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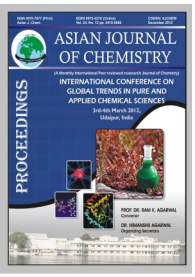

Supported Nano-SiO_2 $H_{14}[NaP_5W_{30}O_{110}]$ Heteropolyacid: A Green and Reusable Catalyst in Oxidation of Aromatic Aldehydes†

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$H_{14}[NaP_5W_{30}O_{110}]$ is deposited on silica nanoparticles and used as recyclable heterogeneous catalysts in the oxidation of benzaldehydes to carboxylic acids both in thermal conditions and microwave irradiation. In catalytic reactions, the effects of various parameters such as catalyst amount, loading percentage and reaction time were examined. We found that the use of nano-SiO_2-supported $H_{14}[NaP_5W_{30}O_{110}]$ coupled to microwave irradiation allows a solvent- free, rapid (4-5 min) and high-yielding reaction. This catalyst can be easily recovered and reused for many times without a significant loss in its activity.

Key Words: $H_{14}[NaP_5W_{30}O_{110}]$, Heteropolyacid, Catalyst, Supported nano-SiO_2, Aromatic aldehydes.

INTRODUCTION

In recent times, inorganic solid acid-catalyzed organic transformations are gaining much importance due to the proven advantage of heterogeneous catalysts, such as simplified product isolation, mild reaction conditions, high selectivities, easy recovery and catalyst reuse and reduction in generation of waste byproducts[1-4].

A common and important class of these inorganic solid acids, which used in the majority of catalytic applications are heteropolyacids[5,6]. They have several advantages, including high flexibility in the modification of the acid strength, ease of preparing, environmental compatibility, non-toxicity and experimental simplicity[7]. These solid acids can be used in bulk or supported forms in both homogeneous and heterogeneous systems[8,9].

Increasing attention has been paid to search for preparing supported heteropolyacid catalysts. Efforts have also been made to study the support of heteropolyacids on suitable nano supports[10]. The use of supported heteropolyacids increases the specific surface area of the catalysts and modifies their catalytic properties.

Recently, we developed an efficient method for oxidation of aromatic aldehydes to corresponding carbonyl compounds using heteropolyacids as catalyst. We studied these reactions in both thermal and photochemical conditions[11-13].

In this research, in continuation of ongoing research[11-17] on the application of heteropolyacids in organic syntheses and due to the importance of derivatives of aldehydes in chemical processes, the applicability of heteropolyacid for efficient oxidation of aldehyde to the corresponding carboxylic acids is reported.

We carried out the successful oxidation of benzaldehydes in both thermal conditions and microwave irradiation using different loading of nano-SiO_2 -supported $H_{14}[NaP_5W_{30}O_{110}]$ catalyst and optimized the reaction conditions.

EXPERIMENTAL

All of the chemicals were commercially available. ^1H NMR spectra were recorded on an FT-NMR Brucker100 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-7Aavartn MAT Breman specterometer. A Milestone APC-55E microwave was used for all of the experiments. Silica nanoparticles were synthesized and characterized according to our earlier published work[13]. For the preparation of supported catalyst, 2.5 g of the synthesized nanosilica was suspended in 20 mL of water and then to this suspension the heteropolyacid in different loadings of tungsten was added. After stirring the heterogeneous solution-support mixture, the solvent was evaporated, samples were dried at 120 ºC and the catalysts were calcined at 250 ºC in a furnace prior to use.

General procedures for the oxidation of benzaldehydes using H_2O_2 as the oxidizing agent: A: microwave irradiation

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benzaldehyde, catalyst and H_2O_2 are mixed thoroughly in a small beaker. The mixture was placed in microwave oven and irradiated for 4-5 min. Then to the final mixture was added 10 % aqueous solution of $NaHCO_3$ 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 H_2O. The products were characterized by comparison of their spectroscopic data (IR, ^1H NMR and MS) and melting points with those of authentic samples.

B: Reflux conditions: The aldehyde (1 mmol) was dissolved in a mixed solvent ($CH_3CN + H_2O$). Then catalyst was added to the solution. The reaction mixture was refluxed in a 25 mL round-bottom flask equipped with a magnetic stirrer, reflux condenser and thermometer. While the solution was vigorously stirred, at equal intervals H_2O_2 was added to the solution. The reaction mixture was stirred and refluxed for 2-8 h.

RESULTS AND DISCUSSION

To optimize the reaction conditions, 4-chloro benzaldehyde was selected as a test substrate and the important factors, such as loading effect, amount of the catalyst and the reaction time were investigated. Among various tested molar ratios of aldehyde to hydrogen peroxide in CH_3CN and H_2O as solvent, 0.217 mol H_2O_2 gave optimum results at reflux temperature in 6 h, which was selected as the reaction conditions in the next reactions. For obtaining the optimum loading percentage, the catalyst with different initial heteropolyacid loadings on nano-silica (10-50 %) was prepared. The results are shown in Fig. 1.

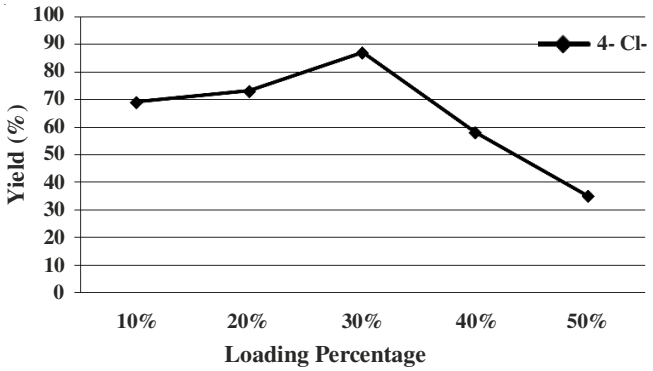

Fig. 1. Effect of loading percentage on yield (%) of carboxylic acids

The results show that the higher yield can be achieved with 30 % loading. As reported in this figure, by increasing the catalyst loading up to 30 %, there is an increase in yield. It is attributed to the increase in the total number of available active catalytic sites for the reaction. The fall of the yields at higher catalyst loading can be attributed to competitive adsorption reactions for the active site on the catalyst surface or physically blocks the catalyst pore by excessive amounts of additives. Thus 30 % loading was selected as the optimum condition for this transformation.

After optimizing the loading percentage, we optimized the amount of the catalyst. The observations are presented in Fig. 2.

Decrease of yields with increase of catalyst amount can be attributed to side reactions by the excess amount of the catalytic sites.

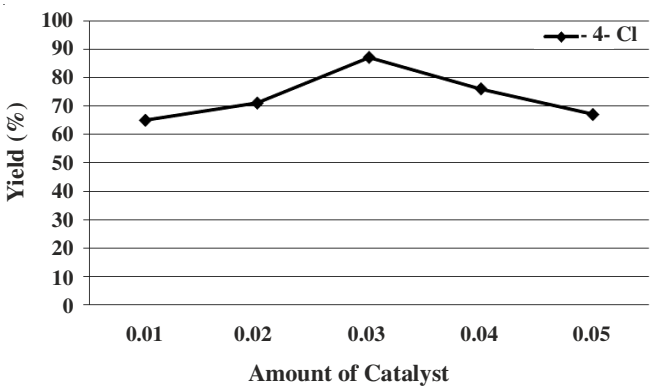

Fig. 2. Relation of catalyst amount with yield (%) of carboxylic acids.

To demonstrate the versatility of the developed protocol, different benzaldehydes were selected (Figs. 3 and 4) and found that moderate to good results were obtained.

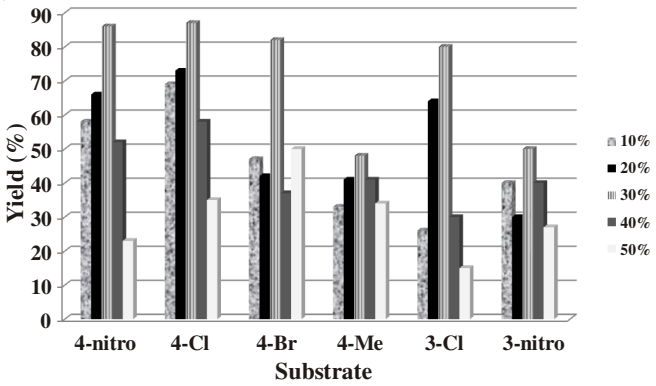

Fig. 3. Yield (%) of carboxylic acids with different loading of catalyst

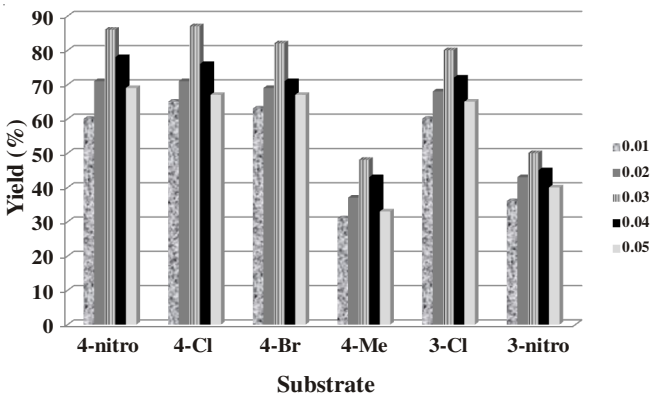

Fig. 4. Yields of carboxylic acids with different amount of the catalyst

Interestingly, in all cases the observed yields were higher with 30 % loading and 0.03 g. In the obtained optimum conditions, effect of the time was studied in the time range of 2-8 h and the results are presented in Fig. 5.

It is observed that the yield of benzoic acids increases with the reaction time. At reaction time of 6 h, the yield increases and it has not increase thereafter. This has been found to be due to the non-availability of enough oxidant in the reaction mixture after 6 h. This is confirmed by the determination of unreacted hydrogen peroxide by titration method that shows little oxidant left in the mixture after 6 h. Addition of fresh oxidant again after 6 h takes reaction to increase of yield.

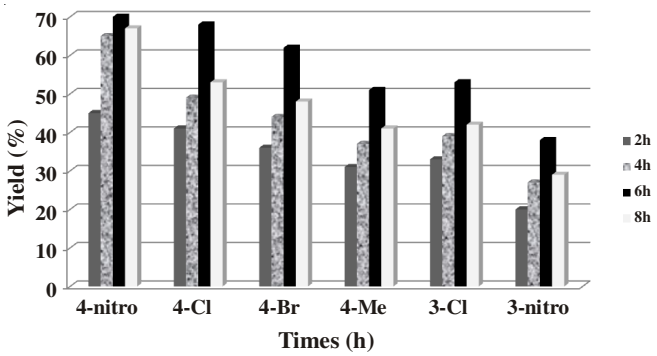

Fig. 5. Effect of time in % yield of carboxylic acids

Effect of microwave irradiation: In recent years, a practical dimension to microwave heating protocols was added by accomplishing reactions on solid supports under solvent-free conditions[18]. These solvent-free microwave-assisted reactions provide an opportunity to work with open vessels, thus avoiding the risk of high-pressure development and increasing the potential of such reactions to large-scale production.

To determine the scope of this catalytic system, all of the aldehydes were oxidized under the optimized conditions in solvent-free conditions under microwave irradiation. The results are summarized in Fig. 6. The results showed that, all of the benzaldehydes could easily be oxidized to the corresponding carboxylic acids in short times (4-5 min).

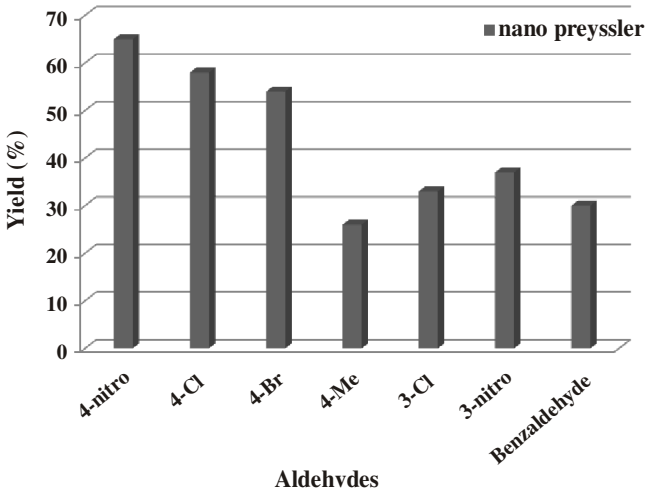

Fig. 6. Yields of the oxidation reactions of benzaldehydes under microwave irradiation (optimum conditions)

A comparison between the methods shows that under microwave irradiation, the oxidation readily proceeds under solvent-free conditions in very short times (4-5 min). This can be due to the polar nature of the reaction intermediates that couple efficiently with the microwaves and hence, increase the yield and accelerate the rate. Clearly, this method minimizes the longer reaction times required under thermal conditions.

Catalyst recyclability: One of the most appreciable properties of a heterogeneous catalyst is its durability. Thus we tested the catalyst on recycling, checking the overall leaching of the $H_{14}[NaP_5W_{30}O_{110}]$ on the used catalyst after several runs. Each run was carried out under identical conditions and reusing the recovered catalyst. The results indicated that the activity of the catalyst was not affected even at the third run with the reused catalyst.

Conclusion

SiO_2 nanoparticles was synthesized and used as a support for the $H_{14}[NaP_5W_{30}O_{110}]$ in different loadings and amounts. The resulting catalysts were used to catalyze the oxidation of benzaldehydes to the corresponding carboxylic acids at reflux temperature and microwave irradiation. The simplest available oxidant, hydrogen peroxide, is used and the oxidative reactions showed good to excellent yields and selectivities. Our findings showed that the loading percentage and catalyst amount as well as the reaction time are important factors.

Good yields, high selectivity, economically convenience, ease of work up, high hydrolytic and thermal stability of the catalyst can extend this reaction to other similar reactions in industry.

REFERENCES

1. B.M. Reddy, P.M. Sreekanth and P. Lakshmanan, *J. Mol. Catal. A*, **237**, 93 (2005).
2. J.H. Clark, *Acc. Chem. Res.*, **35**, 791 (2002).
3. T. Okuhara, *Chem. Rev.*, **102**, 3641 (2002).
4. K. Wilson and J.H. Clark, *Pure Appl. Chem.*, **72**, 1313 (2000).
5. G.D. Yadav and R.D. Bhagat, *J. Mol. Catal.*, **235**, 98 (2005).
6. K. Imamura, K. Tano and S. Kobeppn, JP Patent, 1087811 (1998).
7. M. Langpape and J.C.M. Millet, *Appl. Catal.*, **A 89**, 200 (2000).
8. F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir and A. Gharib, *Appl. Catal. A*, **302**, 42 (2006).
9. F.F. Bamoharram, M.M. Heravi, M. Roshani, A. Gharib and M. Jahangir, *J. Mol. Catal. A*, **252**, 90 (2006).
10. G. Baronetti, H. Thomas and C.A. Querini, *Appl. Catal. A.*, **217**, 131 (2001).
11. F.F. Bamoharram, M. Roshani, M.H. Alizadeh, H. Razavi and M. Moghayadi, *J. Braz. Chem. Soc.*, **17**, 505 (2006).
12. F.F. Bamoharram, M.M. Heravi and S. Mehdizadeh, *Synth. React. Inorg. Met.-Org. Nano-Met. Chem.*, **39**, 746 (2009).
13. F.F. Bamoharram, M.M. Heravi, H. Teymouri, M. Zebarjad and A. Ahmadpour, *Synth. React. Inorg.Met.-Org. Nano-Met. Chem.*, **41**, 1221 (2011).
14. F.F. Bamoharram, M.M. Heravi, M. Roshani and N. Tavakoli, *J. Mol. Catal. A*, **252**, 219 (2006).
15. F.F. Bamoharram, M.M. Heravi, M. Roshani and M. Akbarpour, *J. Mol. Catal. A: Chem.*, **255**, 193 (2006).
16. F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir and A. Gharib, *J. Mol. Catal. A,* **271**, 126 (2007).
17. F.F. Bamoharram, M.M. Heravi, M. Roshani and M. Toosi, *Green Chem. Lett. Rev.*, **2**, 35 (2009).
18. B.L. Hayes, Microwave Synthesis. Chemistry at the Speed of Light, CEM Mattehews, NC, USA (2002).