Accepted Manuscript

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PII: S0022-328X(18)30948-3

DOI: https://doi.org/10.1016/j.jorganchem.2018.12.002

Reference: JOM 20659

To appear in: Journal of Organometallic Chemistry

Received Date: 29 October 2018

Revised Date: 27 November 2018

Accepted Date: 3 December 2018

Please cite this article as: A. Maleki, J. Rahimi, Z. Hajizadeh, M. Niksefat, Synthesis and characterization of an acidic nanostructure based on magnetic polyvinyl alcohol as an efficient heterogeneous nanocatalyst for the synthesis of α-aminonitriles, *Journal of Organometallic Chemistry* (2019), doi: https://doi.org/10.1016/j.jorganchem.2018.12.002.

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Graphical Abstract



Synthesis and characterization of an acidic nanostructure based on magnetic polyvinyl alcohol as an efficient heterogeneous nanocatalyst for the synthesis

of α-aminonitriles

Ali Maleki*, Jamal Rahimi, Zoleikha Hajizadeh, Maryam Niksefat

Catalysts and Organic Synthesis Research Laboratory, Department of Chemistry, Iran University of Science and Technology, Tehran 16846-13114, Iran

*Corresponding author E-mail: maleki@iust.ac.ir; Fax: +98-21-73021584; Tel: +98-21-

77240540-50

Abstract

The present study described design, preparation and characterization of a new magnetic nanocomposite based on polyvinyl alcohol (PVA) as a non-toxic, water-soluble, high mechanical stable and low-cost polymer. Fourier transform infrared (FT-IR) spectroscopy, field-emission scanning electron microscopy (FE-SEM) image, transmission electron microscope (TEM) image, X-ray diffraction (XRD) pattern, energy-dispersive X-ray (EDX) analysis and thermogravimetric (TG) analysis were used to describe the morphological, chemical and physical properties of the prepared nanocatalyst. All these results confirmed the successful synthesis of Fe₃O₄@PVA-SO₃H. This heterogeneous nanocatalyst was then successfully used for the synthesis of α -aminonitrile derivatives by starting from an aldehyde, an aniline and trimethylsilyl cyanide (TMSCN). High efficiency, green chemistry properties, simple and easy separation are the specific properties of this nanocomposite. Fe₃O₄@PVA-SO₃H can be derived out by an external magnet and reused ten times without any changes in its structure.

Keywords: Polyvinyl alcohol; Nanocomposite; Magnetic nanocatalyst; Sulfonic acid; α -Aminonitrile; Green chemistry.

1. Introduction

By looking more closely at the needs of industry, developing new catalysts based on green chemistry principals is urgently needed. Nowadays, nanomaterials have been exhibited significant advantages and features due to their large surface-to-volume ratio [1-15]. The difficulty of separating nanocatalyst from reaction media extremely limits their applications in industry. To conquer this drawback in the last decade's magnetic nanoparticles (MNPs) gained considerable attention [16]. Among the magnetic nanoparticles, Fe₃O₄ nanoparticles have been recognized the most widely used due to its properties such as low cost, relative high magnetic saturation, and easy preparation [17]. To prevent agglomeration and oxidation of Fe₃O₄ NPs coating with organic and inorganic materials including small molecules, silica, polymers, carbon, metal or metal oxide NPs is urgently needed [18, 19]. Also, the coating procedures provide reaction sites or active groups for covalently or no covalently grafting the active catalytic units onto the coated MNPs to construct magnetically recoverable catalysts.

PVA can be used as a high performance polymer because of the unique combination of beneficial properties such as non-toxicity, water-solubility, biocompatibility, biodegradability, low cost and high mechanical efficiency [20]. Its high hydrophilicity and high surface –OH groups lead to easy modification by different nanoparticles and can decrease the aggregation process [21]. The effective immobilization of the Fe_3O_4 inside the PVA was achieved by their bonding with the exposed hydroxyl groups in PVA.

There are several protocols reported in the literature for synthesizing Fe_3O_4/PVA nanocomposites such as in situ [22], ex-situ methods [23], and sonochemical method [24]. The reported methods have their own advantages and disadvantages but, the *in situ* method gives more homogenate composite in relatively short time. The application of this nanocomposite has

been investigated in many different fields such as in drug delivery [25], as membranes for bone regeneration [26], as magneto-thermal for hyperthermia in cancer [25], an enzyme carrier [27] and biomedical application [28].

Recently, due to high reactivity, operational simplicity, low toxicity, non-corrosive nature and recoverable properties heterogeneous acid catalysts are found as an effective catalyst for the organic reactions [29-30]. The three-component synthesis of α -aminonitriles via Strecker reaction was carried out by the combination of aldehydes, amines and TMSCN. Aminonitriles are versatile intermediates for the synthesis of amino acids via hydrolysis of the nitrile moiety [31]. Many methods have been developed for the synthesis of aminonitriles by use of acid catalysts such as InCl₃ [32], BiCl₃ [33] and CoCl₂ [34].

In continuation of last research on green nanocatalyst and organic synthesis [35, 36], herein, the synthesis and characterization of $Fe_3O_4@PVA-SO_3H$ nanocomposite were investigated for the first time and its application as a nanocatalyst was examined in the synthesis of aminonitriles via Strecker reaction (Scheme1).



Scheme 1. Preparation of $Fe_3O_4@PVA-SO_3H$ and catalytic application in the α -aminonitrile derivatives.

2. Experimental

2.1. General

All the solvents, reagents, and chemicals were purchased from Merck, Fluka and Aldrich. FT-IR spectra were recorded on a Shimadzu IR-470 spectrometer by the method of KBr pellets. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Field-emission scanning electron microscopy (FE-SEM) images were taken with KYKY-EM3200. Transmission electron microscope (TEM) image was obtained by Philips CM120. X-ray (EDX) analysis was recorded with a Numerix DXP–X10P. Thermal analysis was taken by Bahr-STA 504 instrument in the air atmosphere. XRD patterns of the solid powders were carried

out using a JEOL JDX–8030 (30 kV, 20 mA). The products were identified by comparison of their spectroscopic and analytical data with those of authentic samples.

2.2. Preparation of Fe_3O_4 @PVA nanocomposite

Fe₃O₄@PVA nanoparticles were synthesized by co-precipitation method. At first, 2.0 g of PVA 72000 M_w was dissolved in 40 mL water at 80 °C for 6 h to achieve homogenous mixture. The homogenous PVA was mixed with 12 mL of NH₃.H₂O in a three-necked flask under nitrogen (N₂) atmosphere. Then, 2.5 g of FeCl₃.6H₂O and 1.0 g of FeCl₂.4H₂O were dissolved in 10 mL of deionized water. The mixture of FeCl₃.6H₂O and FeCl₂.4H₂O was added slowly to the NH₃-PVA solution and the mixture heated at 60 °C for 120 min. The obtained Fe₃O₄@PVA precipitate was washed with deionized water until pH was reached to 7. Finally, it was dried at 80 °C in an oven.

2.3. Preparation of Fe₃O₄@PVA-SO₃H nanoparticles

Functionalizing of prepared Fe₃O₄@PVA nanocomposite with SO₃H, was done by using a suction flask equipped with a constant-pressure dropping funnel and a gas inlet tube for conducting HCl gas over an absorbing solution (i.e., water), charged with the Fe₃O₄@PVA (0.5 g) in CH₂Cl₂ (20 mL) and dispersed by an ultrasonic bath for 30 min. Then, a solution of chlorosulfonic acid (0.25 mL) in CH₂Cl₂ (5 mL) was added dropwise at -10 °C during 30 min. After the addition was completed, the mixture was stirred for 90 min until HCl was fetched up completely. A powder of nano-Fe₃O₄@PVA-SO₃H was obtained. The nanocomposite was

filtered and washed several times with dry CH_2Cl_2 , methanol and distilled water. The precipitate was dried under vacuum at 70 °C.

2.4. General procedure for the synthesis of 2-(N-anilino)-2-phenyl acetonitrile 4a-z

The Mixture of benzaldehyde (0.107 g, 1 mmol), aniline (0.093 g, 1 mmol) and TMSCN (0.120 g, 1.2 mmol) in 3 mL of EtOH was stirred for 10 min at ambient temperature in the presence of $Fe_3O_4@PVA-SO_3H$ nanocomposite (0.050 g). The completion of the reaction was monitored by TLC (ethyl acetate–n-hexane, 1:3). Catalyst was separated easily by an external magnet. The pure crystalline products were achieved from the reaction mixture by recrystallization in hot EtOH.

3. Results and discussion

In this work, Fe₃O₄@PVA-SO₃H heterogeneous acidic nanocatalyst was synthesized for the first time under mild conditions and short reaction times. As can be seen in Scheme 1, Fe₃O₄@PVA-SO₃H nanocatalyst was prepared after two steps. At first, Fe₃O₄@PVA nanoparticles were synthesized by co-precipitation method in presence of PVA and solution of FeCl₃.6H₂O and FeCl₂.4H₂O under N₂. After that, Fe₃O₄@PVA was treated by chlorosulfonic acid to synthesize Fe₃O₄@PVA-SO₃H nanocatalyst. Various methods have been used to confirm synthesis the nanocomposite. FT-IR spectra for confirming the incorporation of SO₃H onto Fe₃O₄@PVA, Energy-dispersive X-ray (EDX) for the elemental analysis, The field emission scanning electron microscopy (FE-SEM) for morphology and the size details of synthesized nanocomposite, X-ray diffraction (XRD) for crystalline phases of Fe₃O₄@PVA-SO₃H and The thermogravimetric analysis (TGA) for thermal stability, which are discussed as follow.

3.1. Characterization of the nanocomposite

3.1.1. FT-IR Analysis

FT-IR spectroscopy, Fig. 1, confirmed the formation of the nanocomposite. The bending vibration band of Fe–O appeared at 584 cm⁻¹. The O–H stretch of Fe₃O₄ and PVA appeared around 3400, and confirm the presence of a great number of PVA hydroxyl functional groups that can be easy modified by SO₃H groups. Stretching vibration band at 2923 is regarding to C–H of PVA [37]. The S-O stretching vibrations of SO₃H groups in Fe₃O₄-PVA-SO₃H nanocomposite on Fe₃O₄@PVA surface appeared at 1124 cm⁻¹ that indicated the synthesis of Fe₃O₄@PVA-SO₃H [38]. Finally, as can be seen, we have characterized the recycled nanocatalyst by FT-IR spectroscopy which showed suitable retention of its structure and there was no considerable deformation or leaching after ten times reusing.



Fig. 1. The FT-IR spectra of $Fe_3O_4@PVA$, $Fe_3O_4@PVA$ -SO₃H and the recycled $Fe_3O_4@PVA$ -SO₃H.

3.1.2. Energy-dispersive X-ray (EDX)

The EDX elemental analysis of the $Fe_3O_4@PVA-SO_3H$ MNPs was shown in Fig. 2. This analysis strongly clarifies that the SO₃H groups were successfully incorporated onto the magnetic PVA. It approved the presence of carbon, oxygen and sulfur elements in the nanocomposite and confirmed the purity of the nanocomposite.



Fig. 2. The EDX analysis of the Fe₃O₄@PVA-SO₃H nanocomposite.

3.1.3. Field-emission scanning electron microscopy (FE-SEM)

The FE-SEM images of the outer surface of the $Fe_3O_4@PVA-SO_3H$ nanocomposite is illustrated in Fig. 3. A close examination of the figure revealed that the iron oxide impregnated in the polymer matrix and embedded in a sponge-like PVA matrix also, The Fe_3O_4 nanoparticles

exhibit cubic structure. Furthermore, iron oxide particles show the uniform size of nanometer dimensions with the range of average diameter 40.27 ± 6 nm.



Fig. 3. The FE-SEM image of Fe₃O₄@PVA-SO₃H nanocomposite.

3.1.4. Transmission electron microscope (TEM)

TEM image micrograph of $Fe_3O_4@PVA-SO_3H$ nanocomposite was illustrated in Fig. 4. It clearly shows considerable exfoliation of PVA after functionalized by Fe_3O_4 and SO_3H by nearly monodisperse in gray colour. This analysis completely can confirm the successful synthesis of the nanocomposite.



Fig. 4. The TEM image of Fe₃O₄@PVA-SO₃H nanocomposite.

3.1.5. Thermogravimetric analysis (TGA)

The thermogravimetric analysis (TGA) curve, display the relation between temperature and weight loss of the nanocatalysts (Fig. 5). Decomposition of the nanocomposite was achieved while heating at a rate of 10 °C/min in the air between 20 °C and 800 °C. As can be seen, the weight loss in the temperature range from 50 to 150 °C is related to the removal of the surface adsorbed water and weakly absorbed impurities. For the Fe₃O₄@PVA-SO₃H, the new weight loss about 40% in the temperature range of 200–550 °C assigned to the decomposition of PVA and SO₃H groups. Moreover, can be seen that the nanocomposite has a higher thermal stability



compared to PVA alone that is decomposition at about 250 °C [39]. This result shows the strong interaction in the nanocomposite.

Fig. 5. The TGA curve of Fe₃O₄/PVA-SO₃H nanocomposite.

3.1.6. X-ray diffraction (XRD)

XRD measurement is used to determine crystalline nature of nanocomposite. Fig. 6 shows the Xray diffraction patterns of Fe₃O₄@PVA-SO₃H and confirm the presence of Fe₃O₄ NPs on PVA. The broad diffraction peak around $2\theta = 20$ corresponds to PVA [40]. All of the observed peaks for the Fe₃O₄ are in perfect match with the characteristic data of magnetite iron oxide (JCPDS card No. 01-075-0449). The crystalline peaks of magnetite iron oxide with cubic structure observed at the diffraction angles (20) of 18.59, 30.53, 35.86, 37.53, 43.54, 54.13, 57.55, and 63.31. Peak broadening and peak high lowering of Fe₃O₄ are due to the grafting of nanoparticles on the surface of the PVA with amorphous nature. Furthermore, the particle size of Fe₃O₄/PVA-SO₃H nanocomposite Debye–Scherrer equation. was calculated by As result, a the average crystallite size was around 28 nm.



Fig. 6. The XRD pattern of: (a) Fe₃O₄@PVA-SO₃H nanocomposite, (b) the reference Fe₃O₄.

3.1.7. Vibrating sample magnetometer (VSM)

VSM analysis was applied at room temperature to measure magnetic properties (Fig. 7). The saturation magnetization values of $Fe_3O_4@PVA$ and $Fe_3O_4@PVA$ -SO₃H nanocomposite were around 32.95 and 24.15 emu g⁻¹. The decrease of the saturation magnetization of $Fe_3O_4@PVA$ after loading to the SO₃H groups confirmed the successful synthesis of the nanocomposite. Moreover, the both of $Fe_3O_4@PVA$ and $Fe_3O_4@PVA$ -SO₃H show an acceptable magnetic property.



Fig. 7. The VSM curves of Fe₃O₄@PVA and Fe₃O₄@PVA-SO₃H nanocomposite.

3.1.8. Back titration of Fe₃O₄@PVA-SO₃H in aqueous media

Acidity ([H⁺]) of the synthesized $Fe_3O_4@PVA-SO_3H$ nanocatalyst was achieved by the back titration method. At first, 0.5 g of $Fe_3O_4@PVA-SO_3H$, 0.5 g of NaCl, and 10 mL of NaOH 0.1 M were added to 35 mL of distilled water and stirred with a magnet for 24 h. After that, a few drops of phenolphthalein were supplemented into the mixture and the colour changed to pink. Finally,

the mixture was titrated by the solution of HCl 0.1 M to reach the neutral pH. Accordingly, the pH of the nanocatalyst was calculated 1.61.

3.2. Application of the nanocatalyst in organic synthetic reaction

In this work, α -aminonitrile derivatives were synthesized by the reaction of different aromatic aldehydes with aniline and TMSCN in the presence of Fe₃O₄@PVA-SO₃H as a recoverable magnetic nanocatalyst in ethanol at room temperature. The work-up procedure of the product was easy as the nanocatalyst can be separated simply by an external magnet. To optimize the reaction conditions, a series of experiments were performed with the variation of different reaction parameters such as solvent and amount of catalyst for a representative condensation of 4-chlorobenzaldehyde (1 mmol), aniline (1 mmol) and TMSCN (1.2 mmol) as the model reaction. The results are summarized in Table 1. Fe₃O₄ NPs and Fe₃O₄@PVA are able to produce relatively low yields in EtOH, but, in the presence of Fe₃O₄@PVA-SO₃H nanocomposite, the yield of the product increased to 99 % (Table 1, entry 5). The model reaction was also studied in various solvents such as H₂O, EtOH, EtOAc, and CHCl₃. The best result was achieved in EtOH. Also, different amount of the catalyst was investigated. As can be seen in Table 1, entry 5, in the presence of 50 mg of the catalyst, a significant yield was obtained. While the yield of the desired product 4b was not significantly improved in presence of excess amount of the catalyst (Table 1, entries 11 and 12). The best result was obtained by carrying out the reaction at ambient conditions in ethanol for 10 min using 50 mg of Fe₃O₄@PVA-SO₃H.

Entry	Solvent	Catalwat	Amount of	Temperature Yield ^a	
		Catalyst	catalyst (mg)	(°C)	(%)
1	EtOH	Fe ₃ O ₄	50	r.t.	50
2	EtOH	PVA	50	r.t.	trace
3	EtOH	Fe ₃ O ₄ @ PVA	50	r.t.	35
4	H ₂ O	Fe ₃ O ₄ @PVA-SO ₃ H	50	r.t.	47
5	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	50	r.t.	96
6	EtOAc	Fe ₃ O ₄ @PVA-SO ₃ H	50	r.t.	55
7	CHCl ₃	Fe ₃ O ₄ @PVA-SO ₃ H	50	r.t.	56
8	Solvent-free	Fe ₃ O ₄ @PVA-SO ₃ H	50	r.t.	45
9	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	20	r.t.	53
10	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	32	r.t.	60
11	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	70	r.t.	96
12	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	100	r.t.	96
13	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	50	60	35
14	EtOH	Fe ₃ O ₄ @PVA-SO ₃ H	50	Reflux	40

Table 1. Optimization of reaction conditions by reaction of 4-chlorobenzaldehyde, aniline andTMSCN at room temperature.

^a Isolated yield.

In order to demonstrate the repeatability of this strategy, a broad variety of aromatic aldehydes possessing electron-withdrawing and electron-releasing substitutions, were employed and a variety of products were synthesized under the optimized conditions at room temperature. The desirable results of study are shown in Table 2. All the utilized aldehydes supplied the desired products in high yields and short reaction times.

				Time	Vield ^b	Mp (°C)	
Entry	\mathbf{R}^1	\mathbf{R}^2	Product	(min)	(%)	Obs.	Lit.
1	Phenyl	Н	4 a	5	96	70-83	73-75 [41]
2	4-Chlorophenyl	Н	4b	5	97	91-93	92-94 [42]
3	4-Bromophenyl	Н	4c	5	98	102-104	100-101 [41]
4	3-Nitrophenyl	H	4d	5	90	88-90	89-90 [41]
5	4-Methoxylphenyl	Н	4 e	10	90	91-92	91-92 [41]
6	4-Nitrophenyl	Н	4 f	5	98	86-88	86-88 [41]
7	4-Hydroxyphenyl	Н	4 g	15	89	124-126	124-125 [41]
8	4-Methylphenyl	Н	4h	15	91	71-73	70-71 [41]
9	4-Fluorophenyl	Н	4i	5	96	101-102	99-101 [43]
10	2-Thienyl–	Н	4j	10	85	97-99	97–99 [44]
11	2-Furanyl	Н	4 k	10	89	73-75	72–74 [44]
12	4-(Dimethylamino)phenyl	Н	41	15	90	107-109	107–110 [44]
13	4-Cyanophenyl	Н	4 m	5	98	112-114	113–115 [45]
14	3,4,5-Trimethoxyphenyl	Н	4n	10	96	146-148	147–149[43]

Table 2. Synthesis of α -aminonitrile derivatives 4a-z in optimal conditions.^a

4-Hydroxy-3-methoxyphenyl	Н	40	20	88	114-116	113–115 [45]
2-Nitrophenyl	Н	4 p	15	89	135-137	135-137 [41]
2,6-Dichlorophenyl	Н	4 q	15	85	74-76	75–78 [44]
Cinnamaldehyde	Н	4r	10	95	118-120	117-118 [46]
2-Chlorophenyl	Н	4 s	20	84	69-71	69-70 [45]
3-Fluorophenyl	Н	4t	5	90	91-93	91-92 [47]
Phenyl	4-Me	4 u	5	97	106-108	105–107 [45]
4-Chlorophenyl	4-Me	4 v	5	97	87-89	85-87 [43]
Cinnamaldehyde	4-Me	4 w	10	96	104-106	103-106 [45]
4-Methylphenyl	4-Me	4 x	10	92	116-118	116-118 [45]
4-Nitrophenyl	4-Me	4 y	5	97	84-86	83-85 [44]
Phenyl	4-NO ₂	4z	30	68	128-129	128-129 [48]
	4-Hydroxy-3-methoxyphenyl 2-Nitrophenyl 2,6-Dichlorophenyl Cinnamaldehyde 2-Chlorophenyl 3-Fluorophenyl 9henyl 4-Chlorophenyl Cinnamaldehyde 4-Methylphenyl 4-Nitrophenyl	4-Hydroxy-3-methoxyphenyl H 2-Nitrophenyl H 2,6-Dichlorophenyl H Cinnamaldehyde H 2-Chlorophenyl H 3-Fluorophenyl H 4-Men 4-Me 4-Chlorophenyl 4-Me Cinnamaldehyde 4-Me 4-Chlorophenyl 4-Me 4-Methylphenyl 4-Me 4-Methylphenyl 4-Me 4-Nitrophenyl 4-Me Phenyl 4-Me	4-Hydroxy-3-methoxyphenylH402-NitrophenylH4p2,6-DichlorophenylH4qCinnamaldehydeH4r2-ChlorophenylH4s3-FluorophenylH4t4-Me4u4u4-Chlorophenyl4-Me4vCinnamaldehyde4-Me4w4-Methylphenyl4-Me4w4-Nitrophenyl4-Me4yPhenyl4-Me4y	4-Hydroxy-3-methoxyphenyl H 40 20 2-Nitrophenyl H 4p 15 2,6-Dichlorophenyl H 4q 15 Cinnamaldehyde H 4r 10 2-Chlorophenyl H 4s 20 3-Fluorophenyl H 4s 20 3-Fluorophenyl H 4t 5 Phenyl 4-Me 4u 5 Cinnamaldehyde 4-Me 4w 10 A-Chlorophenyl 4-Me 4w 10 A-Chlorophenyl 4-Me 4w 10 A-Methylphenyl 4-Me 4w 10 A-Methylphenyl 4-Me 4x 10 A-Methylphenyl 4-Me 4y 5 Phenyl 4-Me 4y 5 Phenyl 4-Me 4y 5	4-Hydroxy-3-methoxyphenyl H 40 20 88 2-Nitrophenyl H 4p 15 89 2,6-Dichlorophenyl H 4q 15 85 Cinnamaldehyde H 4r 10 95 2-Chlorophenyl H 4s 20 84 3-Fluorophenyl H 4s 5 90 Phenyl 4-Me 4u 5 97 4-Chlorophenyl 4-Me 4w 10 96 4-Nethylphenyl 4-Me 4w 10 96 4-Nethylphenyl 4-Me 4w 10 92 4-Nitrophenyl 4-Me 4y 5 97 Phenyl 4-Me 4w 10 96 4-Nethylphenyl 4-Me 4w 10 92 4-Nitrophenyl 4-Me 4y 5 97 Phenyl 4-Me 4w 10 92 4-Nitrophenyl 4-Me 4y 5 97 Phenyl 4-Me 4w 10 95 <td>4-Hydroxy-3-methoxyphenylH402088114-1162-NitrophenylH4p1589135-1372,6-DichlorophenylH4q158574-76CinnamaldehydeH4r1095118-1202-ChlorophenylH4s208469-713-FluorophenylH4t59091-93Phenyl4-Me4u597106-1084-ChlorophenylH4w59787-89Cinnamaldehyde4-Me4w1096104-1064-Methylphenyl4-Me4w1092116-1184-Nitrophenyl4-Me4y59784-86Phenyl4-Mo4z3068128-129</td>	4-Hydroxy-3-methoxyphenylH402088114-1162-NitrophenylH4p1589135-1372,6-DichlorophenylH4q158574-76CinnamaldehydeH4r1095118-1202-ChlorophenylH4s208469-713-FluorophenylH4t59091-93Phenyl4-Me4u597106-1084-ChlorophenylH4w59787-89Cinnamaldehyde4-Me4w1096104-1064-Methylphenyl4-Me4w1092116-1184-Nitrophenyl4-Me4y59784-86Phenyl4-Mo4z3068128-129

^a Reaction conditions: benzaldehyde (1 mmol), aniline (1 mmol) and TMSCN (1.2 mmol) and Fe₃O₄@PVA-SO₃H composite (0.05 g) at room temperature in 5 mL of ethanol.

^b Isolated yield.

3.3. Comparison the efficiency of synthesized nanocatalyst

To investigate the efficiency of Fe_3O_4 @PVA-SO₃H catalyst with some other reported works for the synthesis of α -aminonitrile derivatives, the model reaction of benzaldehyde, aniline and TMSCN was compared with other previous reports. Most of last reports have disadvantages such as long time reaction, toxic solvent and low efficiency can be seen in Table 3, the results of the present work is more reliable than previous ones.

Entry	Catalyst	Condition	Time	Yield (%)	Ref
1	InCl ₃	THF/r.t.	6 h	75	[49]
2	(Bromodimethyl)sulfonium bromide	CH ₃ CN/r.t.	1 h	89	[50]
3	RuCl ₃ (20 mol %)	CH ₃ CN/r.t.	20 h	74	[51]
4	PVP-SO ₂	CH ₂ Cl ₂ /50 °C	6h	86	[52]
5	Fe(ClO ₄) ₃	CH ₃ CN/r.t.	3h	95	[53]
б	Fe ₃ O ₄ @PVA-SO ₃ H	EtOH/r.t.	5min	98	This work

Table 3. Comparison the efficiency of the synthesized nanocatalyst with other reported works.

3.4. Mechanistic evaluation

A proposed mechanism for the formation of α -aminonitrile derivatives is shown in Scheme 2. In the first step, carbonyl of aldehyde was activated by Fe₃O₄@PVA-SO₃H catalyst, intermediate **I** was formed. Iminium intermediate **II** was formed by the condensation reaction between intermediate **I** and different amines **2** in the presence of the catalyst. according to the literature [44], the nucleophilic attack of TMSCN into imine yielded the products **4a-z**.



Scheme 2. Proposed mechanism for the synthesis of 4a-z by using Fe₃O₄@PVA-SO₃H.

3.5. Catalyst recycling

A valuable property for a catalyst is its easy recovery and reusability. Therefore, in order to further evaluation of the nanocatalyst, after completion of the reaction, the catalyst was separated with an external magnet, washed with ethanol and water and dried after each run, and then reused in the next runs under the same ratio of catalyst and other reaction conditions to the model reaction. The results shows that the catalyst show no considerable reduction in activity within 10 cycles (Fig. 8). Also, recoverability and reusability of the catalyst without any decrease in catalytic activity after several times show catalyst stability.



Fig. 8. Recycling diagram of Fe₃O₄@PVA-SO₃H nanocatalyst in the synthesis of 4b.

4. Conclusions

In this research, Fe₃O₄@PVA-SO₃H with particular properties such as eco-friendly, high efficiency, green chemistry properties, non-expensive and easy separation was prepared in two steps. PVA with hydroxyl functional groups can be modified by MNPs and SO₃H groups. The nanocomposite was characterized by FT-IR, EDX, FE-SEM, XRD, TEM and TGA analyses. The FT-IR spectra demonstrated that SO₃H groups were successfully grafted onto the Fe₃O₄@PVA nanocomposite. The two major stages of degradation, corresponding to physical absorption and the organic phase of PVA and SO₃H were clearly displayed in TGA analysis. Also, XRD pattern and FE-SEM images supported the FT-IR and TGA results and confirmed the preparation of the nanocomposite. This efficient nanocomposite was also applied as a novel nanocatalyst for the

synthesis of an important α -aminonitrile derivatives in high yields. The nanocatalyst was derived out by an external magnet and reused ten times with high efficiency. This is the first report on design, synthesis and characterization of the present nanocomposite and its application as an efficient catalyst with high reusability and stability.

Acknowledgements

The authors gratefully acknowledge the partial support from the Research Council of the Iran University of Science and Technology.

Competing interests

None of the authors have any competing or conflict of interests in the manuscript.

References

- [1] D. Ghanbari, M. Salavati-Niasari, J. Ind. Eng. Chem. 24 (2014) 284-292.
- [2] F. Ansari, A. Sobhani, M. Salavati-Niasari, J. Magn. Magn. Mater. 401 (2016) 362–369.
- [3] F. Ansari, A. Sobhani, M. Salavati-Niasari, Compos. Part B. Eng. 85 (2016) 170-175.
- [4] F. Ansari, M. Bazarganipour, M. Salavati-Niasari, Mat. Sci. Semicon. Proc. 43 (2016) 34–40.
- [5] F. Ansari, A. Sobhani, M. Salavati-Niasari, RSC Adv. 4 (2014) 63946–63950.
- [6] M. Salavati-Niasari, Chem. Lett. 34 (2005) 1444-1445.
- [7] M. Salavati-Niasari, Inorg. Chem. Commun. 8 (2005) 174–177.

- [8] M. Salavati-Niasari, Chem. Lett. 34 (2005) 244-245.
- [9] M. Salavati-Niasari, J. Mol. Catal. A 229 (2005) 159-164.
- [10] M. Salavati-Niasari, Microporous Mesoporous Mater. 95 (2006) 248–256.
- [11] M. Salavati-Niasari, M. Shakouri-Aranib, F. Davar, Microporous Mesoporous Mater. 116 (2008) 77–85.
- [12] M. Salavati-Niasari, F. Davar, T. Mahmoudi, Polyhedron. 28 (2009) 1455–1458.
- [13] M. Salavati-Niasari, F. Davar, M. Dadkhah, Inorg. Chim. Acta. 362 (2009) 3969–3974.
- [14] M. Salavati-Niasari, Z. Salimi, M. Bazarganipour, F. Davar, Inorg. Chim. Acta. 362 (2009) 3715–3724.
- [15] S. Zinatloo-Ajabshir, M. Salavati-Niasari, M. Hamadanian, RSC Adv. 5 (2015) 33792– 33800.
- [16] A. Maleki, J. Rahimi, J. Porous Mat. 25 (2018) 1789–1796.
- [17] A. Maleki, Firozi-Haji R, Z. Hajizadeh, Int. J. Biol. Macromol. 116 (2018) 320-326.
- [18] M. Zhang, Y.H. Liu, Z.R. Shang, H.C. Hu, Z.H. Zhang, Catal. Commun. 88 (2017) 39-44.
- [19] A. Maleki, J. Rahimi, O.M. Demchuk, A.Z. Wilczewska, R. Jasiński, Ultrason. Sonochem.43 (2018) 262-271.
- [20] S. Mallakpour, F. Derakhshan, High Perform. Polym. 27 (2015) 458-468.
- [21] S. Xu, W. Yu, X. Yao, Q. Zhang, Q. Fu, Compos. Sci. Technol. 131 (2016) 67-76.
- [22] X. Lu, M. Niu, R. Qiao, M, Gao, J. Phys. Chem. B. 112 (2008) 14390–14394.
- [23] D. Ghanbari, M. Salavati-Niasari, M. Ghasemi-Kooch, Particuology 26 (2016) 87–94.

- [24] D. Ghanbari, M. Salavati-Niasari, M. Ghasemi-Kooch, J. Ind. Eng. Chem. 20 (2014) 3970– 3974.
- [25] S. Kayal, RV. Ramanujan, Mater. Sci. Eng. C 30 (2010) 484–490.
- [26] Y. Wei, X. Zhang, Y. Song, B. Han, X. Hu, X. Wang, Y. Lin, X. Deng, Biomed. Mater. 6 (2011) 055008.
- [27] H. Jia, F. Huang, Z. Gao, C. Zhong, H. Zhou, M. Jiang, P. Wei, Biotechnol. Rep. 10 (2016)49–55.
- [28] P. Mendoza Zélis, D. Muraca, J.S. Gonzalez, G.A. Pasquevich, V.A. Alvarez, K.R. Pirota, Sanchez F.H, J. Nanopar. Res. 15 (2013) 1613-1616.
- [29] A. Maleki, Z. Hajizadeh, R. Firouzi-Haji, Microporous Mesoporous Mater. 259 (2018) 46– 53.
- [30] M. Zhang, P. Liu, Y.H. Liu, Z.R. Shang, H.C. Hu, Z.H. Zhang, RSC Adv. 6 (2016) 106160-106170.
- [31] A. Shaabani, A. Maleki, Appl. Catal. A 331 (2007) 149–151.
- [32] J.S. Yadav, A. Antony, J. George, B.V. Subba Reddy, Curr. Org. Chem. 14 (2010) 414–424.
- [33] S.K. De, R.A. Gibbs, Tetrahedron Lett. 45 (2004) 7407–7408.
- [34] S.K. De, Beilstein J. Org. Chem. 1 (2005) 8.
- [35] A. Maleki, Z. Hajizadeh, H. Abbasi, Carbon Lett. 27 (2018) 42-49.
- [36] M.N. Chen, L.P. Mo, Z.S. Cui, Z.H. Zhang, Curr. Opin. Green Sustain. Chem. 15 (2019) 27–37.
- [37] S-Y. Kim, B. Ramaraj, K.R. Yoon, Surf. Interface Anal. 44 (2012) 1238–1242.
- [38] Z. Hajizadeh, A. Maleki, Mol. Catal. 460 (2018) 87–93.

- [39] T. Abdul Kareem, A. Anu kaliani, Arab. J. Chem. 4 (2011) 325-331.
- [40] H.Z. Li, S.C. Chen, Wang Y.Z, Compos. Sci. Technol. 115 (2015) 60-65.
- [41] A. Maleki, R. Firozi-Haji, M. Ghassemi, H. Ghafuri, J. Chem. Sci. 129 (2017) 457-462.
- [42] A. Maleki, H. Movahed, R. Paydar, RSC Adv. 6 (2016) 13657-13665.
- [43] K. Niknam, D. Saberi, M.N. Tetrahedron Lett. 51 (2010) 2959-2962.
- [44] H. Ghafuri, A. Rashidizadeh, B. Ghorbani, M. Talebi, New J. Chem. 39 (2015) 4821-4829.
- [45] M. Eslami, M.G. Dekamin, L. Motlagh, A. Maleki, Green Chem. Lett. Rev. 11 (2018) 36-46.
- [46] A. Shaabani, A. Maleki, M.R. Soudi, H. Mofakham, Catal. Commun. 10 (2009) 945-949.
- [47] A. Mobaraki, B. Movassagh, B. Karimi, ACS Comb. Sci. 16 (2014) 352-358.
- [48] X.L. Zhang, Q.P. Wu, Q.S. Zhang, J. Chem. Res. 37 (2013) 690-693.
- [49] B.C. Ranu, S.S. Dey. A. Hajra, Tetrahedron 58 (2002) 2529-2532.
- [50] B. Das, R. Ramu, B. Ravikanth, K. R. Reddy, Synthesis 9 (2006) 1419-1422.
- [51] S.K. De, Synth. Commun. 35 (2005) 653-655.
- [52] G.A. Olah, T. Mathew, C. Panja, K. Smith, G.K. Surya Prakash, Catal. Lett. 114 (2007) 1-7.
- [53] H.A. Oskooie, M.M. Heravi, A. Sadnia, F. Jannati, F.K. Behbahani, Synth. Commun. 37 (2007) 2543-2548.

Highlights

- PVA as a high performance polymer was used as non-toxic, water-soluble, high mechanical and low cost.
- Fe₃O₄@PVA-SO₃H polymer nanocomposite was synthesized successfully under mild conditions for the first time.
- The new nanocatalyst was employed as an efficient green magnetic nanocomposite catalyst for the synthesis of α-aminonitriles.
- It was easily separated from the reaction mixture by an external magnet.

• It was recovered and reused without considerable decrease in catalytic activity after ten times.