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Polymer-anchored platinum complexes as catalysts for the Baeyer–Villiger oxidation of ketones: preparation and catalytic properties

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Abstract

The preparation of a variety of catalysts obtained by ion exchange of the complex $[(dppb)Pt(\mu - OH)]_2^{2+}$ with sulfonated styrene–divinylbenzene copolymers is reported. Copolymers used are commercial ion exchange resins containing either 4% or 20% DVB and they were loaded with either Li^+ or NBu_4^+ prior to exchange with the Pt complex. Metal loading in the heterogenized catalysts is in the range 2–8% by weight. Their catalytic properties in the Baeyer–Villiger oxidation of methylcyclohexanone with hydrogen peroxide appear to be best in terms of activity and productivity either in neat ketone or in EtOH as the solvent. The use of commercial resins with high exchange capacity prevents the use of DCE as the solvent, i.e., the optimum conditions for the homogeneous system, thereby leading to activities and productivities that are generally lower than their homogeneous counterpart. A discussion on the influence of the philicity properties of the support with respect to the performance of the catalyst is reported. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Ion-exchange resins; Platinum complexes; Hydrogen peroxide; Oxidation

1. Introduction

The use of polymer-bound complexes in catalysis is about 30 years old and stems from the need to separate soluble catalysts from the reaction mixture [1,2]. We have recently reported the use of cationic complexes of Pt(II) of the type $[(P-P)Pt(\mu - OH)]_2^{2+}$ (P-P = a variety of diphosphines) as efficient catalysts for the Baeyer–Villiger oxidation of ketones to esters [3,4]. These complexes are the most effective catalysts known for this reaction and, together with other cationic Pt species [5,6], constitute the first unambiguous example of transition metal catalysis [7]. Most importantly, they allow the use of a clean but otherwise unreactive oxidant such as hydrogen peroxide because of their ability to increase its nucleophilic character through coordination [8].

However, the interest for practical applications of this class of catalysts could be signifi-

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cantly improved by having the catalyst in a separate (solid) phase. In a mechanistic study of the above system [4] we have been able to demonstrate that the Pt species involved in the catalytic cycle are all cationic in nature, hence this system appears to be suitable for embedding into a solid ion exchanger without leaching of metal in the course of the reaction, at least in principle. In this work we wish to report the preparation of a series of catalysts in which the above complexes have been immobilized into commercial ion-exchange resins along with their catalytic properties in the Baeyer–Villiger oxidation of ketones.

2. Experimental

2.1. Apparatus

IR spectra were taken on a Nicolet FTIR Magna 750 and on a Digilab FTS 40 interferometers either in solid (KBr pellets) or in CH_2Cl_2 solution using CaF_2 windows. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded on a Bruker AC 200 spectrometer operating in FT mode, using as external references TMS and 85% H_3PO_4, respectively. Atomic absorption measurements were made on Perkin-Elmer 3100 and Perkin-Elmer Analyst 100 instruments equipped with acetylene/air and N_2O/acetylene burners, respectively. GC measurements were taken on a Hewlett-Packard 5790A gas chromatograph equipped with a 3390 automatic integrator. GC–MS measurements were performed on a Hewlett-Packard 5971 mass selective detector connected to a Hewlett-Packard 5890 II gas chromatograph. Identification of products was made with GC or GC–MS by comparison with authentic samples.

2.2. Materials

Solvents were dried and purified according to standard methods. Reagents were commercial products (*purum* or *puriss* quality) used without purification. Ion exchange resins BioRad AG 50W-X4, 50–100 mesh, capacity 5.2 meq/g (dry) and Rohm & Haas Amberlite 200, 50–100 mesh, 2.75 meq/g were commercial products and thoroughly washed with water, methanol and acetone and dried in vacuo prior to use.

The complex $[(dppb)Pt(\mu - OH)]_2(BF_4)_2$ was prepared according to literature procedure [4]. Styrene–20% divinylbenzene copolymer (Amberlite XAD-2, 20–50 mesh) was sulfonated according to literature procedure [9].

2.3. Ion exchange procedures

2.3.1. Column operation

The resin in the acid form (30 g, 67% water content) was placed in a chromatography column and thoroughly washed with distilled water. A solution of LiOH (500 ml, 0.2 N) in distilled water was added slowly, followed by washing with water, methanol and acetone. The resin was then dried in vacuo.

The same procedure was followed to exchange Na^+ with H^+. Acid–base exchange was monitored by pH determination of the eluate.

The exchange of Li^+ with NBu_4^+ was performed similarly using methanol as solvent and with a flow rate of 5 ml/min. Aliquots of the eluate were withdrawn for Li analysis with AA.

2.3.2. Batch operation

In a round bottomed flask the Pt complex (50 mg) was dissolved in MeOH (35 ml) and to the solution the resin (Li^+ or NBu_4^+ form, 150 mg) was added. The suspension was gently stirred until equilibrium was attained, then the solid was filtered, washed several times with MeOH followed by acetone and finally dried in vacuo. The Pt content of the resin was calculated by difference after Pt analysis of the filtrate solution with AA.

A similar procedure was performed to introduce $HNBu_3^+$ in the resin. BioRad AG 50W-X4 (1.00 g, 5.2 meq) was suspended in MeOH and

NBu$_3$ (1.86 ml, 7.8 meq) was added followed by dioxane (0.5 ml) as internal standard. Quantitative analysis of the residual NBu$_3$ could be performed by GC using a calibration curve NBu$_3$/dioxane.

2.4. Catalytic reactions

These were carried out in a 25 ml round-bottomed flask equipped with a stopcock for vacuum/N$_2$ operations and a side-arm fitted with a screw-capped silicone septum to allow sampling. Constant temperature (± 0.1°C) was maintained by water circulation through an external jacket connected with a thermostat. For reactions carried out at temperatures > 25°C the reaction vessel was equipped with a reflux condenser. Stirring was performed by a Teflon-coated bar driven externally by a magnetic stirrer. The concentration of the commercial H$_2$O$_2$ solution was checked iodometrically prior to use.

The following general procedure was followed: The required amount of catalyst was placed in the reactor which was evacuated and filled with N$_2$. Purified, N$_2$ saturated ketone was added under N$_2$ flow, followed by the required amount of solvent. After thermostatting at the required temperature for a few minutes, the H$_2$O$_2$ solution in the appropriate amount was injected through the septum and time was started.

All reactions were monitored with GLC by direct injection of samples taken periodically from the reaction mixtures with a microsyringe. Separation of the products was performed on 25 m HP-5 capillary column using a flame ionization detector.

The amount of residual H$_2$O$_2$ at different times was determined by sampling 10 μl aliquots from the aqueous phase. These were diluted in water and titrated iodometrically.

AA analysis for the presence of Pt in randomly selected solution samples gave always negative results.

3. Results and discussion

3.1. Preparation of the catalysts

Initially, a resin with 4% cross-linking was chosen in order to have a swellable material in protic media, having hydrogen peroxide as the oxidant for the subsequent catalytic reaction. Since the resin is purchased in the acid form, acidity was removed by exchange with LiOH in water. The resin loaded with Li$^+$ was subsequently exchanged with the [(dppb)Pt($\mu -$OH)]$_2$(BF$_4$)$_2$ (dppb = 1,2-bis(diphenylphosphino)butane) cationic complex dissolved in methanol. This complex was chosen because it is the most active catalyst known for the catalytic Baeyer–Villiger oxidation in solution [4]. The exchange process was performed at room temperature, varying the reaction time. All samples were prepared starting from 50 mg of complex and 150 mg resin and a profile of the amount of complex exchanged with time is reported in Fig. 1. As shown the exchange is almost complete in 2 h, whereas the use of [(dppe)Pt($\mu -$OH)]$_2$(BF$_4$)$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane), which contains a less sterically demanding diphosphine, leads to complete exchange in less than 1 h.

Since the amount of Pt complex introduced corresponds to a maximum of 8.7% of the total
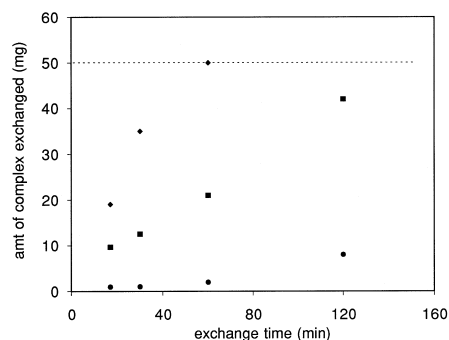

Fig. 1. A comparison between the amount of complex exchange vs. time at 25°C; the broken line indicates the maximum amount. Diamonds [(dppe)Pt($\mu -$OH)]$_2$(BF$_4$)$_2$ on Li exchanged BioRad AG 50W-X4; squares [(dppb)Pt($\mu -$OH)]$_2$(BF$_4$)$_2$ on Li exchanged BioRad AG 50W-X4; circles [(dppb)Pt($\mu -$OH)]$_2$(BF$_4$)$_2$ on Li exchanged Amberlite 200.

exchange capacity of the resin, samples containing alkylammonium cations instead of Li^+ were also prepared in an attempt to have a less hydrophilic environment surrounding the Pt complexes inside the catalyst beads. The exchange between Li^+ and NBu_4^+ was performed both in batch (reaction time 5 days) and using a column until exchange was complete as indicated by AA analysis of the Li content in the eluate. The former procedure led to only 10% exchange, while the latter was impractical, requiring longer than 14 h (of continuous sampling) to go to completion. To overcome this problem a new resin containing $HNBu_3^+$ was prepared in a batch experiment by adding excess NBu_3 to the resin in acid form. The progress of the protonation reaction was monitored quantitatively by analyzing the residual NBu_3 by gas-chromatography. One hundred percent protonation could be attained in a few minutes. Exchange with the Pt complex was performed for 2 h on both NBu_4^+ and $HNBu_3^+$ saturated resins, resulting in samples containing 54% and 44% of the maximum amount of Pt complex, respectively (Table 1). When the exchange time was increased to 6 h all the Pt complex introduced was incorporated in the resin (Table 1).

Finally, a resin containing 20% cross-linking was also used to limit the influence on the performance of the catalysts due to the physical properties of the support. Ion exchange was performed via prior conversion into the Li form
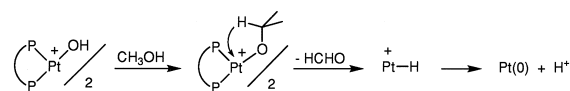
Scheme 1.

following the procedure reported above. However, as shown in Fig. 1, in this case the amount of complex exchanged vs. time is much smaller due to the higher rigidity of the present support and its lower capacity of swelling in MeOH. For this reason the exchange time was increased to 6 h and 4 days and, alternatively, the exchange temperature was increased to 64°C (exchange time 2 h and 18 h). In the latter case prolonged staying (18 h) at a moderately high temperature in MeOH resulted in extensive decomposition of the complex and a very poor incorporation in the resin ($< 5\%$ of the Pt complex introduced). Similarly, a long exchange time (4 days) gave again moderate complex incorporation in the resin (0.11 meq Pt/g catalyst) and evidence for decomposition. On the other hand it is known [10] that this class of Pt(II) bridging hydroxy dimers can exchange with alcohols (see Scheme 1) and it seems plausible that either at high temperatures or for prolonged staying they may undergo β-hydride elimination with formation of Pt(0).

A summary of the analytical properties of the catalysts tested in this work is reported in Table 1.

Table 1
Analytical properties of the catalysts

Catalyst #	Resin cross-linking (%)	Form	Pt content[a] (meq/g)	Exchange time (h)	Exchange temp (°C)
1	4	Li^+	0.37	2	25
2	4	NBu_4^+	0.22	2	25
3	4	$HNBu_3^+$	0.18	2	25
4	4	NBu_4^+	0.37	6	25
5	20	Li^+	0.07	2	25
6	20	Li^+	0.12	2	64
7	20	Li^+	0.16	18	25
8	20	Li^+	0.11	96	25

[a] Expressed as $[(dppb)Pt(OH)]^+$.

3.2. Catalytic reactions

The test reaction chosen was the oxidation of 2-methylcyclohexanone to the corresponding lactone. All reactions were performed at room temperature using a standard reaction mixture as specified in Scheme 2.

The search for the best solvent for the reaction was performed using catalyst **1**. This is an important point because the distribution of reactants inside the resin is strongly solvent-dependent [11] and a good solvent must be able to convey efficiently both the ketone substrate and hydrogen peroxide on the catalytic site inside the resin. A summary of the results obtained is reported in Fig. 2. The first solvent tested was 1,2-dichloroethane (DCE), that is known to be the best solvent when working under homogeneous conditions [4]. However, the use of a three-phase system (H_2O/DCE/resin) did not prove to be very efficient (Fig. 2) because of the high hydrophilicity of the resin that absorbs preferentially H_2O/H_2O_2 with respect to DCE/ketone resulting in poor catalytic activity. The use of some water-miscible solvents such as dioxane or *n*-BuOH gave again modest results, while the use of EtOH resulted in a significant increase in activity (Fig. 2). Under these conditions there is only one liquid phase penetrating the resin ensuring a better mixing of reactants in proximity of the active sites. The observed effect of the solvents on the catalytic activity parallels their swelling ability with respect to the resin bound catalyst (Table 2).

Better results in terms of productivity were obtained using the neat ketone as the reaction medium (Fig. 2). Despite the persistence of two liquid phases (water and 2-methylcyclohexanone are immiscible) and the modest swelling ability (Table 2), the strong concentra-
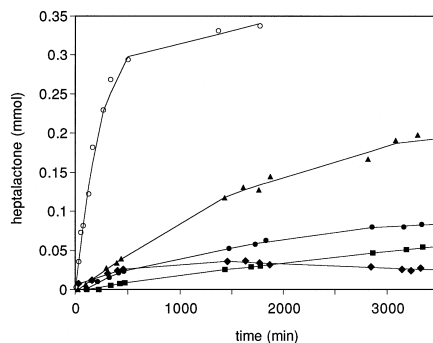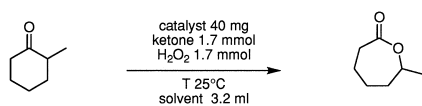

Fig. 2. Lactone formation using catalyst **1** in different solvents. Open circles no solvent; triangles EtOH; circles *n*-BuOH; squares dioxane; diamonds DCE.

tion effect and the lack of competition with the solvent seems to be beneficial for the success of the catalytic reaction. Unfortunately, at variance with the other cases, the use of neat ketone leads to the formation of a significant amount of 6-hydroxyheptanoic acid, which becomes evident after about 250 min. For longer reaction times (> 600 min) the oxidation reaction practically stops but the hydrolysis of the lactone product can continue almost indefinitely.

In general, the activity observed in these experiments is rather moderate (the conversion never exceeds 25%) and is in all cases much lower than the corresponding homogeneous reactions. For example, in Fig. 3 the two parallel reactions in DCE and EtOH using the same amount of free $[(dppb)Pt(\mu - OH)]_2(BF_4)_2$ are reported for comparison. As can be seen the homogeneous system results in much higher rates and, at least in the case of DCE, much higher productivity. The use of EtOH as the solvent leads to a moderate amount of lactone both with the heterogeneous catalyst and in solution. In the latter case small amounts of acetal are also observed, arising from condensa-

Scheme 2.

Table 2
Swelling ability of different solvents on catalyst **1**[a]

DCE	Dioxane	*n*-BuOH	4-Me-Cy-one	EtOH
1.0	1.1	1.15	1.05	2.2

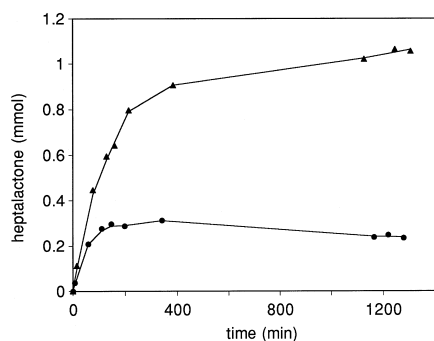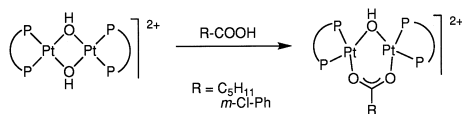[a]Expressed as the volume ratio **1**(wet)/**1**(dry).

Fig. 3. Lactone formation using $[(dppb)Pt(\mu-OH)]_2(BF_4)_2$ as catalyst in solution; triangles DCE; circles EtOH.

tion of EtOH with the ketone, a reaction that is known to be catalyzed by $[(dppb)Pt(\mu-OH)]_2(BF_4)_2$ [10]. This problem appears to be absent in the case of the heterogeneous catalyst.

The amount of hydrogen peroxide consumed at the end of the reaction generally corresponds to the ketone formed, i.e., when the reaction stops there is still a significant amount of unused oxidant. Doubling the amount of hydrogen peroxide does not improve the conversion significantly. These observations seem to suggest that the moderate conversions observed are likely due to a deactivation of the catalyst. It is known [3] that this class of complexes react with carboxylic acids to give bridging carboxylate complexes (Scheme 3) that are catalytically inactive. Indeed, the formation of 6-hydroxy-heptanoic acid observed in some cases as reported above could be a plausible reason for the deactivation of the active species following the reaction reported in Scheme 3 and leading to loss of catalytic activity. An alternative/complementary possibility is related to the formation of Pt(0) as suggested in Scheme 1.

Since the extent of the exchange between the cation in the resin and Pt_2^{2+} is in any case less than 10% of the total capacity of the resin, this implies that each active Pt site is surrounded by a large number of ion pairs that create an environment that is probably not favorable to the coordination of the (relatively hydrophobic) ketone. For this reason we have tested the catalysts loaded with an alkyl ammonium salt and a summary of the results observed with catalysts **2**–**4** is shown in Fig. 4. The tests were performed in EtOH as the reaction medium. As can be seen the activity observed parallels approximately the Pt content of the catalysts. Even in this case the use of neat ketone as the reaction medium results in a much higher activity. An initial rate can be easily extrapolated from the product formed vs. time curves (Figs. 2 and 4). This can be reasonably assumed as the intrinsic activity of the individual catalysts and permits calculation of the specific activity of each catalyst independent of the Pt content. As suggested by Fig. 5, the specific activities of catalysts **2**–**4** fall in the range 0.45–0.58 h^{-1}, only slightly higher than that of catalyst **1** (0.38 h^{-1}). This suggests that the presence of alkylammonium ions inside the resin is not beneficial with respect to Li^+, at least when EtOH is used as the solvent.

3.3. Use of a macroporous resin

In order to test the influence of the physical properties of the support on the activity of the catalyst, a resin containing 20% cross-linking was employed to prepare catalysts **5**–**8**. On the
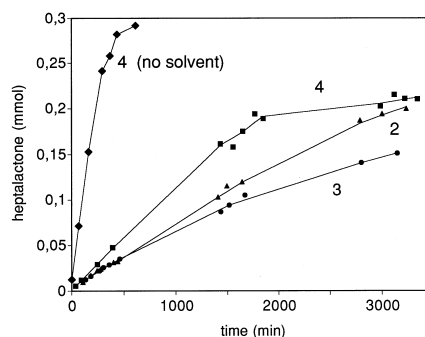

Fig. 4. Lactone formation using catalysts **2**–**4** in EtOH as solvent. The catalyst used is indicated in the individual curves.
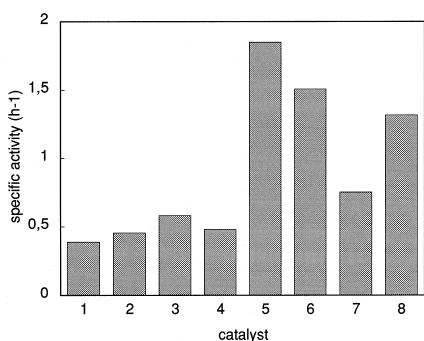

Scheme 3.

Fig. 5. Specific activity of the individual catalysts. Catalyst codes refer to Table 1.

3.4. Nature of the reaction medium

From the above results some considerations concerning the role of the support on the catalytic activity seem in order. The parameter that is mainly responsible for the limited activity of this class of catalysts appears to be the high exchange capacity of commercial resins which determines the philicity properties inside the resin and therefore the nature of the reaction medium where the catalytic reaction occurs. In fact, the substitution with Pt_2^{2+} centers is relatively low (although the Pt content is already in the range 2–8 wt.%) in order to have well separated catalytic centers, leaving some 90% of the original $-SO_3^-$ ^+Li (or NR_4^+) functional groups unchanged. This applies to all the catalysts prepared. The need for a good separation of the active sites is related to the mechanism of the homogeneous reaction [4] which involves bridge-splitting of the $[(dppb)Pt(\mu-OH)]_2^{2+}$ starting complex to give $[(dppb)Pt(ketone)-(OOH)]^+$ units that are the actual catalytically active species (Scheme 4). The large amount of residual $-SO_3^-$ ^+Li (or NR_4^+) functional groups determine: (i) the choice of EtOH as the solvent instead of the more desirable DCE (Fig. 3), (ii) a high affinity for H_2O/H_2O_2, (iii) a relatively poor affinity for the ketone substrate. From the results observed, this protic environment is detrimental for the catalyst because: (i) H_2O and EtOH can compete with H_2O_2 for coordination to platinum, (ii) coordination of the ketone is made more difficult because its concentration in the bulk of the resin is conceivably lower than in solution, (iii) the lactone product is more easily hydrolyzed leading to deactivation of the catalyst. In this respect, it is interesting to observe that when the concentration of ketone inside the resin is increased by using the

basis of the above results, the Li^+ form was used for the preparation of the catalysts.

A summary of the reactivity of these samples under the usual conditions is reported in Fig. 6 and the corresponding specific activities calculated as described above are reported in Fig. 5. As can be seen, the productivity is in general rather modest and, again, the use of DCE as the solvent resulted in very poor activity, although, similarly to the previous cases, the use of pure ketone as the reaction medium allowed to observe a much higher activity and productivity. However, in consideration of the low amount of metal incorporated in the resin, the specific activities are higher than the other catalysts. In other words, a rigid support, the physical properties of which are less sensitive to the effect of solvent, seems to create a better reaction medium in proximity of the active sites.
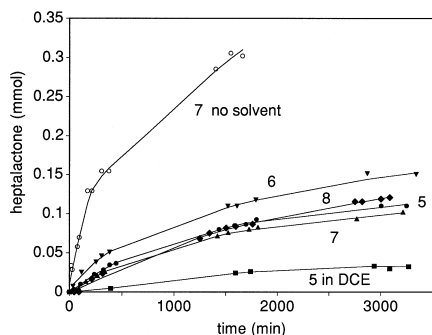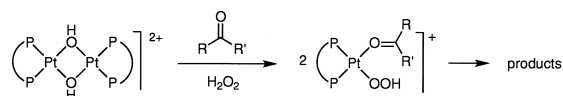

Fig. 6. Lactone formation using catalysts **5**–**8** in EtOH as solvent. The catalyst used is indicated in the individual curves.
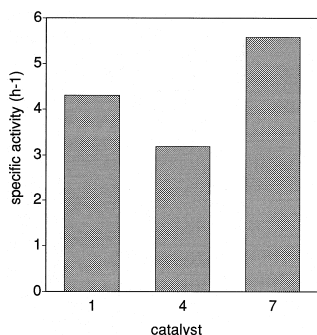

Scheme 4.

Fig. 7. Specific activity of the individual catalysts in reactions performed in neat ketone. Catalyst codes refer to Table 1.

neat ketone as the reaction medium, the corresponding productivities and especially the specific activities (Fig. 7) are significantly increased.

The philicity properties of the resin are probably unaffected by the change of Li^+ with NR_4^+ as cation, as seems to be demonstrated by the corresponding catalytic experiments. On the other hand, the use of a rigid support that is less sensitive to solvent effects seems to relieve, at least in part, the drawbacks summarized above, as is demonstrated by the higher specific activity observed both with EtOH as the solvent and, to a lower extent, in pure ketone.

4. Conclusions

In conclusion, although the results here reported seem to indicate that anchoring to an ion-exchange resin can be a viable way to heterogenize this class of homogeneous catalysts, the loss of catalytic activity with respect to the homogeneous system observed so far appears to be a significant limitation in their possible use towards a practical application. It seems reasonable that this problem may be relieved by the use of more hydrophobic resins, i.e., containing a much lower amount of residual functional groups. Research in this direction is currently underway.

References

[1] F.R. Hartley, Supported Metal Complexes, Reidel, Dordrecht, 1985.
[2] P. Panster, S. Wieland, in: B. Cornils, W.A. Herrmann (Eds.), Applied Homogeneous Catalysis with Organometallic Compounds, Chap. 3.1.1.3, Vol. 2, p. 605, VCH, Weinheim, 1996, and references therein.
[3] A. Varagnolo, F. Pinna, G. Strukul, J. Mol. Catal. A 117 (1997) 413.
[4] R. Gavagnin, M. Cataldo, F. Pinna, G. Strukul, Organometallics 17 (1998) 661.
[5] M. Del Todesco Frisone, F. Pinna, G. Strukul, Organometallics 12 (1993) 148.
[6] A. Gusso, C. Baccin, F. Pinna, G. Strukul, Organometallics 13 (1994) 3442.
[7] G. Strukul, Angew. Chem., Int. Ed. 37 (1998) 1198, and references therein.
[8] G. Strukul, in: G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Chap. 6, Kluwer, Dordrecht, 1992, p. 177.
[9] R. Small, T.S. Stevens, W.C. Bauman, Anal. Chem. 47 (1975) 1801.
[10] M. Cataldo, E. Nieddu, R. Gavagnin, F. Pinna, G. Strukul, J. Mol. Catal. A. 142 (1999) 305.
[11] W. Neier, in: K. Dorfner (Ed.), Ion exchangers, Walter de Gruyter, Chap. 2.11, Berlin, 1991, p. 981.