH\_4 (2 mmol), tmtppa-Zn/DFNS NPs (10 mg), solvent (10 mL).

<sup>b</sup> Isolated yields.

After completing the research on nitrobenzene, the reaction was performed under optimal conditions for a variety of nitro-compounds (Table 3, entry 1) to obtain the best results for each product. Replacement of nitroarene with —Br or —Cl (Table 3, entries 2–5) did not result indehalogenated product (compared to hydrogenation over palladium-on-charcoal) [12]. In addition, when nitrobenzene were used with side groups such as —OMe and —OEt (Table 3, entries 13 and 14), —OH (Table 3, entries 9 and 10), —COOH (Table 3, entries 11 and 12), and —CHO (Table 3, entry 15), the reaction showed good progress and high-efficiency products were obtained.

Extensive biological activity of 3,4-dihydropyrimidinones and its employment as a remarkable precursor in the production of pyrimidine bases [24-31], together with our continued tendency to produce new pyrimidine derivatives [32-36], led us to more in-depth research on the reduction of 3,4-dihydropyrimidin-2(1H)-one (DHPM) derivatives (Scheme 3). The results revealed excessive chemoselectivity of many functional groups. As Table 4 displays, only the nitro group was dropped at various functionalized DHPMs under the ideal reaction states. Ether, cyano, thiocarbonyl, ester, heterocycle, and nitrine groups such as morpholine, pyrimidone showed very high tolerance.

Scheme 4 shows a representation of the reaction along with the hydrides activation on the catalyst surface and their transfer to the nitro group. Actually, based on privious works, during the nitroarenes

#### Table 3

Entry	Nitrobenzene	Aniline	Yield (%)
1		NH <sub>2</sub>	89
		Compound 1a	
2			84
		Compound 1b	
3			81
	CI		
		Compound Ic	
4			79
		Compound 1d	
5	Br-NO2	Br - NH <sub>2</sub>	83
		Compound 1e	
6	Me-NO2	Me-NH <sub>2</sub>	80
		Compound 1f	
7		NH <sub>2</sub>	86
	Me	Me	
		Compound 1g	
8			87
	Me	Me	
		Compound 1h	
9			79
		Compound 1i	
10		NH <sub>2</sub>	80
	ЮН	ЮН	
		Compound 1j	
11			71
	HOOC	HOOC	
		Compound 1k	
12	HOOC	HOOC-NH2	75
		Compound 11	
13	MeO	MeO-NH2	82
		Compound 1m	

Chemo selective Reduction of Nitro-Compounds Catalyzed by tmtppa-Zn/DFNS.<sup>a</sup>

Table 3 (continued)



 $^{\rm a}$  Reaction conditions: nitrobenzene (1 mmol),  $\rm K_2CO_3$  (5 mmol), tmtppa-Zn/ DFNS NPs (10 mg), NaBH\_4 (2 mmol), H\_2O (10 mL).

<sup>b</sup> Isolated yields.



Scheme 3. The reduction of DHPM groups using tmtppa-Zn/DFNS catalysts.

reduction by NaBH<sub>4</sub> catalyzed using nanoparticles of Zn, firstly, a cleavage in B—H bond is the rate-determining stage for giving the Zn-H kinds. In the metal–hydrogen structure, the charged hydrogen, negatively, may attack the positively charged nitrogen, quickly, whive is in the nitro group of nitrobenzene. Therfore, the nitro group was decreased to the nitro so group along with the reductive addition of two hydrogen atoms for forming hydroxylamine. In the last step, the hydroxylamine was more decreased to the aniline derivative. [13]

The lifespan is considered as the most crucial property in industrial usages of a heterogeneous catalyst. Therefore, to study the heterogeneity of our synthesized catalyst, we carried out a hot filtration experiment through the reduction of nitrobenzenein the participation of the tmtppa-Zn/DFNS. At first, the reaction was developed for 7 h under an optimal reaction situation and 42% of the favorable product yield was achieved. Next, the catalyst was isolated by filtration, and the catalyst-free reaction blend was placed in the same reaction environment for another 8 h. No remarkable alteration was seen in the product yield. After the filtration test, the filter was investigated by ICP-MS and no trace of the zinc metal was observed. In addition, TEM and XPS analyses were carried out. According to SEM photos, the morphology of the recycled catalyst was similar to the morphology of the fresh catalyst (Fig. 7a). The XPS analysis of the recovered tmtppa-Zn/DFNS catalyst did not reveal any remarkable alteration in the zinc peak position (Fig. 7b). The inferential spectrum pattern of the reused and fresh catalyst was almost similar. The findings showed that the catalyst maintained its essence after the reaction. The results of the ICP-MS analysis after the first cycle were similar to the results of the synthesized catalyst. In addition, the results of the analysis of the recycled catalyst after the tenth cycle did not reveal a remarkable drop in zinc at the exterior surface of tmtppa. All the findings affirmed that the zinc metal was not drained from the catalyst during the cycle, and therefore, the catalyst regained its heterogeneous essence during the reaction.

Recycling, recovery, and facile isolating are the main properties of a heterogeneous catalyst. Therefore, the reusability of the catalyst in the reduction of nitrobenzene was studied. The catalyst was isolated from the reaction blend after each run by filtration. Next, the isolated catalyst

## Table 4

1

2

3

4

5

Chemoselective reduction of DHPMs catalyzed by tmtppa-Zn/DFNS.



(continued on next page)

#### Table 4 (continued)



<sup>a</sup>Reaction conditions: DHPMs (1 mmol), K<sub>2</sub>CO<sub>3</sub> (5 mmol), tmtppa-Zn/DFNS NPs (10 mg), NaBH<sub>4</sub> (2 mmol), H<sub>2</sub>O (10 mL). <sup>b</sup>Isolated yields.

was cleansed employing distilled acetone,  $H_2O$ , and hot MeOH. Then, it was dried by deploying a vacuum desiccator. As Fig. 8 depicts, the catalyst preserved its efficiency after ten consecutive runs.

# 4. Conclusion

We synthesized tmtppa supported on DFNS, which holds the zinc on itself as a catalyst. Catalyst properties were determined through ICP-MS, AFM, TEM, SEM, XPS, EDX, N<sub>2</sub> adsorption–desorption, TGA, and FT-IR investigations. The catalyst was highly effective for the reduction of Nitro-Compounds. The catalytic reduction of Nitro-compounds took

place under heterogeneous and moderate reaction situations. Our catalyst was highly sustainable as well as detachable and retained its catalytic performance after ten consecutive catalytic runs.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.



Scheme 4. A plausible mechanism for the reduction of nitrobenzene catalyzed by tmtppa-Zn/DFNS NPs.



Fig. 7. SEM photos of reutilized catalyst (a); X-ray photoelectron spectrum of recovered tmtppa-Zn/DFNS catalyst (b).



Fig. 8. Catalyst recyclability for the reduction of nitrobenzene.

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