Journal of the Serbian Chemical Society

H5PV2Mo10O40 as an efficient catalyst for the oxidation of thiols to the corresponding disulfides using hydrogen peroxide as the oxidant

ABDOLLAH FALLAH SHOJAEI[1*], MOHAMAD ALI REZVANI[1] and MAJID HERAVI[2]

[1]*Department of Chemistry, Faculty of Science, University of Guilan, Rasht, 419961-3769 and* [2]*Department of Chemistry, School of Science, Alzzahra University, Vanak, Tehran, Iran*

Abstract: The $H_5PV_2Mo_{10}O_{40}$ catalyzed the oxidation of thiols to their homo-disulfides using hydrogen peroxide as the oxidant under mild conditions is reported. This system provides an efficient, convenient and practical method for the syntheses of symmetrical disulfides. In this work, comparisons of Keggin and Dawson type polyoxometalates are addressed in term of relative stability, hardness and acidity.

Keywords: heteropolyacids; thiols; disulfides; hydrogen peroxide; Keggin type; polyoxometalate; Dawson.

INTRODUCTION

Disulfides play an important role in synthetic organic chemistry[1–3] as well as in biology, notably to control cellular redox potentials in biological systems in which thiols are oxidized to prevent oxidative damage.[4] The disulfide functionality is used as a protecting group under oxidative conditions for thiols, which can be regenerated by S–S bond cleavage.[5] Disulfides have also found industrial applications as vulcanizing agents and as important synthetic intermediates in organic synthesis.[6,7] Thiols can also be over-oxidized to sulfoxides and sulfones; therefore, controlled and selective studies were performed in the present investigation regarding the oxidation of thiols.[8] Various reagents and oxidants have been employed for the oxidation of thiols to homodisulfides.[9–16] Some of these methods suffer from obvious disadvantages, such as long reaction times, limited availability of the oxidant, toxicity of reagents and difficulty in the isolation of the products. Consequently, the introduction of readily available, safe and stable reagents for the oxidation of thiols to disulfide is still a necessity. In continuation of on-going research on the synthetic application of heteropolyacids (HPAs) in

---

* Corresponding author. E-mail: shja47@gmail.com

organic synthesis,[17–23] the applicability of various mixed HPAs for the efficient oxidation of thiols to their homodisulfides using hydrogen peroxide as the oxidizing reagent and under mild conditions is reported herein.

The catalytic function of heteropolyacids (HPAs) and related polyoxometalate compounds has attracted great attention, particularly over the last two decades.[16] In this context, heteropolyacids (HPAs) are promising catalysts. A common and important class of these acids and those used in the majority of catalytic applications is the Keggin class of compounds of general formula $H_nXM_{12}O_{40}$ (X = P, Si, As, Ge, B; M = Mo, W).[24] These solid acids are usually insoluble in non-polar solvents but highly soluble in polar ones. They can be used in bulk or supported forms in both homogeneous and heterogeneous systems. Furthermore, these HPAs have several advantages, including high flexibility in modification of the acid strength, ease of handling, environmental compatibility, non-toxicity, and experimental simplicity.[25] Keggin type polyoxoanions have been widely studied as homogeneous and heterogeneous catalyst for the oxidation of organic compounds.[26]

Another catalytically important subclass of Keggin compounds are the mixed vanadium(V)-substituted HPAs of the general formula $H_{3+n}PV_nM_{12n}O_{40}$ (M = = Mo and W; n = 1–6). These compounds exhibit high activity in acid–base type catalytic reactions; hence they are used in many catalytic areas as homogeneous and heterogeneous catalysts. The most well-known of these HPAs is $H_5PV_2Mo_{10}O_{40}$.

Previously reported procedures for the synthesis of large ring disulfides from thiols using dichlorodioxomolybdenum(VI) as a catalyst produced poor to moderate yields.[13] However, a very efficient and simple method for the oxidative coupling of thiols into the disulfides using hydrogen peroxide as an oxidizing reagent catalyzed by mixed vanadium(V)-substituted HPAs under mild conditions is now reported.

EXPERIMENTAL

All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. Previously reported methods were used to purify the thiols.[24] Preparation of the $H_5PV_2Mo_{10}O_{40}$ catalyst and other mixed heteropolyacids and salts were based on a literature procedure with the following modifications.[25] The acids of $[NaP_5W_{30}O_{110}]^{14-}$, $[P_2W_{18}O_{62}]^{6-}$ and $[P_2Mo_{18}O_{62}]^{6-}$ were prepared according to published methods and were identified by infrared spectroscopy.[26–28] All chemicals were purchased from Merck and used without purification. The ^{1}H-NMR spectra were recorded on a FT-NMR Bruker 100 MHz Aspect 3000 with tetramethylsilane as an internal standard and $CDCl_3$ as the solvent. The IR spectra were recorded on a Buck 500 Scientific Spectrometer in KBr pellets.

Preparation of $H_5PV_2Mo_{10}O_4$[25]

Sodium metavanadate (12.2 g, 100 mmol) was dissolved by boiling in 50 mL of water and then mixed with Na_2HPO_4 (3.55 g, 25 mmol in 50 mL of water). After cooling the solution, concentrated sulfuric acid (5 mL, 17 M, 85 mmol) was added, whereby the solution

developed a red color. Na$_2$MoO$_4$·2H$_2$O (60.5 g, 250 mmol) dissolved in 100 mL of water was added to the red solution under vigorous stirring, followed by the slow addition of concentrated sulfuric acid (42 mL, 17 M, 714 mmol). The hot solution was allowed to cool to room temperature. The 10-molybdo-2-vanadophosphoric acid was then extracted with 500 mL of diethyl ether. Air was passed through the heteropoly etherate (bottom layer) to free it of ether. The solid residue was dissolved in water, concentrated to first crystal formation, as already described, and then allowed to crystallize further. The large red crystals that formed were filtered, washed with water and air-dried.

Preparation of H$_4$PVMo$_{11}$O$_{40}$

Na$_2$HPO$_4$ (3.55 g, 25 mmol) was dissolved in 50 mL of water and mixed with sodium metavanadate (3.05 g, 25 mmol) that had been dissolved by boiling in 50 mL of water. The mixture was cooled and acidified to a red color with concentrated sulfuric acid (2.5 mL, 17 M, 42.5 mmol). To this mixture was added a solution of Na$_2$MoO$_4$·2H$_2$O (66.5 g, 274.8 mmol) dissolved in 100 mL of water. Finally, 42.5 mL of concentrated sulfuric acid was added slowly with vigorous stirring of the solution. With this addition, the dark red color changed to a lighter red. After cooling the aqueous solution, the heteropoly acid was extracted with 200 mL of diethyl ether. In this extraction, the heteropoly etherate was present as a middle layer; the bottom layer (water) was yellow and probably contained vanadyl species. After separation, a stream of air was passed through the heteropoly etherate layer to free it of ether. The orange solid that remained was dissolved in 50 mL of water, concentrated to the first appearance of crystals in a vacuum desiccator over concentrated sulfuric acid, and then allowed to crystallize further. The orange crystals that formed were filtered, washed with water and air-dried.

General procedure for the oxidation of thiols to disulfides

H$_5$PV$_2$Mo$_{10}$O$_{40}$ (0.5 g, 0.2 mmol) was dissolved in a mixture of 25 mL of ethanol and 5 mL of H$_2$O. The substrate thiol (4 mmol) and 1.5 mL (13 mmol) of 30 % H$_2$O$_2$ were added to the solution. The reaction mixture was stirred at room temperature until thin layer chromatography, TLC, indicated the reaction was complete. After completion of the reaction, the solid product was filtered off and recrystallized, while in the case of liquid disulfides, after completion of the reaction, the excess H$_2$O$_2$ was destroyed by 2 mL of 3×10^{-3} M sodium sulfite. The mixture was treated with dichloromethane (2×25 mL). The organic layer was dried by anhydrous MgSO$_4$ and then concentrated to obtain the required product. General reaction for the oxidation of thiols catalyzed by H$_5$PV$_2$Mo$_{10}$O$_{40}$ is shown in Scheme 1.

$$2RSH \xrightarrow[\text{H}_2\text{O}_2,\ \text{Solvent}]{\text{H}_5\text{PV}_2\text{Mo}_{10}\text{O}_{40}} RSSR$$
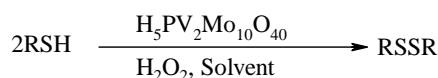
Scheme 1. General reaction for the oxidation of thiols catalyzed by H$_5$PV$_2$Mo$_{10}$O$_{40}$.

Recycling of the catalyst

In order to ascertain whether the catalyst had succumbed to poisoning and lost its catalytic activity during the reaction, the reusability of the catalyst was investigated. For this purpose, after completion of the model reaction (Scheme 1), dichloromethane was added to the solid reaction mixture. All the products were soluble in dichloromethane but the catalyst was not. Thus, the catalyst was separated by simple filtration, washed with dichloromethane and dried at 90 °C for 1 h, and then reused in further reaction with the same substrate.

RESULTS AND DISCUSSION

Effect of the solvent

4-Chlorothiophenol was taken as a model compound and the reaction conditions were optimized by varying the solvent, Table I. In EtOH + H_2O, the reaction was completed within 2 h. The other solvents provided moderate yields with longer reaction times, except CH_3CN and CH_3NO_2, in which the yields were very low even after 5 h (14 %, entry **12** and 18 %, entry **11**, respectively). Notably, in the absence of catalyst, very low yields were obtained (25 %, entry **2** and 21 %, entry **7**).

TABLE I. Results of the oxidation of 4-chlorothiophenol using H_2O_2 as the oxidant and $H_5PV_2Mo_{10}O_{40}$ as the catalyst in different solvents

Entry	Amount of $H_5PV_2Mo_{10}O_{40}$, g	Solvent	Time, h	Temperature, °C	Yield, %[a]
1	0.5	EtOH + H_2O	2	25	97
2	None		5	50	25
3	1.0		2	25	96
4[b]	0.5		2	25	97
5[c]	0.5		2	25	97
6	0.5	MeOH + H_2O	3	25	90
7	None		5	50	21
8	0.5	EtOH	4	25	73
9	0.5	MeOH	2	25	68
10	0.5	H_2O	4	50	45
11	0.5	CH_3NO_2	5	50	18
12	0.5	CH_3CN	5	50	14
13	0.5	CH_2Cl_2	2	50	74
14	0.5	DMF	2	50	63

[a]Isolated yield based on the weight of the pure product obtained; [b]the reaction was performed with the first recycled catalyst; [c]the reaction was performed with the second recycled catalyst

Effect of the catalyst structure

The effect of the structure of the catalyst on the oxidation of 4-chlorothiophenol, as a model compound, in EtOH + H_2O is presented in Table II. The amount of each catalyst was constant throughout the series. In the Keggin-type polyoxometalates series, $H_5PV_2Mo_{10}O_{40}$ showed the highest catalytic activity. In general, the heteropoly salt type catalysts were less efficient than the heteropolyacids. The Keggin-type polyoxometalates led to more effective reactions in comparison with the Wells–Dawson type polyoxometalates. However, $H_6P_2Mo_{18}O_{62}$ was more effective than $H_6P_2W_{18}O_{62}$ in the oxidation of thiols, possibly due to the difference in tungsten and molybdenum reduction potentials. However, the results indicated that the highest yield of disulfide was obtained with $H_5PV_2Mo_{10}O_{40}$ as catalyst (Table II). This behavior was found to be quite general. The high activity of $H_5PV_2Mo_{10}O_{40}$ in comparison of other HPAs (Tab-

Available online at www.shd.org.rs/JSCS/

le II) confirmed that in addition to H^+, V^{5+} probably play a catalytic role in the reaction.

TABLE II. Oxidation of 4-chlorothiophenol by H_2O_2 in the presence of a variety of hetero-polyacids

Entry	Catalyst	Time, h	Temperature, °C	Yield, %[a]
1	$H_5PV_2Mo_{10}O_{40}$	2	25	97
2	$H_4PVMo_{11}O_{40}$	2	25	95
3	$H_6PV_3Mo_9O_{40}$	2	25	96
4	$H_3PMo_{12}O_{40}$	4	45	92
5	$H_3PW_{12}O_{40}$	4	52	90
6	$H_4SiW_{12}O_{40}$	4	50	89
7	$H_{14}[NaP_5W_{30}O_{110}]$	5	70	75
8	$Na_3PMo_{12}O_{40}$	5	80	68
9	$Na_3PW_{12}O_{40}$	5	90	63
10	$(NH_4)_3H[PMo_{11}VO_{40}]$	5	120	56
11	$H_6P_2Mo_{18}O_{62}$	4	90	79
12	$H_6P_2W_{18}O_{62}$	4	90	72
13	None	4	90	28

[a]Isolated product
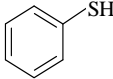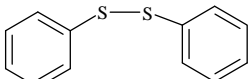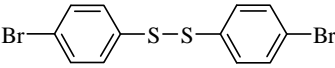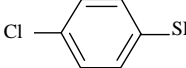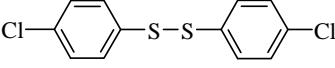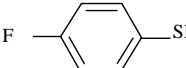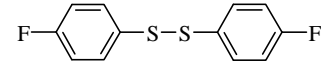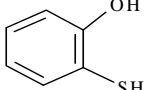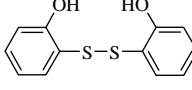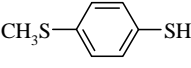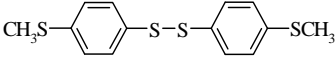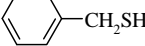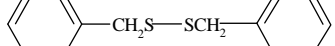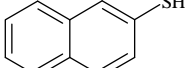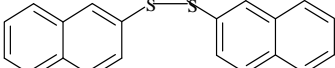
Effect of the substituent

The effects of various substituents on a range of aromatic thiols on the oxidation yield in EtOH + H_2O were examined using $H_5PV_2Mo_{10}O_{40}$ as the catalyst. The results are given in Table III. Halogens were chosen as electron-withdrawing groups (entries **3**–**5**), while methyl, phenolic hydroxyl and methylthio groups (entries **1**, **6** and **7**, respectively) were chosen as electron-donating substituents. One heteroaromatic thiol, *i.e*., pyridine-2-thiol, was successfully oxidized in good yield (entry **9**) as well as benzylthiol (entry **8**) as a benzylic aliphatic representative. The yields were generally very good (>75 %) to excellent (>90 %) with no obvious relationship between the aromatic substituent and yield (compare entries **4** with **5** and **2** with **10**). A highlight of the method is the ease by which the product may be isolated *via* simple filtration followed by removal of the solvent.
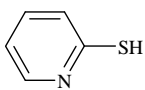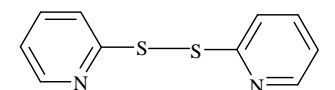
TABLE III. Oxidation of thiols with different substituents by H_2O_2 with $H_5PV_2Mo_{10}O_{40}$ as catalyst

Entry	Thiol	Disulfide	Time h	Yield[a,b] %	M.p., °C Found	M.p., °C Lit.[12,14,29]
1	CH_3—⟨⟩—SH	H_3C—⟨⟩—S–S—⟨⟩—CH_3	2	97	43–44	44–45

TABLE III. Continued

Entry	Thiol	Disulfide	Time h	Yield[a,b] %	M.p., °C Found	M.p., °C Lit.[12,14,29]
2	SH (phenyl)	S—S (diphenyl)	2	96	60–61	61
3	Br—〈〉—SH	Br—〈〉—S—S—〈〉—Br	2	95	90–92	91–93
4	Cl—〈〉—SH	Cl—〈〉—S—S—〈〉—Cl	2	97	72–73	70–71
5	F—〈〉—SH	F—〈〉—S—S—〈〉—F	3	79	49–51	–
6	OH / SH (o-hydroxyphenyl)	OH HO S—S	3	89	Li-quid[29]	–
7	CH$_3$S—〈〉—SH	CH$_3$S—〈〉—S—S—〈〉—SCH$_3$	3	82	40–43	40–43
8	〈〉—CH$_2$SH	〈〉—CH$_2$S—SCH$_2$—〈〉	3	78	69–71	69–70
9	〈N〉—SH (2-pyridyl)	〈N〉—S—S—〈N〉	3	77	55–56	55–57
10	naphthyl—SH	naphthyl—S—S—naphthyl	4	78	144–146	142–145

[a]Isolated yield based on the weight of the pure product obtained; [b]The products were identified by comparison of their physical and spectroscopic properties with the respective authentic compound

Reusability of the catalyst

After recovery of the catalyst, it was repeatedly used for further oxidation reactions. Even after five consequent employments, the catalytic activity of $H_5PV_2Mo_{10}O_{40}$ was almost the same as that of fresh catalyst. The results are summarized in Table IV. The IR spectra of the resulting solids indicated that the catalyst can be recovered without structural degradation.

Structures of the obtained disulfides

The structures and purity of the obtained disulfides were verified by ^{1}H- and ^{13}C-NMR spectroscopy and the obtained data are given in Table V, as well as by their melting points that are given in Table III.

TABLE IV. Reuse of the catalyst for oxidation of chlorothiophenol (see Table III, entry **4**, for the reaction conditions)

Entry	Isolated yield, %
1	96
2	94
3	95
4	96
5	92

TABLE V. ^{1}H-NMR and ^{13}C-NMR spectral data of the products

Entry	Product	^{1}H-NMR δ/ ppm	^{13}C-NMR, δ/ ppm
1	H₃C—⟨⟩—S–S—⟨⟩—CH₃	2.42 (6H, *s*, –CH₃), 7.07–7.14 (4H, *m*, Ar), 7.29–7.33 (4H, *m*, Ar)	135.8 (C1, C1′), 134 (C4, C4′), 130 (C3, C5, C3′, C5′), 127 (C2, C6, C2′, C6′), 21 (C7, C7′)
2	⟨⟩—S–S—⟨⟩	7.11–7.15 (2H, *m*, Ar), 7.29–7.33 (4H, *m*, Ar), 7.44–7.48 (4H, *m*, Ar)	136 (C1, C1′), 129 (C3, C5, C3′, C5′), 126.4 (C4, C4′), 126 (C2, C6, C2′, C6′)
3	Br—⟨⟩—S–S—⟨⟩—Br	7.11–7.16 (4H, *m*, Ar), 7.34–7.39 (4H, *m*, Ar)	135.8 (C1, C1′), 134 (C4, C4′), 130 (C3, C5, C3′, C5′), 127 (C2, C6, C2′, C6′)
4	Cl—⟨⟩—S–S—⟨⟩—Cl	6.57–6.61 (4H, *m*, Ar), 7.21–7.25 (4H, *m*, Ar)	135.3 (C4, C4′), 130 (C2, C6, C2′, C6′), 127 (C3, C5, C3′, C5′), 120 (C1, C1′)
5	F—⟨⟩—S–S—⟨⟩—F	6.37–6.44 (4H, *m*, Ar), 7.33–7.42 (4H, *m*, Ar)	154 (C4, C4′), 132 (C1, C1′), 129 (C2, C6, C2′, C6′), 115 (C3, C5, C3′, C5′)
6	OH HO ⟨⟩—S–S—⟨⟩	4.50 (2H, *s*, –OH), 6.72–6.76 (2H, *d*, Ar), 6.83–6.88 (2H, *t*, Ar), 7.17–7.22 (2H, *d*, Ar)	155.8 (C2, C2′), 131 (C4, C4′), 127 (C6, C6′), 126 (C1, C1′), 120 (C5, C5′), 113 (C3, C3′)
7	CH₃S—⟨⟩—S–S—⟨⟩—SCH₃	2.40 (6H, *s*, –SCH₃), 6.67–6.73 (4H, *m*, Ar), 7.19–7.23 (4H, *m*, Ar)	136 (C4, C4′), 134 (C1, C1′), 130 (C3, C5, C3′, C5′), 129 (C2, C6, C2′, C6′), 16.4 (C7, C7′)

TABLE V. Continued

Entry	Product	^{1}H-NMR δ/ ppm	^{13}C-NMR, δ/ ppm
8		3.53 (4H, *s*, –SCH$_2$), 7.19–7.22 (2H, *m*, Ar), 7.31–7.35 (4H, *m*, Ar) 7.40–7.45 (4H, *m*, Ar)	137 (C1, C1′), 129 (C2, C2′), 128 (C3, C5, C3′, C5′), 127.4 (C4, C4′), 42.6 (C7, C7′)
9		6.89–6.92 (4H, *m*, Py), 7.39–7.41 (2H, *m*, Py), 8.21–8.25 (2H, *m*, Py)	158 (C2, C2′), 147 (C6, C6′), 135 (C4, C4′), 122(C5, C5′), 118(C3, C3′)
10		7.40 (2H, *m*, Ar), 7.45 (2H, *m*, Ar), 7.62 (2H, *m*, Ar) 7.70 (2H, *m*, Ar), 7.74 (2H, *m*, Ar), 7.79 (2H, *m*, Ar), 7.96 (2H, *m*, Ar)	138 (C10, C10′), 137 (C8, C8′), 133 (C3, C3′), 134 (C1, C1′), 129.58 (C4, C4′), 128 (C5, C5′), 127 (C9, C9′), 126 (C7, C7′), 125(C2, C2′), 122(C6, C6′)

CONCLUSIONS

The H$_5$PV$_2$Mo$_{10}$O$_{40}$ heteropolyacid was the most successful heteropolyacid in the oxidation of the thiols. Although it is difficult to offer an explanation for the different activity between these HPAs, certainly there is a complex relationship between the activity and structure of the polyanion. By changing the constituent elements of the polyanion (both hetero and addenda atoms), the acid strength of HPAs as well as their catalytic activity are able to vary over a wide range.[18] For the first time, using an inexpensive and easily prepared H$_5$V$_2$PMo$_{10}$O$_{40}$ solid catalyst, the oxidation of thiols with electron-withdrawing and electron-donating groups to the corresponding disulfides was studied. The results showed that the catalyst type is important as well as solvent and temperature, but that the reaction withstands a range of substituents. Furthermore, the reusability of the catalysts was confirmed.

И З В О Д

H$_5$PV$_2$Mo$_{10}$O$_{40}$ КАО УСПЕШАН КАТАЛИЗАТОР ЗА ОКСИДАЦИЈУ ТИОЛА ДО ОДГОВАРАЈУЋИХ ДИСУЛФИДА ПОМОЋУ ВОДОНИК-ПЕРОКСИДА КАО ОКСИДАЦИОНОГ СРЕДСТВА

ABDOLLAH FALLAH SHOJAEI[1], MOHAMAD ALI REZVANI[1] и MAJID HERAVI[2]

[1]*Department of Chemistry, Faculty of Science, University of Guilan, Rasht 419961-3769 u*
[2]*Department of Chemistry, School of Science, Alzzahra University, Vanak, Tehran, Iran*

H$_5$PV$_2$Mo$_{10}$O$_{40}$ катализује оксидацију тиола до одговарајућих дисулфида помоћу водоник-пероксида као оксидационог средства, под благим реакционим условима. Примењени

реакциони услови омогућавају ефикасну и погодну синтезу симетричних дисулфида. У овом раду извршено је поређење са Keggin-овим и Dawson-овим полиоксометалатима у погледу релативне стабилности, јачине и киселости.

REFERENCES

1. D. C. Jocelyn, *Biochemistry of Thiol Group*, Academic Press, New York, 1992
2. M. C. Carreno, *Chem. Rev.* **95** (1995) 1717
3. N. Iranpoor, B. Zeynizadeh, *Synthesis* **1** (1999) 49
4. J. C. Bardwell, *J. Mol. Microbiol.* **14** (1994) 199
5. A. Ogawa, Y. Nishiyama, N. Kambe, S. Murai, N. Sonoda, *Tetrahedron Lett.* **28** (1987) 3271
6. K. Ramadas, N. Srinivasan, *Synth. Commun.* **25** (1995) 227
7. V. Srivastav, R. Gupta, R. R. Gupta, *Indian J. Chem.* **39B** (2000) 223
8. T. L. Ho, C. M. Wong, *J. Org. Chem.* **39** (1974) 562
9. C. C. Silveira, S. R. Mendes, *Tetrahedron Lett.* **48** (2007) 7469
10. J. Drabowicz, M. Mikolajczyk, *Synthesis* **1** (1980) 32
11. X. Wu, R. D. Rieke, L. Zhu, *Synth. Commun.* **26**(1996)191.
12. A. McKillop, D. Kuyuncu, *Tetrahedron Lett.* **31** (1990) 5007
13. R. Sanz, R. Aguado, M. R. Pedrosa, F. J. Arnaiz, *Synthesis* **7** (2002) 856
14. M. M. Khodaei, I. Mohammadpoor-Baltork, K. Nikoofar, *Bull. Korean Chem. Soc.* **24** (2003) 885
15. V. Kesavan, D. Bonnet-Delpon, J.-P. Begue, *Synthesis* **2** (2000) 223
16. C. A. S. Regino, D. E. Richardson, *Inorg. Chim. Acta* **360** (2007) 3971
17. M. M. Heravi, K. Bakhtiari, F. F. Bamoharram, *Catal. Commun.* **7** (2006) 373
18. F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, M. Jahangir, *J. Mol. Catal. A: Chem.* **252** (2006) 90
19. M. M. Heravi, R. Motamedi, N. Seifi, F. F. Bamoharram, *J. Mol. Catal. A: Chem.* **249** (2006) 1
20. F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Jahangir, A. Gharib, *J. Appl. Catal. A: Gen.* **302** (2006) 42
21. F. F. Bamoharram, M. M. Heravi, *J. Mol. Catal. A: Chem.* **255** (2006) 193
22. M. M. Heravi, S. Taheri, K. Bakhtiari, *Catal. Commun.*, in press
23. M. M. Heravi, F. K. Behbahani, *J. Mol. Catal. A: Chem.* **253** (2006) 16
24. I. V. Kozhevnikov, Chem. Rev. **98** (1998) 171
25. Y. Izumi, K. Urabe, M. Onaka, *Zeolites Clay and Heteropolyacid in Organic Reactions,* Kodansha, Tokyo, 1992, p. 99
26. I. V. Kozhevnikov, *Chem. Rev.* **98** (1998) 171
27. I. V. Kozhevnikov, *Catalysis for Fine Chemical Synthesis, Catalysis by Polyoxometalates*, Wiley, New York, 2002, p. 2
28. X. López, *PhD Thesis*, Universitat Rovira i Virgili, Tarragona, Spain, 2003
29. H. Golchoubian, F. Hosseinpoor, *Catal. Commun.* **8** (2007) 697.