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Silica encapsulated magnetic nanoparticles-supported Zn(II) nanocatalyst: A versatile integration of excellent reactivity and selectivity for the synthesis of azoxyarenes, combined with facile catalyst recovery and recyclability

R.K. Sharma*, Yukti Monga

Green Chemistry Network Centre, Department of Chemistry, University of Delhi, Delhi 11007, India

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ABSTRACT

A novel and highly efficient zinc based nanocatalyst has been synthesized by covalent grafting of 2acetylpyridine on amine functionalized silica@magnetite nanoparticles, followed by metallation with zinc acetate. The resulting nano-composite was found to be highly efficient for oxidation of various aromatic amines to give azoxyarenes. The prepared nanocatalyst was characterized by Electron microscopy techniques (SEM and TEM with EDS), X-ray diffraction (XRD), vibrational sampling magnetometer (VSM), Fourier transform infrared spectroscopy (FT-IR) and atomic absorption spectroscopy (AAS) techniques. High turnover number (TON), mild reaction conditions and high selectivity for azoxyarenes with sustained catalytic activity makes present protocol worthy and highly compliant as compared to the other non-magnetic heterogeneous catalytic system. The acquisition of this nanocatalyst is also exemplified by employing the catalyst in leaching and reusability test and the results from the tests showing negligible zinc leaching and recycling was achieved multiple times just by sequestering using an external magnet.

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1. Introduction

Nanoscience and nanotechnology have become an ideal alternative for raising the industrial core competitiveness. It is also one of the areas where mankind expects to realize the springing development. In fact nanocatalysis, a potent subfield emerged from nanoscience, has enormous potential to provide clean and safe alternatives to existing industrial practices that currently lack solutions [1–3]. The contemporary nano-sized catalysts have replaced the conventional ones owing to their ability of providing greater accessibility of active sites for reaction and thereby, enhancing the contact between reactants and catalyst dramatically. Though, the nanocatalysts have numerous advantages, but their separation and regeneration is not an easy job. The use of magnetic nanoparticles (MNPs) has appeared as a viable solution to the above stated troubles [4-7]. The insoluble and paramagnetic nature of these astonishing MNPs enables easy and efficient separation from the reaction mixture with an external magnet [8]. However, it often shows strong proclivity for aggregation and decomposition. In order to resolve this problem, MNPs are coated with amorphous silica [9–11]. This coating alters the surface properties of MNPs, from hydrophobic to hydrophilic, which screens the magnetic dipolar attraction between nanoparticles [12,13]. It not only provides the stability and inertness but also, assist in grafting of specific ligands to the surface of MNPs [14–16]. Thus silica based magnetically recoverable nanocatalyst meets the following standards of an ideal catalyst [17–20]: (1) uniform distribution of the active species; (2) ease of immobilization of metal complex; (3) good chemical and mechanical stability under reaction conditions; (4) non-hazardous and effortless way of formation; (5) soft ferromagnetism for redispersion.

Oxidation of aromatic amines is one of the imperative functional transformations in terms of industrial applications. Azoxyarenes obtained via this transformation have been utilized as therapeutic medicines, dyes, analytical reagents and photosemiconductors [21,22]. These products are also widely used in the area of organic non-linear optics in modern technology due to their liquid crystalline properties [23–25]. But oxidation of aromatic amines often results in a complex mixture of products. Nevertheless, optimization of reaction conditions leading to the azoxy compound in a quantitative yield has become a research concern, due to its various preceding significant applications. Till now, this transformation







^{*} Corresponding author. Tel.: +91 011 27666250; fax: +91 011 27666250. *E-mail address:* rksharmagreenchem@hotmail.com (R.K. Sharma).

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is catalyzed by a plethora of reagents [26–30]. In spite of their potential utility, these methods have several drawbacks such as unsatisfactory yields, involvement of stringent reaction conditions, use of toxic and expensive organic reagents, co-occurrence of several side reactions and prolonged reaction time. Therefore, improvement of catalytic route in terms of environmentally benign and economical approach is highly desirable.

As a part of our continuing effort [31-40] to utilize heterogeneous organic-inorganic hybrid catalytic systems in various organic transformations and by considering the use of readily available zinc compounds as effective catalyst for various oxidative transformations [41-43]. Herein, we report the synthesis and characterization of zinc nanocatalyst for oxidation of amines to yield industrially worth full azoxyarenes. Literature study reveals that this kind of system has not been reported so far for the oxidation of aromatic amines. The superiority of magnetically driven Zn(II) complex immobilized nanocatalyst, i.e. Zn(II)-AcPy@ASMNPs over other heterogeneous catalyst, is that it makes the work up procedure much simpler due to its ease of recoverability and recyclability. The other benefits with respect to profound use of magnetite based nanocatalyst are due to iron's relative abundance, inexpensiveness and environmental friendliness. Hence the use of magnetic nanoparticles as support makes the synthetic process for industries more appealing from an environmental view point.

2. Experimental

2.1. Materials and reagents

3-aminopropyltriethoxysilane (APTES) and tetraethoxyorthosilicate (TEOS) were purchased from Fluka and Sigma–Aldrich respectively. Hydrochloric acid (36.5%) and nitric acid (69–71%) was obtained from Fischer Scientific. 2-acetylpyridine and zinc acetate were procured from Sisco Research Laboratory. Anhydrous methanol, ethanol, acetone, dichloromethane, and acetonitrile were obtained from Thomas baker.

2.2. Characterizations

The morphology and microstructure of the nanoparticles were examined on a transmission electron microscope (TEM, JEM-2010, JEOL, Japan) operated at 200 kV, equipped with an energydispersive X-ray spectrometer (EDS) and on a high resolution transmission electron microscope (HR-TEM, FEI TECNAIF 30) with HAADF detector operated at 300 kV. Morphology of the silicacoated magnetite nanoparticles was studied by focused ion beamscanning electron microscopy (FIB/SEM) on ZEISS EVO 40 instrument. The samples were placed on a carbon tape and coated with a thin layer of gold using a sputter coater. The phase of the products was examined by XRD on a powder X-ray diffractometer (Bruker, D8 Advance, Germany) using Cu K α radiation (λ = 1.54056 nm) in the 2θ interval (5–80°). Magnetic susceptibility measurements were carried out using a vibrating sample magnetometer (VSM) (EV-9, Microsense, ADE) in the magnetic field range of -20,000 Oe to 20,000 Oe at room temperature. Fourier transform infrared spectra (FT-IR) were recorded using PerkinElmer Spectrum 2000. Digestions were performed in Anton Paar multiwave 3000 microwave reaction system equipped with temperature and pressure sensor. The metal content in supernatant and in catalyst was determined by LAB INDIA AA 7000 atomic absorption spectrophotometer (AAS). The derived products were analyzed and confirmed by using Agilent gas chromatography (6850 GC) with a HP-5MS 5% phenyl methyl siloxane capillary column $(30.0 \text{ m} \times 0.25 \text{ mm} \times 0.25 \text{ mm})$

and a quadrupole mass filter equipped 5975 mass selective detector (MSD) using helium as carrier gas (rate 1 mL min^{-1}).

2.3. Synthesis of amine-functionalized silica coated magnetite supported nanocomposite

Magnetic nanoparticles (MNPs) were synthesized using coprecipitation method [44]. Ferric sulphate (6.0g) and ferrous sulphate (4.2 g) were dissolved in water (250 mL) and stirred at 60 °C to give yellowish-orange solution. Then, 25% NH₄OH (15 mL) was added with vigorous mechanical stirring, with which colour of the bulk solution changed to black. Stirring was continued for another 30 min. The precipitated MNPs were separated magnetically and washed several times with deionized water and ethanol. Silica coating of these MNPs was performed via sol-gel approach [45]. Dispersed solution of activated MNPs with 0.1 M HCl (0.5 g) was prepared in mixture of ethanol (200 mL) and water (50 mL) under sonication; Then, 25% NH₄OH (5 mL) was added to the suspension at room temperature followed by the addition of TEOS (1 mL). Then, the mixture was kept for stirring at temperature of 60 °C for 6 h. The obtained silica coated magnetic nanoparticles (SMNPs) were separated magnetically, washed with ethanol and dried under vacuum.

Finally, in order to introduce the amine groups to the silica surface of the nanoparticles, dispersed solution of SMNPs (0.1 g) in ethanol (100 mL) was made under sonication. APTES (0.5 mL) was then added and resulting mixture was stirred for 6 h at 50 °C. Devised aminopropylated SMNPs (ASMNPs) were separated and washed several times with ethanol to remove the unreacted silylating agent.

2.4. Synthesis of Zn(II)–acetylpyridyl complex grafted silica coated magnetite supported nanocatalyst

For covalent grafting of 2-acetylpyridine on ASMNPs, ASMNPs (2g) and 2-acetylpyridine (4.0 mmol) in ethanol (250 mL) were refluxed for 3 h. Then, the grafted ASMNPs (1g) were stirred with solution of 4 mmol of zinc acetate in acetone for 4 h. The resulted zinc complex grafted nanoparticles (Zn(II)-AcPy@ASMNPs) were separated magnetically, washed thoroughly with water and dried in vacuum oven (Scheme 1).



Scheme 1. The Sequence of events in the preparation of catalyst.



Fig. 1. TEM micrographs of MNPs (a) HR-TEM image, (b) FFTs image, (c) electron diffraction pattern of selected area and (d) large view of MNPs.

2.5. Activity test of the catalysts for oxidation of aromatic amines

An oven dried-flask was charged with substrate (1 mmol) and catalyst (20 mg) in acetonitrile (10 mL). The mixture was stirred at 80 °C. Aqueous 30% hydrogen peroxide (H_2O_2) (2 mmol) was then added drop wise to the reaction mixture. The aliquots for reaction monitoring were taken at appropriate time intervals and were analyzed by GC after catalyst removal. After completion, the reaction mixture was cooled, catalyst was allowed to colonize at the side of the vessel using external magnet. Rest of the solution was taken out with pipette and extracted with dichloromethane, washed with 10% NaHCO₃ and water solution, dried and concentrated to give products. The structure elucidations of the products were confirmed by GC-MS.

2.6. Silica leaching test

The quality of silica coating is evaluated by the acidic leaching test. The property of solubility difference of ferrite core particles and amorphous silica in acidic medium is basis for the given test [46]. The nanoparticles with better coating or more coverage of silica were not soluble in acidic medium than the nanoparticles with less or incomplete coating. For testing the coating process of ferrite nanoparticles with silica, concentration measurement of Fe ions was made in the supernatant solution after leaching the nanoparticles in acidic medium by AAS (i.e. lower the Fe concentration, better is the coating).

For the test, 50 mL of 2 M HCl was added to the 50 mL aqueous suspension of 0.1 g of SMNPs. The mixture was sonicated for 3 h and centrifuged for 2 min at 10,000 rpm. A total of 10 mL of clear



Fig. 2. TEM micrographs of (a) and (b) SMNPs and (c) ASMNPs.

supernatant solution was then taken and diluted to 100 mL. Finally, concentration of Fe ions was measured in AAS. Each test was performed twice. The Fe content in the supernatant came out to be negligible. Hence results showed the uniform and smooth coating of silica over MNPs.

3. Results and discussion

3.1. Shape and morphology of the nanoparticles

The nanocatalyst (Zn(II)-AcPy@ASMNPs) and parent materials (MNPs, SMNPs and ASMNPs) were characterized by transmission electron microscopy (TEM). Fig. 1d shows a representative TEM image of Fe₃O₄ nanocomposites, which clearly indicates that the prepared MNPs shows a typical spherical nanostructure with average size of 8–10 nm. The HR-TEM image (Fig. 1b) and electron diffraction pattern (Fig. 1c) of MNPs confirmed the high crystallinity of the nanoparticles. The electron diffraction pattern can be indexed to highly crystalline reflections, such as (2 2 0), (3 1 1), (4 2 2), (5 1 1) and (4 4 0) of cubic inverse spinel Fe₃O₄ structure. From HRTEM, the average interfringe distance of MNPs was measured to be ~0.3 nm which corresponds to (2 2 0) plane of inverse spinel structured

Fe₃O₄. TEM analysis of SMNPs as shown in Fig. 2a and b, displays a dark nano-Fe₃O₄ core surrounded by a grey silica shell about 3–5 nm thick and the average size of the obtained particles is 12–15 nm (Fig. 2a). Fig. 2c reveals the grafting of organic polymer (APTES) onto the surface of silica coated nanoparticles for the functionalization of SMNPs.

Fig. 3 displays the SEM image at $59.62k \times$ magnification of the prepared nanocatalyst. The spongy surface in SEM images clearly depicts the uniform dispersion of zinc complex over the surface of silica coated magnetite nanoparticles, which is responsible for its high activity as catalyst.

3.2. Phase and structural characterization of the nanoparticles

The materials, both before and after silica coating, were characterized by powder X-ray diffraction (XRD) (Fig. 4). The XRD analysis exhibited the information about the crystallographic structure, chemical composition, and physical properties of the nanocomposites. The pattern of the native iron oxide particles exhibits the characteristic peaks of cubic inverse spinel structure. The positions and the relative intensities in the diffractogram matched well with the standard XRD data of Joint Committee on Powder



Fig. 3. SEM image of prepared nanocatalyst.

Diffraction Standards (JCPDS) card number (19-0629) for Fe₃O₄, which is consistent with the TEM result. The broadening of XRD peaks could be attributed to the decrease in crystalline size of the MNPs [47,48]. The XRD pattern for SMNPs showed a weak broad band at $2\theta = 20-24^{\circ}$ which is due to the amorphous silane shell formed around the magnetic core [49,50]. Other than this, there is no any other appreciable shift in the peak positions, which indicates that the extreme chemical and physical conditions created during silica coating process have no significant effect on crystallographic structural characteristic of magnetite nanoparticles.

EDS analysis in Fig. 5a confirmed the existence of silica (Si) and iron (Fe) in SMNPs, (b) showed decrease in the Fe content and increase in Si and nitrogen (N) in ASMNPs and (c) revealed the



Fig. 4. XRD patterns of (a) MNPs and (b) SMNPs.

presence of zinc over the Zn(II)-AcPy@ASMNPs surface framework; it gave the pivotal evidence of the metal immobilization on the prepared nanocatalyst. The quantitative analysis for zinc content in catalyst was performed using AAS, and sample digestions were carried out in microwave at 400 W for 15 min at constant pressure programme with 5 mL aqua regia. Reference solutions for zinc measurement were made to obtain the calibration curves. 0.13 mmol/g zinc content in catalyst was quantified using calibration curve in duplicate for each sample.



Fig. 5. EDS pattern of (a) SMNPs (b) ASMNPs and (c) Zn(II)-AcPy@ASMNPs.



Fig. 6. FT-IR spectra of (a) MNPs, (b) SMNPs, (c) ASMNPs, (d) AcPy@ASMNPs and (e) Zn(II)-AcPy@ASMNPs.

The FT-IR spectroscopy was used to characterize the functionality of the resulting MNPs, SMNPs, ASMNPs, AcPy@ASMNPs and Zn(II)-AcPy@ASMNPs in Fig. 6. Presence of Fe-O stretching vibration at 588 cm⁻¹ with a slight splitting is attributed to magnetite (Fe₃O₄) [51]. The silica coating of magnetite nanoparticles was confirmed by observation of a broad band at 1090 cm⁻¹ which can be assigned to Si-O stretching vibrations in Fig. 6b. On moving from MNPs to SMNPs, a significant reduction of the intensity of the Fe-O stretching and bending vibrations bands is observed. The characteristic absorption bands observed at 3378 cm⁻¹ and 1625 cm⁻¹ in Fig. 6c, is due to stretching and bending vibrations of physically adsorbed water and surface –OH groups. The band at 2925 cm⁻¹ in Fig. 6c, corresponds to the -CH₂- group of amino-propyl group in functionalized SMNPs (which does not appear in the parent SMNPs spectrum). The spectrum of the acetylpyridine grafted over ASM-NPs in Fig. 6d, showed a strong band at 1647 cm^{-1} due to C=N stretching vibration. This confirms the covalent binding of ligand

Table 1	
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Investigation of different catalysts reaction.^a



Fig. 7. Magnetization curves obtained by VSM at room temperature for (a) MNPs, (b) SMNPs and (c) Zn(II)-AcPy@ASMNPs.

on to the surface of APSCMNPs. On metallation, in Fig. 6e zinc binds to the bidentate complex and prominent C=N stretching frequency was shifted to lower wave number, indicating strong metal-ligand interaction (Supplementary material).

3.3. Magnetic property

Magnetic measurements were carried out using a superconducting quantum interference device with a field of 2 T at room temperature. The magnetization curves of MNPs, SMNPs and Zn(II)-AcPy@ASMNPs showed no hysteresis opening with complete reversibility at room temperature. The coercivity and remanence were not observed in any of the curves which confirmed the superparamagnetism in the nanoparticles. Fig. 7 showed the decrease in saturation magnetism from 53.45 emu/g of MNPs to 14.9 emu/g of Zn(II)-AcPy@ASMNPs. The deviation between them is attributed to the increased mass of diamagnetic silica over MNPs and grafting of metal-ligand complex over ASMNPs [52].

3.4. Catalytic activity of the catalyst in oxidation of aromatic amines

The optimization of catalytic conditions was carried out by employing the oxidation of aniline with H_2O_2 as an oxidant. Aniline was chosen as the test substrate because it is electronically (+R effect or -R effect) and sterically deactivated. Hence, gives accurate assessment of catalytic activity of the nanocatalyst.

Entry	Catalyst	Time (h)	Conversion (%) ^b	Selectivity (%) ^b	H_2O_2 efficiency (%) ^c
1	No	6	Trace	-	-
2	SMNPs	6	Trace	_	-
3	Zinc acetate ^d	1	69	52	66
4	Zn(II)-ASMNPs	1	39	68	36
5	Zn-AcPy@ASMNPs (10 mg)	1	59	95	55
6	Zn-AcPy@ASMNPs (15 mg)	1	81	98	74
7	Zn-AcPy@ASMNPs (20 mg)	1	99	99	89
8	Zn-AcPy@ASMNPs (25 mg)	1	99	99	89

^a Aniline (1 mmol); H₂O₂(2 mmol); catalyst (20 mg); acetonitrile (1 mL); temp. 80 °C.

^b Conversion and Selectivity were determined by GC, Conversion = [(initial moles of substrate – final moles of substrate)/initial moles of substrate] × 100, Selectivity to azoxyarenes = [Azoxyarenes%/(Azoxyarenes% + Azoarenes%)] × 100.

 c H₂O₂ efficiency (%) is calculated as products (mol)/consumed H₂O₂ (mol) × 100 (the remaining H₂O₂ after reaction was estimated by potential difference titration of Ce³⁺/Ce⁴⁺ [0.1 M aqueous Ce(NH₄)₄(SO₄)₄·2H₂O)].

^d 0.00262 mmol.



Fig. 8. Effect of temperature and time on the activity of catalyst.

A control experiment of oxidation of aniline without any catalyst showed negligible conversion even after 6 h of reaction (Table 1). Similarly, the experiment of oxidation in similar conditions using SMNPs also did not undergo any product formation (entry-2). The simple metal salt (zinc acetate) as catalyst was also used for the target reaction which showed formation of desired product with low selectivity (entry-3). Also, this homogeneous catalyst suffers with the problem of separation and recovery. The use of zinc directly attached to amine functionalized silica coated magnetic nanoparticles, i.e. Zn(II)@ASMNPs (without being complexed to acetylpyridine) (entry-4) resulted in azoxyaniline formation with lower conversion (39%). The results from the entries 3 and 4 indicate that though, the reaction was catalyzed by Zn(II) ions but the role of ligand (acetylpyridine) is significant for the transformation (entry-5). Infact, the use of Zn(II)-acetylpyridyl complex grafted nanoparticles over ASMNPs, i.e. Zn(II)-AcPy@ASMNPs for reaction, gave product with highest conversion and selectivity. In this case, acetylpyridine with strong p-donating ability of nitrogen and oxygen donor acted as a co-catalyst and also anchored the Zn(II) in a better way. The quantitative analysis of the nanocatalyst (entries 6-8) was also performed and it was found that the yield increased from 59% to 99% with increasing amount of catalyst from 10 to 25 mg respectively. This could be mainly due to the availability of large number of active sites on the surface of the catalyst, which increases with the amount of the catalyst. For measuring the H₂O₂ utilization in catalytic reaction, its efficiency [53] was also calculated (entries 3–8). The titration of remaining H₂O₂ after reaction was estimated by potential difference titration of Ce^{3+}/Ce^{4+} [54].

To study the effect of temperature and time on the activity of the nanocatalyst, model reaction was carried out at diverse range of temperatures (25–100 °C) for different intervals of time. The conversion of aniline in presence of catalyst and oxidant, as a function of time and temperature is shown in Fig. 8. As shown in Figure, the catalytic activity of prepared nanocatalyst, i.e. Zn(II)-AcPy@ASMNPs enhanced significantly with increasing reaction temperature, Which further has positive effect on conversion.

At room temperature, no change in the conversion of aniline was observed even if the reaction continued for 3 h. So, the temperature of the reaction was raised. Maximum conversion of aniline was obtained, when reaction was carried out at $80 \,^\circ$ C in stirring for 1 h. Moreover, further increase of temperatures leads to no change in conversion but selectivity lowers w.r.t. main product. The catalytic properties of prepared Zn(II)-AcPy@ASMNPs as catalyst

Effect of Solvent



Fig. 9. Effect of the solvent on the yield of Azoxyarenes.

in oxidation of anilines were studied using hydrogen peroxide as oxidant with different solvents at 80 °C (Fig. 9). Depending on the type of solvent used, the rate of the reaction and selectivity towards the product varied. In the presence of acetonitrile as a solvent, azoxyarenes obtained with highest yield as characterized by TLC (60:40 ratio of chloroform/ethyl acetate) and GC analysis. Acetone and ethanol also gave good results in terms of conversion, but lacked the selectivity towards the desired product. Therefore, of all the solvents studied, acetonitrile was found to be most active in terms of conversion and selectivity towards azoxyarenes.

Analysis of the correlation between selectivity and addition of oxidant during the course of the reaction reveals better understanding of mechanism for the reaction. The gradual decrease in concentration of hydrogen peroxide in the course of the reaction was compensated by step-by-step addition of H_2O_2 , which leads to the higher selectivity for azoxyarenes in the reaction. Furthermore, this avoids the direct oxidation of aniline to nitrobenzene in the reaction. The scope of the catalytic activity of Zn(II)-AcPy@ASMNPs in the oxidation of different substituted aniline was studied in

Table 2

Scope of catalytic activity of the Zn(II)-AcPy@ASMNPs nanocatalyst in the oxidation of different substituted aromatic amines.^a

Entry	Anilines	Conv. (%) ^b	Selectivity (%) ^b			TON ^c
			Azoxy	Azo	Nitroso	
1	-	99	100	-	-	377
2	2-Me	96	99	1	-	366
3	4-Me	100	100	-	-	381
4	2,6 Dimethyl	95	96	2	-	362
5	4-OCH ₃	98	99	1	-	374
6	1Napthylamine	94	98	1	-	358
7	4-Cl	90	97	1	2	343
8	3-Cl	87	95	2	2	332
9	2-Cl	82	94	2	4	312
10	4-Br	92	96	2	1	351
11	3-Br	88	93	5	2	335
12	2-Br	82	92	3	5	313
13	4-NO ₂	80	95	1	4	305
14	4-COCH ₃	81	100	-	-	309
15	2-phenyldiamine	Polymer	-	-	-	-
16	4-phenyldiamine	Polymer	-	-	-	-

 a Substrate (1 mmol); 30% aq. H_2O_2 (2 mmol); catalyst (20 mg); acetonitrile (1 mL); temp. 80 $^\circ C$; time 1 h.

^b Conversion and selectivity were determined by GC, Conversion = [(initial moles of substrate – final moles of substrate)/initial moles of substrate] × 100, Selectivity to azoxyarenes = [Azoxyarenes%/(Azoxyarenes% + Azoarenes%)] × 100.
^c TON is the number of moles of product per mole of catalyst.

Table 3	
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A comparisons of the results of the present system with the literature precedents of some recently published catalytic systems for the oxidation of aniline.

Entry	Catalyst	Catalytic conditions	Time (h)	Yield (%)	Ref.
1	Titanium silicate/mol. seives	CH ₃ CN/60 °C	5	21.2	[25]
2	$Na_{12}[WZnZn_2(H_2O)_2(ZnW_9O_{34})_2]$	Water/75 °C	7	95	[26]
3	Co/SBA-15	CH ₃ CN/80 °C	6	98	[27]
4	Zeolite (Ti ⁴⁺ analogues of ZSM-5, TS-1)	Acetone	6	75	[28]
5	Perfluoro-silicate	CH ₃ CN/80 °C	12	100	[29]
6	Heteropolyoxotungstate	H ₂ O/80 °C	4	95	[30]
7	Our catalyst	CH ₃ CN/80 °C	1	99	[This work]

Table 2. It is mandatory to mention here, that the oxidation of less reactive aniline, i.e. phenyl with electron withdrawing groups. underwent lesser conversion as compared to electron rich anilines. i.e. phenyl with electron donating groups. The difference in reactivity as well as selectivity for azoxy product can be attributed to the relative steric and electronic differences amongst the reactants, which affects the reaction mechanism. Conversely, reaction yield is also affected by the steric effect of the substituents. It was confirmed by the oxidation of 2,6-dimethylaniline and other osubstituted anilines, which offered the product with lower yield. Various diamines were also tested in the reaction (entry15-16) but these substrates did undergo coupling reaction to give black polymer material. The TON for azoxy compounds in all the cases (entry1-14) was high and reached up to the maximum TON of 381 for 4-methyl aniline, which is much higher than the previously reported catalyst. As evident from Table 3, the efficiency of the nanocatalyst was compared with other reported catalysts. It showed that our catalyst demonstrated good results in terms of reaction conditions compared to those reported in literature.

3.5. Plausible reaction mechanism

In the present transformation, reaction has not occurred in the absence of catalyst, which indicates that the lewis acidity of the catalyst plays significant role in the transformation. On the other hand the reaction in presence of Zn(II) complex immobilized nanocatalyst (Zn(II)-AcPy@ASMNPs) gave product with the highest conversion and selectivity. As depicted in Scheme 2, in the presence of a surplus amount of H_2O_2 , Zn(II) compounds provide electrophilic activation of hydrogen peroxide [41–43,55–57]. As a results of which, electrons were withdrawn from the peroxyl moiety, thereby enhancing the electrophilic characters of the peroxidic oxygen [41–43,55–57]. The oxidation of nitrogen atom in the aniline, proceeded by nucleophilic attack of an active hydroperoxy intermediate, to form phenylhydroxylamine (2) and regenerates



Scheme 2. Proposed reaction mechanism.

zinc species. Subsequently, the phenylhydroxylamine (2) is further oxidized to nitrosobenzene (3). The condensation of the nitrosobenzene (3) with aniline leads to the formation of azobenzene (4), which on further oxidization gives azoxybenzene (5) or it can also be formed by direct condensation of the two intermediates, phenylhydroxylamine and nitrosobenzene.

3.6. Hot filtration experiment

Hot-filtration based leaching test was conducted to exclude any homogeneous catalytic contribution or lixiviation of catalytic species in the catalyzed reaction. First, AAS analysis of the post reaction mixture after catalyst separation was conducted and the results revealed that concentration of Zn(II) ions in the supernatant correspond to the negligible catalyst leaching (<0.01 ppm). Another reaction was carried out at 80 °C for 30 min with the procured catalyst from previous cycle. After the catalyst was separated using external magnet and the supernatant was again poured back into the reactor and the reaction was continued for additional 3 h. It was found that there was almost no further conversion after separation of the catalyst (Fig. 10). It corroborated that the zinc ions has not been etched out during the course of the reaction which further signifies the stability and heterogeneity of prepared nanocatalyst. To further intensify the fact, catalyst recovered after this run was subjected to digestion using microwave irradiation and metal content analysis using AAS. The result showed that there was barely any change in the amount of zinc compared with the fresh catalyst.



Fig. 10. Percent conversion versus reaction time in a leaching experiment. The blue arrow indicates the time the catalyst was filtered and separated from the reaction mixture and supernatant was then run by itself afterward. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



Fig. 11. (a) TEM and SEM images of recovered catalyst after six successive runs of reaction.

3.7. Recycling of catalyst

The reusability is an important criterion for any catalyst. For performing the reusability experiments, the catalyst was fixed magnetically at the side wall of the vessel and rest of the solution was taken off with a pipette. Then, the vessel was recharged with fresh solvent and substrate. The result from the next run confirmed that the catalyst can be re-used and can be further subjected with fresh substrates for progressive reactions under identical conditions. The experimental results of successive six reactions demonstrated that the reactivity of the catalyst did not undergo any appreciable change in its activity and only a steady decline in the yield was observed in (Supplementary material). The morphology and affectivity of the recovered catalyst isolated after 6th run was assessed from the SEM and VSM analysis. Although during the reaction, nanocatalysts were subjected to continuous stirring; it is evident from SEM image (Fig. 11) of reused catalyst that nanoparticles remain intact confirming its good mechanical strength. Likewise, VSM analysis illustrates that the saturation magnetization values of the reused catalyst almost remains unaltered (14.2 emu/g) (Supplementary material).

4. Conclusions

In summary, we have presented the successful development of a highly efficient and industrially relevant catalyst for the synthesis of azoxyarenes. The unique arrangement of Zn(II)-acetylpyridyl complex over the amine functionalized silica coated magnetic nanoparticle meets the industrial targets under safe and lesscorrosive conditions without any loss of activity during course of the reaction. The stability and rigidity of catalyst, use of economical magnetic nanoparticles as support, easy recoverability and reusability, makes it a valuable green catalyst compared to the other non-magnetic heterogeneous catalytic system. Good yield of products, high TON, reduced reaction time and mild reaction conditions are the other conspicuous advantages of the applied protocol. Conceivably, it is only a matter of time before the real prospective of silica coated magnetic nanocatalysts are realized and implemented on a far-reaching scale.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcata. 2012.12.046.

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