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The Catalytic Performance of Preyssler's Anion, $[NaP_5W_{30}O_{110}]^{14-}$, in the Oxidation of Benzyl Alcohols

Fatemeh F. Bamoharram
Mina Roshani
Department of Chemistry, Islamic Azad University, Mashhad Branch, Mashhad, Iran

Majid M. Heravi
Department of Chemistry, Alzahra University, Vanak, Tehran, Iran

Shahla Safaie
Department of Chemistry, Islamic Azad University, Mashhad Branch, Mashhad, Iran

Under mild conditions, monosubstituted benzyl alcohols were oxidized to benzaldehydes and benzoic acids in the presence of sodium 30-tungstopentaphosphate (Preyssler's anion), $[NaP_5W_{30}O_{120}]^{14-}$*, and hydrogen peroxide as an oxidant. This polyanion with high hydrolytic stability (pH = 0–12), high thermal stability, and high acidic strength shows good activities. The effects of various parameters on the yield of the products, including a catalyst type, a nature of the substitutents, and temperature, were studied. Comparison between Keggin's heteropolyacids,* $H_3[PW_{12}O_{40}]$, $H_3[PMo_{12}O_{40}]$, $H_4[SiW_{12}O_{40}]$*, and* $H_4[SiMo_{12}O_{40}]$*, and Preyssler's anion shows that this polyanion reacts similar to Keggin's acids whitout any degradation of the structure.*

Keywords Benzaldehyde; benzyl alcohol; catalyst; heteropolyacid; Preyssler's anion

INTRODUCTION

In light of the importance of oxidation in industry, there is still a need for new environmentally friendly methods for the oxidation of primary alcohols to carbonyl compounds, especially in the presence of other functional groups.

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Address correspondence to Majid M. Heravi, Alzahra University, Department of Chemistry, School of Sciences, Vanak, Tehran, Iran. E-mail mmh1331@yahoo.com

Carbonyl compounds in the fine-chemicals industry are precursors with wide applicability from drugs to fragrances. The oxidation of alcohols to carbonyl products is an important transformation in organic chemistry,[1] which has received much attention over the years, especially in finding versatile catalysts for catalytic processes.[2] There are many methods for the oxidation of alcohols to the corresponding aldehydes, but there still exists a need for introducing new methods. The main factors, which should be considered, are the simplicity of the method, effectiveness, and mildness of the reaction conditions. Most of the current industrial oxidation processes are using traditional oxidants in solution like the heavy metals Cr(VI) or Mn(VI), and metal nitrates on various inorganic supports.[3–5] According to stringent environmental laws, industries are under pressure to replace them with catalytic processes using clean, inexpensive, and environmentally friendly oxidants.

Heteropolyacids are currently of considerable interest as catalysts for a variety of organic oxidations with the evironmentally acceptable hydrogen peroxide as cooxidant.[6–8] The importance and attractiveness of heteropoly catalysts is due to their variety and high catalytic potential.

It has been known that tungesten and molybdenum compounds are efficient catalysts for oxidations with hydrogen peroxide.[9,10] Tungesten and molybdenum heteropoly acids also catalyze various oxidations of organic substances by hydrogen peroxide.[1] Peroxo polyoxometalates have been shown to be the active intermediates in these reactions.[11–13] Peroxo polyoxometalates are obtained by the degradiation of polyoxometalates.

Although among the wide variety of heteropolyacids much attention has been devoted to the catalytic behavior of Keggin's type polyacids and their derivatives,[14–19] the application of Preyssler's anion has been overlooked and very limited.[20]

Preyssler's heteropolyacid is remarkable due to its exclusive physicochemical properties. They include a strong Bronsted acidity, reversible transformations, solubility in polar and nonpolar solvents, as well as high hydrolytic and high thermal stability, which are very important in catalytic processes.

Nevertheless, for this polyanion no catalytic activity was reported in some cases.[21] The structure of Preyssler's anion is shown in Figure 1. The anion has an approximate D_{5h} symmetry and consists of a cyclic assembly of five PW_6O_{22} units, each derived from the Keggin's anion $[PW_{12}O_{40}]^{3-}$ by the removal of two sets of three corner-shared WO_6 octahedra. A sodium ion is located within the polyanion on the fivefold axis and 1.25 A° above the pseudomirror plane, which contains the

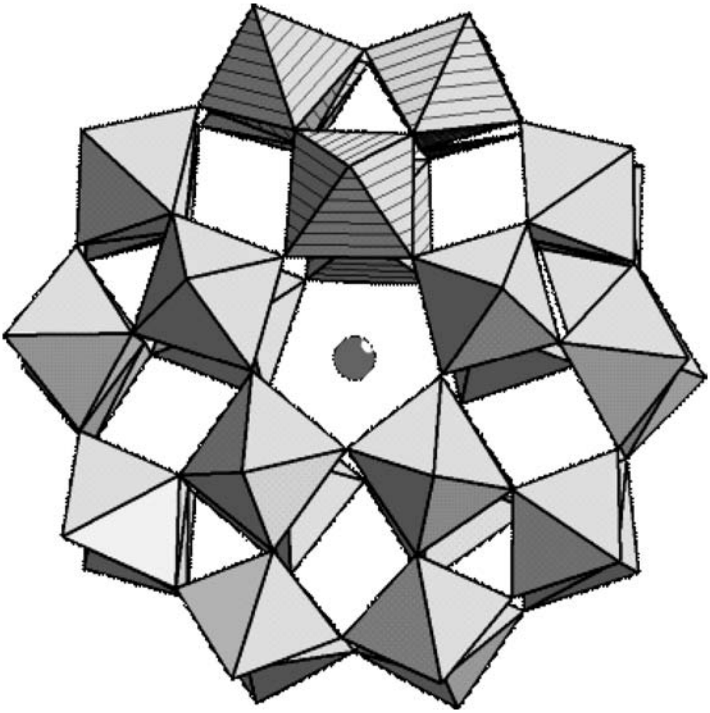

FIGURE 1 The structure of Preyssler's anion.

five phosphorus atoms.[22] Recently, we have reported on the catalytic behavior of Preyssler's anion.[23,24]

Armed with these experiences and in continuation of our investigations on the application of heteropolyanions in organic syntheses;[25] on the development of applications for Preyssler's anion; and also due to the importance of aromatic benzaldehydes in the perfumery, pharmaceutical, dyestuff and agrochemical industries;[26] we describe in this article the catalytic ability of this anion in the oxidation of benzyl alcohols.

RESULTS AND DISCUSSION

The homogeneous catalytic oxidation of monosubstituted benzyl alcohols with electron- donating (CH_3, OCH_3, OH) and electron-withdrawing groups (Cl, Br, NO_2) by Preyssler's anion as the catalyst and hydrogen peroxide as the oxidant are reported. In all cases, the reactions were carried out in mixed solvents including acetonitrile and water over 8 h at 70°C. Benzaldehydes are the major and benzoic acids are the minor reaction products.

All products were isolated, and their purities were checked by their melting points and spectral data. Experiments in the absence of the catalyst yielded no substantial quantity of benzaldehyde or benzoic acid.

THE EFFECT OF THE SUBSTITUENT

The effects of various substituents on the yield of the products have been examined in the presence of Preyssler's catalyst. The results are shown in Table I. The data in Table I indicates that while substrates with electron-withdrawing substituents are converted to the corresponding carboxylic acids and benzaldehydes with good yields, low yields are observed for the oxidation of hydroxy-, methoxy-, and methyl-substituted benzyl alcohols. This behavior may reflect inductive and resonance effects. In hydroxy-substituted benzaldehydes, because of the existance of lone pairs at the oxygen atom, there is a possibility of resonance with the carbonyl group; the ring is stabilized, and poor yields are observed. The results show that both the nature of the substituent and its position are important. Electron-withdrawing substituents result in higher yields than electron-donating substituents. A comparision of the influence of substitutents in the ortho, meta, and para position shows that the largest effect is found for substitutents in the para position. These results indicate that not only the nature of the substituent but also its position has an influence on the yield. The yield of benzaldehydes

TABLE I Yields of the Catalytic Oxidation of Benzyl Alcohols With $H_{14}[NaP_5W_{30}O_{110}]$

Substrate	Aldehyde Yield (%)	Benzoic acid Yield (%)
4-bromo benzyl alcohol	44.5	10.0
4-chloro benzyl alcohol	37.3	30.0
2-chloro benzyl alcohol	35.3	15.0
4-nitro benzyl alcohol	34.5	12.8
3-nitro benzyl alcohol	33.0	28.1
2-nitro benzyl alcohol	31.7	5.0
2-methyl benzyl alcohol	6.7	7.3
2,3,4-methoxy benzyl alcohol	5.2	4.9
2,3,4-hydroxy benzyl alcohol	7.3	4.9

Reaction conditions: catalyst 10^{-5} mol, substrate 10^{-3} mol, solvent acetonitrile (2 mL), H_2O (3 mL), hydrogen peroxide (0.03 mol) reflux for 8 h.

(major products) increased in the order of substitutents:

$$4\text{-Br} > 4\text{-Cl} > 2\text{-Cl} > 4\text{-NO}_2 > 3\text{-NO}_2 > 2\text{-NO}_2$$
$$> 2,3,4\text{-(OH)}_3,\ 2,3,4\text{-(CH}_3)_3,\ \text{and } 2,3,4\text{-(OCH}_3)_3.$$

THE EFFECT OF CATALYST TYPE

In order to compare the Keggin type catalysts with Preyssler's catalyst in the oxidation of benzyl alcohols to benzaldehydes, we selected the Keggin series including $H_n[XM_{12}O_{40}]$ ($X = P^{V}$, Si^{IV}, $M = W^{VI}$, Mo^{VI}, $n = 3, 4$). The results are shown in Figure 2 (data for products with poor yields are not given). The yield of benzaldehyde decreases in the following order:

$$H_3[PW_{12}O_{40}] > H_3[PMo_{12}O_{40}] > H_{14}[NaP_5W_{30}O_{110}]$$
$$> H_4[SiW_{12}O_{40}] > H_4[SiMo_{12}O_{40}].$$

In the Keggin series the results show that the silicon heteropolyacids are far less effective than the phosphorus heteropolyacids. Slightly lower yields were achieved with Preyssler's heteropolyacid.

The low of reactivity of Keggin's acid with X = Si may either reflect the known lower rate of degradation of this complex by aqueous hydrogen peroxide and the lower lability in general relative to

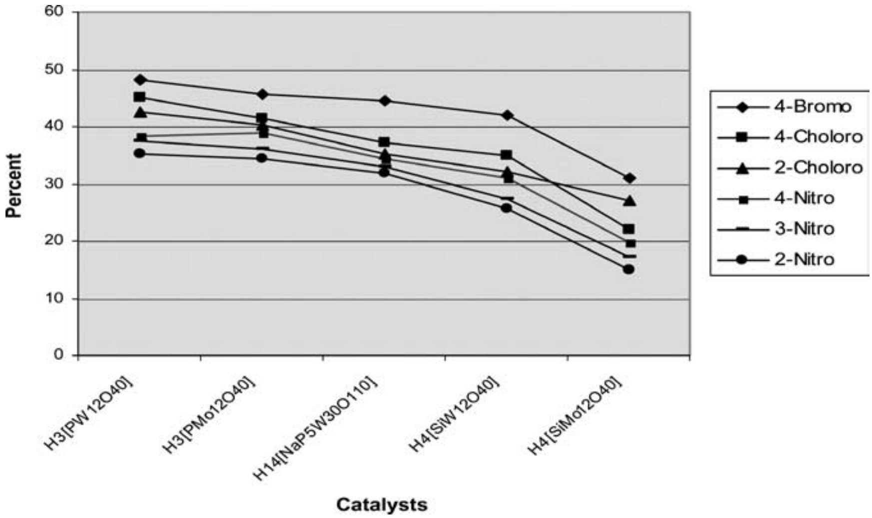

FIGURE 2 A comparison between Preyssler's catalyst and Keggin's catalysts at 70°C.

the phosphorus derivatives or indicate that the silicon analogue of $\{PO_4[WO(O_2)_2]_4\}^{3-}$ does not form. A comparision between $H_3[PW_{12}O_{40}]$ and $H_3[PMo_{12}O_{40}]$ shows for $H_3[PW_{12}O_{40}]$ a higher activity. When tungsten is replaced by molybdenum, the negative charge on the oxygen atoms increases, which leads to a decrease in acidity.[27,28]

It is also interesting to consider that by replacing one of the tungsten atoms of Keggin's acid (X = Si) with molybdenum the yield decreases again.

It is clear that by replacing tungsten with molybdenum the symmetry decreases, and this distortion may affect the nature and acidity of the heteropolyacid along with its catalytic properties.

Although in the Keggin's catalysts the active intermediate is considered to be a peroxo complex, a detailed mechanism in the case of Preyssler's catalyst has not yet been elucidated. It is notworthy that under our conditions Preyssler's catalyst is not degraded during the reaction, which is proven by spectroscopic evidence. The IR spectrum at the end of reactions shows that the catalyst is safe and unchanged.

Preyssler's anion proves to be an efficient catalyst in these reactions with an activity similar to that of the Keggin's acids without any degradation of the structure. The interesting feature of this polyanion compared to Keggin's heteropolyacids is its hydrolytic stability (pH = 0–12), which is very important in catalytic processes. In addition, this polyanion is more stable than the Keggin's catalysts under thermal conditions, which makes high temperature reactions possible.

There is a significant decomposition of H_2O_2 accompanying the oxidation of the benzyl alcohols under reflux conditions. It is proposed that Preyssler's anion catalyzes the oxidation of benzyl alcohols to the corresponding benzaldehydes by H_2O_2 in acetonitrile and water as a mixed solvent at 70°C, with the hydrogen peroxide decomposition being the main reaction. A mechanism for this reaction, including the oxidation of benzaldehydes by HO and HO_2 radicals formed via the hydrogen peroxide decomposition, is suggested.

Usually at temperatures higher than 60°C, HO and HO_2 radicals act as oxidants.[29–31]

THE EFFECT OF TEMPERATURE

The effect of temperature was studied by carrying out reactions at different temperatures in the presence of Preyssler's catalyst. The results showed that this polyanion catalyzes the reaction at r.t. It was observed that the yield increased as the reaction temperature was raised. The results at 70°C and r.t. (highest and lowest temperature) are compared in Figure 3. At higher temperatures, decomposition of hydrogen peroxide

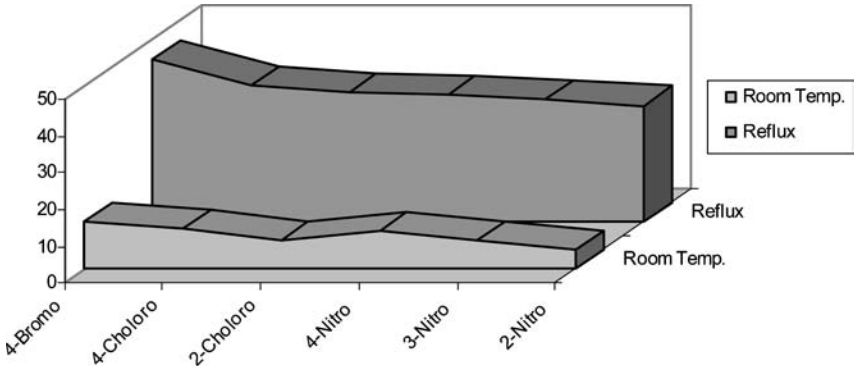

FIGURE 3 A comparison between the yields at r.t. and under reflux conditions (70°C).

may take place, which is undesirable. As expected, with an increase of temperature, the reaction time decreases. Thus, the yield of products is also a function of time: The longer the time, the higher the yield.

EXPERIMENTAL

Chemicals and Apparatus

Keggin's heteropolyacids and benzyl alcohols were commercially available. $H_{14}[NaP_5W_{30}O_{110}]$ was prepared according to the literature.[23] Acetonitrile and sulfuric acid were provided from a commercial source and were used without further purification. Hydrogen peroxide was obtained from Merck Company and was standardized by methods found online (*Hydrogen Peroxide Product Information Manual, Analytical Procedure, Eka Company*)[32].

^{1}H NMR spectra were recorded on a Brucker Aspect 3000 instrument at 100 MHz. IR spectra were recorded on a Buck 500 scientific spectrometer (KBr pellets). Mass spectra were obtained with a Massens POEKTRO METER CH-7A VARIN MAT BREMEN spectrometer.

The Oxidation of Benzyl Alcohols: General Procedure

The oxidation of benzyl alcohols was carried out in a two-necked round-bottom flask equipped with magnetic stirrer, reflux condenser, and thermometer.

In all cases, to a stirred solution of the catalyst (10^{-5} mol), acetonitrile (2 mL) and water (3 mL) were added the benzyl alcohol (10^{-3} mol). In regular intervals, 30% hydrogen peroxide (0.03 mol) was added in small portions. The reaction mixture was stirred and refluxed for 8 h at 70°C. The amount of benzaldehyde formed was determined by the reported 2,4-dinitrophenyl hydrazine method. The quantitative product analysis was carried out with the 2,4-Dinitrophenylhydrazone (DNP) formed.

The aldehyde was isolated as the DNP, vaccum dried, weighed, recrystallized from ethanol, and weighed again. The DNP obtained was found to have an identical melting point and mass spectrum as the DNP of the corresponding benzaldehyde reported in the literature. Benzoic acids were isolated by adding a 5% aqueous solution of $NaHCO_3$ and 2M HCl, respectively. The obtained solid was washed with water, vaccum dried, and weighed.

CONCLUSIONS

For the first time, the oxidation of benzyl alcohols with electron-withdrawing and electron-donating groups to the corresponding benzaldehydes and benzoic acids was achieved using an inexpensive the easily prepared sodium 30-tungstopentaphosphate $H_{14}[NaP_5W_{30}O_{110}]$ as a catalyst with good yields. The results show that the nature and positions of the substituents as well as temperature are important factors. Compared to catalytic procedures using the Keggin's catalysts, $H_{14}[NaP_5W_{30}O_{110}]$ offers the advantages of a higher hydrolytic and thermal stability and of retention of the structure, while its activity is similar to that of a Keggin's catalysts. The salient features of Preyssler's anion are availability, nontoxicity, and reusability. We believe this methodology will find usefulness in organic synthesis.

REFERENCES

[1] B. M. Trost, *Comprehensive Organic Synthesis (Oxidation), Vol. 7* (Pergamon, New York, 1991).
[2] J. Muzart, *Chem. Rev.*, **92,** 113 (1992).
[3] P. Laszlo and A. Cornelis, *Synthesis*, 909 (1985).
[4] B. Khadilkar and S. Borkar, *Synth. Commun.*, **28,** 207 (1998).
[5] M. Hirano, K. Komiya, and T. Morimito, *Org. Prep. Proced. Int.*, **27,** 703 (1995).
[6] C. L. Hil and C. M. Prosser-Mc Cartha, *Coord. Chem. Rev.*, **143,** 407 (1995).
[7] N. Mizuno and M. Misono, *J. Mol. Catal.*, **64,** 1 (1990).
[8] G. P. Romanelli, J. C. Autino, G. Baronetti, and H. J. Thomas, *Synth. Commun.*, **34,** 3909 (2004).
[9] G. Strukul, *Catalytic Oxidations With Hydrogen Peroxide as Oxidant* (Kluwer, Dordrecht, 1992).
[10] R. A. Sheldon, *Stud. Surf. Sci. Catal.*, **55,** 1 (1990).
[11] L. I. Kuznetsova, R. I. Maksimovskaya, and M. A. Fedotov, *Izv. Akad. Nauk SSSR, Ser. Khim.,* 537 (1985).

[12] N. I. Kuznetsova, L. G. Detusheva, L. I. Kuznetsova, M. A. Fedotov, and V. A. Likholobov, *Kinet. Catal.*, **33,** 516 (1992).

[13] C. Venturello, R. D. Aloisio, J. C. J. Bart, and M. Ricci, *J. Mol. Catal.*, **32,** 107 (1985).

[14] Y. Izumi, M. Ono, M. Ogawa, and K. Urabe, *Chem. Lett.*, 825 (1993).

[15] I. V. Kozhevnikov, A. Sinnema, A. J. A. Van der Weerdt, and H. Bekkum, *J. Mol. Catal.*, **120,** 63 (1997).

[16] T. Okuhara, T. Nishimura, K. Ohashi, and M. Misono, *Chem. Lett.*, 1201 (1990).

[17] P. Dupont and F. Lefebvre, *J. Mol. Catal.*, **114,** 299 (1996).

[18] M. N. Timofeeva, R. I. Maksimovskaya, E. A. Paukshtis, and I. V. Kozhevnikov, *J. Mol. Catal.*, **102,** 73 (1995).

[19] T. A. Gorodetskaya, I. V. Kozhevnikov, and K. I. Matveev, USSR Patent 1,121, 255 (1984).

[20] M. K. Harrup, C. Hill, and L. J. Cardona, *Inorg. Chem.*, 33 (1993).

[21] M. A. Fox, R. Cardona, and E. Gaillard, *J. Am. Chem. Soc.*, **109,** 21 (1987).

[22] M. H. Alizadeh, S. P. Harmalker, Y. Jeanenin, J. Martin-Frere, and M. T. Pope, *J. Am. Chem. Soc.,* **107,** 2662 (1985).

[23] (a) M. H. Alizadeh, H. Razavi, F. F. Bamoharram, and M. K. Hassanzadeh, *Kinet. Catal.*, **44,** 524 (2003); (b) F. F. Bamoharram, M. M. Heravi, M. Roshani, M. Gahangir, and A. Gharib, *Appl. Catal.*, **302,** 42 (2006).

[24] (a) M. M. Heravi, R. Motamedi, N. Seifi, and F. F. Bamoharram, *J. Mol. Catal.,* **249,** 1 (2006); (b) F. F. Bamoharram, M. M. Heravi, M. Roshani, and N. Tavakoli, *J. Mol. Catal.,* **252,** 219 (2006); (c) F. F. Bamoharram, M. Roshani, M. H. Alizadeh, H. Razavi, and M. Moghayadi, *J. Braz. Chem. Soc.,* **17,** 505 (2006); (d) M. M. Heravi, F. K. Behbahani, and F. F. Bamoharram, *J. Mol. Catal.,* **253,** 16 (2006); (e) F. F. Bamoharram, M. M. Heravi, M. Roshani, A. Gharib, and M. Gahangir, *J. Mol. Catal.,* **252,** 90 (2006); (f) M. M. Heravi, F. F. Bamoharram, Gh. Rajabzadeh, and N. Seifi, *J. Mol. Catal.,* (2006) in press; (g) F. F. Bamoharram, M. M. Heravi, M. Roshani, and M. Akbarpour, *J. Mol. Catal.,* **255,** 193 (2006); (h) M. M. Heravi, F. Derikvand, L. Ranjbar, and F. F. Bamoharram, *J. Mol. Catal.,* (2006) in press.

[25] (a) M. M. Heravi, Kh. Bakhtiari, and F. F. Bamoharram, *Catal. Commun.,* **7,** 373 (2006); (b) M. M. Heravi, Kh. Bakhtiari, and F. F. Bamoharram, *Catal. Commun.,* **7,** 499 (2006); (c) M. M. Heravi, F. Derikvand, and F. F. Bamoharram, *J. Mol. Catal.,* **242,** 173 (2005); (d) M. H. Alizadeh, H. Razavi, F. F. Bamoharram, and K. Daneshvar, *J. Mol. Catal.,* **206,** 89 (2003); (e) M. M. Heravi, Kh. Bakhtiari, N. M. Javadi, and F. F. Bamoharram, *J. Mol. Catal.,* (2006) in press; (f) M. M. Heravi, F. Derikvand, and F. F. Bamoharram, *J. Mol. Catal.,* (2006) in press; (g) M. M. Heravi, Gh. Rajabzadeh, F. F. Bamoharram, and N. Seifi, *J. Mol. Catal.,* **256,** 238 (2006); (h) M. M. Heravi, V. Zadsirjan, Kh. Bakhtiari, H. A. Oskooie, and F. F. Bamoharram, *Catal. Commun.,* (2006) in press; (i) M. M. Heravi, L. Ranjbar, F. Derikvand, and F. F. Bamoharram, *Catal. Commun.,* (2006) in press.

[26] *Ullmann's Encyclopaedia of Industrial Chemistry, 5th Edition, Vol. A3* (VCH, Weinheim, 1985).

[27] I. V. Kozhevnikov, *Russ. Chem. Rev.*, **56,** 811 (1987).

[28] J. B. Moffat, In B. Imelic (Ed), *Catalysis by Acids and Bases*, pp. 157–165 (Elsevier, Amsterdam, 1985).

[29] T. Yamase, E. Ichicawa, Y. Asai, and S. Kanai, *J. Mol. Catal.*, **114,** 237 (1996).

[30] L. I. Kuznetsova, L. G. Detusheva, M. A. Fedotov, and V. A. Likholobov, *J. Mol. Catal.*, **111,** 81 (1996).

[31] L. I. Kuznetsova, L. G. Detusheva, N. I. Kuznetsova, M. A. Fedotov, and V. A. Likholobov, *J. Mol. Catal.,* **117,** 389 (1997).

[32] Eka Chemicals, Hydrogen Peroxide Product Information Manual. Provided by email.