Pd/polyaniline as the catalysts for 2-ethylanthraquinone hydrogenation. The effect of palladium dispersion

A. Drelinkiewicz[a], M. Hasik[b] and M. Kloc[a]

[a] *Department of Chemistry, Jagiellonian University, ul. Ingardena 3, 30-060 Kraków, Poland*
[b] *Department of Materials Science and Ceramics, Academy of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Kraków, Poland*

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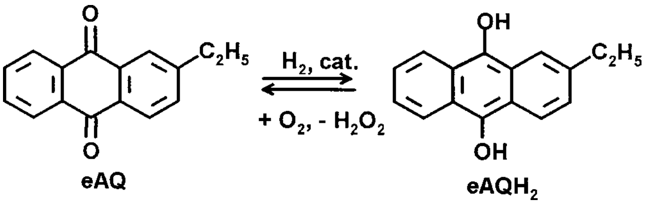
By doping of polyaniline (PANI) in $PdCl_2$ aqueous and ethanol solutions the catalysts containing crystalline and colloidal Pd particles of different sizes were prepared. The size of palladium particles present in Pd/PANI catalysts (characterised by SEM and XRD methods) influenced the course of 2-ethylanthraquinone (eAQ) hydrogenation, a key step in the industrial production of H_2O_2. The presence of large palladium particles promotes reactions leading to the formation of the so-termed "degradation products" not capable of hydrogen peroxide formation.

Keywords: 2-ethylanthraquinone, polyaniline, palladium catalyst, hydrogenation

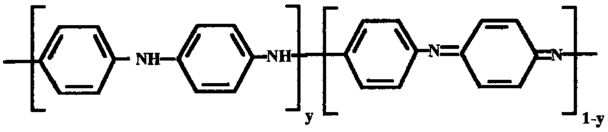
1. Introduction

Catalytic hydrogenation of 2-ethylanthraquinone (eAQ) is the key reaction in the anthraquinone method of H_2O_2 production [1,2] (scheme 1). However, 2-ethylanthrahydroquinone ($eAQH_2$), the primary product of eAQ reduction, is partly hydrogenated to different products, among which only 2-ethyltetrahydroanthrahydroaquinone (H_4eAQH_2) is desired (scheme 2) because it can participate in the oxidation reaction leading to H_2O_2 formation (similar to scheme 1). Therefore, eAQ and H_4eAQ are termed "active quinones" while all other products formed (2-ethyloctahydroanthraquinone, 2-ethylanthrone, 2-ethylanthracene, 2-ethyloxanthrone, dimers [1–4]) not capable of H_2O_2 formation are termed "degradation products". From a technological point of view the formation of low amount of degradation products is required. In the hydrogenation stage of the anthraquinone method palladium catalysts supported on Al_2O_3, SiO_2 and silica–alumina are commonly applied [1,2]. Data presented in patent literature [5] show that also Pd^{2+}–polyethylenimine systems have recently been applied. Therefore, it seems interesting to investigate the possibility of using a palladium catalyst supported on another polymer – polyaniline (PANI) – because PANI was successfully used as a support for Pd and Pt catalysts exhibiting interesting behaviour in hydrogenation of unsaturated hydrocarbons [6] as well as nitrobenzene [7].



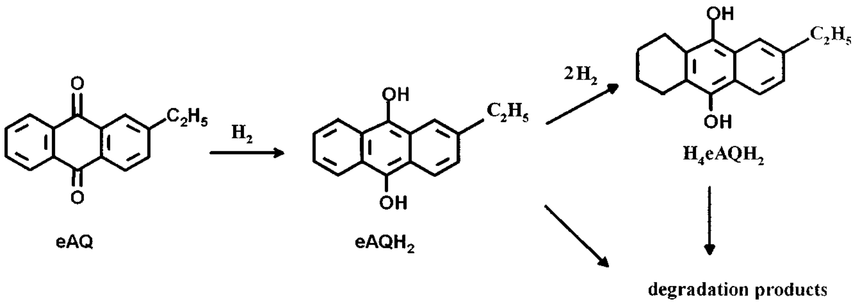
Scheme 1.

On the basis of our previous investigations concerning the nature of interaction in Pd^{2+}–PANI systems [8,9], catalysts with different metal dispersion were prepared. PANI is a conjugated polymer whose repeating unit is represented by the formula



It consists of y reduced and $(1-y)$ oxidized units. Since the value of y lies in the range of $0 \leqslant y \leqslant 1$, the polymer can continuously change its oxidation state from the fully reduced ($y = 1$) to the fully oxidized ($y = 0$) one. Additionally, owing to basic properties (presence of nitrogen atoms) PANI undergoes easily protonation reactions with acids giving PANI salts. Thus, PANI reacts readily in the redox as well as acid–base reactions.

It has been found earlier [8] that depending on the type of Pd^{2+} chlorocomplexes existing in the $PdCl_2$–H_2O–HCl solution (influenced mainly by HCl concentration [8]) the doping process of PANI via an acid–base or redox mechanism was realised. The former was the major one in the $PdCl_2$ solutions of high acidity containing significant amounts of $[PdCl_4]^{2-}$ complexes [10]. In the solutions of low acidity in which the electrically neutral $[PdCl_2(H_2O)_2]$ complexes were the major species [10] the redox reaction was involved resulting in the reduction of Pd^{2+} to Pd^0 accompanied by oxidation of the PANI chain (partial transformation of –NH– to =N– groups [9]). Palladium created in this process was present in the form of large crystalline particles. This latter procedure of catalysts preparation was used in the present investigations. By changing the concen-



Scheme 2.

Table 1
The conditions of catalysts preparation and catalysts properties.

Catalyst	Solvent	$PdCl_2$ (mol/dm^3)	HCl (mol/dm^3)	Pd (%)	Pd^0 (%)	Pd^{2+} (%)	Pd^0/Pd (%)
L	H_2O	1.15×10^{-3}	0.33×10^{-3}	6	3.73	2.27	62.2
M	H_2O	2.3×10^{-3}	0.66×10^{-3}	6	4.35	1.65	72.5
S	H_2O	6.9×10^{-3}	2.0×10^{-3}	6	4.5	1.5	75
E	Ethanol	0.14	–	6	4.25	1.75	70.8

tration of $[PdCl_2(H_2O)_2]$ in the doping solution Pd/PANI catalysts containing palladium crystalline particles of various size were prepared. Additionally, using a solution of $PdCl_2$ in ethanol PANI-supported colloidal Pd was obtained.

The aim of the present research was to study the change of the amount of active quinones (eAQ, H_4eAQ) in the course of eAQ hydrogenation over Pd/PANI catalysts with different palladium dispersion.

2. Experimental

2.1. Preparation procedure

Polyaniline in its polyemeraldine base form ($y = 0.5$, PANI) (BET surface area 46 m^2/g) was prepared according to a standard procedure [11]. Aniline was oxidized with $(NH_4)_2S_2O_8$ in hydrochloric acid followed by deprotonation in an aqueous solution of ammonia.

The conditions of catalysts preparation are given in table 1. Two types of $PdCl_2$ solutions were used, aqueous containing HCl for catalysts **L**, **M** and **S** preparation, and ethanol for catalyst **E** preparation.

In aqueous solutions the concentration of $PdCl_2$ ranged from 1.15×10^{-3} to 6.9×10^{-3} mol/dm^3, while the concentration of HCl was chosen in such a way that the molar ratio HCl : $PdCl_2$ was equal to 0.28 in all solutions. Under such conditions the dominating palladium complex $[PdCl_2(H_2O)_2]$ was the same in all solutions, while its concentration was different. It was the highest in the solution used for the preparation of catalyst **S**. This was spectroscopically (UV-vis) confirmed in our earlier investigation [8]. Doping of PANI by Pd^{2+} ions was performed by exposure of PANI powder at room temperature to the appropriate volume of $PdCl_2$ solution to obtain the same total content of palladium in the final sample equal to 6 wt% (table 1). The suspension was stirred up to the complete disappearance of Pd^{2+} ions in solution. This was achieved after 24 h in solution **S**, while in solution **L** this time period was two times longer. In ethanol solution sorption of palladium was complete after 60 h.

The colorimetric method (based on the reaction between palladium ions and KI leading to the formation of $[PdI_4]^{2-}$ ions [13]) was used for controlling the presence of Pd^{2+} ions in solution during catalysts preparation and for determining the amount of Pd^{2+} in the catalysts. In the latter case the unreduced palladium present in the catalysts was extracted several times with a 2 M solution of HCl. The extraction procedure was repeated until a portion of washing solution free from palladium was obtained. The amount of Pd^0 in the catalysts was calculated as the difference between the total amount of Pd (known from the amount of the solution used for catalyst preparation) and the amount of Pd^{2+} colorimetrically determined.

2.2. Catalysts characterisation

The catalysts were characterised using SEM (Philips XL-30) and X-ray diffraction (HZG 4 diffractometer with Cu K_α radiation) studies. SEM was equipped with an X-ray microprobe which made it possible to carry out Pd element distribution studies.

2.3. Catalytic experiments

2-ethylanthraquinone (eAQ) hydrogenation was carried out under stirred batch reactor conditions at constant atmospheric pressure of hydrogen, temperature 64 °C using as the solvent a mixture of xylene–octanol-2 (1 : 1 volume ratio) [14]. The course of hydrogenation was followed by measuring the volume of hydrogen consumed as a function of reaction time. During the reaction the samples of solution were taken from the reactor, oxidized with air and the amount of H_2O_2 formed was determined by titration (using $KMnO_4$). The concentration of eAQ and H_4eAQ in the oxidized solution was determined by HPLC [4,14]. Since the oxidation of $eAQH_2$ and H_4eAQH_2 is rapid and quantitative it was assumed that the number of moles of $eAQH_2$ and H_4eAQH_2 in the hydrogenated solution was equal to the number of moles of eAQ and H_4eAQ determined with HPLC analysis.

In a typical experiment 40 cm^3 of eAQ solution (eAQ 40 g/dm^3) and 0.2 g of catalyst were used. Pristine samples of all catalysts **S**, **M**, **L** and **E** were used in hydrogenation experiments. It was colorimetrically controlled that no change in Pd^0 and Pd^{2+} content occurred during the hydrogenation tests.

3. Results

In all investigated samples **S**, **M**, **L** and **E**, Pd^0 was formed during catalyst preparation, and its content was practically the same equal to about 4 wt% (table 1). In the catalysts (**S**, **M** and **L**) prepared in aqueous solution of a $PdCl_2$, Pd^0 was formed as the result of a Pd^{2+}–PANI reduction–oxidation process [9]. As the data in table 1 show, about 70% of Pd^{2+} ions were reduced in this process and this amount only slightly increased with the increasing of $PdCl_2$ concentration in the doping solutions. These findings confirmed our earlier XPS studies [8,9] which showed the presence of two peaks: the major one (70%) corresponding to Pd^0 (BE Pd $3d_{5/2} = 335.5$ eV) and the less intensive one characteristic of Pd^{2+} (BE Pd $3d_{5/2} = 337.7$ eV).

Figure 1 presents X-ray diffraction patterns of the catalysts studied. In the spectra of catalysts **S**, **M** and **L** the sharp and narrow peaks at $2\theta = 40.1°$ and $46.6°$ evidently prove the presence of crystalline palladium in the form of large crystals. Palladium peaks are easily detectable above the relatively low background originating from PANI, which exhibits a broad "halo" centred around $2\theta = 20°$. Figure 2 presents the surface morphology of catalysts prepared in aqueous solution of $PdCl_2$. In both samples **S** and **L** distinct Pd particles in the form of white almost spherical spots, exhibiting high contrast against the support, are seen. In both catalysts the distribution of Pd particles seems to be practically uniform. The X-ray microprobe analysis of Pd element (spot, line and surface analyses), carried out in different surface points, indicated that in white spots the content of palladium was in fact the highest. On the other hand, in the analysed points, located beyond the white spots palladium did not practically appear (figure 3). In view of the XRD results it can be supposed that the white spots in the SEM micrographs correspond to the crystalline palladium particles.

SEM micrographs showed also that palladium particles in catalyst **L** (prepared in solution of the lowest $PdCl_2$ concentration) are relatively larger, while their density on the surface of the polymer was lower. Therefore, basing on SEM results, palladium particles size distributions for catalysts **S**, **M** and **L** were calculated (table 2). In the calculations a total number of 174 (catalyst **L**), 535 (catalyst **M**) and 870 (catalyst **S**) individual particles registered by SEM were taken into account. It was found that palladium particles were practically within the same range 60–400 nm in size in all catalysts. However, the detailed analysis indicates that the % contribution of smaller particles 60–240 nm in size increases from 70.7% for catalyst **L** up to 91.9% for catalyst **S**. Additionally, only in the catalyst **L** prepared in solution of the lowest $PdCl_2$ concentration the existence of particles as large as 540–600 nm in size was detected.

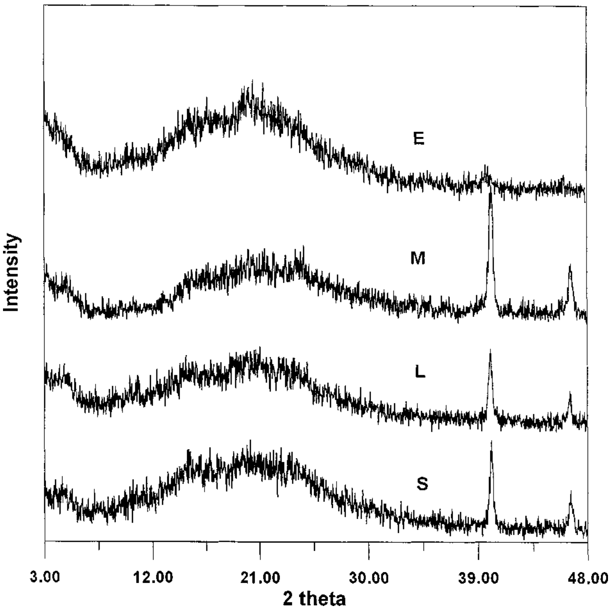


Figure 1. X-ray diffraction patterns of catalysts **S**, **M**, **L** and **E**.

A different surface morphology was observed for catalyst **E** prepared in ethanol solution of $PdCl_2$. In the SEM image of this catalyst (figure 4) palladium particles in the form of irregular aggregates of various shape and size were seen. Their distribution on the polymer surface was not uniform. It seems that the surface covered by Pd agglomerates is low as compared with the total polymer surface. In the XRD spectrum of sample **E** (figure 1) only a small perturbation on the background line at positions corresponding to Pd peaks was visible.

Thus, results of SEM and XRD investigations indicate that conditions of catalysts preparation affected not only the course of Pd^{2+} reduction but also the type and the size of palladium particles existing in the final samples. A plausible explanation for this effect is given below.

When an aqueous solution of $PdCl_2$ was used, as in the preparation of catalysts **L**, **M** and **S**, the PANI chain (–NH– groups) was the only reducing agent. Under such conditions the concentration of $PdCl_2$ in the doping solution and consequently the concentration of $[PdCl_2(H_2O)_2]$ influences the size of Pd crystalline particles formed. The number of palladium crystals formed was small at low concentration

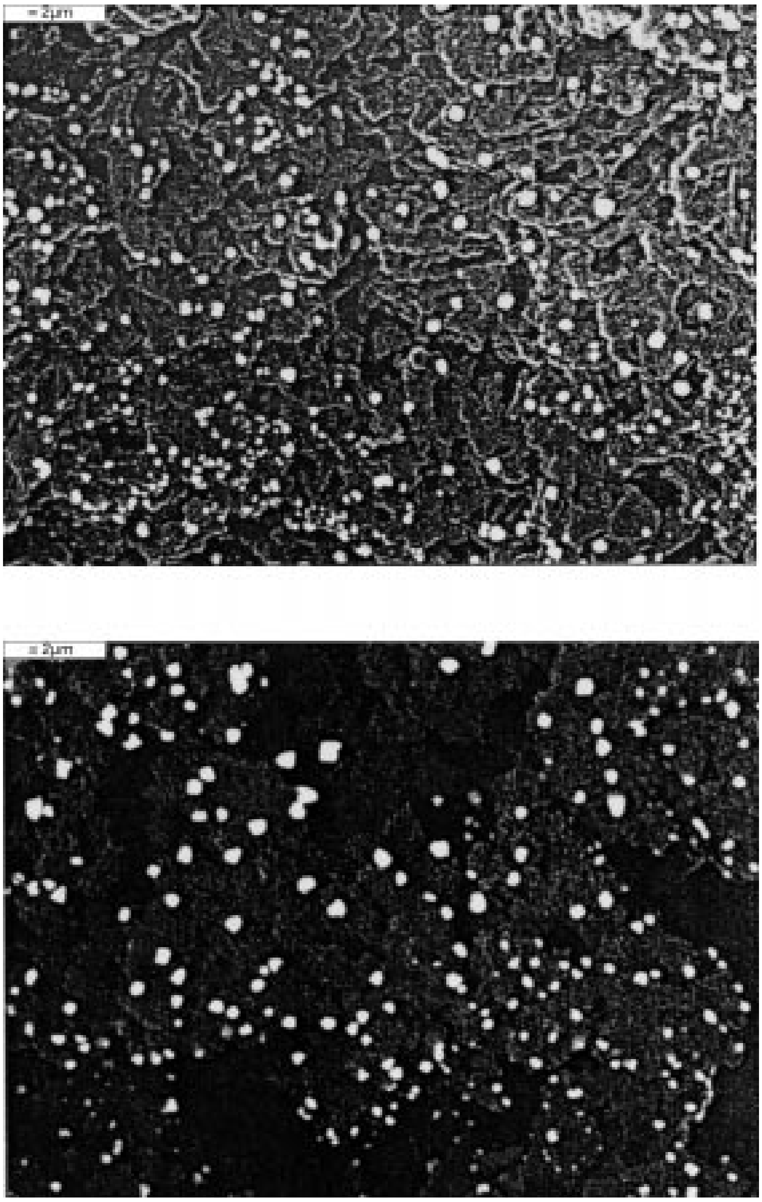


Figure 2. Scanning electron micrographs of catalysts **S** (top) and **L** (bottom) (magnification 8000).

of $[PdCl_2(H_2O)_2]$ in the doping solution (catalyst **L** preparation), large at higher concentration of this complex. This resulted in the formation of larger Pd^0 crystalline particles in catalyst **L** than in catalyst **S**. However, it is not possible to decide whether palladium species were supplied to the reduction centres from the polymer surface as a result of surface migration or from the solution.

It may be supposed that the course of the doping process in the ethanol solution of $PdCl_2$ was different. In this system two reducing agents were present: PANI and ethanol. The presence of the latter decided on the peculiarity of the reduction process. SEM micrographs (figure 4) showed the formation of continuous palladium areas. The bright areas were present only on some polymer grains, while other grains remain completely uncovered by palladium. These effects suggest that colloidal Pd^0 particles were formed in the solution with the participation of ethanol. They sticked to the polymer surface due to adhesion forces.

4. Catalytic activity

In spite of the fact that the size of Pd^0 particles in all samples was larger than that in commonly used palladium supported catalysts, the catalytic ability of prepared Pd/PANI in eAQ hydrogenation was examined. Since all the samples contained the same amount of Pd^0 (4%) it was possible to study the effect of the size of Pd^0 particles on the course of eAQ hydrogenation and, especially, on the change of the amount of active quinones (eAQ, H_4eAQ). It was assumed in these investigations that SEM micrographs were representative for the whole surface of the catalysts and that the total amount of palladium acting in hydrogena-

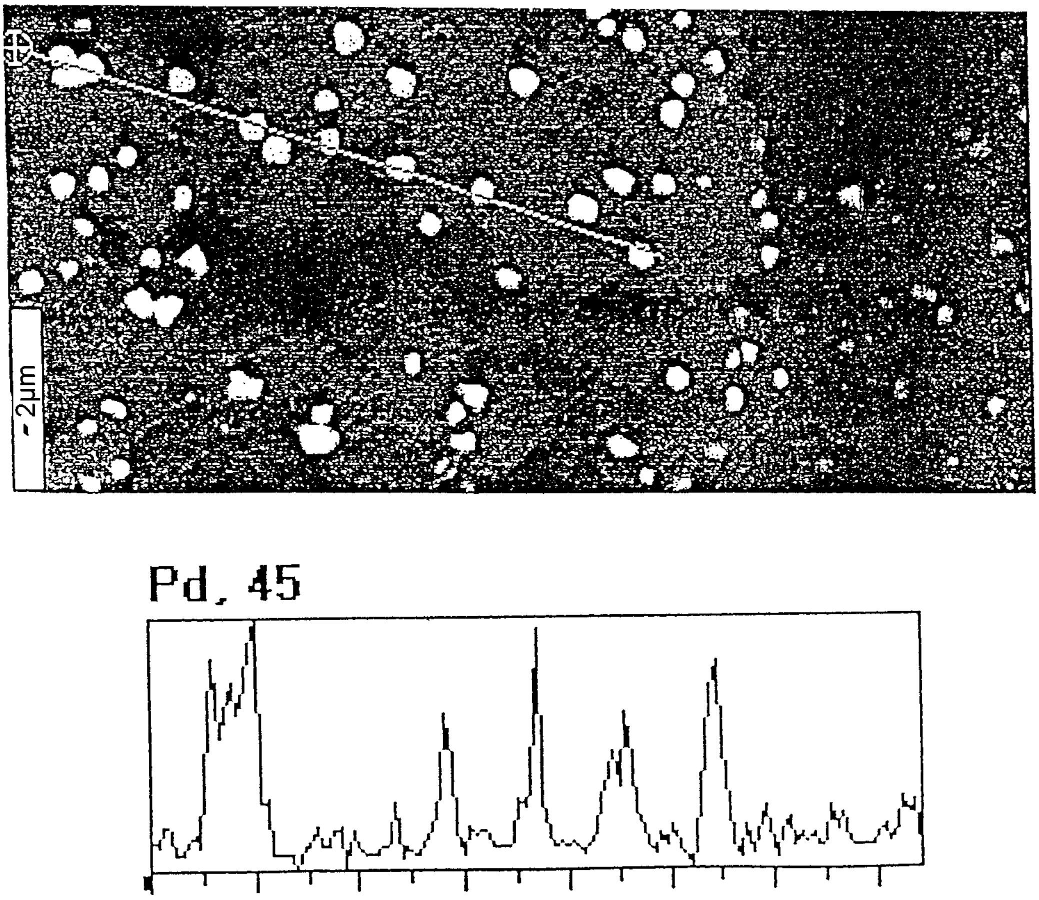


Figure 3. Pd concentration profile, catalyst **M**.

Table 2
Contribution of palladium particles (%) in catalysts.

Particles size (nm)	L	M	S
Up to 61	2.9	11.8	14.7
61–121	22.4	33.6	30.7
121–182	25.3	29.2	27
182–242	20.1	12.3	19.5
242–303	19.5	7.5	6.6
303–364	5.7	4.7	1.3
364–424	1.4	0.4	0.2
424–485	1.2	0.5	–
485–545	0.9	–	–
545–606	0.6	–	–

tion is palladium detected by SEM in the form of distinct particles.

All catalytic results were expressed as a function of parameter β which represents the number of hydrogen moles consumed ($n^t(\mathrm{H_2})$) per one mole of eAQ initially present in the reactor ($n^0(\mathrm{eAQ})$):

$$\beta = n^t(\mathrm{H_2})/n^0(\mathrm{eAQ}).$$

Figure 5 presents the change of the rate of hydrogen uptake ($r(\mathrm{H_2})$, mol H_2/min) in the course of hydrogenation. It is seen, that from the very beginning of the reaction up to $\beta = 1.2$–1.4 the rate of hydrogenation is high. In this first reaction stage the reduction of eAQ to $eAQH_2$ is the main process [1,2,4]. After consumption of 1.2–1.4 mol of H_2 per 1 mol of eAQ ($\beta = 1.2$–1.4) the rate of hydrogen consumption ($r(\mathrm{H_2})$) decreased thus indicating that hydrogenation of eAQ into $eAQH_2$ was almost complete. The second stage ($\beta > 1.2$–1.4) proceeding at distinctly lower rate comprises usually the processes in which the primary product $eAQH_2$ is hydrogenated to H_4eAQH_2 and other side products (degradation products, scheme 2). As figure 5 shows, the highest was the rate over the catalyst containing the smallest Pd^0 particles (**S**), the lowest over catalyst **E** in which the irregular, large Pd^0 particles were present. As has already been said, the main reaction proceeding from the very beginning is reduction of eAQ to $eAQH_2$. In the situation that only this reduction proceeds, the highest possible number of H_2O_2 moles detected at $\beta = 1$ would be equal to the initial number of eAQ moles. This number of H_2O_2 moles was assumed as 100%. In the case of selective hydrogenation of $eAQH_2$ to H_4eAQH_2 (active quinone) also 100% of H_2O_2 would be reached, but at values of β somewhat higher than 1. The change of % H_2O_2 as a function of β is presented figure 6. From the beginning of reaction % H_2O_2 distinctly increased as a result of eAQ to $eAQH_2$ reduction (the main reaction) but at a certain value of β (higher than 1) it reached the maximum value. The β value of reaching the maximum value of % H_2O_2 corre-

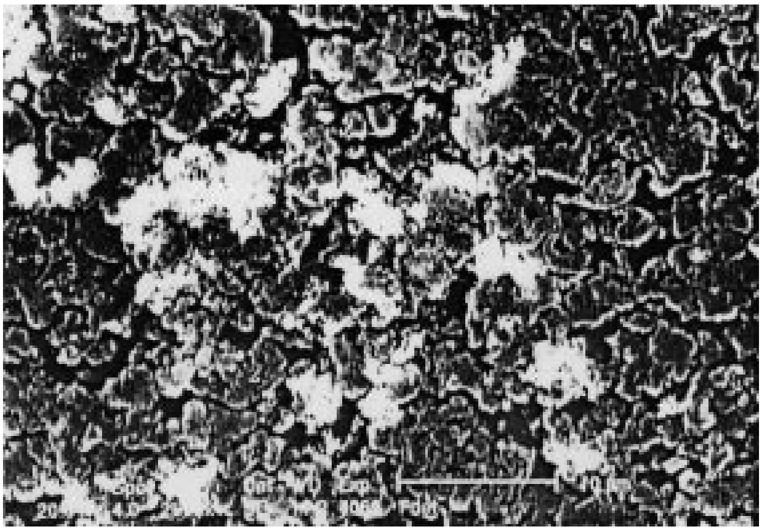


Figure 4. Scanning electron micrograph of catalyst **E** (magnification 2500).

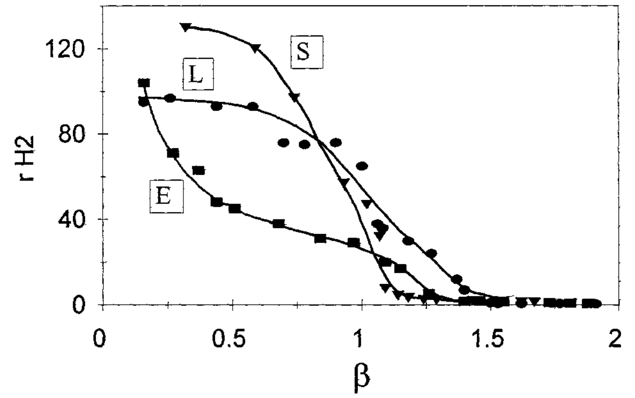


Figure 5. The rate of hydrogen uptake $r(H_2)$ (10^{-5} mol H_2/min) as the function of β.

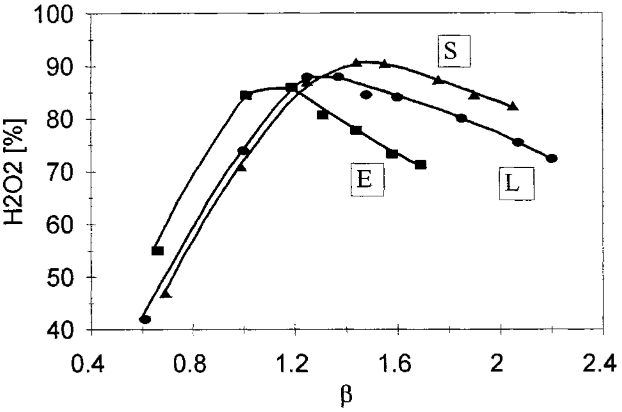


Figure 6. The change of % H_2O_2 as the function of β.

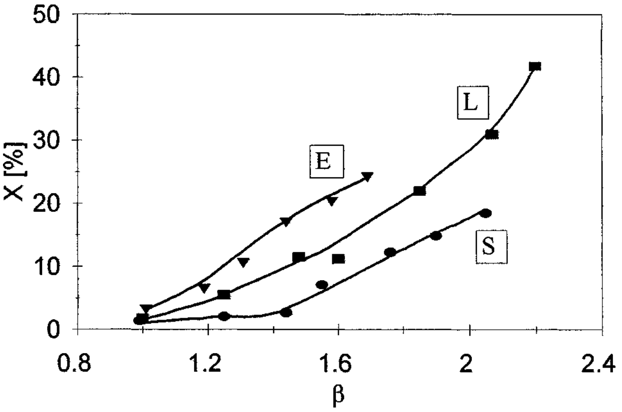


Figure 7. The change of $eAQH_2$ conversion (X) as the function of β.

sponded to the moment of the decreasing of the hydrogenation rate (figure 5). In the second stage of hydrogenation % H_2O_2 decreased as a consequence of active quinone hydrogenation to degradation products. As figure 6 shows, at the presence of all catalysts still before reaching a β value equal to 1, $eAQH_2$ was consumed in an undesired reaction, because in none of the cases the value 100% H_2O_2 was reached. The maximum % H_2O_2 values were obtained at a β value higher than 1 thus indicating that in fact from the beginning of the reaction a part of hydrogen consumed was used for the formation of products other than $eAQH_2$. The highest maximum value of % H_2O_2 (80%) was reached in the presence of catalyst **S**, containing smaller Pd^0 particles, while the progress of undesired reactions was the most intensive over catalyst **E** containing large Pd^0 agglomerates (figure 6).

Figures 7 and 8 present the change of $eAQH_2$ conversion and the number of H_4eAQH_2 moles formed in the course of reaction. At the same value of β the highest number of H_4eAQH_2 moles was formed over catalyst **E**, and in addition the formation of H_4eAQH_2 was observed even at $\beta < 1$. Hence the process of aromatic ring hydrogenation proceeded most intensively over catalyst **E**. The conversion of $eAQH_2$ was also the highest over catalyst **E**. However, in the presence of this catalyst undesired reactions proceeded the most intensively because the selectivity of H_4eAQH_2 formation was the lowest (figure 9). On the other hand, the highest selectivity and simultaneously the lowest $eAQH_2$

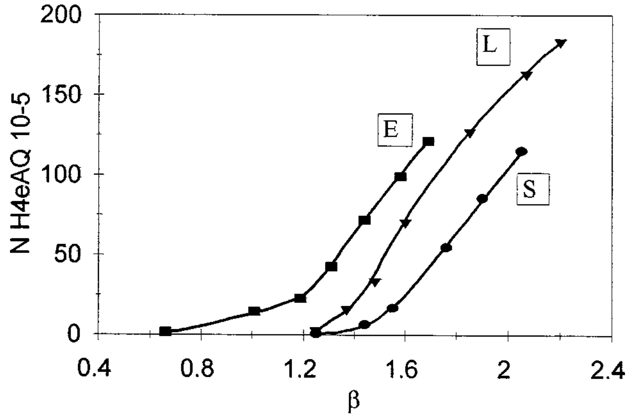


Figure 8. The change of the number of H_4eAQH_2 moles (N $H_4eAQH_2 \times 10^{-5}$) as a function of β.

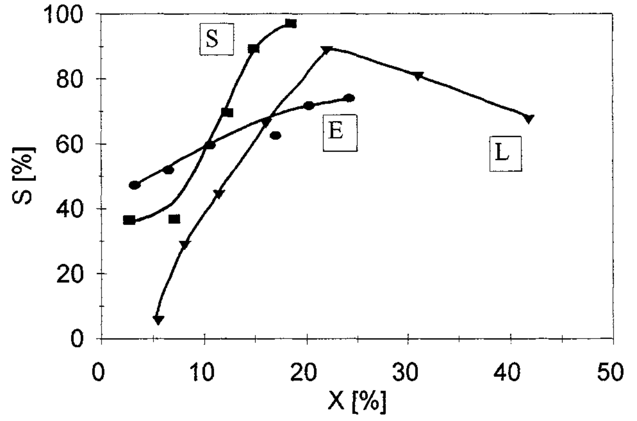


Figure 9. Selectivity of H_4eAQH_2 formation in the course of hydrogenation.

conversion was detected over catalyst **S** in which % contribution of smaller Pd^0 particles was relatively high (table 2).

The results of the catalytic investigations indicate that the presence of large Pd^0 crystalline particles and especially large colloidal palladium agglomerates (catalyst **E**) facilitates aromatic ring hydrogenation as well as the other undesired reactions in which degradation products are formed. This conclusion is in good agreement with our earlier results [9] which showed that distinctly lower ability of $eAQH_2$ degradation exhibited Pd/PANI catalysts prepared in the $PdCl_2$ aqueous solution of strong acidity. In such catalysts uniformly dispersed very small Pd^0 particles of size below the XRD detection limit were presumably present.

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