

FULL PAPER

Producing, characterizing and utilizing a novel magnetic catalyst to promote construction of *N,N'*-alkylidene bisamides

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A novel magnetic material namely $[\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{RNMe}_2\text{-SO}_3\text{H}][\text{Cl}/\text{MeSO}_3]$ (FSRNSCM) was produced. Energy-dispersive X-ray spectroscopy (EDS), field emission scanning electron microscopy (FE-SEM), FT-IR, X-ray diffraction (XRD), vibrating-sample magnetometry (VSM), thermal gravimetric (TG) and differential thermal gravimetric (DTG) analyses were utilized to characterize it. Most of the particles had nano sizes, some of which were more than 100 nm. Thereafter, FSRNSCM was applied as an efficacious and magnetically recyclable catalyst for the solvent-free condensation of arylaldehydes (1 eq.) and primary amides (2 eq.) to construct *N,N'*-alkylidene bisamides.

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KEYWORDS

Magnetic catalyst; solvent-free; $[\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{RNMe}_2\text{-SO}_3\text{H}][\text{Cl}/\text{MeSO}_3]$ (FSRNSCM); *N,N'*-alkylidene bisamide.

Introduction

Performing organic transformations using magnetic catalysts based on Fe_3O_4 core is a practical and attractive field in catalysis researches [1-12]. This class of catalysts has several unique features, including durability at high temperatures and in different chemical conditions, facile recycling, reusability, capability to graft with diverse functional groups and simple preparation of their magnetic core [1-12].

A wide range of applications have been reported for the compounds bearing bisamide functional group [13-24]; they have been used as antiviral [13], selective anion-receptors [14], antitumor [15], insecticide [16], kinase inhibitor [17] and anti-metastasis [18] agents, and for recovery of fuels [19]. Furthermore, complexes of bisamides-metal ions have been applied for absorption and selective isolation of cationic dyes [20], fluorescent sensing [21] and photocatalysis processes [21], and as

reagents in organic transformations [22,23] and MRI contrast agent [24]. A class of bisamide derivatives is *N,N'*-alkylidene bisamides that are constructed *via* the reaction of arylaldehydes (1 eq.) and primary amides (2 eq.), promoted by a catalyst [25-34].

Here, we have reported the production of a novel magnetic catalyst namely $[\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{RNMe}_2\text{-SO}_3\text{H}][\text{Cl}/\text{MeSO}_3]$ (FSRNSCM), and its characterization using EDS, FE-SEM, FT-IR, XRD, VSM, TG and DTG analyses. Thereafter, we have examined its catalytic performance for the solvent-free reaction of arylaldehydes (1 eq.) and primary amides (2 eq.) leading to *N,N'*-alkylidene bisamides.

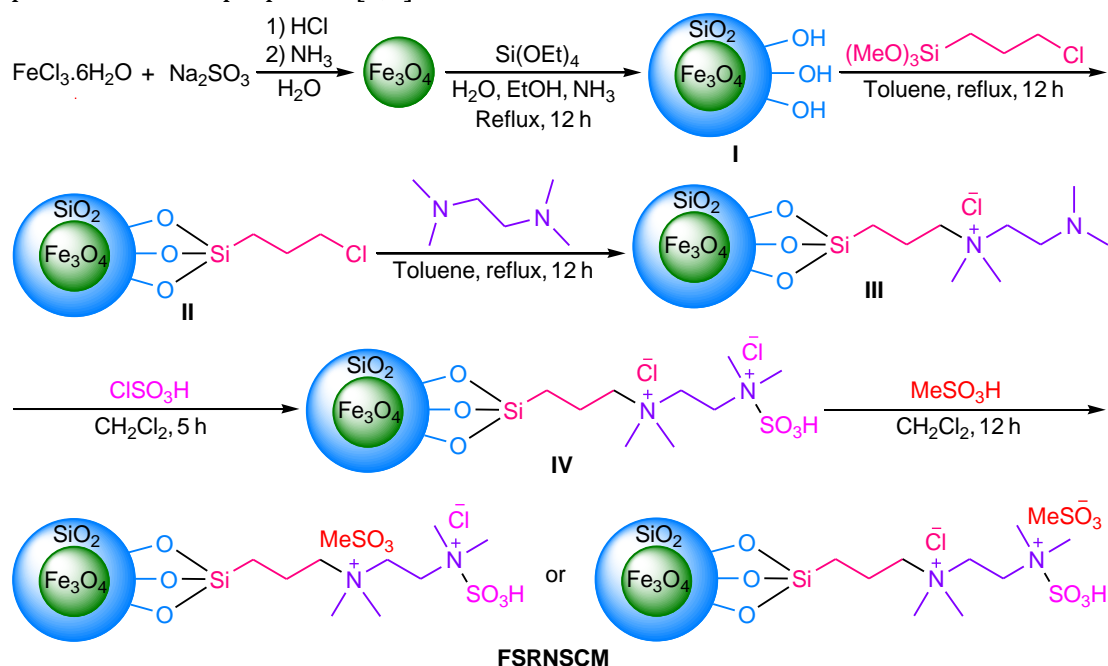
Experimental section*Chemicals and instruments*

Information on chemicals and instruments have been given in supplementary material.

Production of $[Fe_3O_4@SiO_2@RNMe_2-SO_3H][Cl/MeSO_3]$ (FSRNSCM)

Nano- Fe_3O_4 was prepared by the reported protocol [5]. Then, a mixture of nano- Fe_3O_4 (1.16 g), $Si(OEt)_4$ (3.5 mL), NH_3 solution (3.5 mL), H_2O (23 mL) and EtOH (93 mL) was stirred in reflux conditions for 12 h to construct **I** [5]. Compound **I** and (3-chloropropyl) trimethoxysilane (5 mmol, 0.92 g) in dry toluene (40 mL) was stirred and refluxed under a flow of nitrogen gas for 12 h to produce **II** [5]. Then, N^1, N^1, N^2, N^2 -tetramethylethane-1,2-diamine (5 mmol, 0.75 mL) and **II** in dry toluene (30 mL) were stirred (accompanied by refluxing) for 12 h, and compound **III** was prepared [6,7]. **III** was

added gradually to a stirring solution of $ClSO_3H$ (5 mmol, 0.34 mL) in dry methylene chloride (20 mL) at $10^\circ C$, and the mixture was stirred for 5 h at ambient temperature to afford **IV**. Finally, a solution of $MeSO_3H$ (5 mmol, 0.48 g) in dry methylene chloride (15 mL) was gradually added to **IV** at ambient temperature, and stirred for 10 h at this temperature and 2 h under reflux conditions to furnish FSRNSCM (Scheme 1). Before each step, the reaction mixture was dispersed by ultrasound irradiation; furthermore, the produced compound in each step was magnetically isolated, washed by the used solvent in that step, and dried.



SCHEME 1 The production of FSRNSCM.

General method for the construction of N,N' -alkylidene bisamides

A mixture of aldehyde (1 mmol), amide (2 mmol) and FSRNSCM (0.04 g) was stirred by a rod at $90^\circ C$. After consuming the reactants (as seen by TLC) and cooling the mixture to ambient temperature, ethyl acetate (15 mL) was added, and stirred for 2 min in reflux conditions. The unsolvable catalyst was magnetically separated, and the solvent of the

remained solution was distilled; the formed precipitate was recrystallized from ethanol (95%) to produce the pure bisamide. Selected NMR data of the products have been reported in supplementary material.

Results and discussion

The catalyst characterization

Elements including Fe, O, Si, C, N, S and Cl are existing in the structure of FSRNSCM; in the

EDS spectrum, the peaks related to the elements were seen (Figure 1). Additionally, no impurity was observed in the spectrum.

As for the FE-SEM image (Figure 2), nanoparticles and bulk particles are present in

the catalyst powder; nevertheless, most of the particles have nano sizes. In addition, the particles have different crystalline forms.

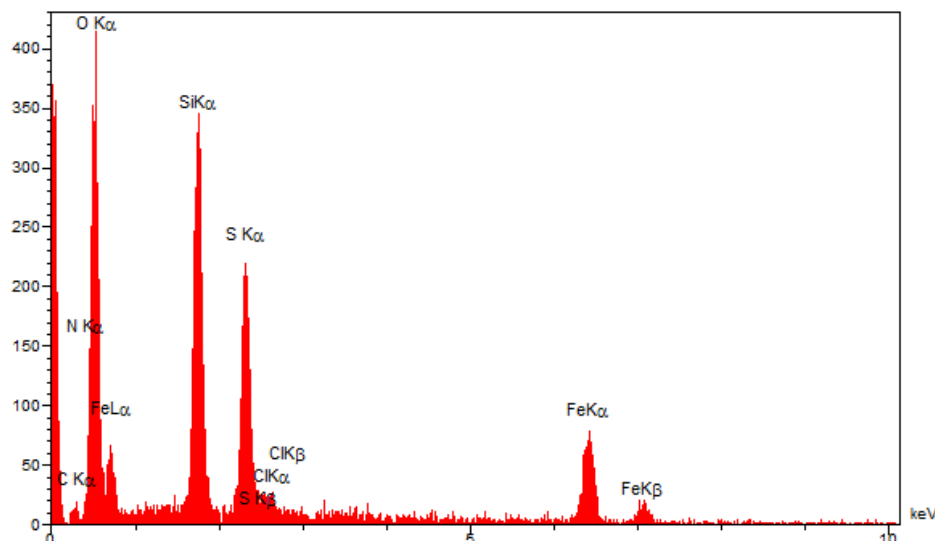


FIGURE 1 The EDS spectrum of FSRNSCM

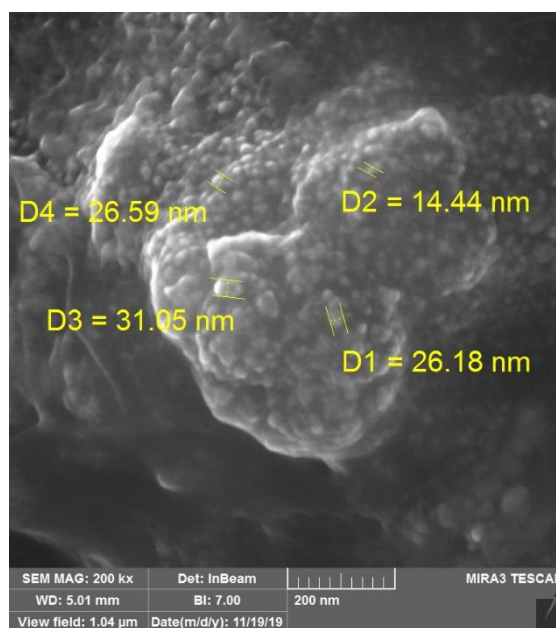


FIGURE 2 The FE-SEM micrograph of the magnetic catalyst

The FT-IR spectrum (Figure 3) confirms that the Fe_3O_4 core has been coated by SiO_2 , and the organic moieties have been anchored to the SiO_2 surface; i.e. the magnetic catalyst has been successfully prepared. The FT-IR results are illustrated in Table 1 that are in agreement with those mentioned in the chemistry sources [7,35,36].

In the XRD pattern of FSRNSCM (Figure 4), some sharp diffraction lines (at $2\theta = 35.4, 40.8, 48.5, 58.8, 62.4$ and 68.1) and a broad one (at $2\theta \approx 21.0\text{--}34.0^\circ$) were observed. The sharp peaks appeared at $35.4, 48.5, 58.8, 62.4$ and 68.1 can be related to Fe_3O_4 in the catalyst structure. The broad peak belongs to the amorphous structure of SiO_2 layer [5,7,37].

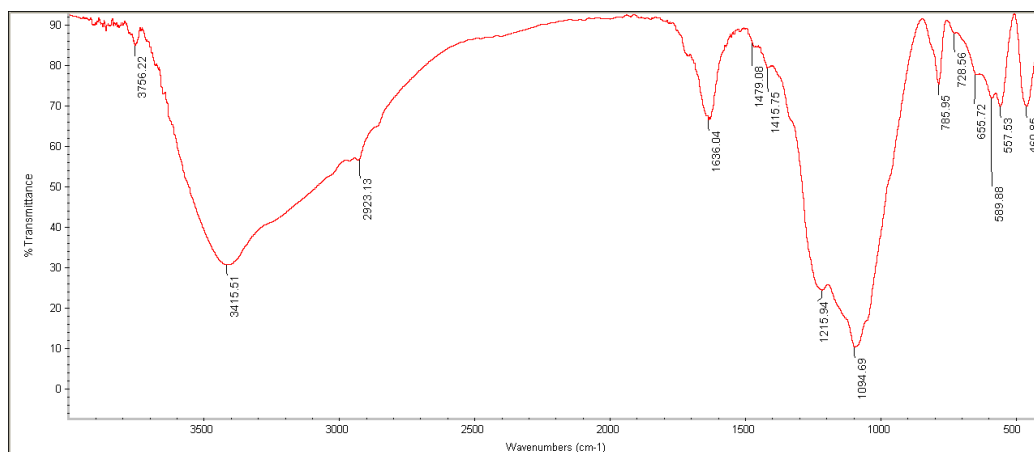


FIGURE 3 The FT-IR spectrum of FSRNSCM

TABLE 1 The FT-IR absorptions and data of FSRNSCM

Absorption (cm ⁻¹)	Relevant bond
461	Si-O (rocking)
558	-SO ₂ - (bending)
590	Fe-O
656	S-O (stretching)
786	Si-O-Si (symmetric stretching)
1095	Si-O-Si (asymmetric stretching)
1216	-SO ₂ - (asymmetric stretching)
1479	C-H (bending)
1636	O-H groups of H ₂ O adsorbed on SiO ₂ (bending)
2923	C-H (stretching)
~2260-3720	O-H groups of SO ₃ H and O-H groups on SiO ₂ (stretching)

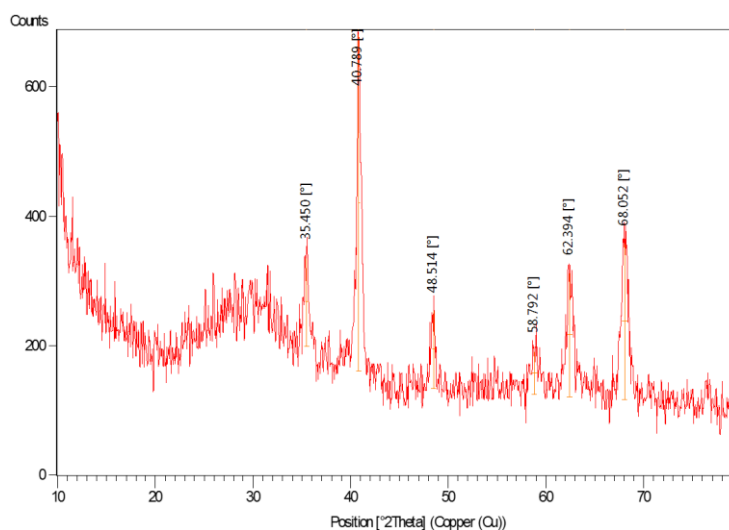


FIGURE 4 The XRD pattern of FSRNSCM

Saturation magnetization (M_s) of Fe_3O_4 which was utilized to prepare FSRNSCM was 52 emu.g^{-1} [5]; however, M_s of FSRNSCM was found to be $\sim 15.2 \text{ emu.g}^{-1}$. Figure 5 represents the VSM diagram of FSRNSCM. Decreasing M_s

of the catalyst with respect to Fe_3O_4 can be ascribed to coating SiO_2 layer on Fe_3O_4 , and bonding the organic groups with the SiO_2 surface.

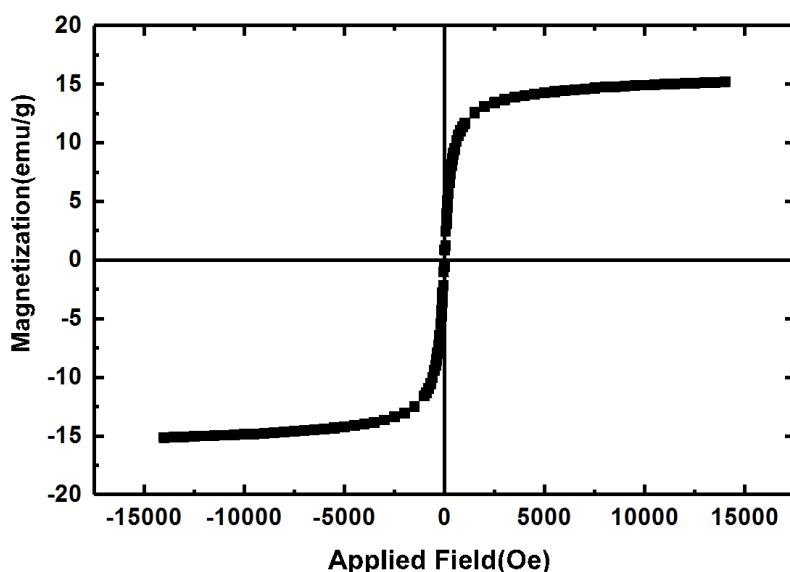


FIGURE 5 The VSM diagram of the magnetic catalyst

During thermal gravimetric analysis, FSRNSCM lost its weight in three stages (Figure 6). Vaporizing the adsorbed solvents on the catalyst surface may be the reason for the weight loss less than ~ 170 °C. During the weight loss at ~ 170 – 405 °C (with T_{\max} at 388 °C in the DTG diagram), the organic

groups bonded with the SiO_2 surface have been decomposed. The weight loss at ~ 405 – 600 °C (with T_{\max} at 478 °C in the DTG diagram) seems to be due to condensing the silanol groups. The literature corroborates these interpretations [7].

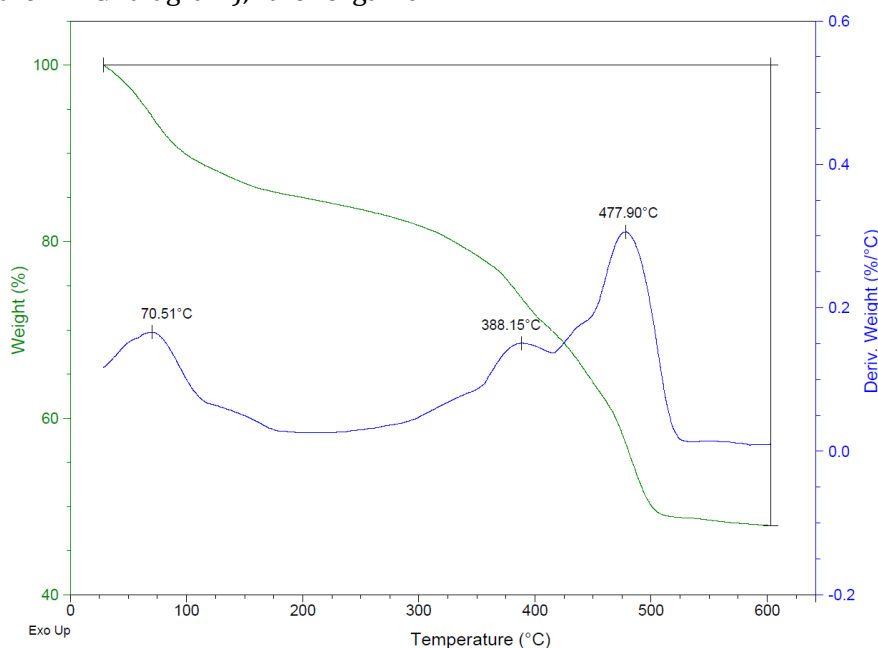


FIGURE 6 The TG and DTG diagrams of FSRNSCM

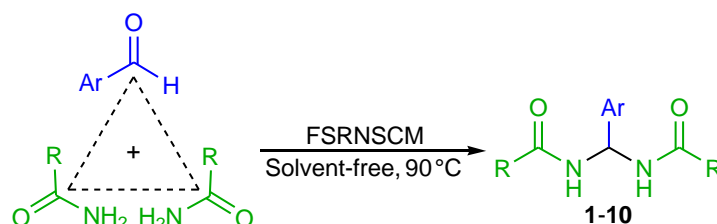
Catalytic performance of FSRNSCM to promote construction of N,N' -alkylidene bisamides

To investigate catalytic performance of FSRNSCM for the construction of N,N' -

alkylidene bisamides, 4-chlorobenzaldehyde (1 mmol) was reacted with benzamide (2 mmol) in the presence of diverse quantities of FSRNSCM (e.g. 0.032 g, 0.040 and 0.048 g) at 80, 90 and 100 °C under solvent-free

conditions (Scheme 2). The optimal reaction time and yield were acquired by application of

0.040 g of the catalyst at 90 °C (time: 15 min; yield: 97%).

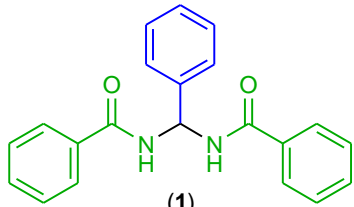
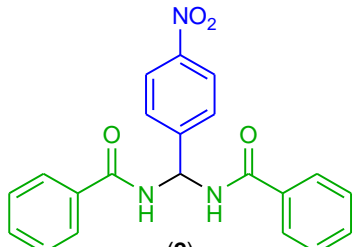
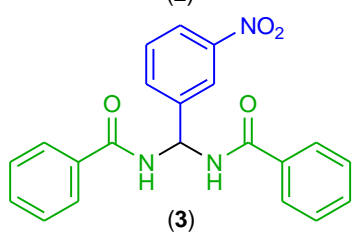
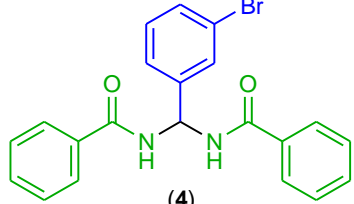


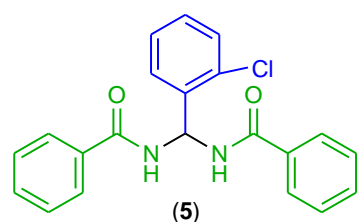
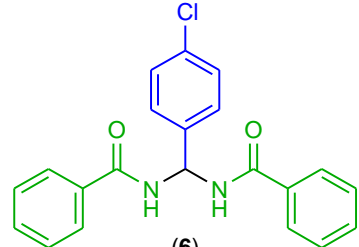
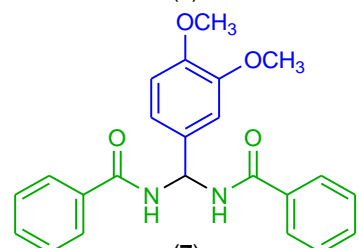
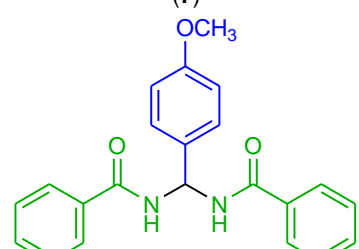
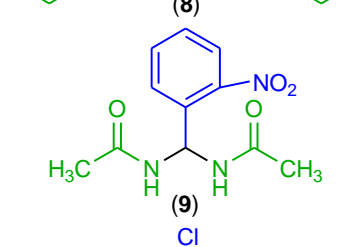
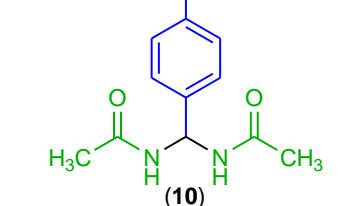
SCHEME 2 The construction of *N,N'*-alkylidene bisamides

Then, the influence of diverse arylaldehydes and primary amides (aromatic and aliphatic) on the construction of *N,N'*-alkylidene bisamides using FSRNSCM were studied; the acquired results are represented in Table 2. All reactions were effectively performed, and the relevant bisamides were constructed in short times and high yields. Nevertheless, the arylaldehydes bearing

electron-releasing substituents gave the related bisamides in longer reaction times in comparison to benzaldehyde and aldehydes possessing electron-withdrawing and halogen substituents (products **7** and **8**). Moreover, aliphatic amide (acetamide) gave the corresponding products in slightly lower yields with respect to benzamide (products **9** and **10**).

TABLE 2 The construction of *N,N'*-alkylidene bisamides using FSRNSCM

Product	Time (min)	Yield ^a (%)	M.p., °C (lit.)
 (1)	15	95	223-225 (222-224) [32]
 (2)	15	97	252-254 (255-257) [27]
 (3)	15	97	225-227 (226-228) [33]
 (4)	15	96	221-223 (223-225) [27]

	15	95	238-241 (241-242) [29]
(5)			
	15	97	253-255 (252-254) [28]
(6)			
	30	91	213-215 (216-218) [25]
(7)			
	25	94	223-225 (225-227) [31]
(8)			
	15	89	236-238 (238-240) [26]
(9)			
	15	93	268-270 (265-267) [32]
(10)			

^aIsolated yield.

The reaction of benzamide with 4-chlorobenzaldehyde was chosen to study reusability of FSRNSCM; the procedure for recycling the catalyst has been mentioned in experimental section. When the fresh catalyst was applied, the reaction time and yield were 15 min and 97%, respectively. In first recycling of FSRNSCM, the reaction time and

yield were 22 min and 93%, respectively. In second recycling, the reaction time increased up to 30 min, and the yield decreased to 78%. So, FSRNSCM was recyclable and reusable for one time with negligible diminution of catalytic activity; but, in second recycling and reusing, its catalytic activity decreased.

Conclusion

Briefly, a novel magnetic catalyst (FSRNCSM) was introduced for the construction of *N,N'*-alkylidene bisamides. This nanomaterial may also catalyze different organic reactions. High efficacy, wide scope, high yields of the products, short reaction times, usage of few amount of the FSRNCSM in the reaction, producing the bisamides without use of solvent, and good appliance with green chemistry principles are the advantages of this methodology.

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