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Fe_3O_4 nanoparticles: A powerful and magnetically recoverable catalyst for the synthesis of novel calix[4]resorcinarenes

Bahador Karami [a,*], S. Jafar Hoseini [a], Shaghayegh Nikoseresht [b], Saeed Khodabakhshi [b]

[a] *Department of Chemistry, Yasouj University, Yasouj 75918-74831, P.O. Box 353, Iran*
[b] *Department of Chemistry, Gachsaran Branch, Islamic Azad University, Gachsaran 75817, Iran*

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Abstract

A simple synthesis of novel and known calix[4]resorcinarenes derivatives has been achieved by the condensation of resorcinol and different aromatic aldehydes in the presence of catalytic amounts of Fe_3O_4 nanoparticles under solvent-free conditions. The experimental conditions have been thoroughly optimized and established, allowing significant rate enhancements and good to excellent yields. The reactions can be run safely without using any toxic organic solvents under mild reaction conditions. The Fe_3O_4 nanoparticles were characterized by powdered X-ray diffraction (XRD), transmission electron microscopy (TEM) and FT-IR spectroscopy.

Keywords: Fe_3O_4 nanoparticles; Calix[4]resorcinarenes; Resorcinol; Arylaldehyde

The challenge in chemistry to develop the practical methods, reaction media, conditions and/or the use of materials based on the idea of green chemistry is one of the important issues in the scientific community. However, in recent years, the concept of ‘‘Green Chemistry’’ has emerged as one of the guiding principles of the environmentally organic synthesis. Recently, preparing and employing the nanoparticles (NPs) in organic synthesis has been the subject of intense interests. Using nanoparticles (NPs) offers advantages in ‘‘clean’’ chemistry since, in addition to being readily recovered; they are non-toxic and widely accessible [1]. The NP surface can be functionalized to allow the attachment of catalytically active groups [2]. Among the organic macrocyclic compounds, calix[4]resorcinarenes, a subclass of calixarenes, are large cyclic tetramers which have found application [3] as macrocyclic receptors and dendrimers in biological systems [4], nanoparticles [5], nano-capsule [6], supramolecular tectons [7], optical chemosensors [8], host molecules [9], as components in liquid crystals [10], photoresists [11], selective membranes [12], HPLC stationary phases [13], surface reforming agents [14], as ion channel mimics [15], and metal ion extraction agents [16]. Besides, some calix[4]arene show metal ions recognition properties [17,18].

It should be noted that the synthesis of calix[4]resorcinarenes was first reported in the late 19th century by Bayer based on the concentrated sulfuric acid catalyzed cyclocondensation of benzaldehyde and resorcinol [19]. Although different synthetic routes have been used for the synthesis of calix[4]resorcinarene derivatives by employing some.

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[*] Corresponding author.
E-mail address: karami@mail.yu.ac.ir (B. Karami).

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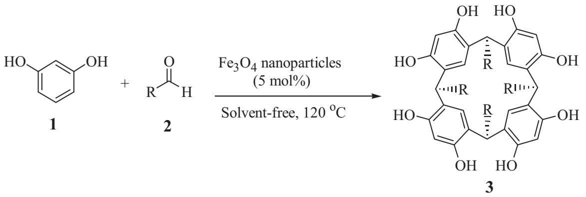


Scheme 1. General procedure for the synthesis of phenyl calix[4]resorcinarenes.

Lewis acid catalyst, however, some of the strategies suffer from the drawbacks such as low product yield, cumbersome isolation of the product and long reaction time. In the past few years, we have been involved in a program directed towards developing simple, novel, and facile methods for the preparation of organic compounds using various catalysts and readily available starting materials [20]. This stimulated our interest for further studies on the chemistry of catalysts.

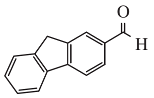
In this work, we describe a new and green strategy based on the condensation of resorcinol **1** with arylaldehyde **2** using Fe_3O_4 nanoparticle as a powerful, safe and recyclable catalyst under solvent-free conditions for the preparation of novel and known calix[4]resorcinarene derivatives **3** (Scheme 1). It should be mentioned that in a previous study, Huanwang Jing and Dongsheng Bai *et al.* reported the synthesis of cyclic carbonate from epoxide and CO_2 catalyzed by magnetic nanoparticle-supported porphyrin [21].

To investigate the suitable reaction conditions, the reaction of benzaldehyde with resorcinol was taken as a model reaction. At first, we found that in the absence of Fe_3O_4 nanoparticles, the reaction did not proceed even at high temperature. After examining the various amounts of Fe_3O_4 nanoparticles at 120 °C, it was found that the reaction can be efficiently carried out by adding 5 mol% of the catalyst under solvent-free conditions in a short time span of 15 min. The use of excessive amounts of the catalyst does not increase the yield and reaction rate. According to Table 1, under the optimized reaction conditions, a number of aromatic aldehydes were allowed to undergo reaction with resorcinol in a molar ratio of 1:1 with catalyst affording calix[4]resorcinarenes **3a**–**3i** in good to excellent yields.

In another variation, in order to comparison of catalytic activity of Fe_3O_4 powder with Fe_3O_4 nanoparticles, two parallel reactions, one through the employing the Fe_3O_4 powder and another by employing the Fe_3O_4 nanoparticles were designed. The Fe_3O_4 nanoparticles catalyst plays an important role in the completion of this process. As shown in Table 2, the product yields were moderate (58–77%) after 43–70 min, when the reactions were carried out with Fe_3O_4 powder whereas the same reactions in the presence of Fe_3O_4 nanoparticles gave good to excellent yields (78–92%) after 15–43 min under solvent less conditions.

It should be reminded that the solids with a smaller particle size (*e.g.* nano chips) react more quickly than solids with a larger particle size (*e.g.* powders). In fact, this is due to the number of sites available for a reaction to occur. So more collisions can occur and therefore more ‘‘Effective Collision’’ can happen.

Table 1
Synthesis of calix[4]resorcinarene derivatives catalyzed with Fe_3O_4 nanoparticles under solvent-free conditions at 120 °C.

Entry	Product	R	Time (min)	Yield (%)[a]	M.p., °C (decompose)
1	**3a**	C_6H_5	15	92	297
2	**3b**		80	85	298
3	**3c**	2-OH–3-MeO–C_6H_5	60	82	264
4	**3d**	2-Cl–C_6H_5	17	90	270
5	**3e**	4-MeO–C_6H_5	40	84	262
6	**3f**	4-Cl–C_6H_5	33	90	264
7	**3g**	3-Br–C_6H_5	30	95	269
8	**3h**	2-NO_2–C_6H_5	60	89	225
9	**3i**	4-Me–C_6H_5	43	78	240

[a] Isolated yields.

Table 2
Comparison of catalytic activity of Fe_3O_4 powder and Fe_3O_4 nanoparticles in the synthesis of phenyl calix[4]resorcinarene **3a**.

Entry	Product	Fe_3O_4		Fe_3O_4 nanoparticles	
		Yield (%)[a]	Time (min)	Yield (%)[a]	Time (min)
1	**3a**	77	43	92	15
2	**3g**	60	56	95	30
3	**3i**	58	70	78	43

[a] Isolated yields.

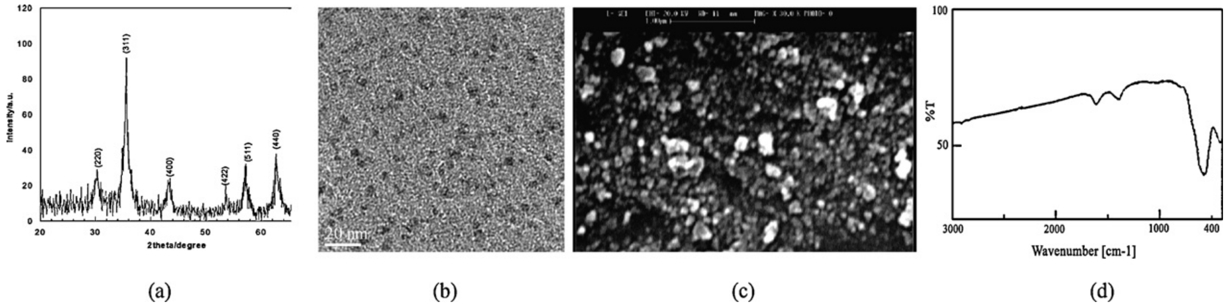


Fig. 1. (a) The powder X-ray diffraction pattern of the Fe_3O_4 nanoparticles; (b) TEM image shows spherical Fe_3O_4 nanoparticles with 10 nm; (c) SEM image of Fe_3O_4 nanoparticles; and (d) FT-IR spectra of Fe_3O_4 nanoparticles.

Fig. 1a shows the XRD patterns of Fe_3O_4 nanoparticles. A number of prominent Bragg reflections by their indices ((2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0)) reveal that the resultant nanoparticles were Fe_3O_4 with a spinel structure [22]. The size of the Fe_3O_4 nanoparticles 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 (Å), λ the X-ray wavelength used (nm), β the angular line width at half maximum intensity (radians) and θ the Bragg's angle (°). For (3 1 1) reflection at $2\theta \sim 36^\circ$, for $\beta = 0.011$ radians (0.64°), $\lambda = 1.54$ Å and $\theta \sim 18^\circ$, the average size of the Fe_3O_4 nanoparticles is estimated to be around 13 nm. Transmission electron microscopy (TEM) analyses were used for characterization (Fig. 1b). The TEM image reveals the spherical Fe_3O_4 nanoparticles with average size 10 nm. In characterization of Fe_3O_4 nanoparticles, in order to observe the morphology of the Fe_3O_4 nanoparticles in larger area, SEM images were also provided (Fig. 1c). The FT-IR spectra of Fe_3O_4 nanoparticles are shown in Fig. 1d. The absorbance bands at 584.3 cm^{-1} ascribed to Fe^{2+}–O^{2-} which are consistent with the reported IR spectra for spinel Fe_3O_4 [23,24].

Although the exact mechanism for this reaction over Fe_3O_4 nanoparticles is not so clear, a feasible pathway might involve the complexation of iron NPs with the carbonyl, thereby acting as a Lewis acid, and also playing a complex role in promoting the dehydration and cyclization steps.

The need to implement green chemistry principles is a driving force towards the development of recoverable and reusable catalysts and avoidance of the use of toxic and inexpensive organic solvents. It should be mentioned that the main disadvantage of many of the reported methods for the synthesis of calix[4]resorcinarenes is that the catalysts are destroyed in the work-up procedure and cannot be recovered or reused. However, we found that magnetic nano particles Fe_3O_4 showed high catalytic activity with short reaction time and can be recovered and reused for five cycles without significant loss of activity.

1. General procedure for the preparation of Fe_3O_4 nanoparticles

To prepare Fe_3O_4 nanoparticles, 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 mol/L HCl. The resulting solution was added dropwise into 250 mL of 1.5 mol/L 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 [25].

2. General procedure for the rapid synthesis of calix[4]resorcinarene derivatives

A mixture of resorcinol **1** (1 mmol), aryl aldehyde **2** (1 mmol), and Fe_3O_4 nanoparticles (5 mol%) was stirred and heated at 120 °C in a preheated oil bath for appropriate time (Table 2). After completion of the reaction as indicated by TLC (ethyl acetate/*n*-hexane 7:3), the reaction mixture was cooled down to room temperature and dissolved in methanol to separate the catalyst through the magnetic absorption by a magnet. After separating the catalyst, the solution was heated and filtered to afford the pure product **3**. At the end of the reaction, the separated catalyst was washed with diethyl ether, dried at 130 °C for 1 h, and reused in another reaction.

To conclude, a green synthetic route to novel and known calix[4]resorcinarene derivatives using Fe_3O_4 nanoparticles under solvent-free conditions was presented. Using this method not only gives high yield and purity but also is a cheap, speedy, facile, and eco-friendly method throughout the course of the reaction.

References

[1] S.M. Baghbanian, M. Farhang, R. Baharfar, Chin. Chem. Lett. 22 (2011) 555.
[2] (a) U. Laska, C.G. Frost, P.K. Plucinski, G.J. Price, Catal. Lett. 122 (2008) 68;
(b) H. Nagabhushana, S. Sandeep Saundalkar, L. Muralidhar, et al. Chin. Chem. Lett. 22 (2011) 143;
(c) P. Tundo, P.T. Anastas, Green Chemistry: Challenging Perspectives, Oxford Science, Oxford, 1999.
[3] (a) H.W. Wang, Y.Q. Feng, J.Q. Xue, et al. Chin. Chem. Lett. 19 (2008) 901;
(b) B.Q. Hong, F.F. Yang, H.Y. Guo, et al. Chin. Chem. Lett. 20 (2009) 1039.
[4] (a) B. Botta, M.D.I. Cassani, D. Misiti, et al. Curr. Org. Chem. 337 (2005) 9;
(b) Y. Ge, C. Yan, J. Chem. Res. 279 (2004) 33.
[5] J.E. Gualbert, P. Shahgaldian, A. Lazar, et al. J. Inclusion Phenom. Macrocycl. Chem. 37 (2004) 48.
[6] M.W. Heaven, C.L. Rastonb, J.L. Atwood, Chem. Commun. 892 (2005) 7.
[7] L.R. MacGillivray, J.L. Atwood, J. Solid State Chem. 199 (2000) 152.
[8] T.W. Bell, N.M. Hext, Chem. Soc. Rev. 589 (2004) 33.
[9] G.M. Martinez, C.R. Teran, O.A. Tlapanco, et al. Fullerene Sci. Technol. 475 (2000) 8.
[10] K. Yonetake, T. Nakayama, M. Ueda, J. Mater. Chem. 761 (2001) 11.
[11] T. Nakayama, D. Takhashi, K. Takeshi, et al. J. Photopolym. Sci. Technol. 347 (1999) 12.
[12] N. Tbeur, T. Rhlalou, M. Hlaibi, et al. Carbohydr. Res. 409 (2000) 329.
[13] O. Pietraszkiewicz, M. Pietraszkiewicz, J. Inclusion Phenom. Macrocycl. Chem. 261 (1999) 35.
[14] K. Ichimura, E. Kurita, M. Ueda, Eur. Pat. EP 671220 (1995).
[15] N. Yoshino, A. Satake, Y. Kobuke, Angew. Chem. Int. Ed. 457 (2001) 40.
[16] E. Gaunert, H. Barnier, L. Nicod, et al. Sep. Sci. Technol. 2309 (1997) 32.
[17] H.W. Wang, Y.Q. Feng, C. Chen, J.Q. Xue, Chin. Chem. Lett. 20 (2009) 1271.
[18] Q. Peng, X.H. Tang, Chin. Chem. Lett. 20 (2009) 13.
[19] (a) A. Bayer, Ber. Dtssch. Chem. Ges. 5 (1872) 25;
(b) A. Bayer, Ber. Dtssch. Chem. Ges. 5 (1872) 280.
[20] (a) B. Karami, S. Khodabakhshi, M. Nikrooz, Polycyclic Aromat. Compd. 97 (2011) 31;
(b) S.E. Mallakpour, B. karami, B. Sheikholeslami, Polym. Int. 98 (1998) 45.
[21] D. Bai, Q. Wang, Y. Song, et al. Catal. Commun. 684 (2011) 12.
[22] J. Park, K. An, Y. Hwang, et al. Nat. Mater. 891 (2004) 3.
[23] Y. Liu, P. Liu, Z. Su, et al. Appl. Surf. Sci. 2020 (2008) 255.
[24] S.C. Wuang, K.G. Neoh, E.T. Kang, et al. J. Mater. Chem. 3354 (2007) 17.
[25] Y.S. Kang, S. Rishbud, J.F. Rabolt, et al. Chem. Mater. 2209 (1996) 8.