Alkane oxidation with hydrogen peroxide catalyzed homogeneously by vanadium-containing polyphosphomolybdates

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Abstract

Alkanes (cyclooctane, *n*-octane, adamantane, ethane) can be efficiently oxidized by hydrogen peroxide in acetonitrile using tetra-*n*-butylammonium salts of the vanadium-containing polyphosphomolybdates $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$ as catalysts. The oxidation of alkanes gives rise to the corresponding alkyl hydroperoxides as the main products, which slowly decompose in the course of the reaction to produce the corresponding ketones (aldehydes) and alcohols. The reaction in acetic acid and water is much less efficient. The oxidation of cyclooctane at 60°C in acetonitrile gives within 9 h oxygenates with turnover numbers >1000 and yields >30% based on the alkane. Pyrazine-2-carboxylic acid added as co-catalyst accelerates the reaction but does not enhance the product yield. The oxidation of the *cis*- and *trans*-isomers of decalin proceeds without retention of configuration. The mechanism assumed involves the reduction of V(V) to V(IV) by a first molecule of hydrogen peroxide, followed by the reaction of V(IV) with a second H_2O_2 molecule to generate hydroxyl radicals. The latter abstract a hydrogen atom from the alkane, RH, leading to alkyl radicals, $R^\bullet$, which rapidly react with aerobic oxygen. The alkyl peroxy radicals thus formed are then converted into alkyl hydroperoxides. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Polyoxometalates are known to catalyze various oxidation reactions [1], in particular, the oxygenation of aromatic hydrocarbons with hydrogen peroxide and *tert*-butyl hydroperoxide [2–11]. Only a few examples for oxidations of saturated hydrocarbons have been reported [12–20]: polyoxomolybdates and polyoxotungstates containing transition metal ions (Co, Mn, Cu, Fe, Ru, Rh, Ni, Cr) have been used in the oxidation of alkanes. Continuing our investigations on vanadium-catalyzed homogeneous alkane oxidations with hydrogen peroxide [21–32], we decided to explore the catalytic activity of vanadium-containing polyoxometalates in homogeneous low-temperature oxidations of saturated hydrocarbons. In particular, it was interesting to compare the activities of the lacunary anion $[PMo_6V_5O_{39}]^{12-}$ [1] and of the non-lacunary anion $[PMo_{11}VO_{40}]^{4-}$ [1], although the lacunary species is not as well characterized as the well known species $[PMo_{11}VO_{40}]^{4-}$. [1]

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[1] When this work has been prepared for publication, two papers by Mizuno and co-workers appeared [44,45] which describe the methane oxidation with hydrogen peroxide in trifluoroacetic acid anhydride as solvent catalyzed by various vanadium complexes, including $H_4PMo_{11}VO_{40}$.

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2. Results and discussion

In the present work, we report the oxidation of alkanes including ethane and methane by hydrogen peroxide in various solvents, catalyzed with vanadium-substituted molybdophosphoric acids. All reactions were carried out in homogeneous phase using the tetra-*n*-butylammonium salts of the anions $[PMo_{11}VO_{40}]^{4-}$ and $[PMo_6V_5O_{39}]^{12-}$ in acetonitrile, or in acetic acid or in water. Higher and light alkanes were used as substrates for the catalyzed H_2O_2 oxidations. Typically, samples of the reaction solution, withdrawn in the course of the oxidation, were analyzed by gas chromatography, using a double-analysis method: the samples were measured before and after treatment with an excess of solid triphenylphosphine (10–20 min at room temperature); for this method, see [12,13,21–27,33–36]. If, prior to GC analysis, triphenylphosphine is added, the ketone (aldehyde) peak decreases, while the alcohol peak increases; this difference is due to the complete decomposition of the primary product (alkyl hydroperoxide) in the GC injector to give the corresponding ketone and alcohol. It should be noted that in some cases, in this and previous work (see, e.g. [23,24]), we were also able to detect directly the alkyl hydroperoxide peak in the chromatogram. Triphenylphosphine reduces the alkyl hydroperoxide easily and quantitatively to the corresponding alcohol, giving triphenylphosphine oxide. By comparing the concentrations of the ketone (aldehyde) and of the alcohol measured before and after the treatment of the sample with PPh₃, it is possible to estimate the real concentrations in the reaction solution, not only of the ketone (aldehyde) and of the alcohol, but also that of the alkyl hydroperoxide.

The oxidation of cyclooctane in acetonitrile solution at 60°C catalyzed by $[PMo_{11}VO_{40}]^{4-}$ gives within 9 h cyclooctyl hydroperoxide as the main product, as well as smaller amounts of cyclooctanol and cyclooctanone. The kinetics of the product accumulation are shown in Fig. 1a. The turnover number (total concentration of all products divided by the catalyst concentration) has attained 1180 after 9 h. After this time, there is no longer an accumulation of oxygenates, but only a slow decomposition of cyclooctyl hydroperoxide to produce additional amounts of both cyclooctanol and cyclooctanone. Previously
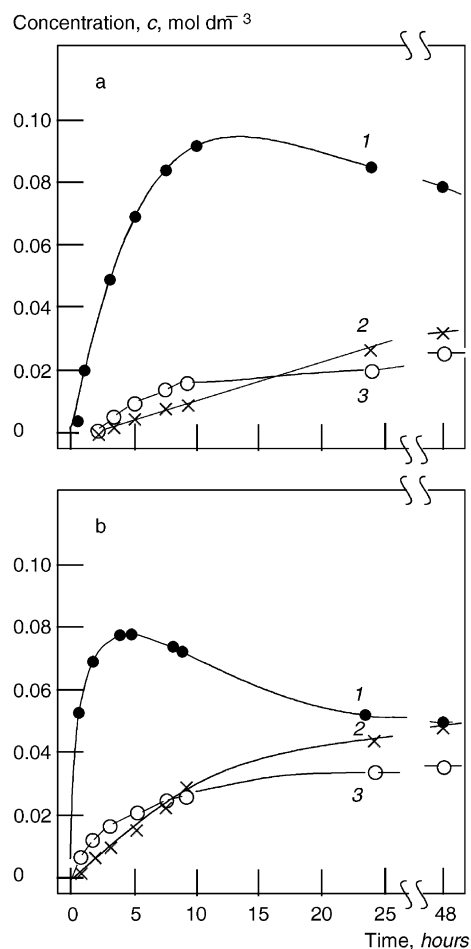

Fig. 1. Reaction profile of the oxidation of cyclooctane (initial concentration $0.37\,mol\,dm^{-3}$) with H_2O_2 ($0.59\,mol\,dm^{-3}$) catalyzed by $[PMo_{11}VO_{40}]^{4-}$ ($1.0 \times 10^{-4}\,mol\,dm^{-3}$) in the absence (a) and in the presence (b) of pyrazine-2-carboxylic acid ($1.0 \times 10^{-3}\,mol\,dm^{-3}$) in MeCN at 60°C. Products: cyclooctyl hydroperoxide (curve 1), cyclooctanone (curve 2) and cyclooctanol (curve 3).

we have demonstrated [21–32] that in the case of the simple vanadate ion (VO_3^-) as the catalyst, addition of pyrazine-2-carboxylic acid (pcaH) dramatically accelerates the alkane oxidation with H_2O_2. Almost no reaction occurs in the absence of pcaH. Therefore, it was interesting to study the effect of pcaH on the oxidation with $[PMo_{11}VO_{40}]^{4-}$. It turned out that the total yield of the reaction products is almost unchanged upon addition of pcaH (with the pcaH:V ratio being 10).

However, the initial reaction rate is higher in this case, and the maximum cyclooctyl hydroperoxide concentration is attained after 5 h (versus 15 h for the oxidation in the absence of pcaH; compare Fig. 1a and b). The oxidation of cyclooctane, catalyzed by $[PMo_6V_5O_{39}]^{12-}$ (without pcaH) gave (under the same conditions) after 2 h (concentration, $mol\,dm^{-3}$) cyclooctyl hydroperoxide (0.013), cyclooctanone (0.027) and cyclooctanol (0.007). The corresponding concentrations obtained from the reaction in the presence of pcaH were 0.012; 0.035 and 0.015, respectively. In this case, pcaH enhances insignificantly the initial reaction rate.

n-Octane is also oxidized under the same conditions ($[n\text{-octane}]_0 = 0.29\,mol\,dm^{-3}$, $[H_2O_2]_0 = 1.1\,mol\,dm^{-3}$, $[catalyst]_0 = 1.0 \times 10^{-4}\,mol\,dm^{-3}$, 60°C, 7 h). The following products are obtained (concentrations, $mol\,dm^{-3}$, measured only after reduction with PPh_3 are given in parenthesis) when $[PMo_{11}VO_{40}]^{4-}$ (first value) or $[PMo_6V_5O_{39}]^{12-}$ (second value) are used as catalysts: octanal (0.0002; 0.0007), octanone-2 (0.0006; 0.003); octanone-3 (0.0007; 0.004), octanone-4 (0.0006; 0.003), octanol-1 (0.0042; 0.003), octanol-2 (0.014; 0.012), octanol-3 (0.013; 0.010), octanol-4 (0.012; 0.009). The turnover numbers for these catalysts, 453 and 447, respectively, indicate that both exhibit the same efficiency. However, a different product distribution is noted: the second catalyst gives rise to higher concentrations of the ketone isomers. This is possibly due to more extensive decomposition of the alkyl hydroperoxide isomers in the course of the reaction to produce the ketone isomers (which cannot be reduced by PPh_3 to the corresponding alcohols). The oxidation of adamantane (0.05 g in 10 ml of the reaction solution) during 7 h catalyzed by the polyoxometalates afforded (product concentrations after reduction with PPh_3, $mol\,dm^{-3}$, for the first and second catalysts, respectively): adamantanol-1 (0.0060; 0.0083), adamantanol-2 (0.008; 0.006) and adamantanone (0.0008; 0.0024). The relative normalized reactivities of hydrogen atoms at secondary and tertiary carbons of adamantane, 2°:3°, calculated from these data are 0.6 and 0.7, respectively. These parameters are very close to those determined for the oxidations by catalytic systems which proceed via hydroxyl radical formation: O_2–H_2O_2–$h\nu$ (2°:3° = 0.7) and O_2–H_2O_2–*n*-Bu_4NVO_3–pcaH (2°:3° = 0.75).

We investigated the stereoselectivity of the oxidation of the *cis*- and *trans*-isomers of decalin catalyzed by $[PMo_{11}VO_{40}]^{4-}$. The oxidation of one of the two tertiary C–H bonds in these compounds gives hydroperoxidated and hydroxylated products and proceeds with epimerization at the tertiary carbon atom. In order to estimate the stereoselectivity quantitatively, we used a simple *trans/cis* parameter which is the ratio [*trans*-decal-9-ol]/[*cis*-decal-9-ol] (ratio of the concentrations of *cis*- and *trans*-isomers). The lower the value of this *trans/cis* parameter, the higher is the stereoselectivity of the reaction. On the other hand, if the oxidation of the *trans*-isomer exhibits a high value of this *trans/cis* parameter, this testifies that the reaction is stereoselective. The oxidation of the decalin isomers by non-stereoselective reagents gives approximately equal *trans/cis* values for both *cis*- and *trans*-hydrocarbons, these parameters being usually different from unity. Stereoselective reactions lead to the predominant formation of the most thermodynamically stable or less strained isomer (usually *trans*-decal-9-ol). The relative concentrations of the tertiary alcohols were measured after reduction of the reaction samples with triphenylphosphine (which converts tertiary hydroperoxides into the corresponding alcohols). The *trans/cis* parameter for the polyoxometalate-catalyzed reaction ($[decalin]_0 = 0.31\,mol\,dm^{-3}$, $[H_2O_2]_0 = 0.6\,mol\,dm^{-3}$, $[catalyst]_0 = 1.0 \times 10^{-4}\,mol\,dm^{-3}$, 60°C, 2 h) was 4.4 (oxidation of *cis*-decalin) and 4.8 (oxidation of *trans*-decalin). We determined the corresponding parameters for the oxidations by hydroxyl-generating systems which turned out similar: O_2–H_2O_2–$h\nu$ (1.3 and 2.7), O_2–H_2O_2–$FeSO_4$ (3.4 and 8.8), O_2–H_2O_2–*n*-Bu_4NVO_3–pcaH (2.1 and 2.4).

Hydrogen peroxide also oxidizes ethane in acetonitrile in the presence of $[PMo_{11}VO_{40}]^{4-}$ as catalyst; the kinetics of the product accumulation are presented in Fig. 2. The TON is 14 after 10 h. Methane (40 bar, $[H_2O_2]_0 = 0.6\,mol\,dm^{-3}$, $[PMo_{11}VO_{40}]^{4-} = 1.0 \times 10^{-4}\,mol\,dm^{-3}$, 60°C, 10 h) gave (without reduction with PPh_3) only a small amount of formaldehyde ($1 \times 10^{-4}\,mol\,dm^{-3}$). Blank experiments (i.e. in the absence of an alkane) showed that, under these conditions, acetonitrile is also oxidized and hydrolized, but the product concentrations are sufficiently lower (formaldehyde, $1.2 \times 10^{-5}\,mol\,dm^{-3}$; acetic acid, $1.2 \times 10^{-5}\,mol\,dm^{-3}$).
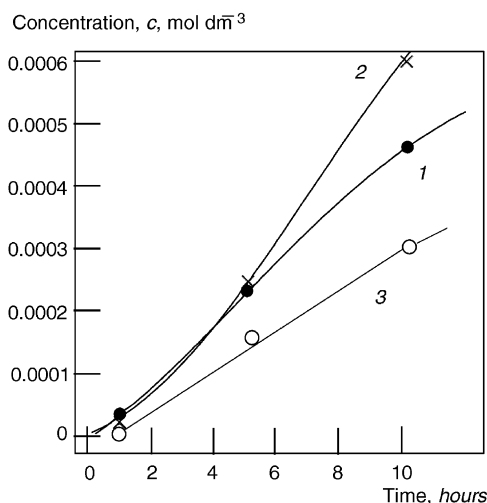
Concentration, c, mol dm^{-3}

Fig. 2. Accumulation of ethyl hydroperoxide (curve 1), acetaldehyde (curve 2) and ethanol (curve 3) in the oxidation of ethane (initial pressure 30 bar) with H_2O_2 (0.59 mol dm^{-3}) catalyzed by [PMo$_{11}$VO$_{40}$]$^{4-}$ (1.0 × 10^{-4} mol dm^{-3}) in MeCN at 60°C.
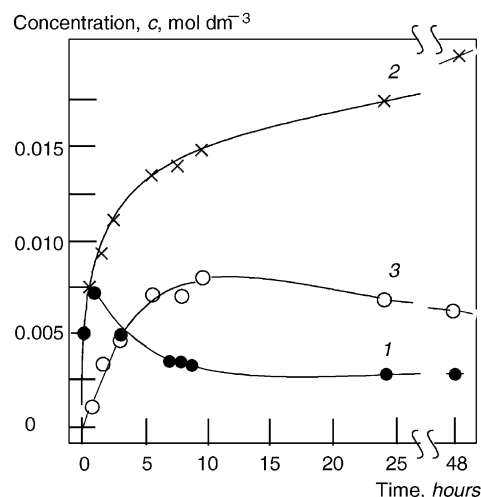
Fig. 3. Reaction profile of the oxidation of cyclooctane (initial concentration 0.37 mol dm^{-3}) with H_2O_2 (0.59 mol dm^{-3}) catalyzed by [PMo$_{11}$VO$_{40}$]$^{4-}$ (1.0 × 10^{-4} mol dm^{-3}) in acetic acid at 60°C. Products: cyclooctyl hydroperoxide (curve 1), cyclooctanone (curve 2) and cyclooctanol (curve 3).

Acetic acid turned out to be much less efficient as solvent in comparison with acetonitrile: the TON of the oxidation of cyclooctane is only 30 after 48 h (the accumulation of the products is shown in Fig. 3). The oxidation of ethane in water solution (ethane, 30 bar; air, 10 bar; [H_2O_2]$_0$ = 2.35 mol dm^{-3}, [PMo$_{11}$VO$_{40}$]$^{4-}$ = 1.0 × 10^{-4} mol dm^{-3}, 100°C, 24 h) afforded only small concentrations of ethanol; acetaldehyde and acetic acid did not exceed the concentrations of the blank experiment in the absence of the catalyst. Thus, it may be concluded that acetonitrile is the solvent of choice for this reaction.

Taking into account the low bond selectivity and the lack of stereoselectivity, we assume that this reaction proceeds via formation of hydroxyl radicals from hydrogen peroxide. Polyoxometalates that do not contain vanadium ions are poor catalysts (compare [2] and [3]) and, consequently, the most reasonable route for the formation of hydroxyl radicals is the interaction of a V(IV) species with H_2O_2. Since in the alkane hydroperoxidation catalyzed by the simple VO$_3^-$ anion [21–32], the rate-limiting step is the monomolecular decomposition of the V(V) complex containing coordinated H_2O_2 molecule, it is probably that in the case of the vanadium-polyoxometalate catalysis, the first slow step is also the coordination of a hydrogen peroxide molecule to vanadium (via inner-sphere mechanism [37]) and the homolytic decomposition of this complex to produce V(IV) and peroxyl radicals. The environment of the oxovanadium ion which consists of many oxomolybdenum fragments definitely facilitates this process, because the VO$_3^-$ anion itself (in the absence of pcaH or HClO$_4$) does not catalyze the alkane oxidation in acetonitrile. Two explanations for this facilitating assistance are possible: first, the Mo=O fragments enhance the oxidizing ability of V(V) toward H_2O_2 (which is a reducing agent in the first step of the process)

$$V^V + H_2O_2 \rightarrow V^V \cdots H_2O_2$$

$$V^V \cdots H_2O_2 \rightarrow V^{IV} + HOO^\bullet + H^+$$
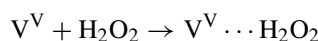
Second, the oxygen atoms of the Mo–O–V moieties in the polyoxometalate can accept hydrogen atoms from H_2O_2 as shown in Scheme 1a. A pcaH molecule (in the zwitterionic form) possibly facilitates the proton transfer from H_2O_2 to the oxygen atom of Mo–O–V moiety as presented in Scheme 1b. The V(IV) species thus formed reacts then further with a sec-
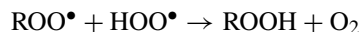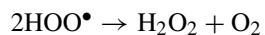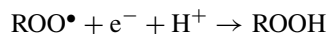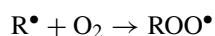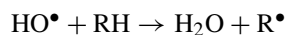
a:

b:
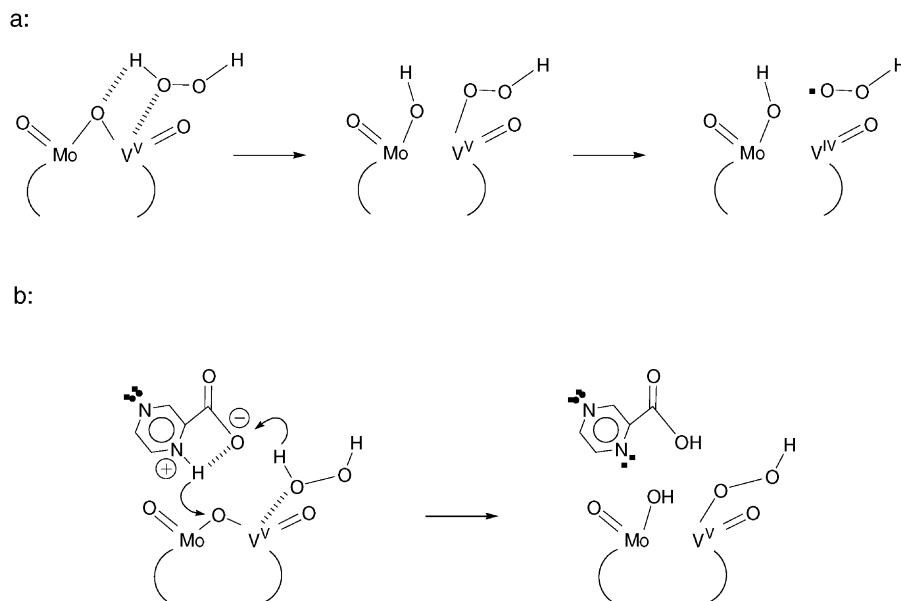
Scheme 1. Tentatively proposed mechanism for MoV-induced decomposition of H_2O_2 to produce a catalytically active species.

ond H_2O_2 molecule to generate the hydroxyl radical according to

$$V^{IV} + H_2O_2 \rightarrow V^V + HO^\bullet + HO^-$$

The following reactions can then lead further to the products

$$HO^\bullet + RH \rightarrow H_2O + R^\bullet$$

$$R^\bullet + O_2 \rightarrow ROO^\bullet$$

$$ROO^\bullet + e^- + H^+ \rightarrow ROOH$$

$$2HOO^\bullet \rightarrow H_2O_2 + O_2$$

$$ROO^\bullet + HOO^\bullet \rightarrow ROOH + O_2$$

Such alkane transformations with participation of free radicals are well-known [38–40]. We should neglect the reaction of hydrogen abstraction from the alkane by alkyl peroxyl radical, $ROO^\bullet$

$$ROO^\bullet + RH \rightarrow ROOH + R^\bullet$$
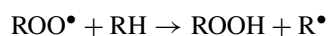
which is the key stage in radical-chain mechanism of alkane autoxidation. Such a mechanism does not operate for the cases of cyclohexane and all alkanes with stronger C–H bonds (e.g. linear alkanes and especially methane) at temperatures $<100°C$ in acetonitrile. It should be noted, however, that in the oxidation of tetralin and cyclohexene, propagation steps with chain lengths >1 cannot be excluded even for relatively low (ca. 50°C) temperatures.

3. Conclusion

Vanadium-containing phosphomolybdates in the form of tetra-*n*-butylammonium salts catalyze efficiently the oxidation of cyclic and linear alkanes with H_2O_2 in acetonitrile to give the corresponding oxygenates.

4. Experimental

The oxidations of higher alkanes were carried out in air in thermostated Pyrex cylindrical vessels with vigorous stirring. The total volume of the reaction solution was 10 ml. In a typical experiment, initially, a portion of 35% aqueous solution of hydrogen

peroxide ("Fluka") was added to the solution of the catalyst and substrate in acetonitrile ("Fluka"). The oxidations of ethane and methane were carried out in a stainless steel autoclave with intensive stirring (volume of the reaction solution was 10 ml and total volume of autoclave was 100 ml).

The samples of the reaction solutions were analysed by GC (chromatograph DANI-86.10; fused silica capillary column 25 m × 0.32 mm × 0.25 μm, CP-WAX52CB; helium; integrator SP-4400) double measurement: before and after addition of an excess of solid triphenylphosphine (which reduces hydrogen peroxide to water and the alkyl hydroperoxide to the corresponding alcohol); this allowed the determination of the real concentrations of the alkyl hydroperoxide, alcohol, and ketone (or aldehyde).

The samples of the catalysts (for synthesis and applications in catalysis see [1,10,11,41–43]) were prepared and characterized in the Institute of Catalysis, Novosibirsk, Russia.

References

[1] I.V. Kozhevnikov, Chem. Rev. 98 (1998) 171, and references therein.
[2] D. Attanasio, D. Orru', L. Suber, J. Mol. Catal. 57 (1989) L1.
[3] R. Neumann, M. de la Vega, J. Mol. Catal. 84 (1993) 93.
[4] N.I. Kuznetsova, L.I. Kuznetsova, V.A. Likholobov, J. Mol. Catal. A: Chem. 108 (1996) 135.
[5] L.I. Kuznetsova, L.G. Detusheva, M.A. Fedotov, V.A. Likholobov, J. Mol. Catal. A: Chem. 111 (1996) 81.
[6] N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fedotov, V.A. Likholobov, J. Mol. Catal. A: Chem. 114 (1996) 131.
[7] K. Nomiya, H. Yanagibayashi, C. Nozaki, K. Kondoh, E. Hiramatsu, Y. Shimizu, J. Mol. Catal. A: Chem. 114 (1996) 181.
[8] L.I. Kuznetsova, L.G. Detusheva, N.I. Kuznetsova, M.A. Fedotov, V.A. Likholobov, J. Mol. Catal. A: Chem. 117 (1997) 389.
[9] K. Nomiya, K. Yagishita, Y. Nemoto, T. Kamataki, J. Mol. Catal. A: Chem. 126 (1997) 43.
[10] K. Nomiya, Y. Nemoto, T. Hasegawa, S. Matsuoka, J. Mol. Catal. A: Chem. 152 (2000) 55.
[11] K. Nomiya, S. Matsuoka, T. Hasegawa, Y. Nemoto, J. Mol. Catal. A: Chem. 156 (2000) 143.
[12] A.E. Shilov, G.B. Shul'pin, Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes, Kluwer Academic Publishers, Dordrecht, 2000.
[13] A.E. Shilov, G.B. Shul'pin, Chem. Rev. 97 (1997) 2879.
[14] M. Faraj, C. Hill, J. Chem. Soc., Chem. Commun. (1987) 1487.
[15] Y. Matsumoto, M. Asami, M. Hashimoto, M. Misono, J. Mol. Catal. A: Chem. 114 (1996) 161.
[16] N. Mizuno, C. Nozaki, T. Hirose, M. Tateishi, M. Iwamoto, J. Mol. Catal. A: Chem. 117 (1997) 159.
[17] M.R. Cramarosa, L. Forti, M.A. Fedotov, L.G. Detusheva, V.A. Likholobov, L.I. Kuznetsova, G.L. Semin, F. Cavani, F. Trifirò, J. Mol. Catal. A: Chem. 127 (1997) 85.
[18] N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, J. Am. Chem. Soc. 120 (1998) 9267.
[19] M.M.Q. Simões, C.M.M. Conceição, J.A.F. Gamelas, P.M.D.N. Domingues, A.M.V. Cavaleiro, J.A.S. Cavaleiro, A.J.V. Ferrer-Correia, R.A.W. Johnstone, J. Mol. Catal. A: Chem. 144 (1999) 461.
[20] T. Hayashi, A. Kishida, N. Mizuno, Chem. Commun. (2000) 381.
[21] G.B. Shul'pin, G.V. Nizova, React. Kinet. Catal. Lett. 48 (1992) 333.
[22] G.B. Shul'pin, D. Attanasio, L. Suber, J. Catal. 142 (1993) 147.
[23] G.B. Shul'pin, M.C. Guerreiro, U. Schuchardt, Tetrahedron 52 (1996) 13051.
[24] M.C. Guerreiro, U. Schuchardt, G.B. Shul'pin, Russ. Chem. Bull. 46 (1997) 749.
[25] G.V. Nizova, G. Süss-Fink, G.B. Shul'pin, Chem. Commun. (1997) 397.
[26] G.V. Nizova, G. Süss-Fink, G.B. Shul'pin, Tetrahedron 53 (1997) 3603.
[27] U. Schuchardt, M.C. Guerreiro, G.B. Shul'pin, Russ. Chem. Bull. 47 (1998) 247.
[28] G. Süss-Fink, G.V. Nizova, S. Stanislas, G.B. Shul'pin, J. Mol. Catal. A: Chem. 130 (1998) 163.
[29] G.B. Shul'pin, Y. Ishii, S. Sakaguchi, T. Iwahama, Russ. Chem. Bull. 48 (1999) 887.
[30] G.V. Nizova, G. Süss-Fink, S. Stanislas, G.B. Shul'pin, Chem. Commun. (1998) 1885.
[31] G. Süss-Fink, S. Stanislas, G.B. Shul'pin, G.V. Nizova, H. Stoeckli-Evans, A. Neels, C. Bobillier, S. Claude, J. Chem. Soc., Dalton Trans. (1999) 3169.
[32] G. Süss-Fink, S. Stanislas, G.B. Shul'pin, G.V. Nizova, Appl. Organometal. Chem. 14 (2000) 623.
[33] G.B. Shul'pin, A.N. Druzhinina, Bull. Russ. Acad. Sci. Div. Chem. Sci. 41 (1992) 346.
[34] G.B. Shul'pin, A.N. Druzhinina, L.S. Shul'pina, Petrol. Chem. (Russ.) 33 (1993) 321.
[35] G.B. Shul'pin, M.M. Bochkova, G.V. Nizova, J. Chem. Soc., Perkin Trans. 2 (1995) 1465.
[36] G.B. Shul'pin, G.V. Nizova, Yu.N. Kozlov, New J. Chem. 20 (1996) 1243.

[37] I.A. Weinstock, Chem. Rev. 98 (1998) 113.

[38] C. Walling, Acc. Chem. Res. 31 (1998) 155.

[39] P.A. MacFaul, D.D.M. Wayner, K.U. Ingold, Acc. Chem. Res. 31 (1998) 159.

[40] H. Hofmann, T. Clark, J. Am. Chem. Soc. 113 (1991) 2422.

[41] M.T. Pope, Heteropoly and Isopoly Oxometalates, Springer, New York, 1983.

[42] M.T. Pope, A Müller (Eds.), Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity, Kluwer Academic Publishers, Dordrecht, 1994.

[43] L.C.W. Baker, D.C. Glick, Chem. Rev. 98 (1998) 3.

[44] N. Mizuno, M. Misono, Y. Seki, Appl. Catal. A: Gen. 13 (2000) 194–195.

[45] Y. Seki, J.S. Min, M. Misono, N. Mizuno, J. Phys. Chem. B. 104 (2000) 5940.