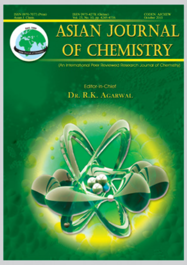
Asian Journal of Chemistry; *Vol. 24, No. 1 (2012), 309-311*

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in



Synthesis of Carbonyl Compounds in the Presence of NanoPreyssler as Green and Recyclable Catalyst by Photocatalytic Oxidation of Benzaldehydes and Benzyl Alcohols

FATEMEH F. BAMOHARRAM

Department of Chemistry, Faculty of Sciences, Mashhad Branch, Islamic Azad University, Mashhad 91735-413, Iran

*Corresponding author: E-mail: fbamoharram@mshdiau.ac.ir; abamoharram@yahoo.com

(*Received*: 21 December 2010; *Accepted*: 19 September 2011) AJC-10423

An efficient, improved and environmentally benign procedure for photocatalytic oxidation of benzaldehydes and benzyl alcohols to related carbonyl compounds was developed in the presence of silica-supported preyssler nanoparticles in photocatalytic conditions. Present data showed that the nano preyssler catalyst in an organic solvent, render effective oxidation reaction better than preyssler catalyst under photocatalytic conditions regarding the yields. The nanocatalyst was easily recovered and reused many times. No significant loss in catalytic activity was observed on recycling.

Key Words: Preyssler, Nanocatalyst, Photocatalytic reaction, Carbonyl compounds, Recyclable.

INTRODUCTION

The photocatalytic reactions of inorganic and organic compounds have been important research topics in many photochemical conversion processes and environmental cleaning. A more complex class of photocatalytically active materials is the heteropoly acid (HPA) compounds. Photocatalysis by solid heteropoly acids is a new branch in the field of photocatalytic chemistry and some attractive researching progresses have developed in recent years. Heteropoly acids are well-defined early transition metal-oxygen clusters with unique structural characteristics and multiple functions, which have been significantly impacting the development of materials with catalytic, photochemical, electrochromic and magnetic properties[1]. While semiconductor materials have been widely studied as photocatalysts[2-5], studies on the photocatalytic behaviour of heteropoly acids have received less attention compared with these materials. In fact, many of heteropoly acids share similar photochemical characteristics of the semiconductor photocatalysts and heteropoly acids represent the analogues of semiconductor metal oxides[6-8]. Many photocatalytic reactions are catalyzed by heteropoly acids including the oxidation of alcohols to aldehydes or ketones[9,10], the functionalization of alkanes to form alkenes or ketones[11], dimerization of alkenes[12] and degradation of all kinds aqueous organic pollutants for advanced oxidation processes[13-15] .

In conjugation of nanostructures with photocatalysts, considerable effort has been devoted to the design and controlled fabrication of nanostructured heteropoly acids for using in green reactions. This interest has resulted in the development of numerous protocols for the synthesis of nanostructured materials over a range of sizes. Therefore the field of nano heteropoly acids and their applications continue to attract significant attention, so the number of publications and patents continue to grow and new researchers are entering the field. Thus, many room exists for expanding the exploration of the opportunities for these materials and further exploring, so developing new heteropoly acids is still a challenge for heteropoly acids chemistry.

Among a wide variety of studied heteropoly acids with different size and structures, the photocatalytic behaviour of preyssler catalyst has been largely overlooked. Recently we have studied catalytic oxidation of aldehydes and alcohols in the presence of preyssler catalyst in both thermal and photocatalytic conditions as well as microwave irradiation[16-19] .

As a part of continuous research on synthesis of carbonyl compounds by green and eco-friendly catalysts, it is great interest to know, what occurs if the nano Preyssler use in these reactions. It was hoped that this would modify the catalytic activity of the preyssler-type heteropolyacid.

Carbonyl compounds are widely used as intermediates both in manufacturing and laboratory[20], thus the development of new catalytic protocols continues to receive attention in spite of the availability of different methods to achieve such objectives[21,22].

Interestingly, we have found that the nano preyssler catalyst in an organic solvent, render effective oxidation reaction better than preyssler catalyst under phtocatalytic conditions regarding the yields.

EXPERIMENTAL

All of the chemicals were commercially available. ^1H NMR spectra were recorded on an FT-NMR Brucker 100 MHZ Aspect 3000 spectrometer. IR spectra were obtained with a Buck 500 scientific spectrometer (KBr pellets). Mass spectra were obtained with a Massens POEKTROMETER CH-7AVARTN MAT BREMAN specterometer. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector.

Preparation of catalyst: Potassium salt of preyssler anion was prepared according to the procedure developed in our laboratory[23]. The free acid was prepared by passage of a solution of the potassium salt in water through a column of Dowex 50WX8 in the H^+ form and evaporation of the elute to dryness under vacuum[23].

Nano catalyst was prepared according to our earlier work[24]. To a solution of sodium bis (2-ethylhexyl) sulfosuccinate as surfactant in cyclohexane (0.2 M) was added a solution of preyssler acid in a specified amount of water. The molar ratio of water to surfactant was selected to be 3, 5 and 7. Tetraethoxysilane was then added into the microemulsion phase. After mixing for various amounts of time (8, 12, 18, 25 and 30 h) at room temperature, dispersed preyssler acid/SiO_2 nano structures were centrifuged (15,000 rpm) and the particles were rinsed with acetone (four times) and dried in a vacuum oven.

Photoreactor: The photoreactor was designed with an internal light source surrounded by a quartz jacket. The temperature of the liquid/solid suspension was maintained at 25 ºC by circulation of water through an external cooling coil. The optical path length was about 2 cm. The light source was a 125 W high-pressure mercury lamp.

General procedure: All reactions were carried out in a glass reactor equipped with magnetic stirrer and inlet gas tube. In a typical reaction, to 6 mL of acetonitrile and 8 mL water, substrate and nano catalyst were added and the mixture was stirred in dark for 0.5 h. Then the mixture was irradiated under conditions mentioned in the results and discussion. High purity oxygen gas was introduced to the stirred reaction mixture *via* an immersed inlet gas tube fitting. For aldehydes, to the final mixture, an solution of $NaHCO_3$ was added and the mixture was filtered. The carboxylic acids were precipitated by adding 2 M HCl to the filtrate. The solid product was collected and washed with water and re-crystallized in ethanol. The products were characterized by comparison of their spectroscopic (IR, H NMR, mass) data and melting points with those of authentic samples. For alcohols, GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector.

RESULTS AND DISCUSSION

Silica-supported preyssler nano structures (**1**) were obtained through a micro emulsion method[24]. The sizes and morphology of products were controlled by changing the water to surfactant, sodium *bis*(2-ethylhexyl) sulfosuccinate molar ratio (S) and reaction time. For a short time, the tubular structure prevails, whereas the spherical shapes dominate at longer times. To optimize the reaction conditions, 4-chlorobenzaldehyde was used as substrate and the photocatalytic oxidation reactions were carried out in the presence of **1** as catalyst and O_2 as oxidant. A mixture of CH_3CN and H_2O has been used as solvent. At first the mixture was stirred in dark for 0.5 h. For a systematic comparison between preyssler and nanopreyssler, we worked in obtained optimum conditions in earlier studies[18,19].

Therefore, all of the studies were performed with the best concentration of catalyst: 1×10^{-3} and 2×10^{-3} M for aldehydes and alcohols, respectively, at 6 h. The results are shown in Table-1.

TABLE-1
PHOTOCATALYTIC OXIDATION OF DIFFERENT ALDEYDES AND ALCOHOLS IN THE PRESENCE OF NANO PREYSSLER CATALYST

Entry	Substrate	Yield (%)
1	4-Chloro benzaldehyde	99
2	3-Chloro benzaldehyde	75
3	3-Bromo benzaldehyde	72
4	4-Methyl benzaldehyde	65
5	3-Methyl benzaldehyde	62
6	2-Hydroxy benzaldehyde	45
7	3-Hydroxy benzaldehyde	40
8	4-Hydroxy benzaldehyde	57
9	4-Nitro benzaldehyde	45
10	4-Nitro benzyl alcohol	95
11	2-Nitro benzyl alcohol	82
12	4-Methyl benzyl alcohol	75
13	2-Chloro benzyl alcohol	70

The results of the comparison between preyssler[18,19] and nano preyssler catalyst showed that, in all cases, the nano catalyst is more active than the bulk form.

Interestingly, it is found that the nano preyssler catalyst in an organic solvent, render effective oxidation reaction better than preyssler catalyst under photocatalytic conditions regarding the yields. It is suggested that, when the particle size decreases, the relative number of surface atoms increases and thus activity increases.

Under illumination of nano preyssler with UV light, a charge transfer (oxygen to tungsten) renders catalyst as a powerful oxidizing reagent that able to oxidize carbonyl compounds. There have been various data suggesting that upon mixing of polyoxometalates (POMs) with organic compounds a pre-associated complex or pre-equilibria is formed and then under UV excitation at the O → M charge transfer band, renders polyoxometalate powerful oxidizing reagents or in similarity with semiconductors, excitation of polyoxometalate can considered as electron (e^-)-hole(h^+). At the other stage, oxidant restores the catalyst to the original oxidized form. In the process dioxygen converts to O_2^-, initiating further oxidations[25].

Conclusion

In this study, a new and green nanocatalyst based on preyssler anion was successfully used as effective and green catalyst for the oxidation of benzaldehydes and benzyl alcohols under UV irradiation. Nanocatalyst was readily recycled and reused to produce almost identical results. The use of this new and novel nanocatalyst in this reaction provides a better and practical alternative to our earlier procedures and provides great promise toward further useful applications. This process will pave a way for large scale applications of synthesis of other carbonyl compounds. Further applications for other reaction systems are currently under investigation.

REFERENCES

1. T. Okuhara, *Appl. Catal*., **256**, 213 (2003).
2. J.M. Herrmann, *Catal. Today*, **53**, 115 (1999).
3. M. Vautier, C. Guillard and J.M. Herrmann, *J. Catal*., **201**, 46 (2001).
4. C. Hu, Y. Wang and H. Tang, *Appl. Catal. B: Environ*., **35**, 95 (2001).
5. M.R. Hoffmann, S.T. Martin, W.Y. Choi and D.W. Bahnemann, *Chem. Rev*., **95**, 69 (1995).
6. D. Sattari and C.L. Hill, *J. Am. Chem. Soc*., **115**, 4649 (1993).
7. C.L. Hill, *Chem. Rev*., **98**, 1 (1998).
8. A. Hiskia, A. Mylonas and E. Papaconstantinou, *Chem. Soc. Rev*., **30**, 62 (2001).
9. M.A. Fox, R. Cardona and E. Gaillard, *J. Am. Chem. Soc*., **109**, 6347 (1987).
10. C.L. Hill and D.A. Ouchard, *J. Am. Chem. Soc*., **107**, 5148 (1985).
11. R.F. Renneke and C.L. Hill, *J. Am. Chem. Soc*., **108**, 3528 (1986).
12. T. Yamase and T. Usami, *J. Chem. Soc. Dalton Trans*., 183 (1988).
13. A. Mylonas and E. Papaconstantinou, *J. Mol. Catal*., **92**, 261 (1994).
14. C. Hu, B. Yue and T. Yamase, *Appl. Catal*., **194-195**, 99 (2000).
15. Y. Guo and Ch. Hu, *J. Mol. Catal*., **262**, 136 (2007).
16. F.F. Bamoharram, M. Roshani, M.M. Heravi and Sh. Safaie, *Phosphorus, Sulfur, Silicon*, **181**, 2833 (2006).
17. F.F. Bamoharram, M. Roshani, M.H. Alizadeh, H. Razavi and M. Moghayadi, *J. Braz. Chem. Soc*., **17**, 505 (2006).
18. F.F. Bamoharram, M.M. Heravi, H.M. Heravi and M. Dehghan, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem*., **39**, 394 (2009).
19. F.F. Bamoharram, M.M. Heravi and S. Mehdizadeh, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem*., **39**, 746 (2009).
20. B.M. Trost, *Synth. Lett*., **7**, 143 (2000).
21. C. Marsden, E. Taarning, D. Hansen, L. Johansen, S.K. Klitgaard, K. Egeblad and C.H. Christensen, *Green Chem*., **10**, 168 (2008).
22. J.M. Grill, J.W. Ogle and S.A. Miller, *J. Org. Chem*., **71**, 9291 (2006).
23. F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir and A. Gharib, *Appl. Catal. A: Gen*, **302**, 42 (2006).
24. F.F. Bamoharram, M.M. Heravi, M. Roushani and M. Toosi, *Green Chem. Lett. Rev*., **2**, 35 (2009).
25. E. Papaconstantinou, A. Hiskia and A. Troupis, *Front. Biosci*., **8**, 813 (2003).