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Organic/Inorganic Fe₃O₄@MCM-41@Zr-Piperazine: An Impressive Magnetite Nanocatalyst for *N-Tert*-Butoxycarbonylation of Amines

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 Fe_3O_4 @MCM-41@Zirconium magnetic nanoparticles modified with piperazine (Fe_3O_4 @MCM-41@Zr-piperazine), as a newly reported catalyst, shows excellent catalytic activity in *N-tert*-butoxycarbonylation of amines under the mild and solvent-free conditions. Accordingly, different derivatives of *N-tert*-butylcarbamates owning diverse aliphatic, aromatic and heteroaromatic amines were prepared efficiently. Good performance of this method for the majority of used complex or acid-sensitive substrates and facile separation of this nanocatalyst due to its superparamagnetic nature from the reaction mixture via an external magnetic field for several times are the most important striking features of this protocol.

Keywords: Fe₃O₄@MCM-41@ZrrMNPs, Piperazine, Superparamagnetic, *N-Tert*-Butoxycarbonylation, Amine. Copyright: American Scientific Publishers Delivered by Ingenta

1. INTRODUCTION

The problem of incompatibility of functional groups in the synthesis of complex organic structures is very important, which makes these syntheses often comprise protectiondeprotection steps, so that by incorporation of an appropriate protecting group that can later be easily separated, an active functional group can be temporarily disabled. This is especially important in designing and manufacturing molecules with a large number of functionalities.

The presence of amine groups in the synthesis of various biological structures such as amino acids, peptides, glycopeptides, aminoglycosides, β -lactams, nucleosides and alkaloids is very important due to their considerable nucleophilicity and basicity. Therefore, the protection of amine groups is of great importance. Amines are effectively protected as *N*-tert-butylcarbamates derivatives through *N*-tert-butoxycarbonylation, which can be related to the stability of *N*-tert-butylcarbamates against nucleophiles, bases, racemization and catalytic hydrogenation.¹⁻⁵

In this regard, different reagents and methods were introduced,^{6–14} in which despite their improvement, some deficiencies such as extended reaction times, low yields, use of organic solvents and tedious work-up

procedures are included. Moreover, being very costly and nonrecoverablity of the previously reported catalysts are as the main disadvantages of most of the existing methods.¹⁰ These negative points prevent such procedures from being perfect. Therefore, the introduction of new catalytic systems which in them the above-mentioned difficulties be excluded is still in demand.

Silica mesoporous compounds are defined as natural and artificial compounds having a pore size of 2–50 nm, classified between the two micro and macroporous classes. The reason for the focus of many studies by researchers and scientists on silica mesoporous materials like MCM-41 is their exclusive characteristics such as high surface area ($\sim 1000 \text{ m}^2 \cdot \text{g}^{-1}$), large pore size (2–50 nm), narrow pore size distribution, high thermal stability and the feasibility of using them in a broad variety of applications such as catalization, sensors, photocatalysis, isolation, absorption, etc.^{15–23}

The susceptibility of transition elements to mediate organic synthesis develops one of the most effective strategies to achieve both selectivity and efficiency in synthetic chemistry.²⁴ Possessing a high coordinating ability of zirconium (IV) compounds due to the higher charge-to-size value of Zr^{4+} in contrast with most of the metal ions leads to displaying a good Lewis acid behavior and high

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catalytic activity. Besides, many zirconium salts are now commercially accessible or reported in the literature.^{25, 26} Notwithstanding its advantages, in contrast with other transition metals, the utility of zirconium (IV) compounds as Lewis acids for organic reactions has not been utilized to a greater extent mainly.^{27–29} In last decade, due to growing environmental concerns and the necessity for efficient and green Lewis acid catalysts for different useful organic transformations, zirconium and its compounds has been more interesting.³⁰

As a proposal way to increase the accessibility of active sites of zirconium to compensate its low surface area, zirconium can be introduced into the framework of molecular sieves during their synthesis as co-condensation or direct ones, by comparison with what had been made with many other elements. In this sort of mesoporous mixed metal materials, metals are extremely dispersed and more active sites can be provided.^{31,32} Furthermore, the thermal and hydrothermal stability can be improved.³³ Moreover, to increase zirconium catalytic activity in organic reactions, functionalization by organic amine groups like piperazine as a basic functional group looks to be a good idea.

On the other hand, the modification of methods that can develop and reuse these nanocomposites at low concentrations in complex matrices will be strongly needed in order to protect the environment and to prevent the attainment of filtration and refinement catalysts. To do this, by heterogenization of the catalyst in the form of magnetic nanoparticles, the catalyst can be recovered using an external magnetic field and increased the performance of the nanocatalysis in subsequent reuses.

Accordingly, very recently we have introduced and identified "piperazine-functionalized Fe₃O₄@MCM-41@Zironium magnetic nanoparticles (Fe₃O₄@MCM-41@Zr-piperazine-MNPs)" as a new stable and highly active superparamagnetic nanocatalyst and inspected its susceptibility in preparing a variety of tetrahydro-4Hchromene and pyrano[2,3-d] pyrimidinone derivatives.³⁴ In continuance of this study and our prior reports on the application of various acidic and basic catalysts, especially zirconium based and supported reagents in organic transformations,34-38 and on the basis of the previously mentioned deficiencies in the N-Boc protection techniques which means there is a necessity to introduce more effective, applicable and environmentally benign method for the synthesis of these compounds, we were interested to investigate the applicability of Fe₃O₄@MCM-41@Zrpiperazine-MNPs in the promotion of the synthesis of N-tert-butylcarbamate molecules.

2. EXPERIMENTAL DETAILS

2.1. Material

All chemicals including $FeCl_3 \cdot 6H_2O$, $FeCl_2 \cdot 4H_2O$, tetraethylorthosilicate (TEOS), cetyl trimethylammonium

bromide (CTAB), NaOH, NaF, $ZrOCl_2 \cdot 8H_2O$, piperazine, amine derivatives, di-*tert*-butyl pyrocarbonate (Boc)₂O, were purchased with high purity from Merck chemical company (Munich). All solvents were prepared from Merck (Munich) and besides getting distilled before being used, they were kept sealed in airtight bottles as well, to minimize the absorption of atmosphere moisturize.

2.2. Characterization Techniques

All obtained products were characterized by comparing their physical constants, and IR and NMR spectroscopy with genuine samples and those reported in the literature. The purity determination of the substrate and reaction monitoring was accompanied by thin-layer chromatography (TLC) on a silica gel Polygram SILG/UV 254 plate. Measuring Melting points were accomplished by applying electrothermal IA9100 melting point device in capillary tubes. The composition and quality of pelletized samples of synthesized nanoparticles were identified via Fourier transform infrared spectroscopy (FT-IR) measurements by Perkin-Elmer Spectrum BX series in the range of 400-4000 cm⁻¹. Analyzing the crystal phases and crystallinity of synthesized MNPs were accomplished by Philips PW1730 (Netherlands) instrument in the range of $0.7^{\circ}-80^{\circ}$ (2 θ). Iron Scanning electron microphotographs (FESEM) and Energy Dispersive Spectrometer (EDS) was performed on a TESCAN MIRA II (Czech) device to study the size and morphology of particles. The pore volume, the BET surface area, and the average pore size obtained before and after the modification was characterized by N₂ adsorption/desorption which was carried out at 77 °K on a BELSORP-mini II apparatus using nitrogen. The samples were outgassed at 393 °K and 1 mPa for 12 h before adsorption measurements. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) was carried out with a Q600 TGA analyzer under argon atmosphere from 25 to 1200 °C with a heating rate of 20 °C \cdot min⁻¹ over. The magnetic properties were determined using vibrating sample magnetometry (VSM; Lake Shore 7200 at 300 kVsm).

2.3. Preparation of Piperazine-Functionalized Fe₃O₄@MCM-41@Zr-MNPs

According to our newly reported literature,³⁴ after synthesizing Fe₃O₄@MCM-41@Zr-MNPs and functionalizing with piperazine, the intended nanocatalyst was successfully prepared and characterized by a variety of techniques such as FT-IR, XRD, TEM, EDX, VSM, TGA. The results validate the structural correctness and justify the accurate performance of the catalyst (Fig. 1).

2.4. General Procedure for *N-tert*-Butoxycarbonylation of Amines

In a round-bottom flask (10 mL), 1 mmol of the amine as the substrate was added to a magnetically

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Figure 1. Preparation of Fe₃O₄@MCM-41@Zr-piperazine-MNPs.

stirred mixture of di-*tert*-butyldicarbonate [(Boc)₂O] (1 mmol, 0.218 g) and Fe₃O₄@MCM-41@Zr-piperazine nanocatalyst (0.03 g) at ambient temperature. When the reaction was fulfilled, as indicated by TLC (*n*-hexane: ethyl acetate; 7:3), the mixture was purified with ethanol. Afterward, in the presence of a magnetic stirrer bar, Fe₃O₄@MCM-41@Zr-piperazine nanocatalyst was separated, concurrently turning clear the reaction mixture. Eventually, after washing the organic phase with 10% aqueous solution of sodium bicarbonate (2×20 mL), it was dried over Na₂SO₄. The solvent was removed under reduced pressure to acquire the favorable product in good to high yields.

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2.5. Characterization of the Catalyst 2.5.1. FT-IR Analysis

Comparison of the FT-IR spectra of the Fe_3O_4 -MNPs, Fe_3O_4 @MCM-41@Zr-MNPs and Fe_3O_4 @MCM-41@Zr-piperazine-MNPs confirm the structure of the synthesized nanoparticles (Fig. 2). For the bare MNPs, Fe_3O_4 usually shows bands at ~560 and 450 cm⁻¹, from Fe–O vibrations at tetrahedral and octahedral sites, respectively.³⁹ In the FT-IR spectra of the finally prepared reagent, there are stretching vibrations of O–H bonds at ~3435 cm⁻¹ and bending vibrations of these bonds at 1635 cm⁻¹.²³ An intense peak at 1000–1250 cm⁻¹ corresponded to the Si–O stretching vibrations in the amorphous silica shell.³² Also,



Figure 2. The FT-IR spectra of (a) Fe_3O_4 -MNPs (b) Fe_3O_4 @MCM-41@Zr-MNPs and (c) Fe_3O_4 @MCM-41@Zr-Piperazine-MNPs.

the external vibrations of SiO₄ chains can be observed at ~ 1200 and 800 cm⁻¹.²³ In this spectra, the angular bending of Si–O units (450 cm⁻¹) is overlapped with the Fe–O vibrations.^{40,41} The band at 980 cm⁻¹ shows the fundamental vibrations of Zr–O–Si which overlaps with the Si–OH vibrations of Fe₃O₄@MCM-41 nanoparticles.⁴² The broad strong bond which appears at 3230 cm⁻¹ is related to the N–H bond of piperazine and the bands at 2810 cm⁻¹ and 2950 cm⁻¹ are due to CH₂ stretching vibrations.⁴³

2.5.2. Powder X-ray Diffraction (XRD) Analysis 2.5.3. BET Analysis

X-ray diffraction (XRD) patterns of the mesoporous $Fe_3O_{4^{-7}}$ MNPs showed peaks that could be indexed both mesoporous structure and MNPs (Fig. 3). The Fe_3O_4 -MNPs indicated peaks with 2θ at 29.72°, 35.57°, 43.17°, 57.15° and 62.77° which are characteristic peaks of Fe_3O_4 and matched well with the XRD pattern of the standard Fe_3O_4 from Joint Committee on Powder Diffraction Standards (JCPDS No. 19-692).⁴⁴ The three peaks with 2θ at 1.5° -10° are characteristic peaks of MCM-41.²² The peaks resemble those of magnetite, indicates the presence of magnetite in the caves of the synthesized nanocomposites. In low angle region, Fe_3O_4 @MCM-41@Zr-MNPs displayed an



Figure 3. The XRD patterns of (a) $Fe_3O_4@MCM-41@Zr-MNPs$ and (b) $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs.

obvious diffraction peak around 0.8°-1°, characteristic of the Bragg plane reflection (100), and one poorly resolved diffraction peak around 2°-4°, indexed as (110) reflection, which indicates the presence of ordered mesostructure and the incorporation of Zr^{4+} in the framework of MCM-41 as a sufficient evidence.42,45 As a more precisely description, consistent with Yang et al. findings,³² after incorporation of ZrOCl₂ into the gels, ordered Zr-MCM-41 was obtained, with the explanation that the peak intensity of (100) plane gradually decreased and the diffraction peaks of (110) and (200) planes gradually disappeared with introducing of Zr, which meant that the ordering of Zr-MCM-41 samples decreased when Zr was introduced into the framework of Fe₃O₄@MCM-41-MNPs. With loading of piperazine, there is decrease of peak intensity as well as a shift of the (100) peak for Fe₃O₄@MCM-41@Zr-MNPs to the low angle degree for Fe₃O₄@MCM-41@Zr-piperazine-MNPs. The results are similar to that observed by Xu et al.⁴⁶ upon the loading of polyethyleneimine (PEI) onto MCM-41. Accordingly, the diffraction patterns of MCM-41 did not change after the piperazine was loaded, which indicated that the structure of MCM-41 was preserved. However, the intensity of the diffraction peaks of MCM-41 did change. After loading of piperazine, the intensity of the diffraction peaks of Fe₃O₄@MCM-41@Zr-MNPs decreased, which was possibly caused by the pore filling by piperazine.

The nitrogen adsorption/desorption isotherms of Fe₃O₄@MCM-41@Zr-MNPs before and after modification with piperazine are shown in Figure 4. The isotherms correspond to type IV (in the IUPAC classification), which is typical of mesoporous materials,⁴⁷ and further confirm that the piperazine was loaded into the pore channels of the MCM-41 support. The Brunauer-Emmet-Teller (BET) surface areas, total pore volume and Barret-Joyne-Halendu (BJH) pore diameter were 597.42 m² \cdot g⁻¹, $0.3912 \text{ cm}^3 \cdot \text{g}^{-1}$, and 2.6196 nm, respectively. After loading of piperazine, the mesoporous pores were filled with piperazine, restricting the access of nitrogen into the pores at the liquid nitrogen temperature.46,48 The surface area was estimated to be 219.57 $m^2 \cdot g^{-1}$ and the residual pore volume of the Fe₃O₄@MCM-41@Zr-piperazine-MNPs is only 0.3072 $\text{cm}^3 \cdot \text{g}^{-1}$. These results correlate with the pore filling effect of the piperazine which was also reflected by the XRD characterization. As we can see, the adsorption curve is identical to the desorption curve, which indicates that materials possess broad mesoporous structure.⁴⁹ Although after piperazine impregnation, the BET surface and total pore volume area were reduced, high surface areas and total pore volume were observed in Fe₃O₄@MCM-41@Zr supported materials. Consequently, it could be concluded that well-organized mesoporous Fe₃O₄@MCM-41@Zr-piperazine-MNPs catalyst with a high surface area could be obtained in the present study.

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Figure 4. The N₂ adsorption/desorption isotherm of (a) Fe₃O₄@MCM-41@Zr-MNPs and (b) Fe₃O₄@MCM-41@Zr-piperazine-MNPs.

2.5.4. Transmission Electron Microscopy (TEM) Analysis

The TEM images of the prepared functionalized $Fe_3O_4@MCM-41@Zr-MNPs$ are shown in Figure 5. The TEM images disclosed the spherical-like particles of all samples including agglomeration of dark MNPs cores

surrounded by lighter a morphous silica shells bearing metals nanoparticles. $^{\rm 22,\,50}$

2.5.5. EDX Analysis

The EDX results of $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs are depicted in Figure 6 indicating the presence of



Figure 5. The TEM images of Fe₃O₄@MCM-41@Zr-piperazine-MNPs.

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Figure 6. The EDX profiles of Fe_3O_4 @MCM-41@Zr-piperazine-MNPs.

all expected elements (Fe, Si, Zr, N and O). The existence of Zr and N elements demonstrates the successful loading of Zr and piperazine in the next step, onto the surface of the materials.

2.5.6. TGA Analysis

Thermogravimetric analysis (TGA) was performed for characterization of Fe₃O₄@MCM-41@Zr-MNPs in



Figure 7. The TGA curves of (a) Fe₃O₄@MCM-41@Zr-MNPs and (b) Fe₃O₄@MCM-41@Zr-piperazine-MNPs.



Figure 8. The magnetic hysteresis curves of $Fe_3O_4@MCM-41@Zr-MNPs$ and $Fe_3O_4@MCM-41@Zr-piperazine-MNPs$.

comparison with Fe₃O₄@MCM-41@Zr-piperazine-MNPs (Figs. 7(a, b)).

Since more than 90% of the structure of Fe₃O₄@MCM-41@Zr-MNPs consists of iron, silica, and zirconium, so there will be no particular weight loss in this range of temperature and the observed change can be related to the desorption of the physically adsorbed water and removal of OH groups of the MCM network. However, in the case of VFe₃O₄@MCM-41@Zr-piperazine-MNPs, due to the addition of piperazine as an organic compound, a larger weight loss is observed, which confirms the catalyst structure.

2.5.7. VSM Analysis

Figure 8 represents the obtained magnetic hysteresis curves of MNPs. Both $Fe_3O_4@MCM-41@Zr-MNPs$ and $Fe_3O_4@MCM-41@Zr-piperazine-MNPs$ exhibit typical superparamagnetic behavior, as evidenced by a zero remanence and coercively on the magnetization loop.²³

The large saturation magnetization values of $Fe_3O_4@MCM-41@Zr-MNPs$ and $Fe_3O_4@MCM-41@Zr-piperazine-MNPs$ were 27.85 emu/g and 35.21 emu/g, respectively, which is sufficiently high for magnetic separation using a conventional magnet. it is deduced that the decrease in saturation magnetization of $Fe_3O_4@MCM-41@Zr-piperazine-MNPs$ is due to the grafted nonmagnetic organic group, piperazine.

3. RESULTS AND DISCUSSION 3.1. Catalytic Activity

According to the high-grade performance of our newly reported nanocatalyst in different organic transformations and due to the lack of an effective catalyst in the *N-tert*-butoxycarbonylation of amines in a method with minimal disadvantages compared to formerly reported

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Table I. <i>N-tert</i> -butoxycarbonylation of amines catalyzed by Fe ₃ O ₄ @MCM-41@Zr-piperazine-MNPs.						
Entry	Amine	Product	Time (min)	Yield (%) ^a		
1	NH ₂	NHBoc	20	80		
2	NH ₂ Me	NHBoc	31	81		
3	NH ₂	NHBoc	25	79		
4	NH ₂	NHBoc	17	85		
5	H N IP: 46.148.112 Copyright	.246 On: Mon, 18 Mar 2019 05:40:47 :: American Scientific Publishers	21	78		
6	NH ₂	Delivered by Ingenta NHBoc	20	75		

Note: a Isolated yields.

catalysts, we were interested to check the efficacy of this catalyst on the aforesaid reaction.

In this line, at first, the efficiency of Fe_3O_4 @MCM-41@Zr in the begetting of *tert*-butyl phenylcarbamate and some other derivatives was surveyed under optimized conditions tabulating in Table I. Due to the weak obtained results of these reactions that were lower than expected and in order to improve the mentioned reactions to proceeding more efficiently, we decided to investigate the influence of Fe_3O_4 @MCM-41@Zr functionalized with piperazine in the aforementioned syntheses. In this regard, to prepare these vintages in a more efficient way with slightest amount of the catalyst and generally for finding the



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most effective reaction conditions, the reaction of aniline (1 mmol) and di-*tert*-butyldicarbonate $(Boc)_2O$ (1 mmol) was chosen as an instance reaction and the various conditions including the quantities of the catalyst, solvent and temperature were tested. eventually, the best conditions are selected on the basis of these outcomes as represented in Scheme 1. Any further increase in the catalyst or temperature did not upgrade the reactions times and yields. The obtained results were tabulated in Table II.

Table II. Optimization of the amount of the catalyst, temperature and solvent in the *N*-*tert*-butoxycarbonylation of aniline catalyzed by $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs.

Entry	Amount of catalyst (g)	Solvent	Temp. (°C)	Time (min.)	Conversion
1	20	_	50	9	100
2	30	_	50	7	100
3	40	_	50	6	100
4	30	_	rt.	10	100
5	30	H_2O	50	11	100

In order to generalize the best conditions, different derivatives of *N-tert*-butylcarbamates owning diverse aliphatic, aromatic and heteroaromatic amines were prepared and the results were summarized in Table III. After termination of the reaction, a small amount of the products wasted through the work-up process and the percentage yields got less than conversion yields. By comparison of the mass of the pure product, we got from the chemical reaction (actual yield) and the theoretical maximum (predicted) yield which was calculated from the balanced equation, the percentage of the product efficiency (percentage yield) was calculated. Importantly, note that the

Entry	Amine	Product	Time (min.)	Yield (%) ^a
1	NH ₂	NHBoc	4	94
2	NH ₂	NHBoc	5	93
3	NH ₂	NHBoc	7	94
4	NH ₂	NHBoc	9	90
5	MeO IP: 46.148.112 OMe	.246 On the second seco	22	87
6	H N N	Boc	10	91
7	H N	Boc	9	89
8	NH ₂	NHBoc	7	94
9	NH ₂	NHBoc	8	91
10	NH ₂ OMe	NHBoc OMe OMe	32	85

Table III. N-tert-butoxycarbonylation of amines catalyzed by Fe₃O₄@MCM-41@Zr-piperazine-MNPs.

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Table III. Co	ntinued.			
Entry	Amine	Product	Time (min.)	Yield (%) ^a
11	NH ₂	NHBoc	30	80
12	Br NH ₂	Br NHBoc	14	91
13	Me NH ₂	Me NHBoc	45	75
14	NO ₂ NH ₂	NO ₂ NHBoc	8	85
15	↓ IP: 46.148.112 H Copyright ↓ N	.246 On: Mon, 18 Mar 2019 05:40:47 :: American Scie _N ific Publishers Delivered by Ligenta	29	86
16	S NH ₂	S NHBoc	60	65
17	NH ₂ NH ₂	NHBoc	20	92
18	N H	N Boc	90	0
19		N Boc	90	0
20	H N	Boc	90	0

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Table III. Continued.						
Entry	Amine	Product	Time (min.)	Yield (%) ^a		
21	NH ₂	NHBoc	90	0		
22	NH ₂ NH ₂	NHBoc NHBoc	90	0		

Note: a Isolated yields.

superparamagnetic nature of the synthesized nanocatalyst, as a beneficial and valuable feature, made the isolation and reuse of this catalyst very easy. As is shown in Figure 9, in the presence of an external magnet,



Figure 9. Photographs of an aqueous suspension of $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs before (a) and after (b) magnetic capture.

Fe₃O₄@MCM-41@Zr-piperazine-MNPs was easily separated from its aqueous suspension in a few minutes.

However, as indicated in Table III, primary and secondary aliphatic amines gave the relevant tertbutoxycarbonylated products in 87-94% yields in 4-22 min. (entries 1-7). Aromatic amines bearing various electron-releasing substituents such as Me, OMe and Br groups were converted to their N-tert-butylcarbamates derivatives efficiently in 75-94% yields in 7-45 min. (entries 8-14). Aromatic amines owning electroned bywithdrawing groups such as 4-nitroaniline (entry 13) proceeded sluggishly in low yield under the stated conditions. Heterocyclic amines like imidazole (entry 15) obtained the favorable products in quantitative yields and the protection of amino groups attached aromatic heterocycle went on temperately (entry 16) and preserving the acid sensitive moieties such as methoxy group is due to enough mildness of the reaction conditions (entries 5, 9 and 10). Also, amines containing two adjacent amino groups were favorably protected (entry 17). No isocyanate or urea formation

Entry	Catalyst	Amount	Condition	Time (min)	Yield (%)	[Ref.]
1	Nano-Fe ₃ O ₄	0.03 mol	EtOH/r.t.	20	99	[51]
2	Yttria-zirconia	0.02 Wt	CH ₃ CN/r.t.	14 (h)	90	52
3	$ZrCl_4$	0.1 mol	CH ₃ CN/r.t.	3	95	[53]
4	Iodine	0.1 mol	Solvent-free/r.t.	30	95	[54]
5	β -Cyclodextrine	0.1 mol	$H_2O/r.t.$	150	75	55
6	RiH	0.05 g	Solvent-free/r.t.	10	95	[56]
7	Thioglycolic acid	0.1 mol	EtOH/30-40 °C	8	95	[57]
8	Saccharin sulfonic acid	0.2 mmol	<i>n</i> -Hexane/r.t.	60	97	[58]
9	$[Dsim]HSO_4^a$	0.1 mol	EtOH/r.t.	15	90	[59]
10	$[H_2$ -cryptand 222] $(Br_3)_2^b$	0.1 mol	CH ₃ CN/r.t.	300	80	[60]
11	Thiourea	0.1 mol	Toluene/60-70 °C	40	95	[61]
12	$[Py][OTf]^c$	0.2 mmol	Solvent-free/r.t.	25	95	[62]
13	Fe ₃ O ₄ @MCM-41@Zr-piperazine	0.03 g	Solvent-free/50 °C	7	94	[This work]

Table IV. Comparison of the proficiency of $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs in the *N-tert*-butoxycarbonylation of aniline with previously reported catalysts in the studied reactions.

Notes: a1,3-Disulfonic acid imidazolium hydrogen sulfate, A kind of macrobicyclic crown ethers, Pyridinium 2,2,2- trifluoroacetate.



Figure 10. Reusability of Fe₃O₄@MCM-41@Zr-piperazine-MNPs in the *N*-*tert*-butoxycarbonylation of aniline.

was observed at all (according to IR and NMR spectroscopies). In this methodology, no rearrangement and elimination by-products were perceived at all. It is notable that bearing low nucleophilicity of some amines due to the probability of strong withdrawing electron and steric impression, cause them to resistant to this conversion and being preserved in the reaction mixture (entries 18–22).

In order to reveal the proficiency of $Fe_3O_4@MCM-41@Zr$ -piperazine-MNPs as a catalyst, this method was compared with previously reported data in terms of gained results and applied reaction conditions for *N*-tert-butoxycarbonylation of aniline (Table IV). Accordingly, it is deduced that the proposed procedure using our mentioned nanocatalyst is preferable in yields, reaction times and catalyst amount in addition to compatibility with the environment and easy separation via an external magnetic field.

3.2. Reusability of the Catalyst

To investigate the recyclability of the catalyst, it was reused five times in the *N-tert*-butoxycarbonylation of aniline. The catalyst was magnetically recovered after each run, washed with ethanol, dried in air prior to use and tested for its activity in the subsequent run. This procedure was repeated five times and each time the mentioned product was obtained by the recovered catalyst with the slight change in the reaction time and yield as shown in Figure 10.

4. CONCLUSION

In conclusion, Fe_3O_4 @MCM-41@Zr modified with piperazine, a stable and highly active superparamagnetic nanocatalyst, has been used to surveying its capability in *N-tert*-butoxycarbonylation of amines. According to the obtained results, this protocol was done successfully and has the following advantages: (i) preparing a variety of *N-tert*-butylcarbamates derivatives under the mild and solvent-free conditions. (ii) moderately short reaction times, (iii) obtaining pure products, (iv) high chemoselectivity, (v) not observing the formation of any side

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products, (vi) the modest to excellent yields of the synthesized products, (vii) good performance of this method for different substrates including the majority of complex or acid-sensitive ones, and (viii) facile separation of this superparamagnetic catalyst from the reaction mixture using an external magnetic field.

Having such superiorities of our newly proposed catalyst makes it a useful substitute to the former methodologies for the scale-up of these reactions. We are probing further applications of this superparamagnetic nanocatalyst for the other sorts of organic reactions in our laboratory.

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References and Notes

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