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Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

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S. Jafar Hoseini $^{\rm a}$, Hasan Nasrabadi $^{\rm a}$, Mahboobeh Azizi $^{\rm a}$, Alireza Salimi Beni $^{\rm a}$ & Reza Khalifeh $^{\rm b}$

^a Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj, Iran

^b Department of Chemistry, Shiraz Uuniversity of Technology, Shiraz, Iran

Accepted author version posted online: 08 Aug 2012. Version of record first published: 06 Mar 2013.

To cite this article: S. Jafar Hoseini , Hasan Nasrabadi , Mahboobeh Azizi , Alireza Salimi Beni & Reza Khalifeh (2013): Fe₃O₄ Nanoparticles as an Efficient and Magnetically Recoverable Catalyst for Friedel-Crafts Acylation Reaction in Solvent-Free Conditions, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 43:12, 1683-1691

To link to this article: http://dx.doi.org/10.1080/00397911.2012.663048

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Synthetic Communications[®], 43: 1683–1691, 2013 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2012.663048

Fe_3O_4 NANOPARTICLES AS AN EFFICIENT AND MAGNETICALLY RECOVERABLE CATALYST FOR FRIEDEL-CRAFTS ACYLATION REACTION IN SOLVENT-FREE CONDITIONS

S. Jafar Hoseini,¹ Hasan Nasrabadi,¹ Mahboobeh Azizi,¹ Alireza Salimi Beni,¹ and Reza Khalifeh²

¹Department of Chemistry, Faculty of Sciences, Yasouj University, Yasouj, Iran

²Department of Chemistry, Shiraz Uuniversity of Technology, Shiraz, Iran

GRAPHICAL ABSTRACT



Abstract Application of Fe_3O_4 nanoparticles (NPs) as a robust, very efficient, and magnetically recoverable catalyst was investigated in Friedel–Crafts acylation (FCA) of ferrocene and aromatic compounds. This reaction was performed with acid chlorides in solvent-free conditions at room temperature. The catalyst was easily separated by an external magnetic field from the reaction mixture. The separated catalyst was recycled for several consecutive runs without appreciable loss of its catalytic activity.

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Keywords Catalyst; Fe_3O_4 nanoparticles; Friedel–Crafts acylation; heterogenous catalysts; solvent free

INTRODUCTION

The application of sustainable, more efficient, and green catalysts for the production of high-quality products with minimum waste and energy demands is a key challenge in the field of chemistry. In this respect, iron catalysts have emerged as ready available, inexpensive, and environmentally friendly catalysts in organic reactions.^[1] Superparamagnetic Fe_3O_4 (NPs) have attracted worldwide attention because of their many biological and technological applications.^[2] Recently, there is growing interest in using of Fe_3O_4 NPs as magnetically supports for catalysts in

Received October 23, 2011.

Address correspondence to S. Jafar Hoseini, Department of Chemistry, Faculty of Science, Yasouj University, Yasouj 74831, Iran. E-mail: jhosseini@mail.yu.ac.ir; sjhoseini54@yahoo.com

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organic synthesis.^[3] This type of catalyst can be easily separated from the reaction mixture by employing an external magnet. Magnetically recoverable catalysts have been used in some reactions, for example, in asymmetric hydrogenation,^[3a] Suzuki coupling reaction,^[3b] and addition of alkoxy diboron reagent to C-C double bonds.^[3c] Also, use of Fe₃O₄ NPs as a catalyst without any modification is in progress because easy large-scale synthesis and facile separation of magnetic NPs with external magnetic fields are promising for industrial applications.^[4]

Friedel–Crafts acylation (FCA) is the main industrial route for the synthesis of aromatic ketones. Typically catalyzed by the Lewis acid AlCl₃, it requires more than a stoichiometric amount of catalyst because of the complexation of the Lewis acid with substrates and/or with the aryl ketone product.^[5] The design and development of a highly reactive catalyst has been an intriguing and challenging goal in FCA.^[6] Most attempts have been directed toward the use of solid acid catalysts.^[7] Different heterogenous catalysts including zeolite, clays, hetropolyacids, metal oxides, sulfated zirconia, and nafion have been studied and utilized in FCA.^[7] So far, metal oxides are particularly useful as catalysts because they are readily available, inexpensive, and noncorrosive, and they exhibit numerous edges and corners for adsorption and activation of the reactants.^[8]

In recent years, many researchers have focused their effort on the application of metal or metal oxide NPs as novel catalysts in various organic transformations. Nanoscale catalysts as a novel family of heterogeneous catalysts have many advantages such as high catalytic activity, good recyclability, and improved selectivity. However, application of nanostructure catalysts in FCA is rare.^[9] To the best of our knowledge, there is no report of application of magnetically recoverable nanocatalyst in FCA. In this article, we report the use of magnetic Fe₃O₄ NPs as an efficient catalyst in the FCA of ferrocene and some aromatic compounds with acid chlorides in solvent-free conditions at room temperature. This catalyst showed two main advantages in FCA reaction: First, it has high surface area because of nanosize of the particles and so the contact between reactants and catalyst increases considerably. Second, because of their insolubility in the reaction mixture and paramagnetic properties of Fe₃O₄ NPs, they can be separated easily from the reaction mixture by applying an external magnet.

RESULTS AND DISCUSSION

The Fe₃O₄ NPs can be easily synthesized by coprecipitation from different chemical sources.^[2] Herein, we prepare Fe₃O₄ NPs by an aging stoichiometric mixture of ferrous and ferric chloride in aqueous solutions without surfactants.^[10] Large-scale synthesis and easy separation of Fe₃O₄ NPs by an external magnetic field from the reaction mixture have encouraged us to investigate the application of Fe₃O₄ NPs as catalyst in organic reactions.^[4a] Figure 1a shows the x-ray diffraction (XRD) patterns of Fe₃O₄ NPs. A number of prominent Bragg reflections by their indices [(220), (311), (400), (422), (511), and (440)] reveal that the resultant NPs were Fe₃O₄ with a spinel structure. The size of the Fe₃O₄ NPs was also determined from x-ray line broading using the Debye–Scherrer formula given as $D = 0.9\lambda/\beta cos\theta$, where D is the average crystalline size, λ is the x-ray wavelength used, β is the angular line width at half maximum intensity, and θ is the Bragg's angle. For (311) reflection, the average size of the Fe₃O₄ NPs is estimated to be around 13 nm. Transmission electron microscopy (TEM) analysis was used for characterization (Fig. 1b). The TEM image reveals the



Figure 1. (a) The powder x-ray diffraction patterns of the Fe_3O_4 NPs. (b) TEM image shows spherical Fe_3O_4 NPs of 20–30 nm.

spherical Fe₃O₄ NPs with average sizes of 20–30 nm. The Fourier transform–infrared (FT-IR) spectra of Fe₃O₄ NPs are shown in Fig. 2. The absorbance bands at 584.3 cm⁻¹ are ascribed to Fe⁺²-O⁻², which are consistent with the reported IR spectra for spinel Fe₃O₄.^[11]

We used anisole as a standard substrate to search for a suitable condition for the Fe_3O_4 NPs to catalyze FCA (Table 1). No desired product was obtained in the absence of Fe_3O_4 NPs (Table 1, entries 1 and 2). Solvents having strong coordination ability such as tetrahydrofuran (THF) or dimethyl sulfoxide (DMSO) gave no products (Table 1, entries 7 and 8). Dichloromethane (DCM) afforded the products in better yield (Table 1, entry 12). A trace product was detected when the reaction was carried out in N,N-dimethylformamide (DMF) (Table 1, entry 10). Among the conditions tested, solvent-free was the most effective for this reaction.

Commercially available bulk powders of Fe_2O_3 and Fe_3O_4 were evaluated as catalysts in the FCA of anisole with acetyl chloride (Table 1, entries 4 and 6). Fe_3O_4 was found to be more active when compared to the other metal oxides tested (Table 1, entry



Figure 2. FT-IR spectra of Fe₃O₄ NPs.

Table 1. FCA of anisole with acetyl chloride in various reaction conditions



Entry Catalyst		Solvent	Temp.	Time (min)	Yield (%) ^a	
1	None	Solvent free	rt	120	0	
2	None	CH ₂ Cl ₂	reflux	120	0	
3	$\operatorname{Fe_2O_3}^b$	Solvent free	rt	120	0	
4	$Fe_2O_3^{b}$	Solvent free	80 ° C	120	32	
5	γ -Fe ₂ O ₃ NPs ^c	Solvent free	rt	5	90	
6	Fe ₃ O ₄	Solvent free	rt	20	70	
7	Fe ₃ O ₄ NPs	THF	rt	120	0	
8	Fe ₃ O ₄ NPs	DMSO	rt	120	0	
9	Fe ₃ O ₄ NPs	n-Hexane	rt	120	30	
10	Fe ₃ O ₄ NPs	DMF	rt	120	Trace	
11	Fe ₃ O ₄ NPs	Acetone	rt	120	Trace	
12	Fe ₃ O ₄ NPs	CH ₂ Cl ₂	rt	120	75	
13	Fe_3O_4 NPs ^d	Solvent free	rt	10	88	
14	Fe_3O_4 NPs ^e	Solvent free	rt	<3	98	

^aIsolated yield.

^bReported from Ref. 8c.

^cSynthesized according to Ref. 10.

 d 0.05 mmol Fe₃O₄ NPs. e 0.1 mmol Fe₃O₄ NPs.

6). To establish the role of nanoparticles, we studied this reaction in the presence of Fe_3O_4 and γ -Fe₂O₃ NPs. Considering the good yield, short time, and easy separation of NPs by an external magnetic field, we conclude that Fe_3O_4 NPs catalyzed the reaction better than other studied catalysts (Table 1, entry 14). Lower yield was observed when slightly decreasing the catalyst loading (0.05 mmol) (Table 1, entry 13). The optimized reaction conditions include 1.0 mmol of aromatic compound, 1.0 mmol of acid chloride, and 0.1 mmol of Fe_3O_4 NPs in solvent-free conditions at room temperature.

To investigate the generality and versatility of this method, the reaction was extended to various aromatic compounds. The results of the FCA of aromatic compounds are collected in Table 2. All of the aromatic compounds reacted very rapidly within 1–30 min. The reactions were remarkably clean, and no chromatographic separation was necessary to get the pure compounds except in entry 7. Acylation occured exclusively at the position para to –OMe and –Me for all of the compounds studied in almost quantitative yields. Also, benzoyl chloride reacted with anisole after vigorous stirring for 5 min and 95% yield of the product was obtained. The acylation of benzene with acetyl chloride was performed in 5 min with good yield (Table 2, entry 4). The FCA of anisole with acetyl chloride on a 100-mmol scale (Table 2, entry 8) proceeded just as well as in the 1-mmol reaction. In general, both aromatic and aliphatic acid chloride underwent the addition reaction smoothly to provide the desired product in moderate to good yields (Table 2, entries 1–7).

FRIEDEL-CRAFTS ACYLATION

Entry	Substrate	Acid chloride	Product	Time (min)	Yield %	Mp (°C) ref.	Ref.
1	OMe	CI	MeO	<3	98	36–39	[12]
2	Me	CI	° ·	<3	96	_	[12]
3	Me	CI	, o	5	91	_	[13]
4		CI	° C	5	94	20	[14]
5	OMe	CI CI	MeO	5	95	58–61	[15]
6	OMe	CI CI	MeO	10	95	85–87	[15]
7	Fe Fe	CI	OMe	30	70	79–81	[16]
8	OMe	CI	MeO	<3	98 ^{<i>a</i>}	36–39	[12]

Table 2. FCA of aromatic compounds

[&]quot;The reaction was carried out on a 100-mmol scale.

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A plausible mechanism for the action of Fe_3O_4 NPs in FCA is shown in Fig. 3. The reaction may proceed through the Lewis acid (Fe^{2+} or Fe^{3+} ion)–catalyzed formation of an acylium ion intermediate. The in situ–generated chloride is adsorbed on the outer surface of Fe_3O_4 NPs. This layer is considered as the first electrical layer providing negative electrical charge on the Fe_3O_4 NPs. Also, the attractive interaction of the negatively charged catalyst with acylium ion (positively charged) then results in the acylinum ion to form the secondary layer on the Fe_3O_4 NP surface. Therefore, this phenomenon precedes the acylation process (Fig. 3).^[8] Also, HCl gas is liberated and may exit the reaction mixture.

The Fe₃O₄ NPs can also be separated easily by magnetic method and reused. The NPs were washed with ethyl acetate, air dried, and used directly for the next round of reactions without further purification. It was shown that the Fe₃O₄ NPs catalyst could be recovered and reused six times without significant loss of catalytic activity (Table 3). The FeCl₃ and FeCl₂ may be generated from the reaction of Fe₃O₄ NPs with hydrogen chloride. Because the formation of ferrous and ferric chloride in the presence of HCl and Fe₃O₄ is an endothermic reaction, formation of these salts under our conditions (room temperature) is low. Also, for further confidence about the lack of responsibility of the FeCl₃ in the acylation process, we have used pure FeCl₃ as catalyst in the FCA but long reaction times are often required. We consider that hydrogen chloride gas is liberated and exit the reaction mixture. Therefore, FeCl₃ is not considered as a true catalyst in the synthesis of organic compounds during the acylation processes.

A comparison of the present protocol employing Fe_3O_4 NPs with previously known procedures shows that the present experiment is better than several known



Figure 3. Mechanism proposed for FCA in the presence of Fe₃O₄ NPs.

Entry	Time (min)	Yield (%)		
1	<3	96		
2	<3	96		
3	3	93		
4	3	90		
5	3	90		
6	3	89		

 Table 3. Reusability of the catalyst for acylation of toluene with acetyl chloride

procedures.^[5–7] According to Table 2, FCA of anisole and toluene is quickly completed at room temperature in 98% and 96% yields, respectively. Most of the other published procedures^[5–7] need long times, preparation of the catalyst support, and toxic solvent with lower isolated yield.

In summary, magnetically recoverable Fe_3O_4 NPs catalyzed the FCA reaction in solvent-free conditions at room temperature. A diverse range of aromatic ketones were obtained in moderate to good yield under mild conditions at room temperature. The separation and reuse of the magnetic Fe_3O_4 NPs were very simple, effective, and economical. In addition, the use of iron oxides as catalysts is more environmentally friendly and safer than other transition-metal catalysts.

EXPERIMENTAL

All of the reagents used in our experiments were of analytical purity from commercial source (Merck). X-ray diffraction (XRD, D8, Advance, Bruker, axs) patterns were obtained for characterization of the heterogeneous catalyst. IR spectra were obtained using a Jasco FT/IR-680 plus spectrometer. NMR spectra were recorded on a Bruker Avance DPX-250 (¹H NMR 250 MHz) or a Bruker Avance DRX 500-MHz spectrometer in CDCl₃ solvent with tetramethylsilane (TMS) as an internal standard. Transmission electron microscopy (TEM) was carried out with a Philips CM-10 TEM instrument.

Synthesis of Fe₃O₄ NPs

To prepare Fe_3O_4 NPs, 5.2 g of $FeCl_3$ and 2.0 g of $FeCl_2$ were successively dissolved in 25 ml of distilled water containing 0.85 ml of 12.1 N HCl. The resulting solution was added dropwise to 250 ml of 1.5 M NaOH solution under vigorous stirring. The last step generated an instant black precipitate. The precipitate was isolated in the magnetic field, and the supernatant was removed from the precipitate by decantation.^[10]

General Experimental Procedure

Acid chloride (1 mmol) was added to a mixture of Fe_3O_4 NPs (0.1 mmol, 10 mol%) and aromatic compound (1 mmol) at room temperature. The reaction mixture was stirred for the appropriate reaction times (monitored by TLC, Table 2).

After completion of the reaction, the magnetic stirring was stopped and the Fe_3O_4 NPs were adsorbed on the magnetic stirring bar. Ethyl acetate and water were added, and the organic phase was separated, dried over anhydrous MgSO₄. Pure corresponding product was obtained after evaporation of solvent. Characterization of these compounds was estabilished by comparison of their ¹H NMR and IR spectra with those of authentic sample.

Representative Spectral Data

Table 2, entry 1: This compound was obtained as white solid in 98% yield, IR (KBr) υ (CO) (cm⁻¹) = 1664 (Fig. S5, available online in the Supplementary Material).

Table 2, entry 2: This compound was obtained in 96% yield, IR (KBr) υ (CO) (cm⁻¹) = 1677 (Fig. S6). ¹H NMR (250 MHz, CDCl₃): δ = 2.1 (s, 3H), 2.52 (s, 3H), 6.92(d, 2H, *J* = 8.0 Hz), 7.85 (d, 2H, *J* = 8.0 Hz) (Fig. S1).

Table 2, entry 3: This compound was obtained in 91% yield, IR (KBr) υ (CO) (cm⁻¹) = 1673 (Fig. S7).

Table 2, entry 4: This compound was obtained in 94% yield, IR (KBr) υ (CO) (cm⁻¹) = 1681 (Fig. S8).

Table 2, entry 5: This compound was obtained as white solid in 95% yield; M.p=58-63 °C, IR (KBr) υ (CO) (cm⁻¹)=1650 (Fig. S9). ¹H NMR (250 MHz, CDCl₃): δ =3.79 (s, 3H), 6.89 (dd, 2H, J_1 =6.8, J_2 =2.0 Hz), 7.39–7.47 (m, 3H), 7.69 (dd, 2H, J_1 =8.5, J_2 =1.7 Hz), 7.76 (d, 2H, J=8.9 Hz) (Fig. S2).

Table 2, entry 6: This compound was obtained as white solid in 95% yield. M.p=85-87°C, IR (KBr) υ (CO) (cm⁻¹)=1654 (Figure S10). ¹H NMR (250 MHz, CDCl₃): δ = 2.35 (s, 3H), 3.81 (s, 3H), 6.89 (d, 2H, *J* = 8.8 Hz), 7.19 (d, 2H, *J* = 7.8 Hz), 7.59 (d, 2H, *J* = 8.3 Hz), 7.73 (d, 2H, *J* = 6.8 Hz) (Fig. S3).

Table 2, entry 7: This compound was obtained as orange crystalline solid in 70% yield. M.p = 79-81 °C, IR (KBr) υ (cm⁻¹): 3105, 1654 (CO), 1456, 1279 (Fig. S11). ¹H NMR (500 MHz, CDCl₃): $\delta = 2.39$ (s, 3H), 4.20 (s, 5H), 4.50 (t, 2H, J = 2.0 Hz), 4.77 (t, 2H, J = 2.0 Hz) (Fig. S4).

ACKNOWLEDGMENTS

We thank the Yasouj University Research Council and the Iranian Nanotechnology Initiative Council for financial support.

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