

Propylene epoxidation with hydrogen peroxide over palladium containing titanium silicalite

W. Laufer, R. Meiers, W. Hölderich *

Chemical Technology and Heterogeneous Catalysis, University of Technology RWTH Aachen, Worringer Weg 1, 52074 Aachen, Germany

Abstract

The epoxidation of propylene to propylene oxide with H_2O_2 was studied over palladium impregnated and reduced titanium silicalite (TS-1), over merely impregnated titanium silicalite and over untreated titanium silicalite. The use of such catalytic systems in the epoxidation of propylene with a $\text{H}_2\text{-O}_2$ mixture motivated us to assess the influence of operating conditions and the effect of the Pd loading on the epoxidation capability of the titanium silicalite catalyst. Concerning the operating conditions TS-1 was found to be very active even at temperatures as low as 10°C . Lowering the H_2O_2 concentrations to only 2 wt.% of H_2O_2 caused the PO yield to increase slightly over TS-1 and 1% Pd/TS-1. TS-1 catalysts that were merely impregnated with $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ were less active than the catalysts that were reduced after impregnation, though the latter is more active in the decomposition of H_2O_2 . The deactivation of TS-1 after impregnation with $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ was probably caused by the blocking of the Ti sites by ammonia, since the impregnation with PdCl_2 did not cause any decrease in activity. Reducing the catalyst removes the ammonia and improves the catalytic performance of the Pd loaded catalyst. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Propylene epoxidation; Hydrogen peroxide; Palladium; Titanium silicalite

1. Introduction

The development of new routes for the synthesis of propylene oxide has been attracting much interest over the recent years [1]. The invention of titanium silicalite-1 (TS-1) by Taramasso et al. [2] offered new opportunities for the epoxidation of olefins with hydrogen peroxide. Especially the epoxidation of propylene has been studied in some detail and has been found to proceed at high conversion rate and high selectivities under mild conditions in the liquid phase [3]. Due to economic considerations it has been tried to substitute the use of

aqueous H_2O_2 solution by the in situ formation of H_2O_2 . Two different approaches are employed for the formation of in situ hydrogen peroxide. The first approach [4] makes use of the conventional anthraquinone (AQ) process for the production of hydrogen peroxide by feeding propylene and oxygen to the oxidation stage of anthrahydroquinone (AHQ). Contacting AHQ with oxygen leads to the formation of hydrogen peroxide, which is then consumed in the oxidation of propylene to PO catalyzed by TS-1. The second concept is based on the oxidation of propylene by a $\text{H}_2\text{-O}_2$ gas mixture over a precious metal containing titanium silicalite [5–8]. Such catalytic systems have also been tested for the oxidation of alkanes, for the hy-

* Corresponding author

droxylation of benzene to phenol and for the oxidation of phenol [4,9]. Hydrogen peroxide is directly synthesized from H_2 and O_2 at the precious metal sites of the bifunctional catalyst and consumed as oxidant at the Ti-sites.

For the epoxidation of propylene with a H_2-O_2 mixture Sato et al. [5–7] and Mueller et al. [8] employ a palladium impregnated TS-1 catalyst suspended in solvents such as water or methanol. The reported conversions for the oxidation of propylene with a H_2-O_2 mixture are below 2% and the selectivity suffers from the hydrogenation of propylene to propane. We have proved that the in situ generation of hydrogen peroxide at the precious metal site is the rate determining step in this reaction [10]. Enhancing the catalytic performance of the catalyst must therefore focus on the impregnation and reduction procedure. We report now how reaction conditions, the impregnation and reduction of a Pd/TS-1 catalyst affects the synthesis of PO with hydrogen peroxide. The objective of this study is to assess the loss of epoxidation capacity of the TS-1 catalyst and the decomposition of H_2O_2 by the Pd loading.

2. Experimental

TS-1 was prepared according to the procedure described in the original TS-1 patent by Taramasso et al. [2]. 499 g of tetraethylorthosilicate were stirred under a CO_2 -free atmosphere and 15 g of tetraethyltitanate were added followed by dropwise addition of 800 g of a 25 wt.% solution of tetrapropylammonium hydroxide. After the alcohol had been distilled off under vacuum at $50^\circ C$, 868 g of distilled water were added to the solution. The mixture was transferred to an autoclave, heated at $175^\circ C$ and stirred under autogenous pressure for 10 d. After cooling down to room temperature, the crystalline product was separated from the liquid by centrifugation, washed with water, dried for 12 h at $120^\circ C$ and finally calcined for 10 h at

$550^\circ C$ in air. As determined by ICP analysis the resulting Si/Ti-ratio was 37.

A $[Pd(NH_3)_4](NO_3)_2$ solution was prepared by dissolving 10 g of $Pd(NO_3)_2$ in 400 g of an aqueous 25 wt.% ammonia-solution. After the mixture had been stirred for 3 d at $50^\circ C$, the solution was filtered and the resulting concentration of Pd was determined by ICP-analysis (21.6 mg/ml). $Pd(NH_3)_4Cl_2$ was prepared by dissolving $PdCl_2$ in aqueous 25 wt.% ammonia-solution.

Pd is supported on TS-1 by suspending 5 g of TS-1 in 20 g of deionized water and adding the appropriate amount of $[Pd(NH_3)_4](NO_3)_2$ or $Pd(NH_3)_4Cl_2$ to the solution. For the impregnation with $PdCl_2$ acetone was used instead of water. The mixture was stirred for 1 d at $80^\circ C$. The solid is recovered by evaporating the solvent under vacuum at $50^\circ C$ and dried at $60^\circ C$ for 1 d. As determined by ICP analysis the resulting catalyst were loaded with 0.1, 0.5, 1 or 2 wt.% Pd.

Reduction was carried out with 5 vol.% H_2 + 95 vol.% N_2 or pure N_2 at a heating rate of 1 K/min from room temperature to $150^\circ C$. Under the pure nitrogen atmosphere the catalyst was autoreduced by the thermal decomposition of the NH_3 ligands.

Catalytic tests were performed as batch reactions in a 75 ml stainless steel autoclave lined with a teflon beaker. 0.075 g TS-1 catalyst, 2 g methanol, 2 g deionized water and 1.2 g aqueous 30 wt.% H_2O_2 solution were charged to the reactor and a stirring bar was placed inside the beaker.

After the autoclave was cooled down in an ice bath, 8 g propylene were filled into the reactor by condensation. The reaction was started by immersing the autoclave into an oil bath. The stirring bar, which was driven by a magnetic stirrer, provided the necessary agitation. Standard reaction temperature was $50^\circ C$ and the standard reaction time were 3 h. At the end of the reaction the autoclave was cooled down again. A sample was withdrawn over a filter and mixed with a defined amount of methyl

tert-butyl ether, which acted as external standard. GC analysis was performed on a Carlo Erba Z 2300 gas chromatograph, using a flame ionization detector and 4 m column containing Carbowax 1500 as stationary phase.

The decomposition reaction of H_2O_2 was carried out similar to the epoxidation reaction except that no propylene was charged to the reactor. Reaction temperature was kept at $50^\circ C$ for 0.5 h. H_2O_2 was determined by iodometric titration.

3. Results and discussion

The catalytic activity of palladium free TS-1 was assessed by running the epoxidation reaction at different reaction times. After 3 h 99% of the hydrogen peroxide was consumed with a PO-yield of 67% based on H_2O_2 added. The hydrogen peroxide that did not react with propylene decomposed to water and oxygen.

The selectivity of propylene oxide based on all organic products (molar amount of produced PO to molar amount of the all organic products) was 97% (Fig. 1). Propylene glycol, 1-methoxy-2-propanol and 2-methoxy-1-propanol were the main by-products. All identified by-products were formed from propylene oxide by epoxide ring opening and reaction with a nucleophile. As the results in Fig. 1 indicate the standard reaction time of 3 h is sufficient to complete the reaction.

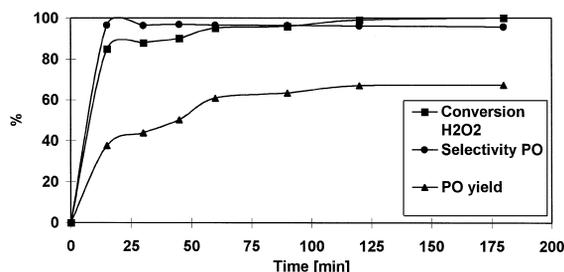


Fig. 1. Epoxidation of propylene with H_2O_2 over TS-1. Conditions: 0.075 g TS-1, 1.2 g aq. 30 wt.% H_2O_2 -solution, 8 g propylene, 2 g MeOH, 2 g H_2O , $50^\circ C$.

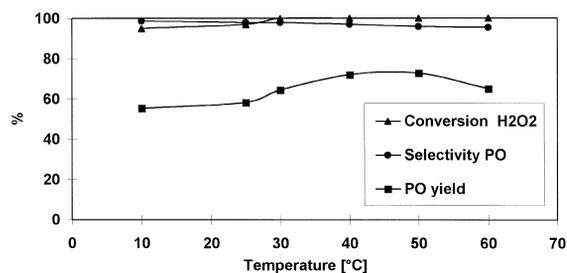


Fig. 2. Epoxidation of propylene with H_2O_2 over TS-1 at different temperatures. Conditions: 0.075 g TS-1, 1.2 g aq. 30 wt.% H_2O_2 -solution, 8 g propylene, 2 g MeOH, 2 g H_2O , 3 h.

For the intended use of the Pd/TS-1 catalyst in the oxidation of propylene with a H_2-O_2 mixture we were interested in the effect of reaction temperature on the catalytic performance of TS-1, because the direct synthesis of H_2O_2 is usually carried out at $0-10^\circ C$ [11–13] whereas epoxidation with H_2O_2 is performed at $40-50^\circ C$ [3]. The catalytic results of temperature variation is presented in Fig. 2. In accordance to literature data [3] the maximum PO yields (67%) were obtained at temperatures in the range of $40-50^\circ C$. Higher temperatures lead to a decrease in the PO yield which can be attributed to the enhanced decomposition of H_2O_2 . Lowering the reaction temperature results only in a slight decrease of the PO yield. Even at $10^\circ C$ a PO yield of 55% was obtained. Since the TS-1 catalyst is also very active at subambient temperatures it is possible to conduct the direct oxidation of propylene with a H_2-O_2 mixture at those temperatures, too.

With respect to the oxidation of propylene with a H_2-O_2 mixture it is furthermore interesting to study the effect of H_2O_2 concentrations on the catalytic performance of TS-1. When a H_2-O_2 mixture is used as the oxidant, the H_2O_2 formed in situ reacts with the propylene to yield PO thus leading to very low concentrations of H_2O_2 in the solution. We have investigated the influence of the initial H_2O_2 concentrations for the epoxidation of propylene with H_2O_2 by varying the H_2O_2 concentration from 2 to 15 wt.%. The epoxidation was catalyzed over TS-1 and over 1% Pd/TS-1. The latter of

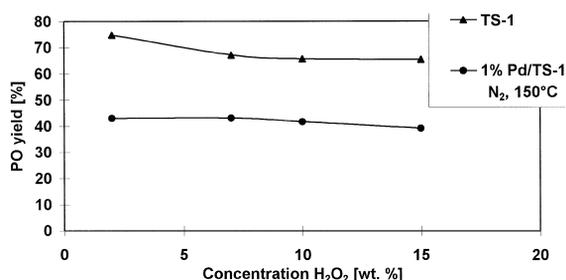


Fig. 3. Epoxidation of propylene with H₂O₂ over TS-1 and 1% Pd/TS-1.

the two catalysts was loaded with 1% Pd ([Pd(NH₃)₄]Cl₂) and autoreduced at 150°C under nitrogen. For the palladium free TS-1 we observed the PO yield to decrease with increasing H₂O₂ concentrations: from 75% PO yield for 2 wt.% H₂O₂ to 65% PO yield for 15 wt.% H₂O₂ (Fig. 3). The 1% Pd/TS-1 catalyst seems to be less affected by the H₂O₂ concentrations: the PO yield decreases from 43% to 39%. The fact that the PO yield increases with lower H₂O₂ concentrations should also favour the generation of PO in the oxidation of propylene with a H₂-O₂ mixture. However, the palladium loading caused the PO yield to decrease by ca. 40% compared to the unloaded TS-1. This result motivates a more detailed inspection of the possible causes for the decrease in epoxidation capacity.

For the loss of epoxidation capacity one can imagine two different reasons:

1. The Pd loading enhances the H₂O₂ decomposition
2. The epoxidation activity itself is negatively affected by the Pd impregnation.

In order to examine both possibilities we conducted epoxidations reactions and decomposition tests with four different catalytic systems:

- unloaded TS-1
- [Pd(NH₃)₄]Cl₂ in solution with TS-1
- TS-1 impregnated with 1% Pd (Pd was provided in the form of Pd(NH₃)₄]Cl₂)
- TS-1 impregnated with 1% Pd (Pd was provided in the form of [Pd(NH₃)₄]Cl₂) and subsequently autoreduced at 150°C.

The results of the epoxidation reaction is shown in Fig. 4 while the results of the decomposition tests are presented in Fig. 5.

The results in Fig. 4 show that the H₂O₂ conversion was not affected by the different catalytic systems whereas the PO yields exhibited a strong dependence on the catalysts employed. As expected the highest PO yield, 67%, was obtained with the untreated TS-1 catalyst. The PO yield dropped to 43% for the impregnated and reduced 1% Pd catalyst. The merely impregnated 1% Pd catalyst achieved only a PO yield of 37%. This result is rather surprising as the decomposition tests demonstrate that the

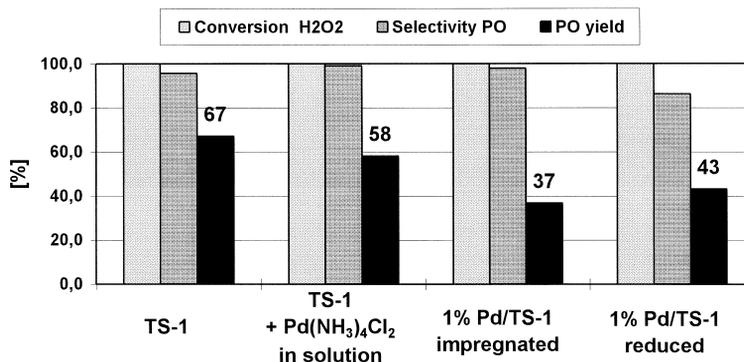


Fig. 4. Epoxidation of propylene with H₂O₂ over various catalytic systems. Conditions: 0.075 g catalyst (+ 1.7 mg [Pd(NH₃)₄]Cl₂), 1.2 g H₂O₂, 8 g propylene, 2 g MeOH, 2 g H₂O, 3 h, 50°C.

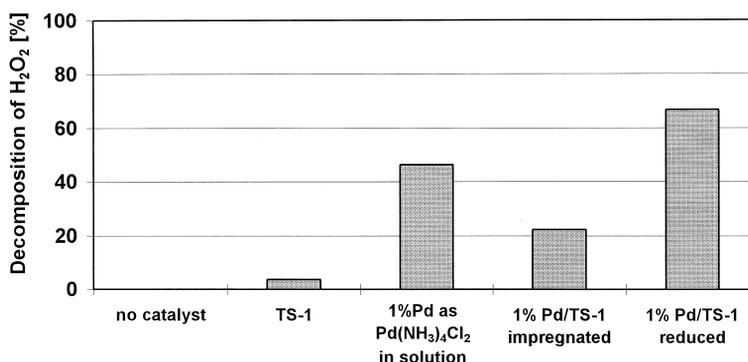
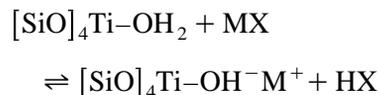


Fig. 5. Decomposition of H₂O₂ over various catalytic systems. Conditions: 0.075 g catalyst (+ 1.7 mg [Pd(NH₃)₄]Cl₂), 1.2 g H₂O₂, 2 g MeOH, 2 g H₂O, 0.5 h, 50°C.

reduced 1% Pd catalyst decomposes H₂O₂ more than three times faster than the merely impregnated catalyst. More H₂O₂ was decomposed by the reduced catalysts due to the presence of metallic Pd, which is well known for catalyzing the H₂O₂ decomposition [14]. Since the reduced 1% Pd/TS-1 catalysts performs better in the epoxidation reaction in spite of its H₂O₂ decomposition ability, we must assume that the epoxidation capacity of the impregnated 1% Pd/TS-1 was lowered drastically and that the loss in epoxidation capacity surpasses the decomposition effect by far. The Pd precursor itself lowers the PO yield only by 9% when brought into solution with TS-1, which is most probably caused by the decomposition of H₂O₂ by the Pd ions in solution.

The decrease in epoxidation capacity can be attributed to the blocking of the active sites by the ammonia solution and the Pd precursor [Pd(NH₃)₄]Cl₂. Thiele and Roland [15] observed also that the TS-1 activity decreased drastically after ammonia treatment and was regained by calcining the TS-1 at 550°C. They ascribe this effect to the deprotonation of the titanium site by a base, which causes blocking of the catalytic activity for epoxidation:



Calcining the ammonia treated TS-1 drives off ammonia as does the autoreduction at 150°C and thus shifts back the equilibrium back to the

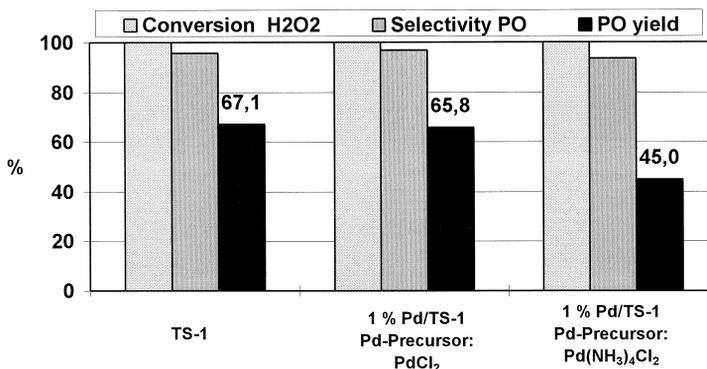


Fig. 6. Epoxidation of propylene with H₂O₂ over 1% Pd/TS-1 using different Pd precursors. Conditions: 0.075 g catalyst, 1.2 g H₂O₂, 8 g propylene, 2 g MeOH, 2 g H₂O, 3 h, 50°C. Reduction of impregnated catalysts: 150°C under 5% H₂/95% N₂.

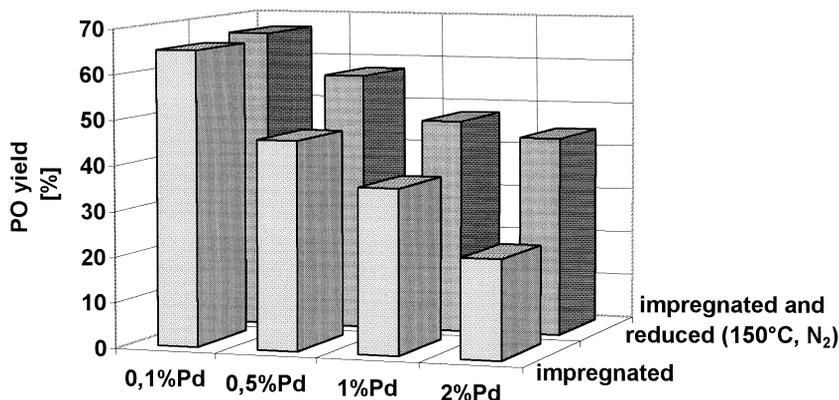


Fig. 7. Epoxidation of propylene with H_2O_2 over TS-1 catalysts loaded with different amounts of Pd. Conditions: 0.075 g catalyst, 1.2 g H_2O_2 , 8 g propylene, 2 g MeOH, 2 g H_2O , 3 h, 50°C. Conversion H_2O_2 : 100%.

left. According to this concept impregnation with an ammonia-free Pd precursor should yield a more active catalyst for the epoxidation reaction. For this purpose TS-1 was impregnated with PdCl_2 dissolved in HCl and reduced with 5% H_2/N_2 at 150°C. As a reference catalyst TS-1 was impregnated with $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and reduced in the same way, leading also to a 1% Pd/TS-1 catalyst. As shown in Fig. 6 the ammonia free catalyst, prepared with PdCl_2 , is indeed superior and yields 66% PO compared to 45% for the catalyst impregnated with $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$. The catalyst impregnated with PdCl_2 is even as active as the untreated TS-1 catalysts, which indicates that H_2O_2 decomposition on the Pd surface of this catalyst is rather negligible for the epoxidation reaction.

The best reduction method of catalyst for the direct oxidation of propylene with $\text{O}_2\text{--H}_2$ is the autoreduction under N_2 (decomposition of NH_3 -ligand [16,17]). Unfortunately the catalyst impregnated with PdCl_2 must be reduced under H_2/N_2 .

Apart from the effect of the Pd precursor on the propylene epoxidation we have investigated the relationship between the amount of Pd loading and catalytic activity. It is known from the oxidation of propylene with a $\text{H}_2\text{--O}_2$ mixture that PO yield increases digressively with Pd loadings ranging from 0.01 to 2 wt.% Pd [5–7]. For this purpose TS-1 was impregnated with

$[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$ and autoreduced at 150°C under nitrogen yielding catalyst with 0.1, 0.5, 1 and 2 wt.% Pd. Catalysts were tested in the merely impregnated and in reduced form for the epoxidation reaction with H_2O_2 under standard reaction conditions.

As demonstrated by the results presented in Fig. 7 the merely impregnated and the reduced catalyst exhibited two different trends with increasing Pd loading. The PO yield decreased almost linearly over the impregnated form while the PO yield levels off at 1–2% Pd over the reduced form. Due to these different relations the difference in PO yield was most pronounced, i.e., 22%, for the 2% Pd/TS-1 catalyst and was almost neglectable for the 0.1% Pd/TS-1 catalyst. These results clearly show that the removal of the ammonia from the Ti sites becomes more important for higher Pd loadings.

4. Conclusions

The impregnation of TS-1 with Pd tetramine ligands leads to a significant loss of the catalyst's activity, which is probably due the blocking of the active Ti site by ammonia. The activity can partially be restored by reducing the impregnated catalyst and thus removing the ammonia. The reduced catalyst is still less active as the

untreated TS-1 because of the decomposition of H_2O_2 by palladium.

Acknowledgements

Financial support of the Hoechst is gratefully acknowledged. The authors express their sincere thanks to Prof. Kühlein, Dr. Dingerdissen and Dr. Schulz for helpful and stimulating discussions.

References

- [1] Ullmanns Encyclopedia of Industrial Chemistry, 5th edn., Vol. 22, VCH Weinheim, 1993, p. 239.
- [2] M. Taramasso, G. Perego, B. Notari, U.S. Patent 4,410,501 to Snamprogetti, 1983.
- [3] M.G. Clerici, G. Belussi, U. Romano, *J. Catal.* 129 (1991) 159.
- [4] P. Ingallina, M.G. Clerici, L. Rossi, G. Belussi, *Science and technology in catalysis, Stud. Surf. Sci. Catal.* 92 (1995) 31.
- [5] M. Sato, T. Miyake, JP Patent Application 4 352771 to Tosoh, 1992.
- [6] A. Sato, M. Oguri, M. Tokumaru, T. Miyake, JP Patent Application 269029 to Tosoh, 1996.
- [7] A. Sato, M. Oguri, M. Tokumaru, T. Miyake, JP Patent Application 269030 to Tosoh, 1996.
- [8] U. Müller, P. Lingelbach, P. Baßler, W. Harder, E. Karsten, V. Kohl, J. Dembowski, N. Rieber, M. Fischer, German Patent Application DE 44 25 672 A1 to BASF, 1996.
- [9] T. Tatsumi, K. Yuasa, H.J. Tominaga, *J. Chem. Soc., Chem. Commun.*, 1992, 1446.
- [10] R. Meiers, R.P. Schulz, W. Hölderich, Epoxidation of propylene and direct synthesis of hydrogen peroxide by hydrogen and oxygen, *J. Chem. Soc., Chem. Comm.*, submitted.
- [11] L.W. Grosser, J.-A.T. Schwarz, U.S. Patent 4,832,938 to Du Pont, 1989.
- [12] H. Nagashima, Y. Ishiuchi, Y. Hiramatsu, M. Kawakami, Europ. Patent Application 539 846 A1 to Mitsubishi Gas Chemical, 1992.
- [13] M. Kawakami, Y. Ishiuchi, H. Nagashima, T. Tomita, Y. Hiramatsu, Europ. Patent Application 623 552 A1 to Mitsubishi Gas Chemical, 1994.
- [14] J. Schirrmann, S.Y. Delavarenne, *Hydrogen Peroxide in organic chemistry, Elfa Oyxchemie Handels Arau (CH)*, 1979.
- [15] G.F. Thiele, E. Roland, *J. Mol. Catal. A* 117 (1997) 351.
- [16] W.M.H. Sachtler, Z. Zhang, in: D. Eley, P. Weisz (Eds.), *Advances in Catalysis*, Vol. 39, Academic Press, New York, 1993, p. 129.
- [17] P. Albers, J. Kiwi, *J. Mol. Catal.* 58 (1990) 115.