

Short communication

A catalytic method for synthesis of γ -butyrolactone, ϵ -caprolactone and 2-cumaranone in the presence of Preyssler's anion, $[\text{NaP}_5\text{W}_{30}\text{O}_{110}]^{14-}$, as a green and reusable catalyst

Fatemeh F. Bamoharram^{a,**}, Majid M. Heravi^{b,*}, Mina Roshani^a,
Ali Gharib^a, Manouchehr Jahangir^a

^a Department of Chemistry, School of Sciences, Islamic Azad University, Mashhad Branch, Mashhad, Iran

^b Department of Chemistry, School of Sciences, Azahra University, Vanak, Tehran, Iran

Received 21 November 2005; received in revised form 31 January 2006; accepted 31 January 2006

Available online 24 March 2006

Abstract

γ -Butyrolactone, ϵ -caprolactone and 2-cumaranone are synthesized from related diols, using Preyssler heteropolyacids, $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ and $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$ as catalyst, and hydrogen peroxide as oxidizing agent. The performance of eco-friendly Preyssler catalysts was compared with H_2SO_4 and the catalytic activity of H_2SO_4 is found to be lower than Preyssler catalysts. The effects of various parameters such as amount of diol, temperature, solvent and time were studied. In all cases, the Preyssler catalyst was easily recovered and recycled with retention of their initial structure and activity.

© 2006 Elsevier B.V. All rights reserved.

Keywords: Preyssler; Catalyst; Lactone; Diol; Heteropolyacid

1. Introduction

Lactones of five, and larger rings, are of interest because of their applications in building up biologically active compounds which exhibit various pharmacological activities [1–5]. They can be also used for the synthesis of polyesters [6,7].

There are a number of methods concerning the lactonization of diols. Many catalytic methods including heterogeneous liquid phase lactonization of diols using vanadomolybdophosphoric acid immobilized on polyaniline [8], lactonization of α -, ω -diols by use of the sodium bromate–hydrobromic acid system [9], cyclo carbonylation of allylic alcohols [10,11], and direct insertion of carbon monoxide into cyclic ethers [12], with palladium-based catalysts have been reported. Most of these catalysts are expensive and the applications of them cause some drawbacks such as environmental problems, long reaction times and tedious work up procedure.

Green/sustainable chemistry (GSC) is, in a word, chemistry and chemical technology for environmentally friendly products and processes. Green chemistry has been defined as a set of principles that reduces or eliminates the use or generation of hazardous substances throughout the entire life of chemical materials [13,14]. If one compares the technology with medical care, GSC focuses on precaution (or prevention) rather than diagnosis and cure. Here, the idea of placing more stress on the stage of design, as stated in the definition [13,14], is important and useful. Heteropolyacids as solid acid catalysts are green with respect to corrosiveness, safety, quantity of waste, and separability and it is well known that the use of heteropolyacid catalysts for organic synthesis reactions can give a lot of benefits. Heteropolyacids are widely used in variety of acid catalyzed reactions [15–20].

It is known that heteropolyacid catalysts are active in the lactonization of 1,4-butanediol into γ -butyrolactone, which is an important chemical as a solvent and as a precursor for the synthesis of *N*-methyl-2-pyrrolidone and 2-pyrrolidone [21–23].

One of the unique features that make solid heteropolyacids economically and environmentally attractive is their stability and Bronsted acidity.

* Corresponding author. Tel.: +98 9121329147; fax: +98 218047861.

** Corresponding author.

E-mail addresses: fbamoharram@mshdiau.ac.ir (F.F. Bamoharram), mmh1331@yahoo.com (M.M. Heravi).

Although a wide variety of heteropolyacids have been reported as green and effective catalysts [24–28], there are only a few reports for application of Preyssler catalyst. This heteropolyacid with fourteen acidic protons is an efficient “supper acid” solid catalyst with unique hydrolytic stability (pH 0–12) [29].

Recently, we have been exploring the application of this catalyst and have found that this catalyst in different forms are very effective in catalytic processes [30–33].

Because of interesting importance of lactones and in continuation of our interest in application of heteropolyacids in organic synthesis [34,35], specially, in this article we wish to report our results for the synthesis of lactones using Preyssler catalyst in various conditions.

Our findings indicate that Preyssler catalyst render effective lactonization of 1,4-butanediol, 1,6-hexanediol and 1,2-benzene dimethanol to γ -butyrolactone, ϵ -caprolactone and 2-cumaranone respectively with high yields and excellent selectivity by using hydrogen peroxide. Also we have found that, in spite of degradation of the Keggin heteropolyacids in the presence of hydrogen peroxide [36], Preyssler catalyst catalyzes the lactonization reactions with complete retention of structure. The effects of various parameters such as amount of diol, temperature, solvent and time were studied. For expanding of our work we studied, using urea-hydrogen peroxide (UHP- H_2O_2) and DABCO- H_2O_2 . In the last few years, several reports appeared on the use of UHP and DABCO- H_2O_2 for the conversion of amines to nitroalkanes, Bayer–Villiger oxidations of ketons to lactones, oxidations of sulfides to sulfones, conversion of pyridines to pyridine *N*-oxides, epoxidation of styrene and alkenes, epoxidation of allylic alcohols and alkenes, oxidation of diols with methyltrioxo rhenium, oxidation of thiols to disulfides, oxidation of aromatic aldehydes, oxidation of imines to oxaziridines and nitrores, and asymmetric epoxidation catalyzed by oligopeptides [37–50].

Hence, it was thought that instead of aqueous hydrogen peroxide, anhydrous UHP- H_2O_2 or DABCO- H_2O_2 can be used as the oxidizing agent. A major advantage of UHP lies in its potential for releasing anhydrous H_2O_2 into solution in a controlled manner [51]. Literature survey, revealed that UHP and DABCO- H_2O_2 are insoluble in common organic solvents such as chloroform as solvent of choice in our reactions [52,53].

The major aim described in this work is the design and development of applications for Preyssler catalyst with exclusive properties including high thermal and hydrolytic stability and strong acidity.

2. Experimental section

2.1. Chemicals and apparatus

All solvents and diols were purchased from commercial sources. $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ was prepared by passage of a solution of the potassium salt in water through a column (50 cm \times 1 cm) of Dowex 50w \times 8 in the H^+ form and evaporation of the elute to dryness under vacuum [30].

Molybdenum substituted Preyssler heteropolyanion, $\text{H}_{14}[\text{NaP}_5\text{W}_{29}\text{MoO}_{110}]$, was prepared as follow: 2.8 g (0.169 mol)

$\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ and 2 g (0.008 mol) $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ were dissolved in 35 ml water and mixed at 60 °C for 30 min. The solution was cooled to room temperature, and 25 ml concentrated phosphoric acid was added. The resulted yellow solution was refluxed for 18 h. The solution was brought to room temperature, diluted with water and during stirring 10 g KCl was added. The mixture was stirred and then evaporated to dryness. The product was dissolved in warm water and upon cooling to room temperature yellow crystals formed. Acidic form of molybdenum substituted heteropolyacid was obtained as described above for unsubstituted analogue.

Supported heteropolyacid catalyst was synthesised according to our previous report [30] using impregnating a support in the form of powder (SiO_2) with an aqueous solution of the $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$. After stirring of the mixture, the solvent was evaporated, dried at 120 °C and was calcined at 250 °C in a furnace prior to use. Hydrogen peroxide was obtained from Merck Company and was standardized by online internet methods (Hydrogen Peroxide Product Information Manual, Analytical Procedure).

2.2. Instruments

IR spectra were obtained with a buck 500 scientific spectrometer. GLC analysis was performed on a Pu 4500 gas chromatograph with FID detector. ^1H NMR spectra were recorded on a FT NMR Bruker 100 MHz Aspect 3000 spectrometer.

2.3. General procedure for lactonization reaction

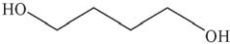
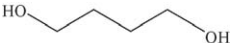
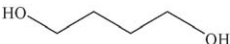
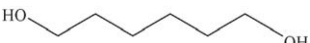
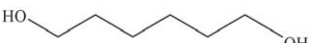
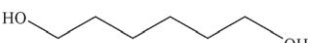
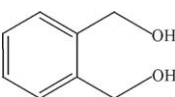
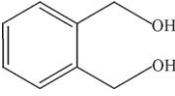
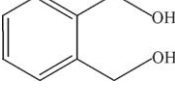
In a round-bottom flask equipped with a thermometer and reflux condenser, diol (1.15×10^{-2} mol), catalyst (0.15×10^{-4} mol) and solvent (10 ml) were placed and the hydrogen peroxide 30% (0.046 mol) was added. The reaction mixture was heated with stirring for 6 h at reflux temperature (boiling point of solvents). The progress of reaction was followed by measuring the amount of produced water by Karl–Fisher titration. After 6 h, the reaction mixture was cooled to room temperature. To this mixture saturated sodium carbonate and sodium sulfite 20% were added respectively, and the solution was extracted with dichloromethane (3×10 ml). The organic phase was dried on magnesium sulfate and evaporated under reduced pressure. The lactones were purified by column chromatography using petroleum ether and diethyl ether as eluant.

3. Results and discussion

As mentioned earlier, we have previously explored the esterification reaction of salicylic acid with aliphatic and aromatic alcohols in the presence of Preyssler catalyst in homogeneous and heterogeneous conditions to produce esters [31].

In continuation of our interest in this area, we have explored the dimeric esterification of butanol to butylbutanoate and we have found a good selectivity and yield for the preparation of butylbutanoate [32].

Table 1
Lactonization of diols by Preyssler catalyst in various solvents at reflux temperature for 4 h

Entry	Solvent	Substrate	% Product yield	
			H ₁₄ -P ₅	H ₁₄ -P ₅ Mo
1	Chloroform		88.50	96.00
2	1,2-Dichloroethan		86.80	93.50
3	Tetrachloride carbon		82.90	90.70
4	Chloroform		90.00	98.50
5	1,2-Dichloroethan		83.80	97.50
6	Tetrachloride carbon		79.80	95.50
7	Chloroform		82.90	96.70
8	1,2-Dichloroethan		78.30	94.40
9	Tetrachloride carbon		71.30	94.40

In continuation of our investigation on application of heteropolyacid catalysts [33–36], we wish to report an efficient and green method for the synthesis of cyclic esters, known as lactones.

The results for lactonization of 1,4-butanediol, 1,6-hexanediol and 1,2-benzene dimethanol with Preyssler catalyst and hydrogen peroxide in various solvents under reflux temperature (boiling point of solvents) at 6 h are shown in Table 1. As shown in Table 1, the lactonization reaction was proceeded with a higher yield using chloroform as solvent. It can be attributed to the increased solvent polarity under the same reaction conditions.

Comparison between H₁₄[NaP₅W₃₀O₁₁₀] and H₁₄[NaP₅W₂₉MoO₁₁₀], shows that H₁₄[NaP₅W₂₉MoO₁₁₀] produces higher yield. This activity of H₁₄[NaP₅W₂₉MoO₁₁₀], is expected because, lactonization of diols is an catalytic-oxidative reaction. Since a heteropolyacid with molybdenum atom shows higher reduction potential [54], the higher yields was expected to be obtained with H₁₄[NaP₅W₂₉MoO₁₁₀].

Surprisingly and interestingly, in the same condition, we found out that H₂SO₄ is less active than the Preyssler catalyst. In optimum conditions (chloroform as solvent and 6 h) in the presence of H₂SO₄ the yield of γ -butyrolactone, ϵ -caprolactone and 2-cumaranone was obtained in 77%, 80% and 71%, respectively. The results are compared in Fig. 1.

Preyssler polyanion as a large anion can provide many “sites” on the oval-shaped molecule that are likely to render the catalyst effective.

Table 2 shows the dependence on the amount of the diol in optimum conditions. The results show that the yield increases with increase of the diol amount. Interestingly, in all cases the yields are higher with H₁₄[NaP₅W₂₉MoO₁₁₀].

We also observed the lactonization is depend on temperature. In all solvents in the presence of Preyssler catalyst the maximum yield of lactones is obtained at reflux temperature, and the lower temperatures does not have any affect on the reaction.

For all diols in the presence of Preyssler catalyst, the effect of reaction time on the % yield of lactones was studied. The results are shown in Figs. 2–7. It seems clear that there is an increase in the yields with increase in reaction times in the presence of both

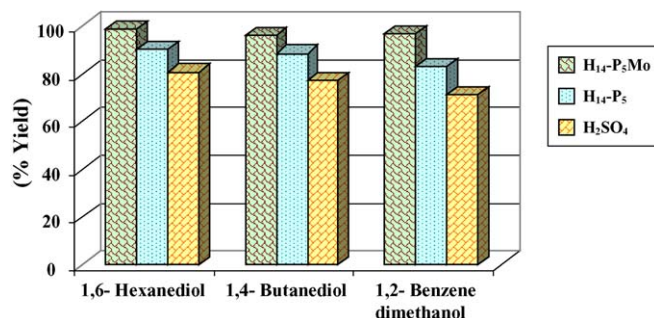
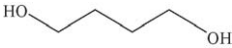
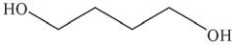
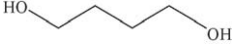
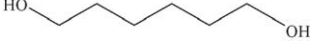
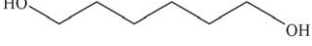
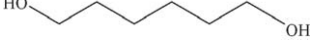
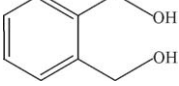
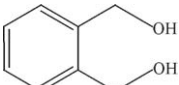
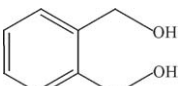
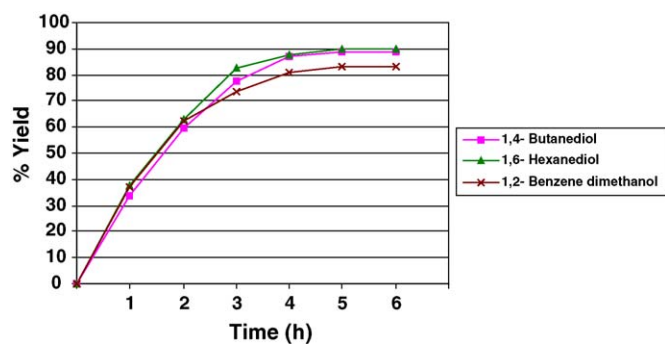
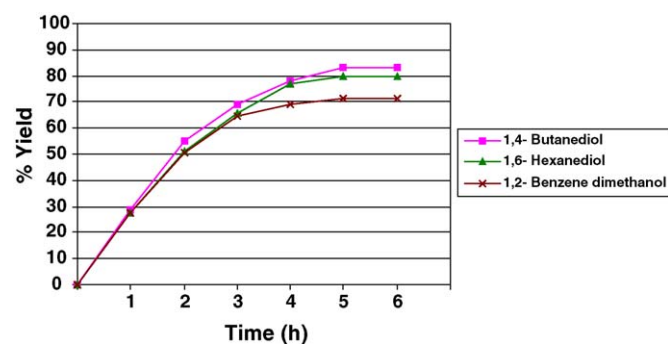
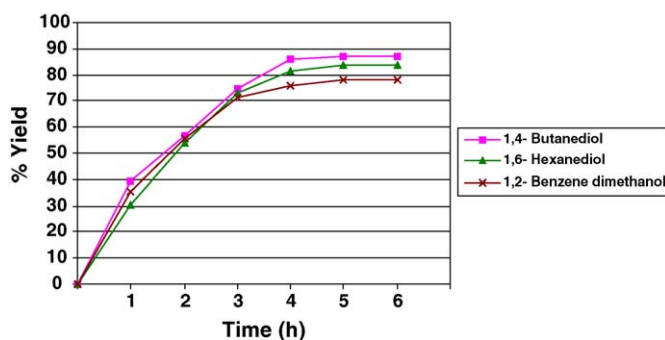
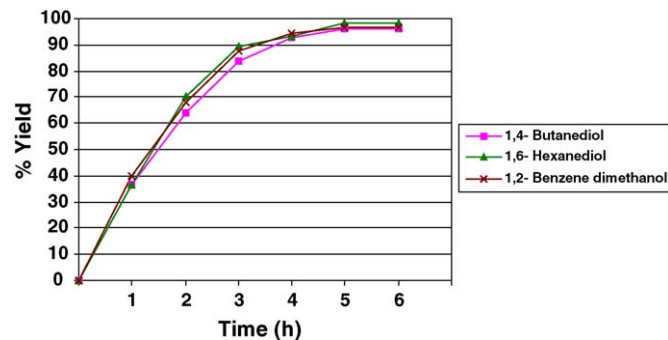


Fig. 1. Comparison between Preyssler catalyst and sulfuric acid in lactonization reactions.

Table 2

Lactonization with different moles of diols in the presence of Preyssler catalyst at reflux temperature in chloroform

Entry	Number of moles	Substrate	% Product yield	
			H ₁₄ -P ₅	H ₁₄ -P ₅ Mo
1	1.15×10^{-2}		88.50	96.00
2	0.575×10^{-2}		80.10	89.40
3	0.287×10^{-2}		70.50	81.20
4	0.869×10^{-2}		90.00	98.50
5	0.434×10^{-2}		85.20	91.00
6	0.217×10^{-2}		77.60	89.90
7	0.723×10^{-2}		82.90	96.70
8	0.361×10^{-2}		64.10	75.60
9	0.180×10^{-2}		60.80	69.90

Fig. 2. Yield of homogeneous catalytic lactonization of diols in chloroform and in the presence of H₁₄[NaP₅W₃₀O₁₁₀].Fig. 4. Yield of homogeneous catalytic lactonization of diols in tetrachloride carbon and in the presence of H₁₄[NaP₅W₃₀O₁₁₀].Fig. 3. Yield of homogeneous catalytic lactonization of diols in 1,2-dichloroethane and in the presence of H₁₄[NaP₅W₃₀O₁₁₀].Fig. 5. Yield of homogeneous catalytic lactonization of diols in chloroform and in the presence of H₁₄[NaP₅W₂₉MoO₁₁₀].

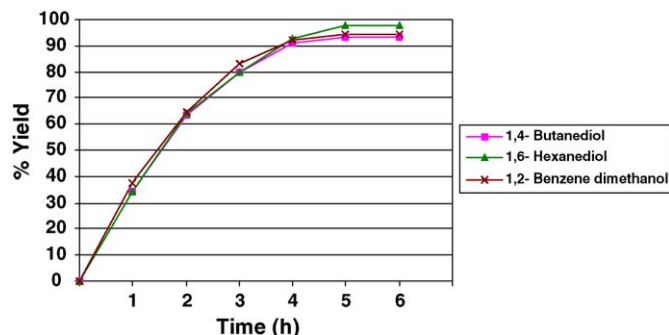


Fig. 6. Yield of homogeneous catalytic lactonization of diols in 1,2-dichloroethane and in the presence of $H_{14}[NaP_5W_{29}MoO_{110}]$.

Preyssler catalysts. The optimum reaction time has been found to be 5.5 h. The selectivity towards obtained esters remains 100% in all cases.

We have found that the Preyssler catalyst can be recovered at least five times and reused without any appreciable loss of activity. This result is very important because, in the presence of H_2O_2 as oxidizing agent most of the heteropolyacids degrade to the peroxopolyoxometalates [36].

In all cases, the IR spectra showed the absence of alcoholic OH band and appearance of carbonyl band in $1700\text{--}1800\text{ cm}^{-1}$. IR spectra of γ -butyrolactone and ϵ -caprolactone were showed, stretching vibration band of carbonyl group in the range of $1770\text{--}1790$ and $1700\text{--}1735\text{ cm}^{-1}$, respectively. IR spectra of 2-cumaranone showed stretching vibration band of carbonyl group in $1700\text{--}1800\text{ cm}^{-1}$. This shift is attributed to conjugation of benzene ring with carbonyl group.

In conclusion, although other procedures for the lactonization of diols have been reported, our method is more effective because of their ease, simplicity, mildness of conditions, good product yields and catalyst type. The salient features of this catalyst, are simple experimental set-up and procedure, high yields and eco-friendly conditions. We believe this applicability of Preyssler's anion with strong acidic properties, highly thermal stability and functionality over a wide range of pH makes our method superior over other reported methods to synthesis lactones and find usefulness in organic methodologies.

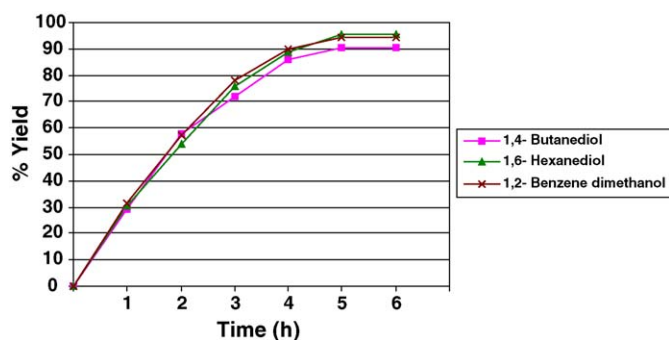


Fig. 7. Yield of homogeneous catalytic lactonization of diols in tetrachloride carbon and in the presence of $H_{14}[NaP_5W_{29}MoO_{110}]$.

References

- [1] R.A. Raphael, P. Ravenscroft, *J. Chem. Soc. Perkin Trans. 1* (1988) 1823.
- [2] K.L. Dueholm, L.B. Pederson, *Synthesis* (1992) 1.
- [3] D.W. Robertson, J.H. Krushinski, B.G. Utterback, R.F. Kauffman, *J. Med. Chem.* 32 (1989) 1476.
- [4] L.F. Bjeldanes, *J. Org. Chem.* 42 (1977) 2333.
- [5] M.A. Weidner-Wells, A. Decamp, P.H. Mazzocchi, *J. Org. Chem.* 54 (1989) 5746.
- [6] T.F. Al-Alzemi, L. Kondaveti, K.S. Bisht, *Macromolecules* 35 (2002) 3380.
- [7] M. Trollasas, J.L. Hedrick, D. Mecerreyes, P. Dubois, R. Jerome, H. Ihre, A. Hult, *Macromolecules* 31 (1998) 2756.
- [8] S.S. Lim, G.I. Park, J.S. Choi, In.K. Song, W.Y. Lee, *Catal. Today* 74 (2002) 299.
- [9] S. Kajigaeshi, T. Nakagawa, N. Nagasaki, H. Yamasaki, *Bull. Chem. Soc. Jpn.* 59 (1986) 747.
- [10] T. Hosokawa, S.I. Murahashi, *Heterocycles* 33 (1992) 1079.
- [11] C. Coperet, T. Sugihara, G. Wu, I. Shimayama, E.I. Negishi, *J. Am. Chem. Soc.* 117 (1995) 3422.
- [12] B. El Ali, H. Alper, *J. Org. Chem.* 56 (1991) 5357.
- [13] P.T. Anastas, J.C. Warner, *Green Chemistry, Theory and Practice*, Oxford University Press, 1998.
- [14] J.H. Clark, *Green Chem.* 1 (1999) 1.
- [15] C. Hu, M. Hashimoto, T. Okuhara, M. Misono, *J. Catal.* 143 (1993) 437.
- [16] T. Okuhara, A. Kasai, M. Misono, *Shokubai (Catalyst)* 22 (1980) 226.
- [17] T. Yamada, *Peterotech (Tokyo)* 13 (1990) 627.
- [18] T. Okuhara, T. Nishimura, K. Ohashi, M. Misono, *Chem. Lett.* (1990) 1201.
- [19] T. Okuhara, T. Nishimura, K. Ohashi, M. Misono, *Chem. Lett.* (1995) 155.
- [20] A. Aoshima, S. Tonomura, S. Yamamatsu, *Adv. Technol.* 2 (1990) 127.
- [21] Y. Ishii, T. Yoshida, K. Yamawaki, M. Ogawa, *J. Org. Chem.* 53 (1988) 5549.
- [22] Y. Ishii, K. Yamawaki, T. Yoshida, T. Ura, M. Ogawa, *J. Org. Chem.* 52 (1987) 1868.
- [23] B. Torok, I. Busci, T. Beregszaszi, I. Kapocsi, A. Molnar, *J. Mol. Catal.* 107 (1996) 305.
- [24] M. Misono, *Mater. Chem. Phys.* 17 (1987) 103.
- [25] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [26] H. Hayashi, J.B. Moffat, *J. Catal.* 81 (1983) 66.
- [27] N. Mizuno, M. Misono, *Chem. Rev.* 98 (1998) 199.
- [28] C.L. Hill, C.M. Prosser-McCarthy, *Coord. Chem. Rev.* 143 (1995) 407.
- [29] M.H. Alizadeh, S.P. Harmalkar, Y. Jeannin, J. Martin-Frere, M.T. Pope, *J. Am. Chem. Soc.* 107 (1985) 2662.
- [30] M.H. Alizadeh, H. Razavi, F. Farrash Bamoharram, M.H. Hassanzadeh, *Kinet. Catal.* 44 (2003) 524.
- [31] F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir, A. Gharib, *Appl. Catal.* 302 (2006) 42.
- [32] F.F. Bamoharram, M.M. Heravi, M. Roshani, M. Jahangir, A. Gharib, *J. Mol. Catal.* (2006), submitted for publication.
- [33] F.F. Bamoharram, M. Roshani, M.H. Alizadeh, M. Moghayadee, *J. Braz. Chem. Soc.* (2006), in press.
- [34] M.H. Alizadeh, H. Razavi, F.F. Bamoharram, K. Daneshvar, *J. Mol. Catal.* 206 (2003) 89.
- [35] (a) M.M. Heravi, F. Derikvand, F.F. Bamoharram, *J. Mol. Catal.* 242 (2005) 173;
(b) M.M. Heravi, Kh. Bakhtiari, F.F. Bamoharram, *Catal. Commun.* (2006), in press.;
(c) M.M. Heravi, R. Motamedi, N. Seifi, F.F. Bamoharram, *J. Mol. Catal.* (2006), in press.
- [36] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [37] R. Ballini, E. Marcantoni, M. Petrini, *Tetrahedron Lett.* 33 (1992) 4835.
- [38] L. Astudillo, A. Galindo, A.G. Gonzalez, H. Mansilla, *Heterocycles* 36 (1993) 1075.
- [39] R. Balicki, *Synth. Commun.* 29 (1999) 2235.

- [40] R.S. Varma, K.P. Naicker, *Org. Lett.* 1 (1999) 189.
- [41] H. Heaney, A.J. Newbold, *Tetrahedron Lett.* 42 (2001) 6607.
- [42] P. Pietikainen, *J. Mol. Catal.* 165 (2001) 73.
- [43] R.I. Kureshy, N.H. Khan, S.H.R. Abdi, S.T. Patel, R.V. Jasra, *Tetrahedron: Asymmetry* 12 (2001) 433.
- [44] J.A. Damavandi, B. Karami, M.A. Zolfigol, *Synlett* (2002) 933.
- [45] D.R. Kelly, S.M. Roberts, *Pept. Sci.* 84 (2006) 74.
- [46] S.C. Laha, R. Kumar, *J. Catal.* 204 (2001) 64.
- [47] W. Adam, C.R. Shaha-Moller, K.S. Schmid, *J. Org. Chem.* 66 (2001) 7365.
- [48] A. Omar Bouh, J.H. Espenson, *J. Mol. Catal.* 200 (2003) 43.
- [49] B. Karami, M. Montazerzohori, M. Moghadam, M.H. Habibi, K. Niknam, *Turk. J. Chem.* 29 (2005) 539.
- [50] S. Carno, N.M. Do, J.E. Sieser, *Tetrahedron Lett.* 41 (2000) 2299.
- [51] A.M.A.R. Gonsalves, R.A.W. Johnstone, M.M. Pereira, J. Shaw, *J. Chem. Res. (S)* (1991) 208.
- [52] C.S. Lu, E.W. Hughes, P.A. Giguere, *J. Am. Chem. Soc.* 63 (1941) 1507.
- [53] J.A. Dobado, J. Molina, D. Portal, *J. Phys. Chem. A* 102 (1998) 778.
- [54] I.V. Kozhevnikov, *Russ. Chem. Rev. (English translation)* 56 (1987) 811.