

# Heteropoly acid cesium salt/cetyltrimethylammonium bromide a catalytic heterogeneous system which highly controls regioselective bromination of aromatic compounds with bromine

Habib Firouzabadi\*, Nasser Iranpoor<sup>1</sup>, Kamal Amani

Department of Chemistry, Shiraz University, Shiraz 71454, Iran

Received 7 August 2002; accepted 21 October 2002

## Abstract

Regioselective and high-yielding bromination of aromatic compounds especially phenols is an important protocol from different point of views. In this article, we have reported regioselective mono-bromination of phenol, its derivatives and some aromatic compounds with bromine in the presence of a heterogeneous catalytic system which is composed of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /cetyltrimethylammonium bromide (CTAB) in high yields. For reactions performed on 1 mmol scale of phenol, the optimum  $\text{PhOH}/\text{Br}_2/\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}/\text{CTAB}$  molar ratio was found to be 1:1.1:0.05:0.025. Phenols with electron-releasing groups were rapidly and selectively mono-brominated at their *para* positions in good to excellent yields. 2-Chlorophenol and 2,6-dichlorophenol were also mono-brominated at *para* positions in high yields. In the presence of this catalytic system, bromination of polycyclic aromatic compounds proceeded efficiently and furnished mono-brominated products by the control of bromine concentration.

© 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Phenol; Bromination; Heteropoly acid cesium salt; Cetyltrimethylammonium bromide; Heterogeneous catalysis

## 1. Introduction

Bromoarenes are widely used intermediates of commercial importance [1,2] and methods reported in the literature for the electrophilic bromination of aromatic compounds include: (i) solid brominating agents such as  $\text{PyHBr}_3$  [3],  $\text{DBUHBr}_3$  [4],  $\text{Me}_4\text{NBr}_3$  [5],  $\text{PhMe}_3\text{NBr}_3$  [6]; (ii)  $\text{Br}_2$ -Lewis acids [7],  $\text{Br}_2$ -zeolite [8–10],  $\text{Br}_2$ -silica or clay supported  $\text{ZnBr}_2$  [11]  $\text{Br}_2$ -supported resin [12]; (iii) oxidative nuclear bromination using metal-oxo catalysts [13–17]; (iv)

*N*-bromosuccinimide, NBS in solid state reactions [18], NBS-HZMS-5 zeolite [19], NBS-Amberlyst [20], NBS-HCl [21], NBS-SiO<sub>2</sub> [22], and NBS-HBF<sub>4</sub>·Et<sub>2</sub>O [23].

Heteropoly acids and their acidic salts having the Keggin structure are known to be excellent acid catalysts [24–26]. Tungstophosphoric acid ( $\text{H}_3\text{PW}_{12}\text{O}_{40}$ ) that belongs to Keggin type heteropoly acids has low surface area (ca.  $5\text{ m}^2\text{ g}^{-1}$ ), whereas its cesium salt has much higher surface area (ca.  $150\text{ m}^2\text{ g}^{-1}$ ) [27,28]. This high surface area makes it a more active catalyst than the parent acid and also other known solid acid catalysts such as zeolites [27,28]. Heteropoly acid cesium salt has been used for decomposition of cyclohexyl acetate into cyclohexene and acetic acid [29], alkylation and acylation of aromatics [30–32],

\* Corresponding author. Tel.: +98-711-2284822;

fax: +98-711-2280926.

E-mail address: firouzabadi@chem.susc.ac.ir (H. Firouzabadi).

<sup>1</sup> Co-corresponding author.

alkylation of isobutane [33–35], skeletal isomerization of *n*-butane [36–38], hydrolysis of esters [39] and hydration of olefins [40]. Oxidative bromination of a range of aromatics with HBr in the presence of oxygen catalyzed by heteropoly acids [41] and regioselective oxybromination of phenols with HBr gas catalyzed by  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$  (HPA-2) is also reported [42].

We have recently initiated studies on the use of tungstophosphoric acid as a Brønsted acid for the catalysis of oxidation of anilines to their corresponding nitro derivatives [43], thioacetalization of carbonyl compounds [44] and highly efficient solvent-free oxidation of hydroxy groups to their corresponding carbonyl compounds with ferric nitrate [45]. In this article, we have introduced a new heterogeneous catalytic system which is composed of the cesium salt of the heteropoly acid and cetyltrimethylammonium bromide (CTAB) for the highly controlled regioselective bromination of phenols and some aromatic compounds with molecular bromine.

## 2. Experimental

Tungstophosphoric acid cesium salt,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , was prepared according to the known procedure [46]. All the products are known and therefore, their physical data are not reported. The products were purified by column chromatography on silica gel and the purity was checked by GC on a Shimadzu model GC-14A instrument or by TLC on silica gel polygram SIL G/UV 254 plates. The IR spectra were recorded on a Perkin-Elmer 781 spectrophotometer. The NMR spectra were recorded on a Bruker avance DPX 250 MHz spectrometer.

### 2.1. General experimental procedure for mono-bromination of aromatic compounds

The catalyst (0.05 mmol, 0.160 g) and CTAB (0.025 mmol, 0.01 g) were placed in a round bottom flask (25 ml) containing  $\text{CH}_2\text{Cl}_2$  (5 ml) and was stirred for 5 min. Substrate (1 mmol) was then added to the resulting mixture and the mixture was stirred for extra 5 min. To the mixture, bromine (1.1 mmol, 0.058 ml) in  $\text{CH}_2\text{Cl}_2$  (5 ml) was added dropwise with rapid stirring at room temperature over a period of 10–30 min and stirring was continued for the appropriate reaction time

(Table 2). The reaction mixture was filtered and the filter cake was washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 25$  ml). The resulting organic layer was washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$ . Filtration and evaporation of the solvent afforded pure product (Table 2). When necessary, further purification could be achieved by column chromatography on silica gel (70–230 mesh) with an appropriate solvent. In the case of bromination of 2-naphthol, *n*-hexane was used as a solvent.

### 2.2. Larger-scale mono-bromination of phenol

The catalyst (0.25 mmol, 0.80 g) and CTAB (0.125 mmol, 0.05 g) were placed in a round bottomed flask (200 ml) containing  $\text{CH}_2\text{Cl}_2$  (50 ml) and was stirred for 5 min. Then phenol (50 mmol, 4.7 g) was added to the mixture and the resulting heterogeneous mixture was stirred for another 5 min. To the resulting mixture, dropwise addition of bromine (55 mmol, 2.75 ml) in  $\text{CH}_2\text{Cl}_2$  (50 ml) with rapid stirring at room temperature was continued for 20 min. Completion of the reaction (1 h) was monitored by TLC or GC. The resulting mixture was filtered and the filter cake was washed with  $\text{CH}_2\text{Cl}_2$  ( $2 \times 25$  ml). The resulting organic phase was separated, washed with  $\text{H}_2\text{O}$  and dried over anhydrous  $\text{MgSO}_4$  and filtered. Evaporation of the solvent under vacuum afforded the almost pure 4-bromophenol (8.15 g, 94%).

## 3. Results and discussion

Bromination of phenol with molecular bromine is an easy process and gives 2,4,6-tribromophenol and with the extra amount of bromine produces 2,4,4,6-tetrabromo-2,5-cyclohexadienone. Therefore, the regioselective and high-yielding bromination of aromatic compounds especially phenols is an important protocol from different points of view. In this paper, we reported a regioselective mono-bromination of phenol and phenol derivatives and some aromatic compounds with molecular bromine in the presence of this heterogeneous catalytic system [ $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ /CTAB] in high yields in dichloromethane at room temperature. This double catalytic system conducts reactions cleanly leading to the complete conversion of the starting materials and isolation of a single product. Optimization of the reaction conditions was studied on

Table 1  
Effects of binary catalyst system on the regioselectivity and activity of some bromination reactions

| Entry | Substrate                            | Sub./Br <sub>2</sub> /Cs <sub>2.5</sub> H <sub>0.5</sub> PW/CTAB | Time (min) | Conversion (%) | GC yield (%) ( <i>para</i> isomer) |
|-------|--------------------------------------|--|------------|----------------|------------------------------------|
| 1     | PhOH                                 | 1:1.1:0.000:0.025  | 90         | 88             | 85.5                               |
| 2     |                                      | 1:1.1:0.050:0.000  | 2          | 100            | 89 <sup>a</sup>                    |
| 3     |                                      | 1:1.1:0.025:0.000  | 5          | 73             | 66                                 |
| 4     |                                      | 1:1.1:0.001:0.000  | 15         | 62             | 43                                 |
| 5     |                                      | 1:1.1:0.050:0.025  | 2          | 100            | 97                                 |
| 6     | PhOCH <sub>3</sub>                   | 1:1.1:0.000:0.025  | 10         | 65             | 57                                 |
| 7     |                                      | 1:1.1:0.050:0.000  | 5          | 90             | 85.5                               |
| 8     |                                      | 1:1.1:0.025:0.000  | 5          | 83             | 77.5                               |
| 9     |                                      | 1:1.1:0.050:0.025  | 10         | 100            | 97 <sup>a</sup>                    |
| 10    |                                      | 1:1.1:0.025:0.025  | 10         | 83             | 79                                 |
| 11    | 2-BrC <sub>6</sub> H <sub>4</sub> OH | 1:1.1:0.000:0.025  | 180        | 61             | 56                                 |
| 12    |                                      | 1:1.1:0.050:0.000  | 35         | 50             | 41                                 |
| 13    |                                      | 1:1.1:0.050:0.025  | 35         | 58             | 56                                 |
| 14    |                                      | 1:1.1:0.100:0.025  | 35         | 77             | 75.5                               |
| 15    |                                      | 1:1.1:0.200:0.025  | 35         | 90             | 86                                 |

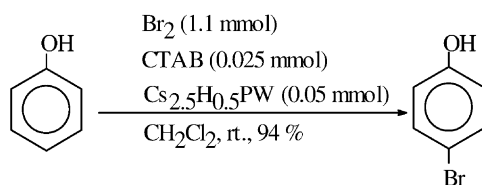
<sup>a</sup> Isolated yield.

phenol, as a model compound, in the presence of this catalytic system. Termination of the reaction was monitored by TLC and GC. For the reactions performed on a 1 mmol scale of the substrate, the optimum molar ratio of PhOH/Br<sub>2</sub>/Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>/CTAB was found to be 1:1.1:0.05:0.025 (Table 1, Scheme 1). With this ratio, immediate mono-bromination of phenol was occurred (100% conversion) with absolute regioselectivity at *para* position and the brominated phenol was isolated in 94% yield at room temperature. We observed that an immediate color change from white to a faint yellowish color by the addition of phenol to the catalytic system in dichloromethane. This observation indicates that an interaction has occurred between phenol molecules and the catalytic system.

We have also studied the application of this catalytic system for a large-scale bromination of phenol (50 mmol), with the molar ratio of 50:55:0.25:0.125

(PhOH/Br<sub>2</sub>/Cs<sub>2.5</sub>H<sub>0.5</sub>PW/CTAB) at room temperature. The reaction proceeded smoothly with the similar selectivity in >95% yield in 10 min with stirring at 1200 rpm. The reaction time, in this operation, was dependent on the rate of the stirring. The calculated turnover number for this reaction was around 190 with respect to Cs<sub>2.5</sub>H<sub>0.5</sub>PW and 380 with respect to CTAB.

In order to show the importance of the regioselectivity and activity of this binary catalytic system, we have studied the bromination of phenol, anisole and 2-bromophenol with different ratios of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>/CTAB (Table 1). The first reaction was conducted with PhOH/Br<sub>2</sub>/CTAB with the molar ratio of 1:1.1:0.025 in the absence of heteropoly acid cesium salt. Bromination at *para* position was occurred in longer reaction time (1.5 h) and the reaction was accompanied with the evolution of bromine fume which makes the handling of the reaction for the large-scale operation uneasy. Secondly, similar reaction was performed with PhOH/Br<sub>2</sub>/Cs<sub>2.5</sub>H<sub>0.5</sub>PW with the molar ratio of 1:1.1:0.05 in the absence of CTAB. By this system, immediate reaction occurred with 100% conversion of phenol with the production of 4- and 2-bromophenols in 89 and 11% isolated yields, respectively. Therefore, by lowering the concentration of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub> the yield, rate, and the regioselectivity of the reaction were decreased. In



Scheme 1.

Table 2

Bromination of phenols and some other aromatic compounds with bromine in the presence of Cs<sub>2.5</sub>H<sub>0.5</sub>PW<sub>12</sub>O<sub>40</sub>/CTAB system at room temperature in CH<sub>2</sub>Cl<sub>2</sub> and comparison of the results with some other reported methods

| Entry | Substrate                   | Br <sub>2</sub> addition time (min) | Time (min) <sup>a</sup> | Product                              | Yield (%) <sup>b</sup> |   |
|-------|-----------------------------|-------------------------------------|-------------------------|--------------------------------------|------------------------|---|
|       |                             |                                     |                         |                                      | This method            | Other method  |
| 1     | Phenol                      | 15                                  | Im.                     | 4-Bromophenol                        | 94                     | 99 <sup>c</sup> , 20 <sup>d</sup> , 83 <sup>e</sup>                   |
| 2     | <i>o</i> -Cresol            | 20                                  | Im.                     | 4-Bromo- <i>o</i> -cresol            | 92                     | 97 <sup>c</sup> , 92 <sup>d</sup>                                     |
| 3     | 2-Ethylphenol               | 20                                  | Im.                     | 4-Bromo-2-ethylphenol                | 91                     |   |
| 4     | 2-Methoxyphenol             | 30                                  | Im.                     | 4-Bromo-2-methoxyphenol              | 96                     | 72 <sup>e</sup>   |
| 5     | 2-Chlorophenol              | 15                                  | 15                      | 4-Bromo-2-chlorophenol               | 96                     | 78 <sup>e</sup>   |
| 6     | 2,6-Dichlorophenol          | 10                                  | 30                      | 4-Bromo-2,6-dichlorophenol           | 88                     |   |
| 7     | 2-Naphthol <sup>f</sup>     | 15                                  | Im.                     | 1-Bromo-2-naphthol                   | 91                     | 76 <sup>d</sup> , 60 <sup>g</sup>                                     |
| 8     | Anisole                     | 10                                  | 10                      | 4-Bromoanisole                       | 97                     | 98 <sup>c</sup> , 93 <sup>h</sup> , 70 <sup>i</sup> , 99 <sup>h</sup> |
| 9     | Anthracene                  | 20                                  | Im.                     | 9-Bromoanthracene                    | 90                     | 70 <sup>j</sup>   |
|       |                             | 20                                  | Im.                     | 9,10-Dibromoanthracene               | 98 <sup>k</sup>        | 93 <sup>d</sup> , 95 <sup>j</sup>                                     |
|       |                             | 20                                  | Im.                     | 9,10-Dibromophenanthrene             | 96 <sup>k</sup>        | 95 <sup>j</sup>   |
| 10    | Phenanthrene                | 20                                  | Im.                     | 9-Bromophenanthrene                  | 73                     | 60 <sup>j</sup>   |
| 11    | Fluorene                    | 10                                  | 4 (h)                   | 2-Bromofluorene                      | 94                     |   |
| 12    | Naphthalene                 | 10                                  | 6 (h)                   | 1-Bromonaphthalene                   | 59                     | 65 <sup>j</sup> , 98 <sup>l</sup>                                     |
| 13    | Aniline                     | 15                                  | Im.                     | 4-Bromoaniline                       | 43                     | 82 <sup>d</sup>   |
| 14    | 2-Chloroaniline             | 10                                  | Im.                     | 4-Bromo-2-chloroaniline              | 91                     |   |
| 15    | <i>N,N</i> -dimethylaniline | 10                                  | 10                      | 4-Bromo- <i>N,N</i> -dimethylaniline | 97                     | 98 <sup>c</sup> , 80 <sup>i</sup> , 70 <sup>l</sup>                   |
| 16    | Acetanilide                 | 10                                  | 5                       | 4-Bromoacetanilide                   | 98                     | 92 <sup>d</sup> , 99 <sup>l</sup>                                     |

<sup>a</sup> Reactions performed on 1 mmol of substrate. Im. stands for immediate work up after addition of bromine.

<sup>b</sup> Isolated yields.

<sup>c</sup> Conditions: substrate (20 mmol), tetraglyme (5 mmol), PMoV-2 (0.1 mmol), (CH<sub>2</sub>Cl)<sub>2</sub>, HBr (g), air, 20 °C, 5 h, (GLC data) [42].

<sup>d</sup> Conditions: substrate (1 mmol), TBAB (3 mmol), V<sub>2</sub>O<sub>5</sub> (0.5 mmol), H<sub>2</sub>O<sub>2</sub> (16 mmol), CH<sub>3</sub>CN/H<sub>2</sub>O (1:1), 5 °C, 0.5–2 h [17].

<sup>e</sup> Conditions: substrate (2 g), NBS (1–1.2 eq.), HBF<sub>4</sub>·Et<sub>2</sub>O (1–1.1 eq.), –20 °C to room temperature, CH<sub>3</sub>CN (20 ml), N<sub>2</sub>, 1.5–24 h [23].

<sup>f</sup> Reaction performed in *n*-hexane.

<sup>g</sup> Conditions: substrate (1 mmol), NBS (1 mmol), solvent-free, room temperature, 2 min [18].

<sup>h</sup> Conditions: substrate (0.84 mmol), Br<sub>2</sub> (0.93 mmol), NaY zeolite (0.55 g), CH<sub>2</sub>Cl<sub>2</sub> (8 ml), 20 °C, 5 h [8,9].

<sup>i</sup> Conditions: substrate (10 mmol), NBS (10 mmol), HZSM-5 (0.1 g), CCl<sub>4</sub> (30 ml), reflux, 5 h [19].

<sup>j</sup> Conditions: substrate (10 mmol), DBUHBr<sub>3</sub> (10–20 mmol), DMF/H<sub>2</sub>O (1:1, 25 ml), room temperature, 0.25–3 h [4].

<sup>k</sup> Reaction performed with 2.2 mol eq. of bromine.

<sup>l</sup> Conditions: substrate (4.63 mmol), CAN (5.1 mmol), LiBr (5.1 mmol), CH<sub>3</sub>CN (20 ml), room temperature, N<sub>2</sub>, 1–7 h [13].

the absence of CTAB, a lower selectivity has been observed. More or less, similar trend has been also observed for anisole and 2-bromophenol (Table 1).

In order to show the general applicability of the present method, we have studied the bromination of some other aromatic compounds. The results of this study are shown in Table 2. Phenols with electron-releasing groups such as *o*-cresol, 2-ethylphenol, and 2-methoxyphenol were rapidly and selectively mono-brominated at their *para* positions in good to excellent yields (Table 2, entries 2–4). 2-Chlorophenol and 2,6-dichlorophenol were mono-brominated at *para* positions with high yields.

We have also studied the bromination of polycyclic aromatic compounds such as naphthalene, anthracene,

phenanthrene, and fluorene in the presence of this catalytic system. The results show that bromination proceeded efficiently and furnished mono-brominated products by the control of bromine concentration.

In the bromination of anthracene and phenanthrene, 9-bromo and 9,10-dibromo derivatives can be prepared in excellent yields by controlling the molar ratio of bromine with respect to the substrate (Table 2, entries 9 and 10). Fluorene gave 2-bromofluorene and naphthalene gave 1-bromonaphthalene in 94 and 59% yields, respectively (Table 2, entries 11 and 12). Aniline, even in the presence of BaCO<sub>3</sub> as an acid scavenger, was quantitatively converted to 4-bromoaniline in 43% yield, plus other unidentified by-products. We believe that the high reactivity of aniline towards

electrophilic substitution reactions resulted in uncontrolled by-product formation in this reaction. Bromination of 2-chloroaniline and acetanilide which are less reactive compounds than aniline towards electrophilic reactions proceeded well and produced 4-bromo-substituted products in 91 and 98% yields, respectively (Table 2, entries 14 and 16). Bromination of benzene and its derivatives such as toluene, chlorobenzene and bromobenzene, 2-nitrophenol were unsuccessful by this binary catalytic system. We have also tried bromination of 2-naphthol in  $\text{CH}_2\text{Cl}_2$  which resulted in a mixture of unidentified products. We found that this reaction was a highly solvent dependent and in a non-polar media such as *n*-hexane, it proceeded well and 1-bromo-2-naphthol was isolated in a high yield (Table 2, entry 8). Comparison of our results with some of those reported in the literature shows the advantages of the present binary catalytic system. To the best of our knowledge, the only method which is comparable to the present protocol involves the use of  $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}/\text{O}_2/\text{HBr}$  gas/tetraglyme/ $\text{CH}_2\text{Cl}_2$  for 5 h [42]. However, the reaction condition used by this method is harsh and the reaction times are much longer.

#### 4. Conclusion

In this article, we have introduced a new binary catalytic system, tungstophosphoric acid cesium salt/CTAB for the high-yielding regioselective bromination of phenol and phenol derivatives and some other aromatic compounds with molecular bromine at room temperature. Comparison of the results obtained by the other methods shows that the present protocol is simpler and more efficient than other catalytic systems used for this purpose in many instances.

#### Acknowledgements

The authors are thankful to the Shiraz University Research Council for the partial support of this work.

#### References

- [1] C. Christophersen, *Acta Chem. Scand.* 39B (1985) 515.
- [2] A. Butler, J.V. Walker, *Chem. Rev.* 93 (1993) 1937.
- [3] L.F. Fieser, M. Fieser, *Reagents for Organic Synthesis*, Wiley, New York, 1967, p. 967.
- [4] H.A. Muathen, *J. Org. Chem.* 57 (1992) 2740.
- [5] M. Avramoff, J. Weiss, O. Schachter, *J. Org. Chem.* 28 (1963) 3256.
- [6] S. Kajigaeshi, T. Kakinami, H. Tokiyama, T. Hirakawa, T. Okamoto, *Chem. Lett.* (1987) 627.
- [7] H. Schmid, *Helv. Chim. Acta* 29 (1946) 1144.
- [8] K. Smith, G.A. El-Hiti, M.E.W. Hammond, D. Bahzad, Z. Li, C. Siquet, *J. Chem. Soc., Perkin Trans. 1* (2000) 2745.
- [9] K. Smith, D. Bahzad, *Chem. Commun.* (1996) 467.
- [10] F. Vega, Y. Sasson, K. Hhuddersman, *Zeolite* 13 (1993) 341.
- [11] J.H. Clark, J.C. Ross, D.J. Macquarrie, S.J. Barlow, T.W. Bastock, *Chem. Commun.* (1997) 1203.
- [12] Z.-X. Chen, G.-C. Yang, *Hecheng Huaxue* 7 (1999) 435.
- [13] S.C. Roy, C. Guin, K.K. Rana, G. Maiti, *Tetrahedron Lett.* 42 (2001) 6941.
- [14] J.R. Hanson, S. Harpel, I.C. Rodriguez Medina, D. Rose, *J. Chem. Res. (S)* (1997) 432.
- [15] M.H. Clague, A.J. Butler, *Am. Chem. Soc.* 117 (1995) 3475.
- [16] D. Roche, K. Prasad, O. Repic, T.J. Blacklock, *Tetrahedron Lett.* 41 (2000) 2083.
- [17] U. Bora, G. Bose, M.K. Chaudhuri, S.S. Dhar, R. Gopinath, A.T. Khan, B.K. Patel, *Org. Lett.* 2 (2000) 247.
- [18] J.A.R.P. Sarma, A. Nagaraju, *J. Chem. Soc., Perkin Trans. 2* (2000) 1113.
- [19] V. Paul, A. Sudalai, T. Daniel, K.V. Srinivasan, *Tetrahedron Lett.* 35 (1994) 7055.
- [20] Y. Goldberg, H. Alper, *J. Mol. Cat.* 88 (1994) 377.
- [21] B. Andersh, D.L. Murphy, R.J. Olson, *Synth. Commun.* 30 (2000) 2091.
- [22] H. Konishi, K. Aritomi, T. Okano, J. Kiji, *Bull. Chem. Soc. Jpn.* 62 (1989) 591.
- [23] T.J. Oberhauser, *J. Org. Chem.* 62 (1997) 4504.
- [24] M. Misono, *Chem. Commun.* (2001) 1141, and references therein.
- [25] T. Okuhara, H. Watanabe, T. Nishimura, K. Inumaru, M. Misono, *Chem. Mater.* 12 (2000) 2230.
- [26] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171, and references therein..
- [27] T. Okuhara, T. Nishimura, M. Misono, in: J.W. Hightower, W.N. Delgass, E. Iglesia, A.T. Bell (Eds.), *Proceedings of the 11th International Congress on Catalysis*, Elsevier, Amsterdam, 1996, p. 581.
- [28] T. Okuhara, A. Kasai, N. Hayakawa, Y. Yoneda, M. Misono, *J. Catal.* 121 (1983) 83.
- [29] T. Okuhara, T. Nishimura, K. Ohashi, M. Misono, *Chem. Lett.* (1990) 1201.
- [30] T. Okuhara, T. Nishimura, H. Watanabe, M. Misono, *J. Mol. Catal.* 74 (1992) 247.
- [31] T. Nishimura, T. Okuhara, M. Misono, *Appl. Catal.* 73 (1991) L7.
- [32] Y. Izumi, M. Ogawa, W. Nohara, K. Urabe, *Chem. Lett.* (1992) 1987.
- [33] T. Okuhara, M. Yamashita, K. Na, M. Misono, *Chem. Lett.* (1994) 1451.
- [34] P. Guyraud, N. Essyem, J.C. Vadrine, *Catal. Lett.* 56 (1999) 35.

- [35] A. Corma, M. Martinez, C. Martinez, *J. Catal.* 164 (1996) 422.
- [36] K. Na, T. Okuhara, M. Misono, *J. Chem. Soc., Faraday Trans. 1* 91 (1995) 367.
- [37] K. Na, T. Iizaki, T. Okuhara, M. Misono, *J. Mol. Catal.* 115 (1997) 449.
- [38] N. Essayem, G. Coudurier, M. Fournier, J.C. Vedrine, *Catal. Lett.* 34 (1995) 223.
- [39] M. Kimura, T. Nakato, T. Okuhara, *Appl. Catal.* 165 (1997) 227.
- [40] T. Okuhara, M. Kimura, T. Nakato, *Chem. Lett.* (1997) 839.
- [41] T.A. Gorodetskaya, I.V. Kozhevnikov, K.I. Matveev, USSR Patent 1,121,255 (1984).
- [42] R. Neumann, I. Assael, *J. Chem. Soc., Chem. Commun.* (1988) 1285.
- [43] H. Firouzabadi, N. Iranpoor, K. Amani, *Green Chem.* 3 (2000) 131.
- [44] H. Firouzabadi, N. Iranpoor, K. Amani, *Synthesis* (2001) 59.
- [45] H. Firouzabadi, N. Iranpoor, K. Amani, *Synthesis* (2002), in press.
- [46] S. Tatematsu, T. Hibi, T. Okuhara, M. Misono, *Chem. Lett.* (1984) 865.