Heterogenization of $H_6PMo_9V_3O_{40}$ and palladium acetate in VPI-5 and MCM-41 and their use in the catalytic oxidation of benzene to phenol

Luís César Passoni, Fernando J. Luna, Martin Wallau, Regina Buffon,
Ulf Schuchardt *

Instituto de Química, Universidade Estadual de Campinas, P.O. Box 6154, 13083-970 Campinas, SP, Brazil

Abstract

The heteropolyacid $H_6PMo_9V_3O_{40}$ (HPA) was encapsulated in MCM-41 and VPI-5. When HPA/MCM-41 is used in the direct oxidation of benzene to phenol, the heteropolyacid leaches from the MCM-41 and oxidation takes place in the homogeneous phase. VPI-5 retains the HPA and palladium acetate more efficiently than MCM-41, and can be used as a heterogeneous oxidation catalyst for benzene. However, its activity is very low since only the active species at the pore entrances of VPI-5 are accessible to the reactants. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Encapsulation; Heteropolyacids; VPI-5; MCM-41; Benzene oxidation; Phenol

1. Introduction

In a recent paper [1], we described the direct oxidation of benzene to phenol by molecular oxygen, catalyzed by palladium acetate in the presence of molybdovanadophosphoric heteropolyacids (HPA) with the general formula $H_{3+x}[PMo_{12-x}V_xO_{40}]$, where $x = 2, 3, 4$ or 6. Using 0.02 mmol palladium acetate, 0.3 g $H_6PMo_9V_3O_{40}$, 10 mmol lithium acetate and 150 mmol benzene in 200 mmol acetic acid and 400 mmol water, at 130°C, and an oxygen pressure of 60 bar, 12 mmol of phenol are produced with 75% selectivity, which corresponds to a turnover number of 800. However,

the system deactivates after 4 h of reaction time due to the irreversible reduction of the HPA and the palladium acetate. The addition of a fresh portion of HPA results in a non-selective oxidation to overoxidation products. Here, we describe attempts to heterogenize the catalytic system by incorporation of the HPA and palladium acetate in mesoporous MCM-41 and microporous AlPO₄-VPI-5 molecular sieves. This is, to the best of our knowledge, the first report of the encapsulation of a heteropolyacid into the VPI-5 aluminophosphate molecular sieve.

2. Experimental

The $H_6PMo_9V_3O_{40}$ was synthesized according to a procedure described by Tsigdinos and

---

* Corresponding author. Fax: +55-19-7883023; e-mail: ulf@iqm.unicamp.br

Hallada [2] and characterized by X-ray diffraction and X-ray fluorescence. Following a modified procedure of Beck et al. [3], mesoporous MCM-41 containing HPA with and without palladium were prepared from gels with the following molar composition: SiO_2: 0.5; CTMABr: 3.5; HCl: 52; H_2O: 0.01; HPA: 0 or 0.0012 Pd, which were reacted at 100°C under autogenous pressure for 72 h. Tetraethoxysilane (sample A) and sodium metasilicate (sample B) were used as silica sources, and cetyltrimethylammonium bromide (CTMABr) as template. In the palladium-containing molecular sieve (sample C), palladium acetate was used as the Pd source. The solid obtained was filtered, washed exhaustively with water, dried and characterized by X-ray diffraction, scanning electron microscopy and X-ray fluorescence. Microporous VPI-5 containing palladium and HPA was prepared following a procedure based on that described by Davis et al. [4], from a gel containing the HPA and palladium acetate. The gel, with the molar composition P_2O_5:Al_2O_3:DPA:40 H_2O:0.24 HPA:0.16 Pd, was crystallized at 140°C for 4 h in a PTFE-lined steel autoclave. Phosphoric acid (85%) and pseudoboehmite Condea were used as the P and Al sources, respectively, palladium acetate as the Pd source and di-*n*-propylamine (DPA) as template. The solid material obtained was filtered, washed, dried in an oven for 2 h at 100°C under atmospheric pressure, and characterized by X-ray diffraction, scanning electron microscopy, X-ray fluorescence, and ^{31}P MAS NMR. The ^{31}P MAS NMR spectra were recorded at room temperature on a Bruker AC 300 spectrometer operating at 121.5 MHz, using zirconia rotors and allowing spinning rates up to 4000 Hz. A single pulse and high power decoupling were used and the delay between scans was fixed to 20 s. The chemical shifts are given with respect to H_3PO_4 using $NH_4H_2PO_4$ as an external reference.

The oxidation of benzene was carried out in a PTFE-lined Parr 4842 reactor under an oxygen pressure of 60 bar using 1.02 g of lithium acetate, 11.7 g of benzene, 0.5 g of HPA-containing MCM-41 and 0.07 mmol of palladium acetate or 2 g of VPI-5 loaded with HPA and Pd suspended in a mixture of 12 g of acetic acid and 7.2 g of water. The reaction mixture was stirred at 600 rpm at 130°C for 4 h. The products were analyzed by HPLC using a Waters system equipped with two model 510 piston pumps, a 100 mm × 5 mm i.d. C-18 Radial Pak Cartridge, and a PDA 991 detector to record the UV-VIS spectra. A methanol/water gradient, starting at 60/40 (v/v) and reaching 100% methanol within 9 min was used for elution. The samples were prepared by dissolution in methanol/water (60/40, v/v). The products were quantified using calibration curves. The UV-VIS spectra of the products were recorded and compared with those of authentic samples. The identification of the reaction products was carried out by GC-MS.

3. Results and discussion

In preliminary experiments, HPA and palladium acetate were impregnated onto active carbon, alumina and silica (Aerosil 200) and tested as catalysts in the oxidation of benzene. However, both the impregnated HPA and palladium were found to leach completely from these supports under the reaction conditions employed. The conversions of benzene, as well as the selectivities for phenol formation were identical to the values found for the analogous reaction in the homogeneous phase [1]. We, therefore, decided to heterogenize the HPA and palladium acetate in molecular sieves with pore sizes large enough to accommodate the bulky Keggin ions.

The X-ray diffractograms of MCM-41 prepared in the presence of HPA and palladium acetate, and in the absence of the later, are shown in Fig. 1. The 2θ reflections at 2.3° (100) and 4.6° (110) observed for the samples prepared without palladium acetate (samples A and B) point to the existence of ordered mesopores, which are typical for MCM-41 type materials. The broad reflection observed at $2\theta \sim 9°$
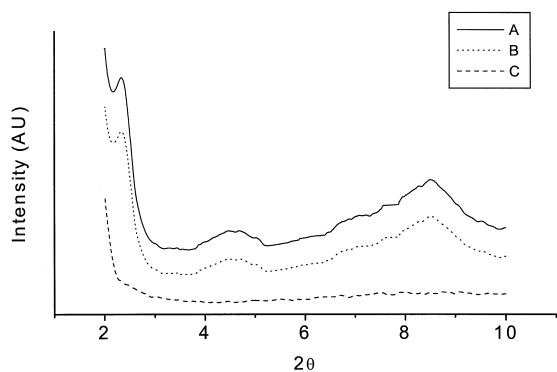
Fig. 1. X-ray diffractograms of MCM-41 prepared in the presence of HPA (sample A and B) and of HPA and palladium acetate (sample C).

cannot be attributed to the MCM-41 structure. However, this reflection has been reported by Kozhevnikov et al. [5] for MCM-41 containing $H_3PW_{12}O_{40}$ and can be attributed to the incorporation of the HPA into the MCM-41 structure. The lack of any reflection associated with mesopores and the very low specific surface area (5 m^2/g) of sample C obtained in the presence of palladium acetate indicate that only a dense-phase silicate is produced in this case. Scanning electron microscopy studies support these observations. While the micrograph of sample C (Fig. 2b) shows only amorphous material, the micrograph of sample A prepared without palladium acetate (Fig. 2a) shows uniform particles shaped as ca. 10 μm long cylinders. The Mo:V ratio of sample A measured by X-ray fluorescence indicates that the HPA is preserved after its encapsulation into MCM-41 and that 0.13 g (0.07 mmol) of HPA are incorporated per gram of MCM-41. Although the procedure described above allows the incorporation of HPA into MCM-41, all attempts to include palladium acetate as well resulted in amorphous material.

The X-ray diffractogram of HPA/Pd/VPI-5, recorded after drying the sample at 100°C under atmospheric pressure for 2 h, is given in Fig. 3. It shows that only crystalline VPI-5 was formed, free of any contamination with other crystal phases. Due to adsorbed water, VPI-5 trans-

forms into $AIPO_4$-8 under these drying conditions, so that the preservation of the structure under these conditions indicates the replacement of the adsorbed water by the HPA in the HPA/Pd/VPI-5 sample, which is confirmed by the ^{31}P NMR spectroscopy (see below). The scanning electron micrograph (Fig. 4) shows that the HPA/Pd/VPI-5 material crystallizes in a single phase consisting of long needles agglomerated into sphere segments with a length of approximately 70–80 μm, typical for molecular sieves with the VFI structure. The existence of both tetrahedral and octahedral aluminum, as well as four and six-membered rings in VPI-5 originates phosphorus atoms having three different types of neighborhood, which causes the three ^{31}P NMR signals at ca. -23, -27 and -33 ppm shown in the spectrum of VPI-5 (Fig. 5a). In the spectrum of HPA/VPI-5, shown in Fig. 5b, the peak at -23 ppm disappears, while the peaks originally at -27 and -33 ppm broaden and become one single peak centered at ca. -29 ppm. Ryoo and Chon [6], and Parton et al. [7] reported similar observations after loading Co(saloph) and phthalocyanine, respectively, into VPI-5. Parton et al. [7] attributed the loss of resolution to a local deformation of the framework, caused by a tight fit between the encapsulated species and the walls of the VPI-5 channels. A tight fit can also be expected between the 1.23-nm wide VPI-5 channels [8] and the HPA, which is reported to measure 1.2 nm in diameter [5]. On the other hand, Akporiaye and Stöcker [9], Martens et al. [10], and Perez et al. [11] followed the reversible dehydration of VPI-5 by ^{31}P NMR and observed the reduction of the peak at ca. -23 ppm and the broadening of the peaks at ca. -27 and -33 ppm into a large peak centered at ca. -30 ppm. All these findings point to the same direction, i.e., the removal of water from the channels either by extraction or by its replacement for an encapsulated species causes a loss of resolution in the NMR spectrum, as observed in this work, and can be considered as a strong evidence of the successful incorporation of the HPA into the
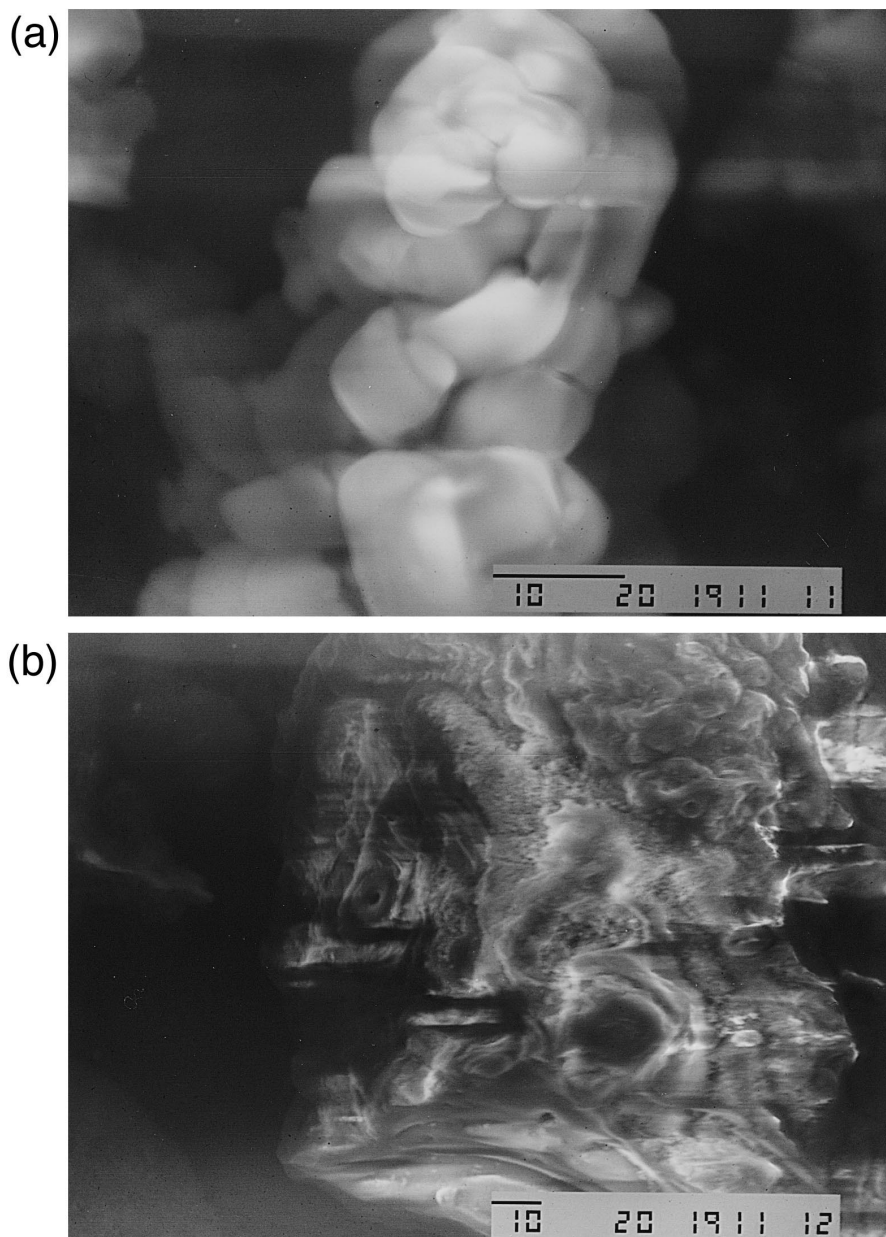
Fig. 2. (a) Scanning electron microscopy of HPA/MCM-41 (sample A) and (b) of sample C, prepared with HPA and palladium acetate.

VPI-5 structure. No signal due to the phosphorus atom of the Keggin-type HPA, which would be expected between -3 and -4 ppm, was observed. However, the concentration of HPA phosphorus is only ca. 0.4% of the concentration of the VPI-5 lattice phosphorus. Furthermore, Sulikowski et al. [12] showed that the ^{31}P

signal is largely broadened for heteropolyacids encapsulated in zeolites with FAU structure. Therefore, the absence of the HPA signal cannot be considered contradictory to the incorporation of the HPA into the VPI-5 structure. The HPA-VPI-5 sample submitted to X-ray fluorescence contained relative quantities of Mo and V
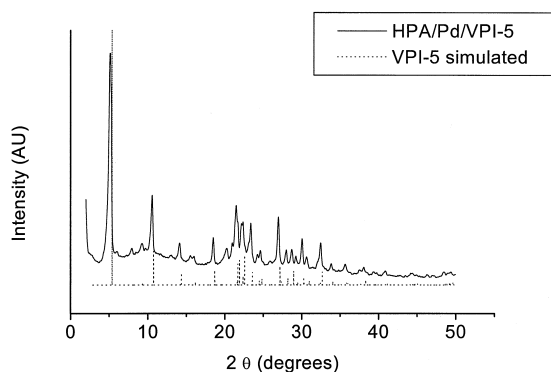
Fig. 3. X-ray diffractograms of VPI-5 prepared in the presence of HPA and palladium acetate.

Fig. 5. ^{31}P MAS NMR spectra of (a) VPI-5 (40 scans) and (b) HPA/Pd/VPI-5 (95 scans).

similar to those found in the HPA added to the synthesis gel, thus confirming the incorporation of the HPA into VPI-5.

The results of the oxidation of benzene catalyzed by palladium acetate in the presence of HPA and HPA/MCM-41 are summarized in Table 1. These results show that both the free HPA and the HPA incorporated in MCM-41 catalyze the production of phenol with a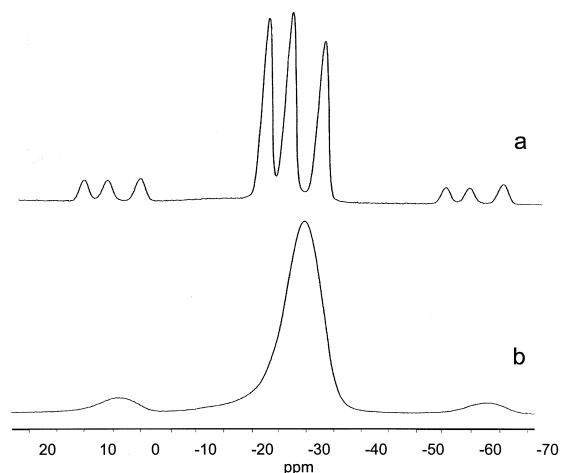 similar selectivity. However, phenol production is 2–3 times higher when the HPA is used in homogeneous solution instead of incorporated in MCM-41, which can be explained by the reduced quantity of HPA incorporated. Analysis of the HPA/MCM-41 recovered after the reaction showed that most of the HPA leached to the solution. The oxidation of benzene should therefore be considered homogeneous.
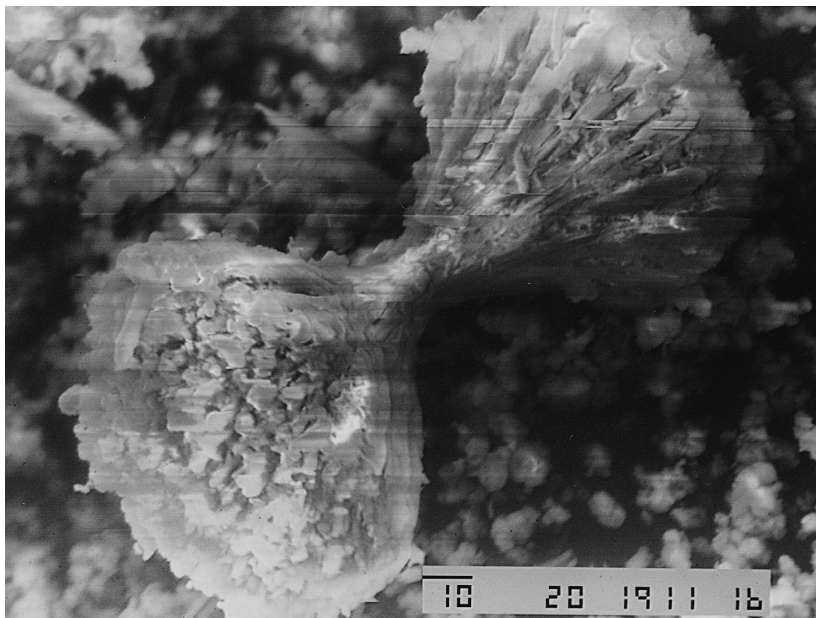

Fig. 4. Scanning electron microscopy of HPA/Pd/VPI-5.

Table 1
Results of the oxidation of benzene catalyzed by Pd in the presence of HPA and HPA/MCM-41

Catalyst	HPA content (g)	Phenol (mmol)	Other products (mmol)	Phenol selectivity (%)	Turnover number
0.07 mmol Pd	0.3	13.8	5.9	70	282
HPA/MCM-41 (A)[a]	0.06	4.5	1.2	79	82
HPA/MCM-41 (B)[a]	0.08	7.1	1.6	82	124

150 mmol of benzene, 60 bar O_2, 130°C, 4 h ([a]) and 0.07 mmol Pd.

Table 2
Oxidation of benzene catalyzed by Pd/HPA/VPI-5

Reaction cycle	Phenol (mmol)	Others (mmol)	Phenol selectivity (%)	Turnover number
1	0.63	0.25	72	7
2	0.21	0.06	78	2
3	0.12	0.04	75	1
4	0.02	0	–	–

150 mmol of benzene, 60 bar O_2, 130°C, 4 h.

When the amorphous silica prepared in the presence of HPA and palladium acetate (sample C) is used as catalyst, the activity is very low (turnover number = 26) and no phenol is observed. Hydroxybenzoic acids, cresols, hydroxybiphenyls and other coupling products become the main products. Since the palladium is heterogenized in the silica, the loss of selectivity is probably due to a closer interaction between the initially formed phenol and the hydroxyl groups of the silica surface. This interaction allows methyl radicals and formaldehyde, formed in a side reaction from acetic acid [1], to attack the immobilized phenol, producing the overoxidation and coupling products.

The results of the oxidation of benzene catalyzed by HPA/Pd/VPI-5 are given in Table 2. This catalyst produces phenol as the main product, with a selectivity comparable to that found in the homogeneous system [1]. Nevertheless, the activity is very low and a turnover number of only 7 is observed. It must be noted, however, that the pores of the VFI structure are blocked by the occluded HPA and that only the palladium atoms located near the surface of the VPI-5 aggregates are catalytically active. Estimating that less than 1% of the palladium is located at the surface of the VPI-5 aggregates with diameters around 70 μm [7], one can

calculate a turnover number that reaches 700, which is in the same range as that observed for the optimized homogeneous system [1].

HPA/Pd/VPI-5 cannot be recycled without loss of activity and turns inactive after the third reaction cycle, as shown in Table 2. The results of the elemental analysis, shown in Table 3, reveal that the building elements of the HPA (Mo and V) leach slowly during the catalytic cycles. However, V leaching is more significant than that of Mo, causing the HPA formula to change from $H_6PMo_9V_3O_{40}$ (I) to $H_4PMo_{11}VO_{40}$ (II). Consequently, the redox potential decreases from 0.7 V in (I) to 0.4 V in (II) [13]. This decrease may account for the loss of activity observed, since a strong oxidant is needed to oxidize Pd(II) to the Pd(IV) which is involved in the oxidation of benzene [1]. It is interesting to remark that no Pd leaching occurred during the four reaction cycles. This

Table 3
Content of HPA, Mo, V and Pd of Pd/HPA/VPI-5 as a function of the reaction cycles

Reaction cycle	HPA (wt.%)	Mo (wt.%)	V (wt.%)	Pd (wt.%)
1	5.5	2.9	0.4	0.7
2	5.2	2.8	0.3	0.7
3	5.0	2.7	0.3	0.7
4	4.7	2.6	0.2	0.7

stability might be an indication that the palladium was incorporated into the VPI-5 structure, replacing Al and/or P in the lattice. Furthermore, most of the VPI-5 underwent transformation to AIPO-8 after four reaction cycles.

4. Conclusions

Addition of the heteropolyacid $H_6PMo_9V_3O_{40}$ to the synthesis gels of MCM-41 and VPI-5 allows its successful incorporation into the molecular sieves. However, under the conditions of benzene oxidation, the heteropolyacid leaches from the MCM-41 and the oxidation of benzene takes place in the homogeneous phase. VPI-5 retains the heteropolyacid to a larger extent and, if palladium acetate is also added to the synthesis gel, it heterogeneously oxidizes benzene to phenol. However, its activity is strongly reduced as the heteropolyacid blocks the pores of the molecular sieve and the oxidation takes place only at the pore entrances.

Acknowledgements

References

[1] L.C. Passoni, A.T. Cruz, R. Buffon, U. Schuchardt, J. Mol. Catal. A 120 (1997) 117.
[2] G.A. Tsigdinos, C.J. Hallada, Inorg. Chem. 7 (1968) 437.
[3] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.
[4] M.E. Davis, C. Montes, P.E. Hathaway, J.M. Garces, Stud. Surf. Sci. Catal. 49 (1989) 199.
[5] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen, K. Pamin, H. van Bekkum, Catal. Lett. 30 (1995) 241.
[6] M.-H. Ryoo, H. Chon, Microporous Mater. 10 (1997) 35.
[7] R.F. Parton, F. Thibault-Starzyk, R.A. Reynders, P.J. Grobet, P.A. Jacobs, C.P. Bezoukhanova, W. Sun, Y. Wu, J. Mol. Catal. A 97 (1995) 183.
[8] W.M. Meier, D.H. Olson, Zeolites 12 (1992) 449.
[9] D. Akporiaye, M. Stöcker, Zeolites 12 (1992) 351.
[10] J.A. Martens, E. Feijen, J.L. Lievens, P.J. Grobet, P.A. Jacobs, J. Phys. Chem. 95 (1991) 10025.
[11] J.O. Perez, P.J. Chen, A. Clearfield, J. Phys. Chem. 55 (1991) 9994.
[12] B. Sulikowski, J. Haber, A. Kubacka, K. Pamin, Z. Olejniczak, J. Ptaszynski, Catal. Lett. 39 (1996) 27.
[13] I.V. Kozhevnikov, Russ. Chem. Rev. 56 (1987) 811.