ICC

Iranian Chemical Communication

Original Research Article

Payame Noor University *http://icc.journals.pnu.ac.ir*

A comparative study of catalytic properties of ZnO and FeZnO nanoparticles on oxidation of Benzylic alcohols: Influence of doped metal

Hamid Reza Mardani[a,*], Mehdi Forouzani[a], Mitra Ziari[a], Azim Malekzadeh[b], Pouria Biparva[c]

[a]*Department of Chemistry, Payame Noor University, P.O. BOX 19395-4697 Tehran, Iran*

[b]*Department of Chemistry, Damghan University, Iran*

[c]*Department of Basic and Agricultural Sciences and Natural Resources University, Sari, Iran*

Received: 15 August 2014, Accepted: 20 November 2014, Published: 1 January 2015

Abstract

Novel nano-catalysts (Nano ZnO and Fe doped ZnO ($Fe_{(0.1)}Zn_{(0.99)}O$) were synthesized by co-precipitation method in aqueous solution as new nanocatalysts and characterized by common techniques as FTIR, XRD, SEM and UVD. The size of particles obtained from XRD data is 27 and 16 nanometers for ZnO and Fresno respectively. Influences of doped Fe on ZnO catalytic properties in oxidation of Benzylic alcohols were studied. The oxidation was carried out under mild and green conditions as solvent free, at room temperature and with H_2O_2. The results show, that FeZnO is better than ZnO as nanocatalyst in oxidation reaction. The rate, of %conversion and %selectivity of reaction is improved in the presence of Fe atoms than ZnO only. The main product of oxidation reactions is Benzaldehyde and/or its derivatives.

Keywords: Nanocatalyst; ZnO; FeZnO; doped nanoparticles; oxidation; green oxidation; benzylic alcohols.

Introduction

Recently, Nanoparticles are used widely and efficiently as catalyst in organic synthesis because of the increase in the interface of catalyst with substrates [1-7].

---

*Corresponding author: Hamid Reza Mardani
Tel: +98 (11) 33232392, Fax: +98 (11) 33211514
E-mail: hamidreza.inorg@yahoo.com

In the past few years, spinel and perovskite type metal oxides have been extensively used as catalysts for various organic transformations [8-11]. These types of metal oxides have good thermal and chemical stability and can be employed for a wide range of temperatures in various reactions [12-14].

Oxidation of alcohols is one of important transformation in organic synthesis. The products of this reaction are commonly benzoic acid, but production of aldehydes is essential in the synthesis of other organic compounds. Therefore, catalyst and oxidant are effective on the main product of oxidation reaction [15-19].

Recently, nano-transition metal oxide materials, like ZnO, CuO and NiO have attracted intense interest by the following facts. First, these metal oxides are a non-toxic, green synthesis, inexpensive and non-hygroscopic powder. Second, the nanostructure and surface geometry of the material are modified by the addition of suitable dopant. Third, many physical and chemical properties are arisen by doped metal [20]. ZnO has been used for a number of organic syntheses in combination with other metal oxides, Such as; ZnO-CuO-alumina, FeZnO and CuZnO [21]. Many previous studies have disadvantages, for example, using a BuOOH (TBHP) as Oxidant and performed oxidation in different solvents, such as acetonitrile and/ or oxidation at high temperature condition [22-24].

Few studies were performed on the oxidation of alcohols by using nano-materials with H_2O_2 [25- 33], but selective oxidation of benzylic alcohols by nano-ZnO and doped Cu metal-ZnO under eco-friendly condition such as with H_2O_2 oxidant, solvent free and in room temperature, were not reported yet.

Herein we report the oxidation of benzylic alcohols to carbonyls using H_2O_2 as a clean oxidant with nano crystalline ZnO and FeZnO catalyst. Also, we investigated the influence of Fe atom on ZnO catalytic properties.

Experimental

General

All chemicals were of reagent grade (Merck and/or Aldrich). All compounds were used without further purification.

IR spectra were recorded as pressed KBr discs using a PerkinElmer RXI, FT-IR instrument. Diffuse reflectance spectra were recorded on an Analytikjena (Specord 205) UV–Vis in the range of 200– 900 nm. The XRD data of synthesized nanoparticles were obtained with a Bruker X-ray diffractometer (Advanced-D8) using Cu-Kα radiation.

Synthesis of ZnO nanoparticles:

Pure ZnO was prepared through hydrolysis and oxidizing process. $Zn(NO_3)_2$ (1 mmol) dissolved in 100 mL of distilled water with continuous stirring. NaOH solution was added into the former solutions drop by drop until the pH of the solution became 12. White particles were washed three times with distilled water and dried for 24 h at 80 ^{o}C.

Synthesis of FeZnO nanoparticles

Synthesis of $Fe_xZn_{(1-x)}O$ (1% Fe-doped) nanopowder was carried out using a modified procedure [34]. The targets were specifically designed using high purity $Zn(NO_3)_2\cdot 6H_2O$ (99.99%) and $FeCl_2\cdot 6H_2O$ (99%) powders. The Fe-doped ZnO catalyst was prepared by a two-step procedure: (1) preparation of the precursor by co-precipitation; (2) formation of the Fe/ZnO nanopowder by thermal decomposition. This method has been considered to be efficient and inexpensive, allowing for the production of high purity, homogeneous, and fine crystalline powders.

Stoichiometries quantities of Zn and Fe salts were dissolved in 100 mL of deionized double distilled water (solution A). Separately, a solution was prepared by dissolving appropriate amounts of NaOH and Na_2CO_3 in deionized double distilled water (solution B). Solution A was heated to 85 °C and solution B was added dropwise into it with constant stirring. The temperature was maintained at 85 °C and the reaction mixture was stirred for 1 h and refluxed through a water condenser. The resulting solution was cooled to room temperature and the green precipitate formed was washed with 3 × 20 mL of de-ionized water and dried under vacuum overnight at 50 °C. Finally, the precursors were calcined at 450 °C for 90 min in a muffle furnace under air atmosphere to obtain the nanocrystalline Fe/ZnO powder.

Oxidation Reaction:

With a mixture of benzyl alcohol (1 mmol) and 30% H_2O_2 (10 mmol) was added (10 mg) of nano-catalyst. The reaction mixture was stirred at room temperature. The progress of the reaction was monitored by TLC n-Hexane/Ethyl acetate (4:1) solvents. After an appropriate time, the catalyst was separated by filtration and extracted by Diethyether.

Results and discussion

Characterization of catalysts

The XRD patterns and SEM images of ZnO and FeZnO are shown in Figures 1 and 2 respectively. The patterns of two samples are closely the same without any impurity peak; therefore all samples have a wurtzite hexagonal phase and Zn and substituted Fe metal are distributed homogeneously along the whole crystal [35]. The general morphology of nano samples is similar and has mushroomed-shaped.

The crystallite sizes of the catalysts were calculated using the Scherrer's formula:

$$D = K\lambda/(\beta\ Cos\theta)$$

where D is taken as crystallite size, K is a constant equals to 0.9, λ is 1.5406 Ȧ, $\boldsymbol{\beta}$ is the FWHM measured in radians on the 2θ scale, θ is the Bragg angle for the diffraction peaks. The results are tabulated in Table 1. ZnO crystallite sizes decreased as Fe-oxide loading. Detected phases are observed to be in nanosized scale. Results show a considerable effect of metal oxide dopant on ZnO particle size. Thus, the presence of small parts of a different metal oxide has a characteristic effect on the particle size of the sample.

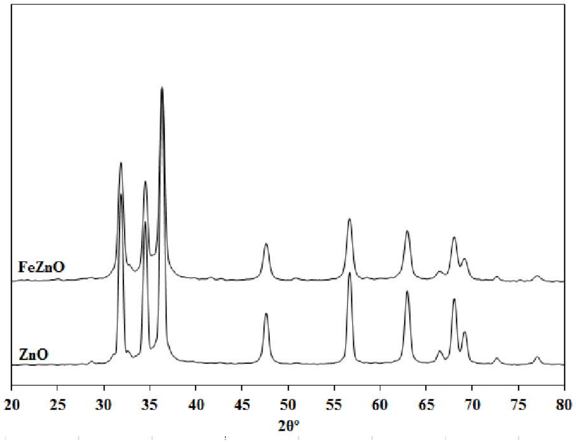
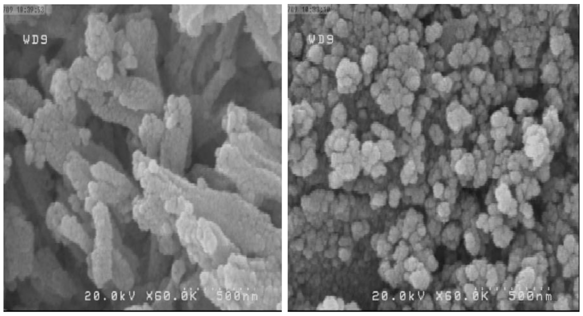


Figure 1. XRD data of ZnO and FeZnO



ZnO FeZnO

Figure 2. SEM images of ZnO and FeZnO.

Table 1. Crystallite size[a] (nm) of synthesized samples.

Sample	ZnO	FeZnO
Crystallite size (nm)	28	16

[a] Calculations were done using Scherrer equation.

The absorption spectra of 2 samples are the same (Figure 3). The absorption edge (oxygen to Zn) showed 376 and 359 nm and the energy of Band Gap was calculated 3.15 and 2.52 ev for ZnO and FeZnO respectively [36, 37]. Then, the Band Gap of ZnO was reduced by doped Fe metal.

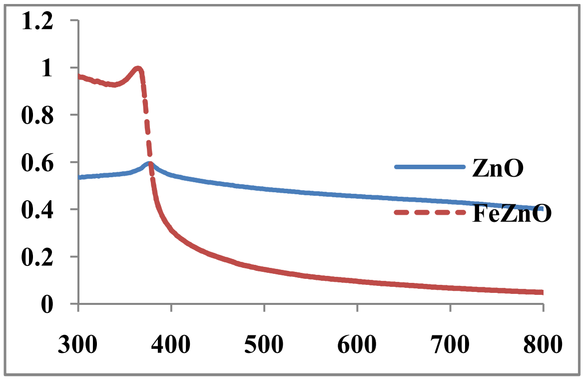


Figure 3. UV-Visible diffuse reflectance spectra of ZnO and FeZnO

The FTIR of samples is shown in Figure 4. The spectra of tow samples are exactly the same and several well-defined bands at 460, 1120, 1650 and 3450 cm^{-1} have been appearing in the FTIR spectrum. The band at 460 cm^{-1} is due to metal–oxygen modes and hence confirms the formation of ZnO and Fe doped ZnO [26]. The broad absorption peaks around 3450 cm^{-1}, 1120 and 1650 cm^{-1} are attributed to O–H stretching and H–O–H bending vibration of H_2O in Fe-Zn–O or Zn-O lattice [38-40].

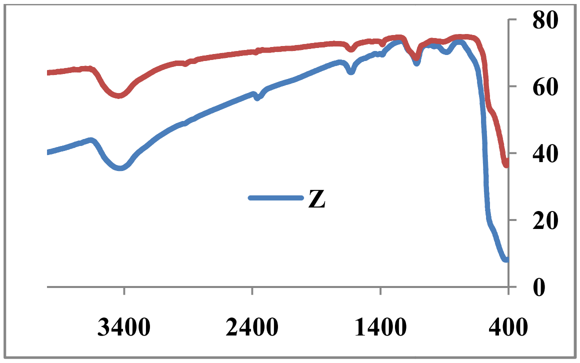


Figure 4. FTIR spectrum of ZnO and FeZnO

Influence of doped Fe metal

The influence of doped Fe metal on the catalytic properties of nano ZnO was studied. First of all, the catalytic properties of both catalysts were compared after 4 times in oxidation reaction. ZnO and FeZnO can be easily recovered from the reaction mixture by filtration and reused as catalyst. Herein, the reusability of the ZnO and FeZnO were evaluated for 4 runs, and the results are shown in Figure 5. During the four runs, the conversion of reaction decreased with ZnO in a range from 100% to 80%, probably due to the change in surface (loss of surface) of ZnO [41], but it is fixed for FeZnO because the size of FeZnO is smaller than ZnO and the loss of surface is poor in FeZnO in the presence of ZnO. Also, the selectivity of Benzaldehyde is motionless in 4 runs for both catalysts. The result is indicating that the FeZnO catalyst has a good reproducibility and stability than ZnO.

In the second comparative study, ZnO and FeZnO were evaluated by the catalytic activity in the oxidation reaction of benzyl alcohol fter 3 h (Figure 6). The same amount of ZnO and FeZnO is used in the same condition reaction. The conversion of FeZnO is more than ZnO catalyst (100% and 70% respectively). In addition, the rate of reaction remarkably increased in ZnO by doping Fe metal ion, perhaps it is due to the changes on surface and nature's ability of Fe^{2+} ion in oxidation reaction to Zn^{2+} ion.

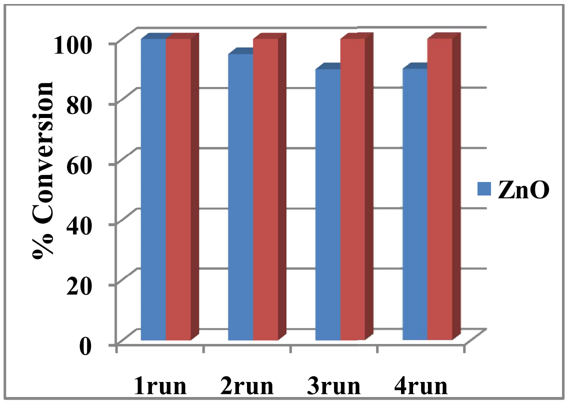


Figure 5. Compare the reusability of the nano ZnO and FeZnO in oxidation of benzyl alcohol after 4 times.

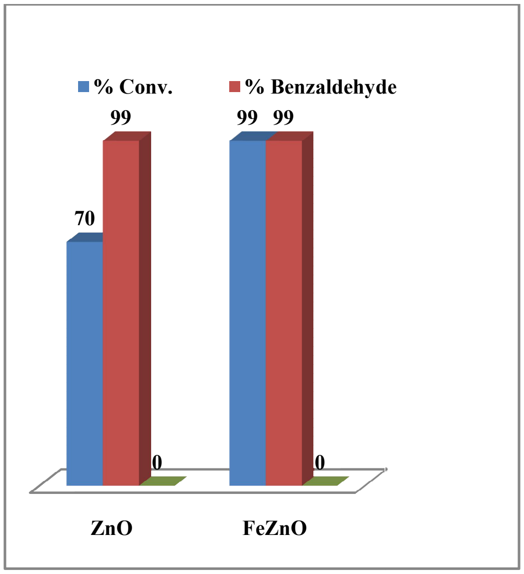
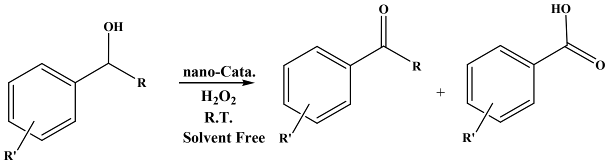


Figure 6. Comparable catalytic properties of ZnO and FeZnO for 3 h.

Finally, the third comparative study was performed between both catalysts in oxidation of other benzylic alcohols under similar conditions after 2 h, as shown in Table 2. Notable results were obtained as follows: first, no oxidation was observed in the aromatic rings of the benzylic substrates. Second, oxidation of phenol group doesn't occur (Entry 4). Third, the secondary benzylic alcohol was converted to the corresponding ketones and don't observed each benzoic acid (Entries 5, 6 and 7). Fourth, FeZnO is better than ZnO as nano catalyst.

Table 2. Oxidation of other benzylic alcohols after 2 h



2 3

Entry[a]	Substrate		Nano-Cat.	%Conv.	Ratio (%2: 3)
	R'	R			
1	H	-H	ZnO	60	>99
			FeZnO	> 99	>99
2	*p*-NO_2	-H	ZnO	50	>99
			FeZnO	> 99	>99
3	*P*-Cl	-H	ZnO	50	>99
			FeZnO	> 99	>99
4	*O*-OH	-H	ZnO	60	>99
			FeZnO	> 99	>99
5[b]	H	-Ph	ZnO	60	>99[c]
			FeZnO	> 99	>99[c]
6	H	$-CH_3$	ZnO	50	>99[c]
			FeZnO	> 99	>99[c]
7[b]	H	-CO-Ph	ZnO	70	>99[c]
			FeZnO	> 99	>99[c]

[a] (1 mmol) alcohol, (10 mg) catalyst and (10 mmol) H_2O_2 (30%) was stirred at room temperature in solvent free.
[b] in (2mL) CH_3CN.
[c] Converted to corresponding ketone.

Conclusion

In conclusion, we introduced novel, efficient and recyclable nano-catalyst for the solvent free oxidation of benzylic alcohols by H_2O_2 at room temperature. We evaluated the catalytic properties of ZnO with the Fe doped ZnO in these oxidation reactions. The catalytic activity of ZnO is significantly increased by slight changes in their physical and chemical properties by doped Fe metal ion. Also, we have developed a green chemistry, because the reaction was carried out under solvent-free and green oxidant. The catalysts were prepared in aqueous phase or a green solvent too.

Acknowledgement

We are grateful for the financial support of Payame Noor University of Iran.

References

[1] N. Salam, B. Banerjee, A.S. Roy, P. Mondal, S. Roy, A. Bhaumik, S.M. Islam; *Applied Catalysis A: General*, **2014**, *477*, 184-194.

[2] M. Esmaeilpour, J. Javidi, M. Zandi; *Materials Research Bulletin*, **2014**, *55*, 78-87.

[3] C.W. Lim, I.S. Lee; *Nano Today*, **2010**, 5, 412-434.

[4] R.K. Sharma, Y. Monga, A. Puri; *Catalysis Communications*, **2013**, *35*, 110-114.

[5] V. Polshettiwar, R. Luque, A. Fihri, H. Zhu, M. Bouhrara, J. M. Basset*;* *Chem. Rev.*, **2011**, *111*, 3036–3075.

[6] F. Sadri, A. Ramazani, A. Massoudi, M. Khoobi, V. Azizkhani, R. Tarasi, L. Dolatyari, B. Min; *Bull. Korean Chem. Soc.,* **2014**, *35*, 2029-2032.

[7] F. Sadri, A. Ramazani, A. Massoudi, M. Khoobi, R. Tarasi, A. Shafiee, V. Azizkhani, L. Dolatyari, S. W. Joo; *Green Chemistry Letters and Reviews,* **2014***, 7*, 257-264.

[8] A.S. Reddy, C.S. Gopinath, S. Chilukuri; *Journal of Catalysis,* **2006**, *243*, 278–291.

[9] A.H. de Morais. Batista, F.S.O. Ramos, T. P. Braga, C.L. Lima, F. F. de Sousa, E. B.D. Barros, J.M. Filho, A.S. de Oliveira, J.R. de Sousa, A. Valentinia, A.C. Oliveira; *Applied Catalysis A: General*, **2010**, *382*, 148–157.

[10] K. Sreekumar, T. Mathew, B.M. Devassy, R. Rajgopal, R. Vetrivel, B. S. Rao; *Applied Catalysis A: General*, **2001**, *205*, 11–18.

[11] A.S. Kulkarni, R.V. Jayaram; *Applied Catalysis A: General*, **2003**, *252*, 225–230.

[12] R. Sumathi, K. Johnson, B. Viswanathan, T. K. Varadarajan;

Applied Catalysis A: General, **1998**, *72*, 15–22.

[13] M. Ilyas, M. Saeed; *International Journal of Chemical Reactor Engineering,* **2010**, *8*, 1–19.

[14] K.S.R.C. Murthy, J. Ghose, *Journal of Catalysis,* **1994**, *147*, 171–176.

[15] J.L. Kroschwitz, 4th ed., Encyclopedia of Chemical Technology, vol. 4, Wiley- Interscience Publications, New York, **1992**.

[16] T. Mallat, A. Baiker; *Chem. Rev.,* **2004**, *104*, 3037–3058.

[17] M. Musawir, P.N. Davey, G. Kelly, I.V. Kozhevnikov; *Chem. Commun.,* **2003**, *12*, 1414–1415.

[18] K. Chritz, A. Sebek, M. Dittmar, A. Radnik, J. Bruckner, A. Bentrup, U. Pohl, M.M. Hugl, H. Magerlein;. *J. Mol. Catal. A: Chem.,* **2006**, *246*, 85–99.

[19] D. Lenoir; *Angew. Chem. Int. Ed.,* **2006**, *45*, 3206–3210.

[20] Z. Zhang, J.B. Yi, J. Ding, L. M. Wong, H. L. Seng, S.J. Wang, J.G. Tao, G.P. Li, G.Z. Xing, T.C. Sum, C.H.A. Huan, T. Wu; *J. Phys. Chem.,* **2008**, 112, 9579–9585.

[21] M. Gupta; *Tetrahedron Lett.*, **2005**, *46*, 4957–4960.

[22] A.S. Burange, R.V. Jayaram , R. Shukla, A.h K. Tyagi; *Catal. Commun.*, **2013**, *40*, 27–31.

[23] P. Sharma, G. Darabdhara, T.M. Reddy, A. Borah, P. Bezboruah, P. Gogoi, N. Hussain, P. Sengupta, M.R. Das; *Catal. Commun.,* **2013**, *40*, 139–144.

[24] P. Das, N. Aggarwal, N.R. Guha; *Tetrahedron Lett.,* **2013**, *54*, 2924–2928.

[25] A.S. Burange. R.V. Jayaram, R. Shukla, A.K. Tyagi; *Catal. Commun.,* **2013**, *40*, 27–31.

[26] V.R. Choudhary, D.K. Dumbre; *App. Catal. A: General,* **2010**, *375*, 252–257.

[27] S. Prakash. C. Charan, A.K. Singh; *Applied Catalysis B: Environmental,* **2013**, *132*, 62-69.

[28] F. Shi, M.K. Tse, M.M. Pohl, J. Radnik, A. Brückner, S. Zhang, M. Beller; *J. Mole. Catal. A: Chem.,* **2008**, *292*, 28–35.

[29] D. Habibi, A.R. Faraji, J.L.G. Fierro; *J. Mole. Catal. A: Chem.,* **2013**, *372*, 90-99.

[30] D. Habibi, A.R. Faraji; *App. Surf. Sci.,* **2013**, *276*, 487-496.

[31]J. Albadi, A. Alihoseinzadeh, A. Razeghi; *Catal. Commun.*, **2014**, *49*, 1–5.

[32] R.V. Choudhary, K. De. Dumbre; *Catal. Commun.,* **2011**, *13*, 82-86.

[33] R.V. Choudhary, K. De. Dumbre; *Catal. Commun.,* 2009, *10*, 1738-1742.

[34] D. Jung; *solid state science*, **2010**, *12*, 466-470.

[35] R. Kumar G. Kumar, A. Umar; *Materials Letters*, **2013**, *97*, 100–103.

[36] S. Sakthivel, H. Kisch; *Angew. Chem. Int. Ed.,* **2003**, *42*, 4908-4912.

[37] S. Muthukumaran, R. Gopalakrishnan; *Optic. Mat.,* **2012**, *34*, 1946–1953.

[38] K. Nakamoto; *Infrared and Raman Spectra of Inorganic and Coordination Compounds,* Parts A and B, John Wiley & Sons, New York, **1997**.

[39] A.J. Reddy, M.K. Kokila, H. Nagabhushan, R.P.S. Chakradhar, C. Shivakumar, J.L. Rao, B.M. Nagabhushan; *J. Alloys Compd.*, **2011**, *509*, 5349– 5355.

[40] R. A. Nyquist, R. Kagel; *Infrared spectra of inorganic compounds*, p. 220. New York, London: Academic Press, Inc.; **1971**.

[41] J. Luo. F. Peng, H. Yu, H. Wang; *Chemical Engineering Journal,* **2012**, *204*, 98–106.