The influence of zinc ions discharged in a non-aqueous cell on a copper catalyst on the rate of cyclohexanol dehydrogenation reaction

Andrzej Stokłosa, Janusz Zajęcki, Grzegorz Wilczyński, Anna Wójtowicz and Stefan S. Kurek

Institute of Chemical Engineering and Physical Chemistry, Cracow University of Technology, ul. Warszawska 24, 31-155 Krakow, Poland

Received 8 August 1995; accepted 7 November 1995

Results of studies on the influence of a copper catalyst modification with zinc ions on the activity in the reaction of cyclohexanol dehydrogenation are presented. The modification has been performed by electrochemical discharging–insertion of zinc ions on a copper electrode in a non-aqueous cell. It has been demonstrated that the catalyst activity depends on the amount of discharged zinc ions as well as on the nature and concentration of the electrolyte. In the case of zinc ions discharged from a solution of $ZnCl_2$ in propylene carbonate, the yield of cyclohexanone increased up to five times and using $Zn(BF_4)_2$ in dimethylformamide almost twenty times. The activity of the system in the competing reaction of dehydration was low, hence the selectivity in the dehydrogenation reaction was high.

Keywords: zinc/copper catalyst; cyclohexanol dehydrogenation; zinc electrochemical discharging on copper

1. Introduction

There has been a growing new interest in metallic catalysts both in the research and technology over recent years [1,2]. The higher thermal conductivity of metals, the relative easiness with which forms of optimal shape could be obtained and the possibility of the formation of various complex surface systems, all that makes metals interesting materials for catalyst preparation. On the other hand, the availability of relatively easy methods of single crystal preparation or monolithic systems in the form of large crystals makes it plausible to study those well defined surfaces with modern techniques. Complex metallic catalysts are obtained as alloys, by using surface modification techniques like vacuum deposition [2] or by the reaction of organometallic complexes with the surface of metallic particles [3] etc. Some electrochemical processes and modification of the electrode surface by using them is employed in electrocatalysis [4]. Forcing a surface to a determined catalytically active state may be accomplished in solid cells by non-Faradaic electrochemical modification [5,6]. Similar processes which in effect modify electrode surfaces are spontaneous processes occurring in galvanic cells during discharging. These processes occurring in non-aqueous cells with electrodes made of compounds with layered structure lead to intercalation and are widely studied with the objective to obtain reversible secondary cells (alkaline rechargeable cells). The discharging of ions on metallic surfaces may lead to their insertion into the metal lattice, at least into subsurface layers, giving rise to their stable incorporation or to a bimetallic system. In effect we obtain novel surface properties and hence catalytic properties.

The process of chemical intercalation mainly into graphite [7,8], tungsten bronzes [9,10] and aluminosilicates [11] has been extensively studied and applied in catalysis. The advantage of the electrochemical intercalation technique is the possibility to precisely control the process by discharging the optimal amount of ions. It is also possible to control the surface state by measuring the electrode-catalyst potential, what might prove to be useful in catalyst preparation. Electrochemistry has already been applied to study redox transformations of semiconductor oxide catalysts [12].

During the process of electrochemical intercalation the guest ion is inserted into the structure of the host compound, at the same time, electrons flowing in an external circuit occupy permitted states in the electrode material. Thus for the intercalation process, except for the crystallographic structure its electronic structure is important [13,14]. Metals clearly show that latter feature but they usually have close packed structures which are not structurally advantageous. Thus on metallic electrodes one should expect the formation of surface solid solutions or bimetallic systems.

The goal of this research was to investigate the influence of zinc ion discharging on the activity and selectivity of a copper catalyst in the dehydrogenation of cyclohexanol.

2. Experimental

The copper catalyst was prepared from a copper sheet of spectral purity supplied by Johnson-Matthey. The sheet was obtained by rolling rods to get strips with dimensions 0.002 × 1 × 20 cm. Prior to use the sheet was

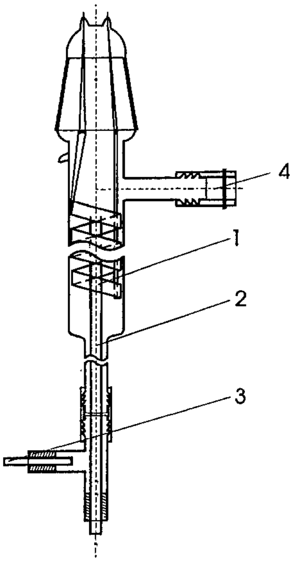

Fig. 1. Tubular reactor for intercalation and catalytic studies: (1) copper electrode, (2) zinc electrode, (3) copper reference electrode, (4) feed inlet.

polished with 600–1000 grit SiC paper and then washed with acetone and ethanol.

The deposition of zinc ions was performed directly in the tubular catalytic flow reactor shown in fig. 1. The coiled copper strip, (1), was placed in the central tubing of the reactor. A zinc electrode, (2), in the form of a rod of 0.5 cm diameter was inserted from the bottom. The reference electrode, (3), in the form of a copper rod was placed in a side tubing. The reactor was filled with electrolyte and then it was degassed under vacuum (below 1 Pa). The cell discharging was carried out with a current of constant density in the range of 0.5–1 $\mu A/cm^2$. The electric circuit is schematically shown in fig. 2. The discharging was stopped when the cell voltage fell to 10% of its initial value, usually after 7–9 h. Then, the reactor was emptied of the electrolyte, leaving the electrode-catalyst in the final state of the cell discharging. Afterwards the catalyst was washed with acetone and ethanol and eventually dried.

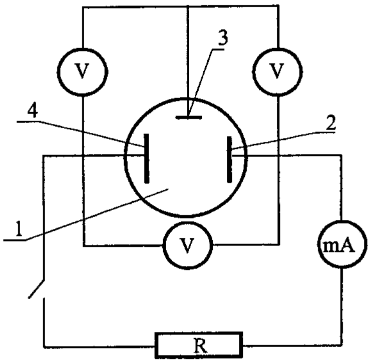

Fig. 2. Electric circuit used for intercalation: (1) gas tight chamber, (2) catalyst electrode, (3) reference electrode, (4) zinc electrode, (R) galvanostat.

Before the start of catalytic studies, the zinc electrode in the reactor was replaced by a small tubing with a thermocouple that served as a temperature measuring device inside the reactor. Then, the reactor was placed in an oven. Cyclohexanol was fed from the top (fig. 1, (4)) with a micropump. The reaction products were collected through the tubing (fig. 1, (3)) previously used for the reference electrode.

The analysis of the products was performed using a HP 5890 Chromatograph fitted with an FID detector. A 30 m Stabilwax capillary column (0.53 ID, 10 μmDF), temperature program: 70 to 230°C, 10°C/min; inlet/detector temperature: 240°C; and helium carrier gas were applied.

During the oven heat up period the reactor was filled with hydrogen. Afterwards it was kept at the reaction temperature in flowing hydrogen for a further half hour. The objective of the above treatment was the reduction of the catalyst surface and its standardization. The reaction was carried out at 693 K. Cyclohexanol was fed at the rate of 0.08 cm^3/min. The reaction was conducted for 3.5 to 8 h. Then the reactor was cooled down in flowing hydrogen. The catalyst (copper electrode) was then washed with acetone and the electrochemical discharging of zinc ions was carried out again.

Zinc ions were discharged from 0.3 M $ZnCl_2$ in propylene carbonate (PC) and 0.1 M $Zn(BF_4)_2$ in dimethylformamide (DMF).

3. Results and discussion

The electrochemical studies carried out by the authors [15] demonstrated that during the discharging of the cell:

$Zn|Zn^{2+}$(non-aqueous electrolyte)|Cu(Zn)[catalyst]

with a current of constant density, a cell voltage fall is observed that is due to an electrode-catalyst potential reduction caused by the deposition of zinc ions. During the relaxation of the electrode its potential increases above its initial value, which indicates that a part of zinc ions may be inserted into the copper lattice forming a surface solid solution, while another part leaves the surface. The above behaviour indicates a complexity of the electrode discharging and relaxation processes. The properties of the modified catalysts containing maximum amounts of zinc on the surface were studied first. To achieve this, the discharging was stopped by emptying the reactor of the electrolyte, thus skipping the relaxation step at least in the presence of the electrolyte.

Representative results of the studies on the catalytic activity of two copper catalysts modified with zinc ions from $ZnCl_2$ in PC (cat. PC) and $Zn(BF_4)_2$ in DMF (cat. DMF) are presented in table 1. The electrode potentials reported in table 1 are potentials of the copper catalyst versus the reference copper electrode measured

Table 1
Representative results of the studies on the catalytic dehydrogenation of cyclohexanol at 693 K on two copper catalysts modified by zinc ions

Catalyst	Cu electrode potential (V)	n_{Zn} (μmol/cm^2)	Cyclohexene (%)	Cyclohexanone		
				minimum (%)	mean value (%)	maximum (%)
Cat. PC 1	−0.0872	0.0282	0.57		9.69	
Cat. PC 2	−0.2153	0.0780	0.87		15.34	
Cat. PC 3	−0.1599	0.1051	0.43		17.30	
Cat. PC 4	−0.3270	0.1248	0.34		18.03	
Cat. PC 5	−0.3239	0.1355	0.39		18.90	
Cat. PC 6	−0.1875	0.1523	0.49		18.02	
Cat. PC 7	−0.1098	0.1643	0.91		17.00	
Cat. PC 8	−0.1759	0.1792	0.52		17.23	
Cat. DMF 1	+0.0304	0.4680	0.335	2.677		5.893
Cat. DMF 2	−0.0558	0.6864	0.317	6.705		10.543
Cat. DMF 3	−0.0471	0.8450	0.768	19.740		39.209
Cat. DMF 4	−0.1344	1.1148	1.826	21.789		35.620
Cat. DMF 5	−0.1490	1.2317	3.044	34.433		50.098
Cat. DMF 6	−0.2780	1.3290	5.054	49.203		57.183
Cat. DMF 7	−0.2890	1.6011	9.246	22.731		73.296
Cat. Cu	0	0	1.40		4.50	

after the catalytic reaction. These values could be related to zinc concentration variation or some catalyst surface changes resulting from the processes occurring during the catalytic reaction. The main reactions occurring on the catalyst were the dehydrogenation of cyclohexanol yielding cyclohexanone and the dehydration giving cyclohexene. The ratio of cyclohexene to cyclohexanone was small, in the range of 0.03 to 0.2.

The yields in the dehydrogenation reaction and the potentials of the electrode-catalyst versus the copper reference electrode after successive runs of the catalytic reaction (before the following discharging of zinc ions) as a function of the total amount of discharged zinc ions are depicted in figs. 3a ($ZnCl_2$ in PC) and 3b ($ZN(BF_4)_2$ in DMF). As can be seen from the figure there is an apparent correlation between the potential of the electrode-catalyst and its catalytic activity. In the case of the catalyst of fig. 3c, the same number of the discharging processes was performed as in the case of the catalyst of fig. 3b, except for the catalytic reaction, which was carried out only once, at the end of the experiment. As can be seen, the electrode potentials had similar values and the catalytic activity was also high. The obtained results indicate that the electrode potential measurement can give some information about the state of the surface of the electrode-catalyst.

A pure untreated copper sheet had low, 4%, catalytic activity in the dehydrogenation of cyclohexanol under the same conditions. Similar results were obtained in the case of a copper sheet immersed only in a solution of $ZnCl_2$ and then heated. Similar activity was observed in the case of zinc electrochemically deposited on an iron sheet. Thus copper modified with zinc exhibits much more enhanced activity as compared with pure copper. Yet this activity is a strong function of the nature of the solution employed for the discharging of zinc ions (figs. 3a and 3b).

It was also observed that the catalytic activity is affected by the way of discharging the zinc ions. If they are discharged with a large current, then the catalyst is less active than in the case of applying a small current for longer periods of time.

Catalysts obtained by using $ZnCl_2$ in PC and $Zn(BF_4)_2$ in DMF behave differently during the reaction as depicted in figs. 4a and 4b. The catalyst modified with zinc ions from $ZnCl_2$ solution in PC shows decaying oscillations, below 1%, in its activity around a constant value. In the case of the catalyst obtained by using a $Zn(BF_4)_2$ solution in DMF a faster fall in activity is observed, especially for catalysts with higher initial activity.

The relation between the cyclohexanone yield and the total charge passed in the successive processes of the cell discharging using $ZnCl_2$ in PC is depicted in fig. 3a. These values are equivalent to the amount of the discharged zinc ions. As can be seen, there is an increase in the activity up to a certain point. The results of a study on a catalyst on which a relatively large amount of zinc had been deposited are presented in fig. 5. In the case of this system, further amounts of zinc do not enhance the activity. A copper catalyst modified with zinc ions from a solution of $Zn(BF_4)_2$ in DMF showed significant variation in catalytic activity (fig. 4b). Maximum and minimum yields achieved are shown in fig. 6. As can be seen, much higher activities in the dehydrogenation were gained than for the catalysts obtained from a $ZnCl_2$ solu-

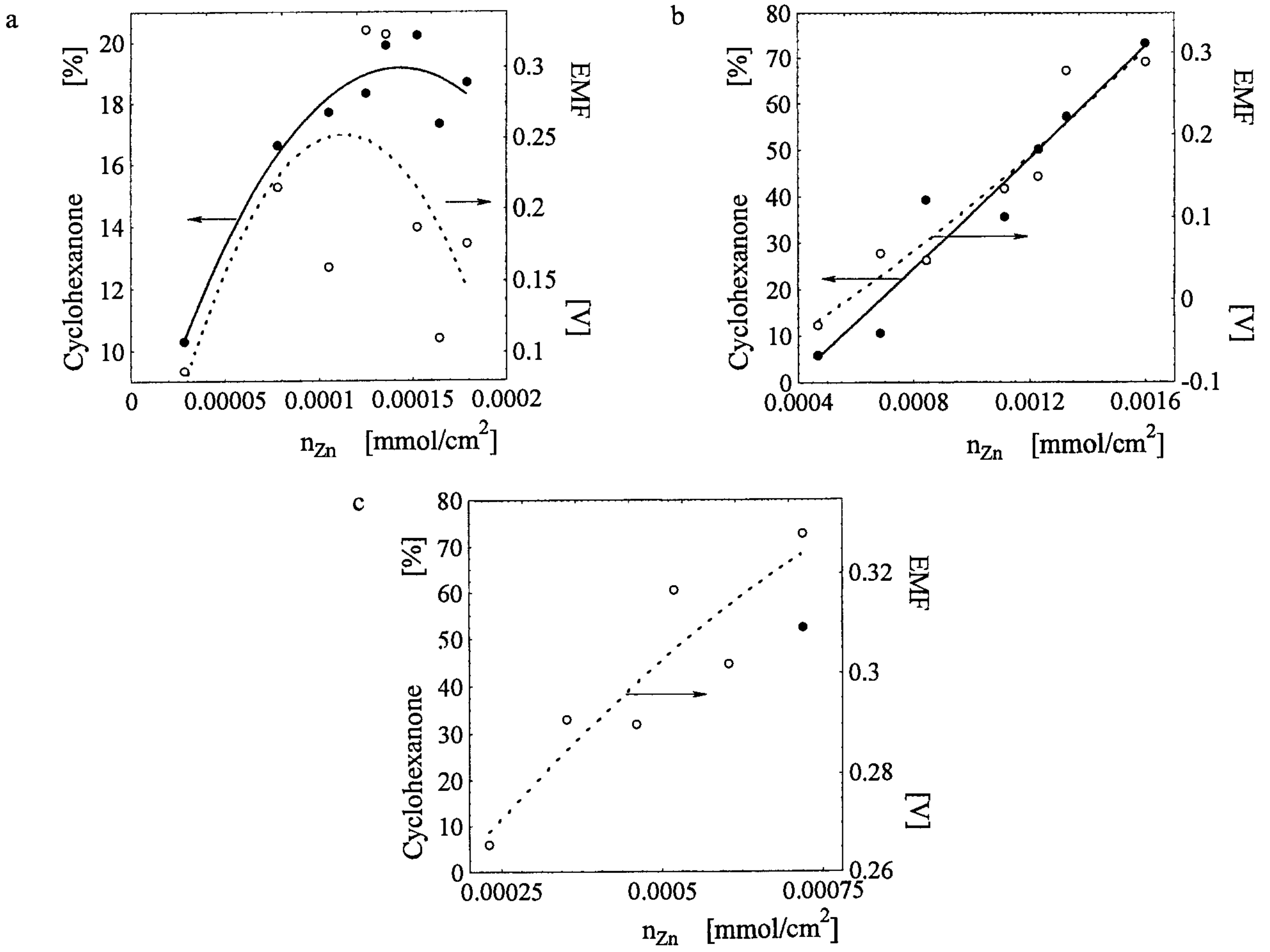

Fig. 3. Variation of electrode potential and yield in dehydrogenation versus the total amount of zinc deposited (a) from 0.3 M $ZnCl_2$ in PC and (b) 0.1 M $Zn(BF_4)_2$ in DMF, (c) 0.1 M $Zn(BF_4)_2$ in DMF but with five successive discharging–relaxation processes without catalytic reactions.

tion in PC, especially the initial values (maximum). The minimum values, achieved after 3.5 h, are also significant, yet they are much scattered, which demonstrates that the properties of the studied surface layers are affected by the method of preparation and they change during the catalytic reaction. A possible reason for the low stability of the surface layer may be the relatively high temperature which may cause evaporation of a significant amount of zinc. In order to check this effect a series of experiments was carried out in which the same amounts of zinc were discharged successively and the temperature of the reaction was decreased. At all the

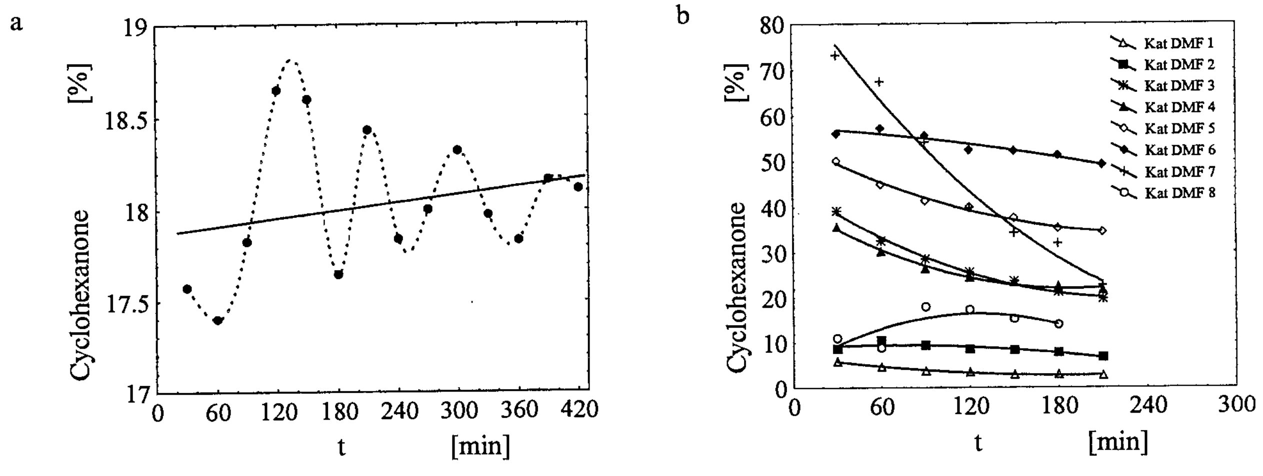

Fig. 4. Yields in dehydrogenation of cyclohexanol catalyzed by zinc modified copper using (a) 0.3 M $ZnCl_2$ in PC (solid line – linear regression, dotted line – cubic spline to show oscillatory character of the process), (b) 0.1 M $Zn(BF_4)_2$ in DMF, at 693 K versus reaction time.

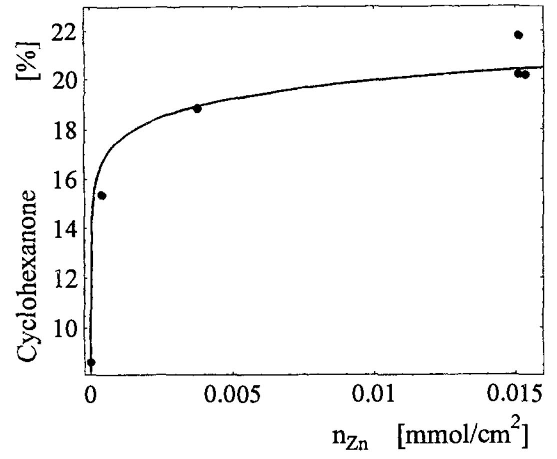

Fig. 5. Variation of the catalytic activity in cyclohexanol dehydrogenation at 693 K on copper with the total amount of discharged zinc ions from 0.3 M $ZnCl_2$ for larger amounts of zinc.

temperatures, low stability of the catalyst during the reaction was demonstrated. In fig. 7, the maximum (initial) and minimum yields in the dehydrogenation reaction at various temperatures are shown. As can be seen, despite the increasing amount of zinc discharged on copper, the yield decreases significantly. The difference between the maximum and minimum yield decreases with decreasing temperature, yet still remains significant. When the temperature was raised back to 690 K, a relatively high yield was observed again. The obtained results demonstrate that the surface layer obtained by discharging zinc ions from a DMF solution showed rather low catalytic stability.

4. Conclusions

The obtained results in the studies on modification of a copper catalyst by an electrochemical discharging method indicate its significant impact on the catalytic activity in the dehydrogenation of cyclohexanol. The activity of the catalyst can be precisely varied by controlling the electrochemical process. It was demonstrated that the catalytic activity is affected by the nature and concentration of the solution used for the discharging of zinc ions. It is also influenced by the magnitude of the current used and hence the duration of surface layer formation. The electrochemical process of discharging of zinc ions is complex, yet due to the possibility of controlling it by the magnitude of the current, duration of the process, as well as the possibility of the measurement of the electrode-catalyst potential, it is conceivable to obtain reproducible catalytic surfaces.

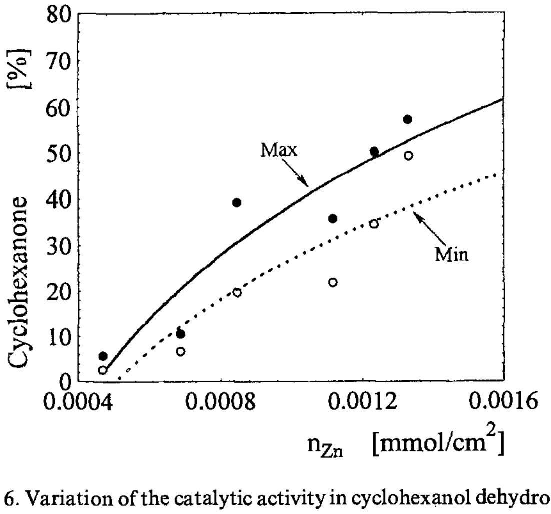

Fig. 6. Variation of the catalytic activity in cyclohexanol dehydrogenation at 693 K on copper with the total amount of discharged zinc ions from 0.1 M $Zn(BF_4)_2$ in DMF: (●) initial values, (○) minimum values.

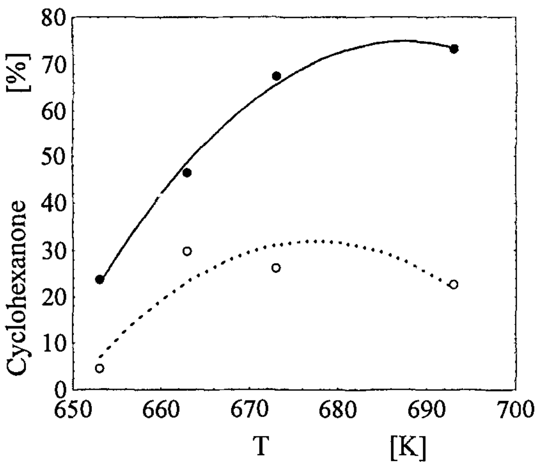

Fig. 7. Effect of temperature on the yield of cyclohexanol dehydrogenation. The amount of discharged zinc increased with decreasing reaction temperature from 693 to 653 K: (●) initial values, (○) minimum values.

Acknowledgement

Support for this work was provided by the Committee for the Scientific Research under Grant No. 2 P303 16404.

References

[1] M. Stoukides, Ind. Eng. Chem. Res. 27 (1988) 1745.
[2] J.A. Rodriguez and D.W. Goodman, J. Phys. Chem. 95 (1991) 4196.
[3] J.P. Candy, B. Didillon, E.L. Smith and T.B. Shay, J. Mol. Catal. 86 (1994) 179.
[4] B.J. Podlovchenko, A.G. Pshenichnikov and A.M. Skundin, Russian Electrochemistry 29 (1993) 534.
[5] C.G. Vayenas, S. Bebelis and S. Ladas, Nature 343 (1990) 625.
[6] C.G. Vayenas, S. Ladas, S. Bebelis, I.V. Yentekatis, S. Neophytides, J. Yi, C. Karavasilis and C. Pliangos, Electrochim. Acta 39 (1994) 1849.
[7] A. Fürstner, F. Hofer and H. Weidmann, J. Catal. 118 (1989) 502.
[8] F. Notheisz, A. Mastalir and M. Bartok, J. Catal. 134 (1992) 608.

[9] W.J. Wolfson, L.N. Ganiuk and S.F. Totskaya, Kinet. Katal. 5 (1964) 1100.
[10] J.O'M Bockris, R.A. Fredlein and A. Damajanovic, US Govt. Res. Develop. 70 (1970) 60.
[11] J.M. Thomas and Ch.R. Theocharis, in: *Perspectives in Catalysis*, eds. J.M. Thomas and K.I. Zamaraev (Blackwell, Oxford, 1992) p. 465.
[12] J. Haber and P. Nowak, Catal. Lett. 27 (1994) 369.
[13] J. Molenda, Phys. Stat. Sol. (b) 122 (1984) 591.
[14] J. Molenda, Solid State Ionics 21 (1986) 263.
[15] A. Stokłosa, S.S. Kurek, A. Wójtowicz and J. Zajęcki, Electrochim. Acta, submitted.