Scientia Iranica C (2012) 19 (6), 1597–1600

Sharif University of Technology

Scientia Iranica

Transactions C: Chemistry and Chemical Engineering

www.sciencedirect.com

Research note

Controlled microwave-assisted synthesis of $ZnFe_2O_4$ nanoparticles and their catalytic activity for O-acylation of alcohol and phenol in acetic anhydride

F. Matloubi Moghaddam [a,*], M. Doulabi [a], H. Saeidian [b]

[a] *Department of Chemistry, Sharif University of Technology, Tehran, P. O. Box 11155-9516, Iran*

[b] *Department of Science, Payame Noor University (PNU), Zanjan, Iran*

Received 12 March 2012; revised 28 July 2012; accepted 15 September 2012

KEYWORDS

Zinc ferrite;
Controlled microwave heating;
Nanoparticles;
Catalytic activity;
Co-precipitation.

Abstract $ZnFe_2O_4$ nanoparticles have been successfully prepared through a controlled microwave–assisted co-precipitation. X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FT-IR), Scanning Electron Microscopy (SEM) and Vibrating Sample Magnetometer (VSM) were used for the structural, morphological and magnetic investigation of the product. SEM micrographs of $ZnFe_2O_4$ nanopowder also reveal that nanoparticles have spherical shape. Average particle size was obtained as 12 nm from XRD. Catalytic activity of $ZnFe_2O_4$ nanopowder for *O*-acylation of alcohol and phenol has been investigated. A trace amount of $ZnFe_2O_4$ has been effectively used as a nanocatalyst for the acylation of alcohol and phenol in acetic anhydride.

© 2012 Sharif University of Technology. Production and hosting by Elsevier B.V. All rights reserved.

1. Introduction

Nanocrystalline spinel ferrites belong to a family of magnetic materials that can be used in many areas, such as magnetic devices, permanent magnets, hard disc recording media, read–write heads, active components of ferro fluids, color imaging, magnetic refrigeration, detoxification of biological fluids, magnetically controlled transport of anti-cancer drugs, Magnetic Resonance Imaging (MRI) contrast enhancement and magnetic cell separation [1–8]. Recently, some composite oxides such as spinel AB_2O_4 were found to be more attractive than single-metal oxides for their better selectivity and/or sensitivity to certain gases. In particular, the spinel-structured $ZnFe_2O_4$, in which the transition metal cation Zn^{2+} was incorporated into the lattice of the parent structure of ($Fe^{2+}Fe_2^{3+}O_4$), was established to be a promising material in detecting reducing gases such as CO, CH_4 and in the chemistry as catalyst [9–12]. Zinc ferrite has long attracted interests because of its intriguing magnetic properties compared with other spinel ferrites. The traditional bulk $ZnFe_2O_4$ belongs to the normal spinel type with antiferromagnetic properties below the Neel temperature of about 10.5 K and behaves paramagnetic at room temperature. All Zn^{2+} ions reside in the tetrahedral sites (*A* sites) and Fe^{3+} ions are in the octahedral sites (*B* sites). In 1961, Neel suggested that small antiferromagnetic particles can exhibit super-paramagnetism and weak ferromagnetism due to uncompensated spins in the two sublattices.

In recent years, $ZnFe_2O_4$ nanoparticles prepared using varied methods, such as traditional ceramic synthesis, [4] aerogel procedure, [3] low-temperature hydroxide co-precipitation and hydrothermal synthesis, [13,14] have been studied and observed to be ferrimagnetic or super-paramagnetic. Development of new routes for the synthesis of solids is an integral aspect of materials chemistry and physics. Some of the important reasons for this are the continuing need for fast and energy-efficient techniques, and the necessity to avoid competing reactions in the known processes. Recently, a new deposition technique has reported: microwave activated chemical bath deposition (MW-CBD). This technique is based on the microwave heating of a precursor solution in which the substrate is immersed [15–17]. Microwave-hydrothermal synthesis is generally quite faster, simpler and more energy-efficient. The exact

* Corresponding author. Tel.: +98 2166165309; fax: +98 2166012983.
E-mail address: matloubi@sharif.edu (F. Matloubi Moghaddam).

Peer review under responsibility of Sharif University of Technology.

Production and hosting by Elsevier

1026-3098 © 2012 Sharif University of Technology. Production and hosting by Elsevier B.V. All rights reserved.
doi:10.1016/j.scient.2012.10.013

Archive of SID

www.SID.ir

nature of microwave interaction with reactants during the synthesis of materials is somewhat unclear and speculative. Energy transfer from microwave to the material is believed to occur either through resonance or relaxation, which results in rapid heating. This knowledge is widely used as the basis in the discussion of the reaction mechanism.

In our previous works, we have reported the synthesis of some nanoparticles and their application in organic reactions [18–20] *and have explored potential ability of microwave as an energy source for synthesis in our laboratory* [21,22]. Herein, we combined co-precipitation method with microwave technique (thereafter named microwave co-precipitation) and synthesized uniform $ZnFe_2O_4$ nanoparticles. This technique involves nucleation and growth from homogeneous solution. In this method, processes such as coarsening and aggregation can compete with nucleation and growth in modifying the particle size distribution. The micelles, [23] capping agents [24] and polymer stabilization [25] could be used to arrest the growth. We used sodium dodecylsulfate to create the micelles. The catalytic activity of $ZnFe_2O_4$ nanopowder for O-acylation of alcohol and phenol has also been studied.

2. Experimental

2.1. General

The microwave-assisted reactions were performed in a single-mode microwave cavity (Ethos, MR, 2.45 GHz, maximum power 1000 W), producing controlled irradiation. Reaction temperatures were determined and controlled *via* the built-in, on-line sensor. The microwave synthesis reactor was equipped with a water-cooled condenser. X-ray diffraction was preformed with a Siemens D5000 X-ray diffractometer using graphite-monochromatized high-intensity Cu Kα radiation. Scanning electron microscopy images were obtained using a Vega Tscan. Fourier transform infrared spectroscopy was performed using a Nicollet (Magna 500). The magnetic measurements were carried out with a Superconducting Quantum Interference Device (SQUID) magnetometer.

2.2. Synthesis of $ZnFe_2O_4$ nanoparticles

$ZnFe_2O_4$ nanoparticles were synthesized *via* a controlled microwave-assisted co-precipitation. The microwave co-precipitation process was similar to the conventional co-precipitation. In a typical synthesis procedure, $Fe(NO_3)_3 \cdot 9H_2O$ (1.25 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.625 mmol) were dissolved in 10 mL water. Sodium dodecylsulfate (SDS, 7.5 mmol) was dissolved in 20 mL water and was added to the solution. After 10 min stirring, the PH 11 of the solution was adjusted by adding the solution of sodium hydroxide 2 M. The final mixture was heated in a controlled microwave cavity for 20 min. During the microwave irradiation in the first 5 min, the temperature of the solution reached to 90 °C, then the temperature is maintained at 90 °C for further 15 min. The resulting solid product was collected by filtration, washed several times with deionized water and ethanol, then powders calcined at 400 °C for 4 h.

2.3. General procedure for O-acylation alcohol and phenol in acetic anhydride

In a general experimental procedure, to a mixture of $ZnFe_2O_4$ nanoparticles (12 mg) and acetican hydride (2 mmol), alcohol or phenol (1 mmol) was added. The reaction mixture was stirred for the required period of time at 55 °C. The progress of the reaction was followed by TLC or GC. After completion of the reaction, the product was extracted with CH_2Cl_2 and filtered to remove $ZnFe_2O_4$. The organic phase was treated with saturated sodium bicarbonate solution and dried over anhydrous sodium sulfate. The solvent was removed under vacuum to afford the pure product. The products are characterized on the basis of 1_H NMR and GC-MS.

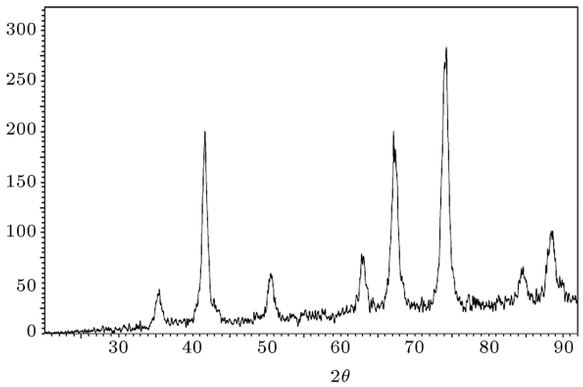

Figure 1: XRD powder pattern of $ZnFe_2O_4$.

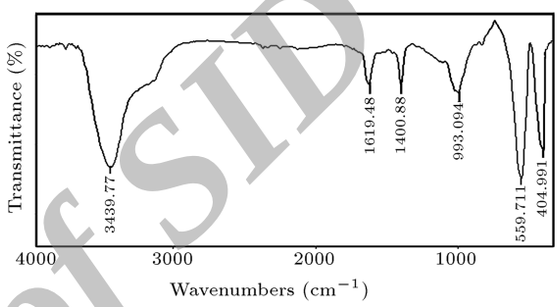

Figure 2: The FT-IR spectra of $ZnFe_2O_4$ nanoparticles.

3. Results and discussion

3.1. X-ray analysis

The XRD powder pattern of the synthesized $ZnFe_2O_4$ is shown in Figure 1. All the diffraction peaks can be indexed to the cubic structured $ZnFe_2O_4$ with cell constant $a = 8.350 \pm 0.02$ Å. The average crystallite size was estimated by the Scherrer equation, $L = 0.9\lambda/\beta \cos\theta_B$, from the X-ray peak broadening (full-width at half maximum, FWHM) of the most intense peak (4 4 0), where λ is the wavelength $= 1.7889$ Å, θ_B is the angle of Bragg diffraction, and $\beta = B - b$. B is the full FWHM and b represents the instrumental line broadening [26]. Crystallite size of synthesized $ZnFe_2O_4$ powder, based on this equation, was calculated as about 12 nm.

3.2. Fourier transform infrared spectroscopy

Two main broad metal-oxygen bands are seen in the FT-IR spectra of all spinels and ferrites in particular [27]. The band, observed at around 559 cm^{-1} for $ZnFe_2O_4$ can be assigned to tetrahedral Zn^{2+} stretching and the band observed at 405 cm^{-1} involves the Fe^{3+} vibration at the octahedral site (Figure 2).

Archive of SID

www.SID.ir

Table 1: The results of O-acylation of alcohol and phenol using $ZnFe_2O_4$ nanopowder in acetic anhydride.

$$ROH + A_{C2}O \xrightarrow[\text{Solven-free, 55 °C}]{\text{Catalyst (5 mol\%)}} ROAc + AcOH$$

$$R = Ph, n\text{-}Bu, Benzyl$$

Entry	*R*	Catalyst	Reaction time (min)	Yield (%)
1	N-butyl	$ZnFe_2O_4$	150	≥96
2	Benzyl	$ZnFe_2O_4$	150	≥96
3	Phenyl	$ZnFe_2O_4$	240	≥96

3.3. SEM observations

The morphology and particle sizes of the prepared sample were determined by SEM. The SEM micrograph of $ZnFe_2O_4$ is shown in Figure 3. It indicates that sphere-like $ZnFe_2O_4$ nanostructures obtained by this method are uniform in both morphology and particle sizes. The regular distribution of nanoparticles is attributed to the uniform temperature gradient maintained on the substrate by controlled microwave heating.

3.4. Magnetic studies

Magnetization measurement of the prepared sample was carried out using a SQUID magnetometer with a magnetic field up to 8 kOe. The section of hysteresis loops of $ZnFe_2O_4$ are shown in Figure 4. As shown in Figure 4, the magnetization curves at 300 K show the absence of hysteresis, immeasurable remanence and coercivity. This is a typical characteristic of nano-sized particles that are superparamagnetic at room temperature and present finite coercivity below the blocking temperature.

3.5. Evaluation of catalytic activity of $ZnFe_2O_4$ nanoparticles for o-acylation alcohol and phenol

The surface of metal oxides exhibit both acid and base character [28]. This is the characteristic of many metal oxides, especially TiO_2, Al_2O_3, ZnO, *etc*.. We report herein, our results onthe O-acylation of alcohol and phenol using catalytic amount of $ZnFe_2O_4$ nanopowder at 55 °C under solvent-free conditions. In any metal oxide, surface atoms make a distinct contribution to its catalyst activity. In powder particles, the number of surface atoms is a large fraction of the total. Therefore, catalytic activity of nanopowder is more than bulk powders. As a result, $ZnFe_2O_4$ nanopowder is coordinated better than bulk one, while the $ZnFe_2O_4$ nanopowder has more surface atoms, participating at the reaction (see Table 1).

A brief comparison of catalytic activity of some recently reported catalyst for acetylation of phenol with Ac_2O is given in Table 2. It is obvious from the data that the $ZnFe_2O_4$ nanoparticles prepared in the present work exhibit a good catalytic activity for acetylation of phenol. Easy magnetic separation of the catalyst eliminates the catalyst filtration process after completion of the reaction, which is an additional suitable aspect of our catalyst.

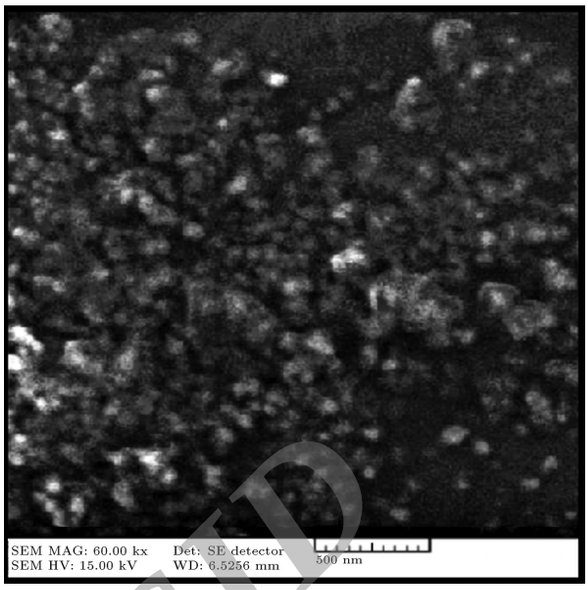

Figure 3: SEM micrograph of the $ZnFe_2O_4$ nanoparticles in the presence of SDS.

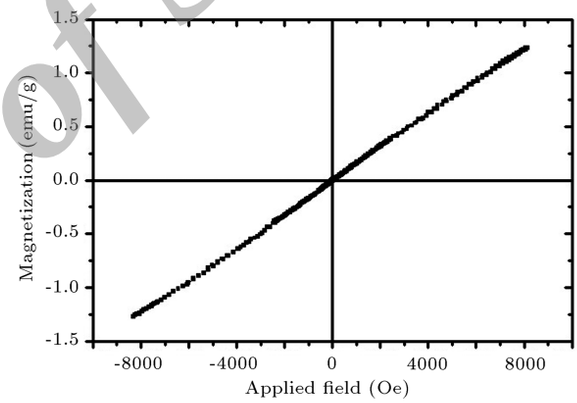

Figure 4: Hysteresis loops of the $ZnFe_2O_4$ nanoparticles at 300 K.

The reusability of catalyst ($ZnFe_2O_4$ nanoparticles) was checked in the acetylation of benzyl alcohol with acetic anhydride. The obtained results showed that after using the catalyst for several times (three consecutive times were checked), the corresponding acetate was obtained without any decrease in its yield.

Table 2: Acetylation of phenol with Ac_2O catalyzed by $ZnFe_2O_4$ nanoparticles prepared in the present work in comparison with that of some recently reported catalyst.

Catalyst	Condition	Amount of catalyst	Solvent	Time (min)	Yield (%)
$Bi(TFA)_3$ [29]	Reflux	5 (mol%)	CH_3CN	120	90
SiO_2-$ZnCl_2$ [30]	80 °C	0.4 g	CH_3CN	3.5 h	83
$CuSO_4 \cdot 5H_2O$ [31]	*rt*	2 (mol%)	–	90	92
$(NH_4)_2 \cdot 5H_{0.5}PW_{12}O_{40}$ [32]	*rt*	0.5 (mol%)	CH_3CN	120	40
$RuCl_3$ [33]	40 °C	5 (mol%)	[bmim][PF_6]	120	89
$ZnFe_2O_4$	55 °C	5 (mol%)	–	240	≥96

Archive of SID

www.SID.ir

4. Conclusions

$ZnFe_2O_4$ nanoparticles were successfully prepared by a controlled microwave–assisted co-precipitation. According to the results, the microwave co-precipitation inclined to form homogeneous particles which are about 12 nm in size. $ZnFe_2O_4$ nanoparticles have strong catalytic activity for O-acylation of alcohols and phenols.

References

[1] Nikolaev, V.I., Bushina, T.A. and Chan, K.E. "On magnetic properties of superparamagnets in the Curie point region", *J. Magn. Magn. Mater.*, 213(1), pp. 213–218 (2000).

[2] Kodama, R.H. and Bushina, T.A. "Magnetic nanoparticles", *J. Magn. Magn. Mater.*, 200(1), pp. 359–372 (1999).

[3] Lue, J.T. "A review of characterization and physical property studies of metallic nanoparticles", *J. Phys. Chem. Solids*, 62(9), pp. 1599–1612 (2001).

[4] Kim, D.K., Zhang, Y., Kehr, J., Klason, T., Bjelke, B. and Muhammed, M. "Characterization and MRI study of surfactant-coated superparamagnetic nanoparticles administered into the rat brain", *J. Magn. Magn. Mater.*, 225(1), pp. 256–261 (2001).

[5] Zhou, Z.H., Xue, J.M., Wang, J., Chan, H.S.O., Yu, T. and Shen, Z.X. "$NiFe_2O_4$ nanoparticles formed in situ in silica matrix by mechanical activation", *J. Appl. Phys.*, 91(9), pp. 6015–6020 (2002).

[6] Misra, R.D.K., Kale, A. and de Hosson, J.Th. "Some aspects of nanocrystalline nickel and zinc ferrites processed using microemulsion technique", *Mater. Sci. Technol.*, 19(11), pp. 1617–1621 (2003).

[7] Köseoğlu, Y. and Aktas, B. "ESR studies on superparamagnetic Fe_3O_4 nanoparticles", *Phys. Status Solidi C*, 1(12), pp. 3516–3520 (2004).

[8] Köseoğlu, Y., Kavas, H. and Aktas, B. "Surface effects on magnetic properties of Fe_3O_4 nanoparticles", *Phys. Status Solidi A*, 203(7), pp. 1595–1601 (2006).

[9] Chu, X.F., Liu, X.Q. and Meng, G.Y. "Preparation and gas sensitivity properties of $ZnFe_2O_4$ semiconductors", *Sensor. Actuat. B-Chem.*, 55(7), pp. 19–22 (1999).

[10] Manorama, S.V., Satyanarayana, L. and Reddy, K.M. "Synthesis of nanocrystalline $Ni_{1-x}Co_xMn_xFe_{2-x}O_4$: a material for liquefied petroleum gas sensing", *Sensor. Actuat. B-Chem.*, 89(1), pp. 62–67 (2003).

[11] Klimkiewicz, R., Wolska, J., Przepiera, A., Przepiera, K., Jablonski, M. and Lenart, S. "The zinc ferrite obtained by oxidative precipitation method as a catalyst in *n*-butanol conversion", *Mater. Res. Bull.*, 44(1), pp. 15–20 (2009).

[12] Woslka, J., Przepiera, K., Grabowska, H., Przepiera, A., Jablonski, M. and Klimkiewicz, R. "$ZnFe_2O_4$ as a new catalyst in the C-methylation of phenol", *Res. Chem. Intermediat.*, 34(1), pp. 43–52 (2008).

[13] Nathani, H. and Misra, R.D.K. "Surface effects on the magnetic behavior of nanocrystalline nickel ferrites and nickel ferrite-polymer nanocomposites", *Mater. Sci. Eng. B*, 113(3), pp. 228–235 (2004).

[14] Kasapoglu, N., Birsöz, B., Köseoglu, Y., Baykal, A. and Toprak, M.S. "Synthesis and magnetic properties of octahedral ferrite $Ni_\chi Co_{1-\chi}Fe_2O_4$ nanocrystals", *Cent. Eur. J. Chem.*, 5(2), pp. 570–580 (2007).

[15] Zhu, Y.J., Wang, W.W., Hu, X.L. and Qi, R.J. "Microwave-assisted synthesis of single-crystalline tellurium nanorods and nanowires in ionic liquids", *Angew. Chem. Int. Ed.*, 43(11), pp. 1410–1414 (2004).

[16] Wang, W.W., Zhu, Y.J., Cheng, G.F. and Huang, Y.H. "Microwave-assisted synthesis of cupric oxide nanosheets and nanowhiskers", *Mater. Lett.*, 60(5), pp. 609–612 (2006).

[17] Shao, M., Li, Q., Xie, B., Wu, J. and Qian, Y. "The synthesis of CdS/ZnO and CdS/Pb_3O_4 composite materials via microwave irradiation", *Mater. Chem. Phys.*, 78(1), pp. 288–291 (2002).

[18] Moghaddam, F.M. and Saeidian, H. "Controlled microwave-assisted synthesis of ZnO nanopowder and its catalytic activity for O-acylation of alcohol and phenol", *Mater. Sci. Eng. B*, 139(2), pp. 265–269 (2007).

[19] Mirjafary, Z., Saeidian, H., Sadeghi, A. and Moghaddam, F.M. "ZnO nanoparticles: an efficient nanocatalyst for the synthesis of β-acetamido ketones/esters via a multi-component reaction", *Catal. Commun.*, 9(2), pp. 299–306 (2008).

[20] Saeidian, H., Moghaddam, F.M., Pourjavadi, A., Barzegar, S., Soleyman, R. and Sohrabi, A. "Superabsorbent polymer as nanoreactors for preparation of hematite nanoparticles and application of the prepared nanocatalyst for the Friedel–Crafts acylation", *J. Braz. Chem. Soc.*, 20(3), pp. 466–469 (2009).

[21] Moghaddam, F.M. and Dekamin, M.G. "Thia-Fries rearrangement of aryl sulfonates in dry media under microwave activation", *Tetrahedron Lett.*, 41(18), pp. 3479–3481 (2000).

[22] Moghaddam, F.M. and Zali-Boinee, H. "A versatile one-pot synthesis of 2, 3, 5-tri-substituted thiophenes from thiomorpholides", *Tetrahedron Lett.*, 44(33), pp. 6253–6255 (2003).

[23] Joselevich, E. and Willner, I. "Photosensitization of quantum-size TiO_2 particles in water-in-oil microemulsions", *J. Phys. Chem.*, 98(31), pp. 7628–7635 (1994).

[24] Murrag, C.B., Norris, D.B. and Bawendi, M.G. "Synthesis and characterization of nearly monodisperse CdE(E = S, Se, Te) semiconductor nanocrystallite", *J. Am. Chem. Soc.*, 115(19), pp. 8706–8715 (1993).

[25] Taubert, A., Glasser, G. and Palms, D. "Kinetics and particle formation mechanism of zinc oxide particles in polymer-controlled precipitation from aqueous solution", *Langmuir*, 18(11), pp. 4488–4494 (2002).

[26] Chae, K.P., Lee, J., Kweon, H.S. and Lee, Y.B. "The crystallographic, magnetic properties of Al, Ti doped CoFe2O4 powders grown by sol–gel method", *J. Magn. Magn. Mater.*, 283(1), pp. 103–108 (2004).

[27] Hafner, S. and Krist, Z. "Order/disorder and IR-absorption IV. The absorption of some metal oxides with spinel structure (Ordnung/unordnung und ultrarotabsorption IV, die absorption einiger metalloxyde mit spinellstruktur)", *Scripta Mater.*, 115(5), pp. 331–358 (1961).

[28] Tanabe, K., *Solid Acids and Bases*, Academic Press, New York (1970).

[29] Mohammadpoor-Baltork, I., Aliyan, H. and Khosropour, A.R. "Bismuth (III) salts as convenient and efficient catalyst for the selective acetylation and benzoylation of alcohols and phenols", *Tetrahedron*, 57(1), pp. 5851–5854 (2001).

[30] Gupta, R., Kumar, V., Gupta, M., Paul, S. and Gupta, R. "Silica supported zinc chloride catalyzed acetylation of amines, alcohols and phenols", *Indian J. Chem.*, 47(5), pp. 1739–1743 (2008).

[31] Heravi, M., Behbahani, F., Zadsirjan, V. and Oskooie, H. "Copper (II) sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), a green catalyst for solventless acetylation of alcohols and phenols with acetic anhydride", *J. Braz. Chem. Soc.*, 17(5), pp. 1045–1047 (2006).

[32] Jitendra, R.S. and Radha, V.J. "Acetylation of alcohols, phenols and amines using ammonium salt of 12-tungstophosphoric acid: environmentally benign method", *Catal. Commun.*, 9(11), pp. 2365–2370 (2008).

[33] Xi, Z., Hao, W., Wang, P. and Cai, M. "Ruthenium (III) chloride catalyzed acylation of alcohols, phenols, and thiols in room temperature ionic liquids", *Mol.*, 14(9), pp. 3528–3537 (2009).

Firouz Matloubi Moghaddam was born in Maragheh, Iran. He obtained his B.S. in Chemistry and M.S. in Organic Chemistry from Tabriz University. Thereafter, he joined the group of Prof. G. Solladie in the University of Louis Pasteur Strasbourg France and obtained a 'Doctorat d'Etat' (Habilitation) in 1982. He also obtained an M.Sc in Medicinal Chemistry from the same University. *After three years of postdoctoral appointments at University of Zurich (Prof. C.H. Eugster and Prof. A. Vasella), he began his own career at the Sharif University of Technology*. Currently, He is Full Professor of Organic Chemistry and his scientific interests include total synthesis of bioactive compounds, isolation, structure elucidation and synthesis of bioactive natural products, heterocyclic chemistry, and catalysis.

Malihe Doulabi studied at Sharif University of Technology, Tehran, Iran from 2003 to 2009, where she received a bachelor's degree in Chemistry in 2007, and her master's degree in Organic Chemistry in 2009. Currently, she is Ph.D. student on Polymer Science at Sharif University of Technology.

Hamdollah Saeidian was born in Tarom, Zanjan Iran, in 1981. He received his B.S. degree in applied Chemistry from K.N. Toosi University of Technology (K.N. Toosi), Tehran, Iran, and his M.S. degree in organic chemistry from Sharif University of Technology, Tehran, Iran, in 2005. He completed his Ph.D. degree in 2009 under the supervision of Professor F. Matloubi Moghaddam and Professor D. Enders. He had received research grant from the German Academic Exchange Service (DAAD) in 2008. Now he is working at Payame Noor University as Assistant Professor. His research interests include new methodologies in organic chemistry and mass spectral studies of organic compounds.

Author's copy

www.SID.ir