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Liquid-Phase Hydrogenation of 2-Ethylanthraquinone over Pd/Polyaniline Catalysts

A. Drelinkiewicz,* M. Hasik,† and M. Kloc*

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

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The conjugated polymer polyaniline (PANI) has been used as the support for palladium catalysts. It was found that the dispersion of Pd in Pd/PANI catalysts depends on the nature of Pd^{2+}–PANI interactions proceeding upon catalyst preparation. The type of interaction (protonation or oxidation–reduction process) was influenced mainly by the acidity of the precursor solution containing $PdCl_2$–H_2O–HCl. Under various conditions of acidity, two series of catalysts, A and B (0.8–10 wt% Pd), were prepared. In catalysts of series A, prepared using a strongly acidic solution (2 M HCl), the dispersion of Pd was high. On the other hand, in catalysts of series B, prepared using a weakly acidic $PdCl_2$ solution (0.66×10^{-3} M HCl), large Pd particles (100–600 nm) were present. They were formed as the result of an oxidation–reduction process proceeding with the participation of PANI chain. The physicochemical properties of catalyst were characterized by XRD and SEM methods. All catalysts exhibited activity in 2-ethylanthraquinone (eAQ) liquid-phase hydrogenation. The catalysts of series A were more active and the selectivity of eAQ hydrogenation in their presence was higher than that seen for catalysts of series B. © 1999 Academic Press

Key Words: **2-ethylanthraquinone; polyaniline; palladium catalysts.**

INTRODUCTION

In recent years the application of polymer-immobilized transition-metal catalysts has been extensively studied. In this type of catalyst, the polymer plays the role of a ligand, forming a surface complex with the metal atom or ion. Such complexes are isolated from each other by the polymer, which may enhance their catalytic activity and also facilitate their reduction. Even though several papers concerning the electrochemical doping of the conjugated polymer polyaniline (PANI) with Pd and Ag have been published (1–3), information on the use of PANI in catalytic systems is scarce (4, 5).

As Scheme 1 shows, PANI in its polyemeraldine base form (**I**) can be easily protonated by acid–base type doping with the formation of polyaniline salt (Scheme 1, **II**). This type of doping takes place during the treatment of PANI with an aqueous solution of $PdCl_2$ of high HCl concentration (6), when anionic complexes $[PdCl_4]^{2-}$ and $[PdCl_3(H_2O)]^-$ dominate in the solution (7). Nitrogen atoms (=N–, –NH–) in the polymer chain are protonated while Cl^- or $[HPdCl_4]^-$ ions act as a counterions. In some cases also coordination of Pd^{2+} ions to nitrogen atoms was established (6). In addition to acid–base doping, PANI can be oxidized, which involves transformation of –NH– groups into –N= (Scheme 1, **III**). This type of process takes place when PANI is treated with a $PdCl_2$ solution of low acidity, containing predominantly electrically neutral $[PdCl_2(H_2O)_2]$ complexes (8).

The aim of the present paper was to describe in a more detailed way the method of preparation and the properties of PANI-supported Pd catalysts obtained through the reduction of different chlorocomplexes of this metal at the surface of the polymer. As a model reaction for testing the catalytic ability of Pd/PANI, the liquid-phase hydrogenation of 2-ethylanthraquinone (eAQ), the main reaction of H_2O_2 production in the anthraquinone method (9), was chosen.

In a cyclic process, eAQ is catalytically hydrogenated to yield 2-ethylanthrahydroquinone ($eAQH_2$) (Scheme 2, reaction 1). Upon oxidizing of $eAQH_2$, hydrogen peroxide is formed and eAQ is regenerated (Scheme 3). However, the primary product $eAQH_2$ is also partly hydrogenated into different compounds, among which are the products of aromatic ring hydrogenation (2-ethyltetrahydroanthrahydroquinone, H_4eAQH_2) as well as the products of hydrogenolysis (2-ethylanthrone, 2-ethylanthracene) (10–13). From the technological point of view the formation of H_4eAQH_2 with high selectivity is required because only $eAQH_2$ and H_4eAQH_2 can participate in the oxidation process leading to H_2O_2 formation (Scheme 3). All other compounds formed, termed “degradation products,” are undesirable, because upon oxidation they cannot produce H_2O_2.

METHODS

Catalysts Preparative Procedure

The powdered PANI (BET surface area 46 m^2/g) was prepared according to standard procedure (14). Aniline was

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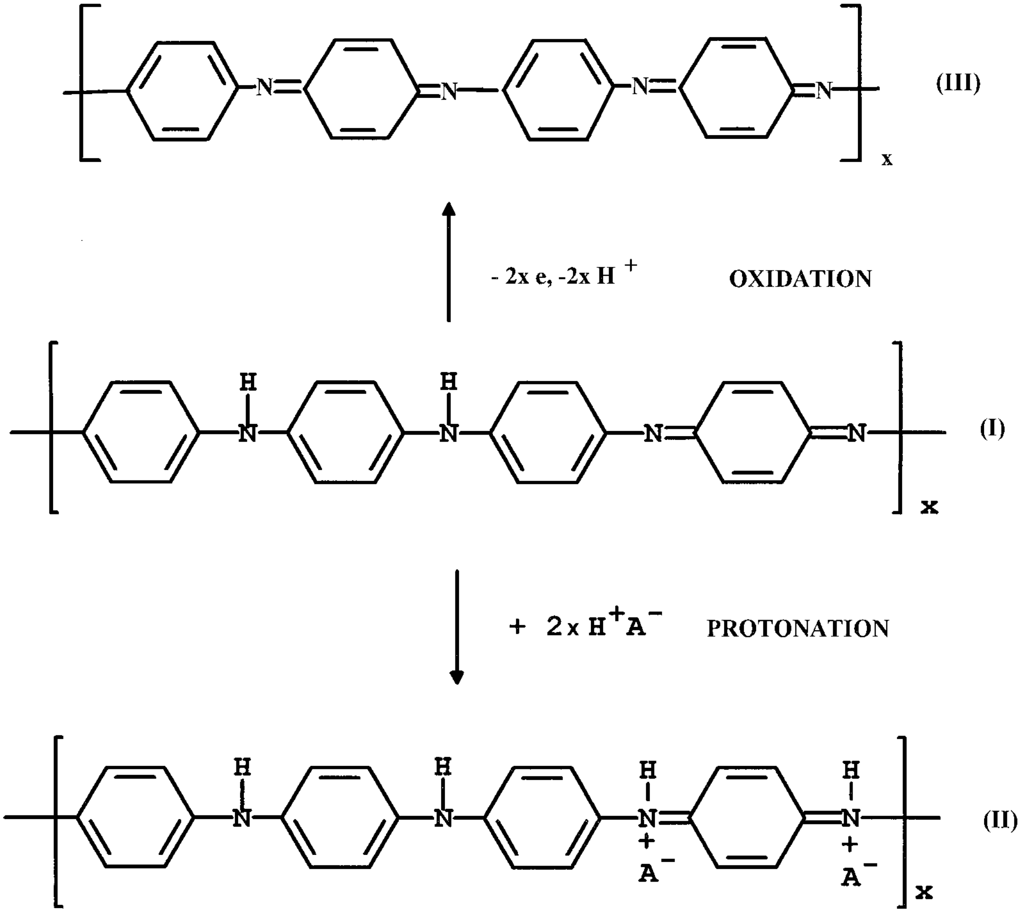
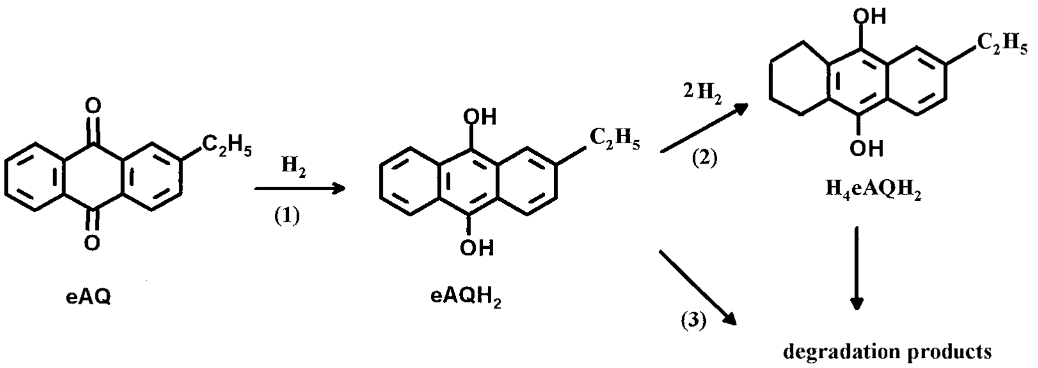


SCHEME 1. Reactions of polyaniline.

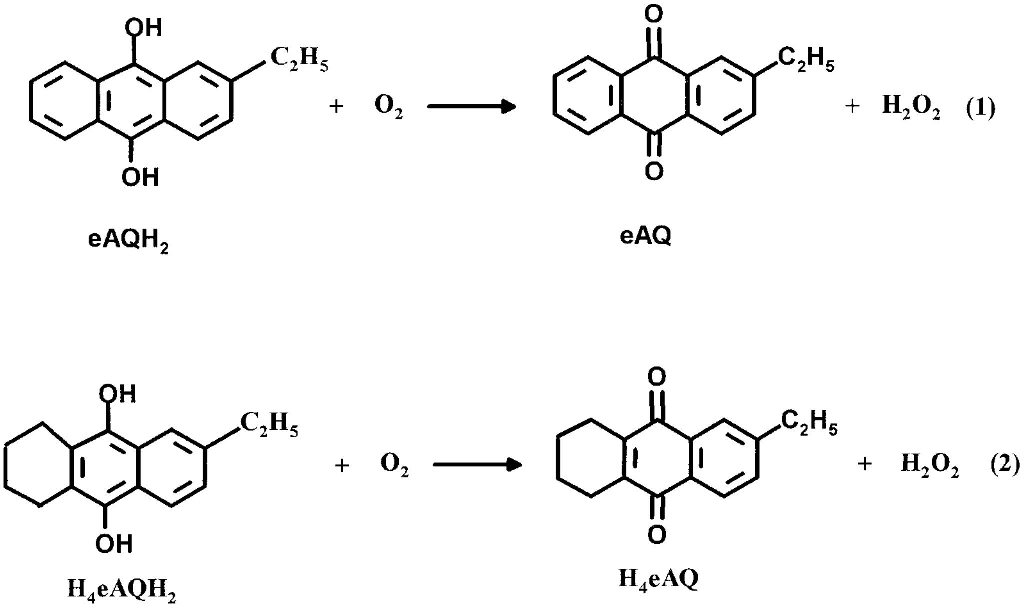
oxidized with $(NH_4)_2S_2O_8$ in hydrochloric acid followed by deprotonation in the aqueous solution of ammonia.

According to earlier observations (6) the doping of PANI by Pd^{2+} ions strongly depends on the concentration of HCl in the doping solution. Two solutions of $PdCl_2$ strongly differing in the concentration of HCl were used for catalyst preparation (in both solutions the $PdCl_2$ concentration was 2.3×10^{-3} mol/dm^3): (A) HCl concentration, 2 mol/dm^3; (B) HCl concentration, 0.66×10^{-3} mol/dm^3.

Doping of PANI was performed by exposure of PANI powder at room temperature to the solution of $PdCl_2$ (A or B). The suspension was stirred until the total disappearance (96 h) of Pd^{2+} ions in solution (controlled by colorimetric method). The appropriate volume of solution to give



SCHEME 2. Hydrogenation reactions.



SCHEME 3. Oxidation reactions.

1–10 wt% of Pd in the finished sample was used (Tables 1 and 2). After palladium sorption was complete, the samples were filtered, washed with water until the Cl^- ions were eliminated, and dried for 2 h at 110°C. No difficulty was encountered in repeatability of series A catalyst preparation. The reproducibility of the preparation of series B was satisfactory only when exactly the same conditions of synthesis were kept, especially the concentration of both HCl and $PdCl_2$ precursor solution and the intensity of mixing of PANI suspension in the doping solution.

The colorimetric method (based on the reaction between palladium ions and KI leading to the formation of $[PdI_4]^{2-}$ complexes (15)) was used to control the presence of Pd^{2+} ions in the solution during catalyst preparation and to determine the amount of Pd^{2+} in the catalysts. In the latter case, the unreduced palladium present in catalysts was extracted several times with a 2 M solution of HCl. The extraction procedure was repeated until a portion of washing solution free of palladium was obtained. The amount of extracted Pd^{2+} was colorimetrically determined. The amount of Pd^{2+} was determined in the pristine samples of series B. In the samples of series A the Pd^{2+} ions remaining after their reduction with NaH_2PO_2 were determined.

The amount of Pd^0 in catalysts was calculated as the difference between the total amount of Pd (known from the catalyst preparation) and the amount of Pd^{2+} colorimetrically determined. As the data in Table 2 show, in series B catalysts practically the same amount of Pd^{2+} was reduced to Pd^0 ($\%R = 80$) during sample preparation. It should be noted that the analytically determined content of Pd^0 and Pd^{2+} is in accordance with that obtained earlier by XPS (6).

Characterization of Catalysts

XRD studies were carried out using a HZG-4 diffractometer with Cu$K\alpha$ radiation. The surface morphology of the catalysts was investigated by means of a scanning electron microscope (Philips XL-30). The microscope was equipped with an X-ray microprobe which made it possible to carry out Pd$L\alpha$ elemental distribution studies (spot, surface, line profiles) as well as quantitative analysis.

TABLE 1

Series A Catalysts

Catalyst	Pd (wt%)	Pd^0 (wt%)	Pd^0/Pd (%)
1 A	1	0.83	83.0
2 A	2.5	2.40	96.3
3 A	4	3.80	95.2
4 A	6	5.80	96.2
5 A	10	9.40	94.0

TABLE 2

Series B Catalysts

Catalyst	Pd (wt%)	Pd^0 (wt%)	Pd^0/Pd (%)
1 B	1	0.93	93.5
2 B	2.5	2.05	82.2
3 B	4	3.32	82.9
4 B	6	4.63	77.2
5 B	10	8.32	83.2

Catalytic Experiments

2-Ethylanthraquinone hydrogenation was carried out under agitated batch reactor conditions under a constant atmospheric pressure of hydrogen and temperature of 64°C as described earlier (10). As the solvent, a mixture of xylene–octanol-2 (1 : 1 volume ratio) was used. The course of hydrogenation was followed by measuring the volume of hydrogen consumed as a function of reaction time. The precision of this measurement was 0.1 cm^3 H_2/min. In all experiments, hydrogenation was carried out until the consumption of 1.8 mol of H_2 per 1 mol of eAQ initially present in the reactor. After the experiments the hydrogenated solution was oxidized with air, the H_2O_2 formed according to reaction 1 or 2 (Scheme 3) was extracted with water, and its amount was determined by titration using $KMnO_4$. The composition of the hydrogenated solution (eAQ and H_4eAQ concentration) was determined by HPLC (10). The precision of HPLC analysis was 5%. In the oxidized solution used for HPLC analysis, the quinone forms eAQ and H_4eAQ are present. The hydroquinone forms $eAQH_2$ and H_4eAQH_2 (Scheme 2) present in the solution taken from the reactor react rapidly with atmospheric oxygen, thus forming H_2O_2 and regenerating quinones (eAQ and H_4eAQ, respectively; Scheme 3). Reaction with oxygen is quantitative and complete even before HPLC analysis. Thus, it has been 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 by HPLC. In a typical experiment 10 cm^3 of the solution (eAQ concentration equal to 25 g/dm^3) and 0.075 g of catalyst were used.

To control the interaction between the support PANI and the reagents (eAQ, solvents), PANI and catalysts 3A and 3B were contacted for a long time (6 h) with eAQ solution under a He atmosphere and conditions similar to those used in hydrogenation experiments. No change in PANI structure (FTIR) or eAQ concentration was detected.

Series B catalysts in which Pd^{2+} ions were reduced to Pd^0 (Table 2) during their synthesis were used in hydrogenation tests without any preliminary reduction. In contrast, pristine samples prepared according to procedure A in which only Pd^{2+} appeared (6) did not exhibit catalytic activity and therefore it was necessary to reduce them before catalytic experiments. In the presence of commonly used reducing agents, such as hydrazine, formaldehyde, $NaBH_4$, or H_2, at 220°C a change in polymer structure occurred (most probably due to the polymer degradation), accompanied by partial dissolution of the catalyst. Therefore, a weaker reducing agent, NaH_2PO_2, was subsequently used. The reduction was carried out at room temperature by contacting catalysts with a 0.1 M solution of NaH_2PO_2 (2 h). No change in polymer structure was observed (confirmed by IR, XRD) but the reduction of Pd^{2+} ions was never complete (Table 2).

After the hydrogenation test the amount of Pd^{2+} in selected catalysts of both series (3A, 5A, 3B, 5B) was colorimetrically controlled as described earlier. It was practically the same as before the hydrogenation reaction, indicating that no reduction of Pd^{2+} occurred during the catalytic tests. It was also observed that the activity of catalysts 4A and 4B was practically the same after their repeated use in hydrogenation reactions. This effect may indicate that no significant changes in Pd^0 morphology occurred under the conditions used in the reaction. The unchanged activity of the catalysts in the consecutive tests may also suggest that no significant leaching of Pd^0 into the hydrogenation solution took place.

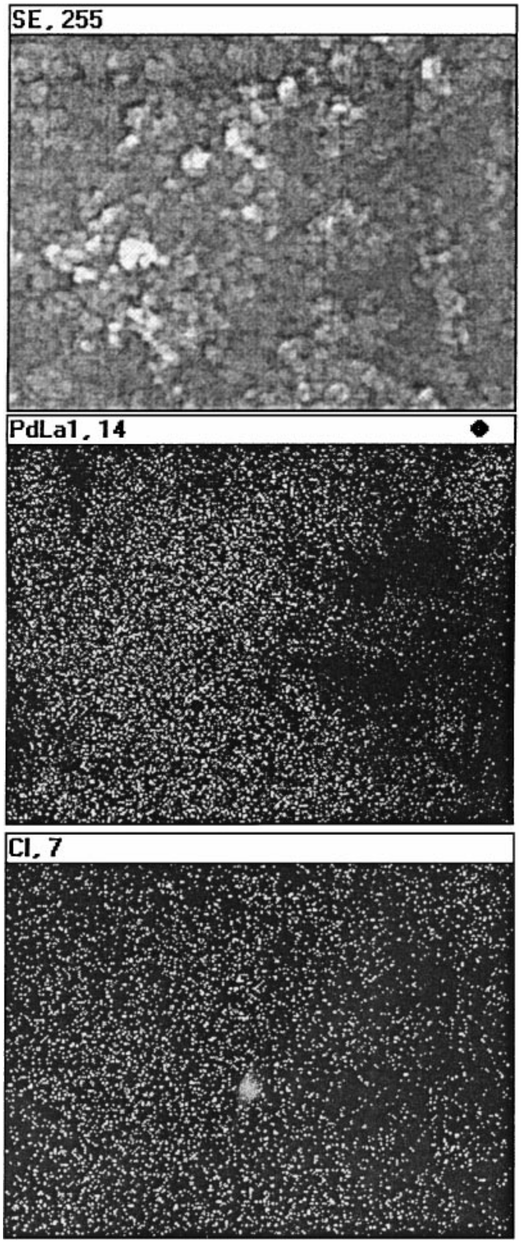


FIG. 1. SEM distribution of Cl and Pd, catalyst 5A containing 9.4% Pd^0 (original magnification, ×4000).

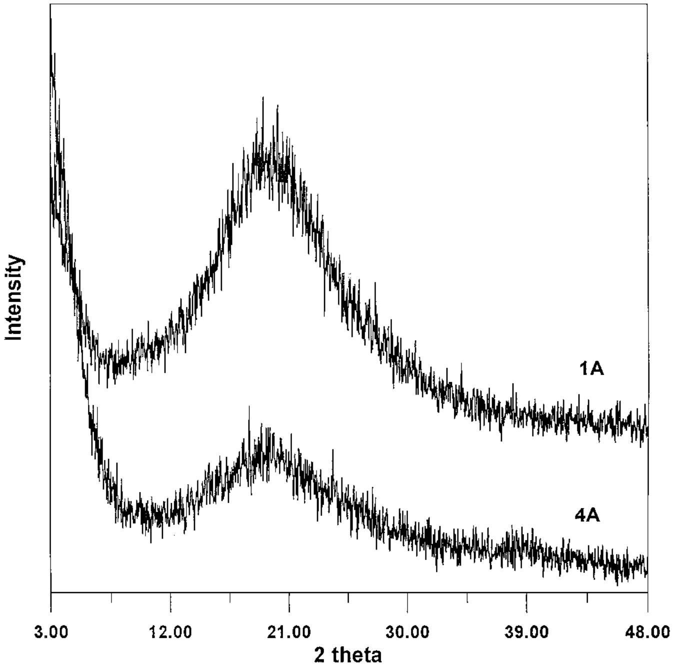


FIG. 2. X-ray diffraction patterns of catalysts 1A (0.83% Pd^0) and 4A (5.8% Pd^0).

RESULTS AND DISCUSSION

Physicochemical Properties of Pd/PANI Catalysts

As already noted, the procedures used to prepare series A and B catalysts differed only in the HCl concentration

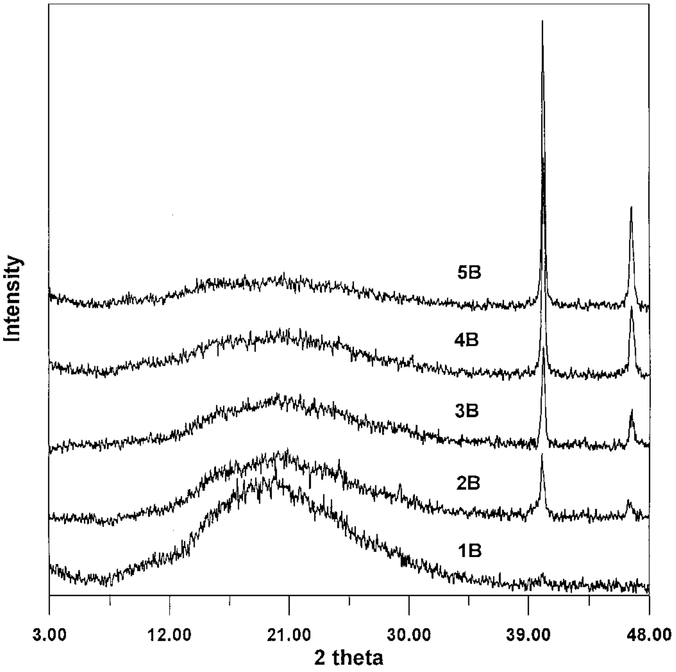


FIG. 3. X-ray diffraction patterns of catalysts of series B: 1B (0.93% Pd^0), 2B (2.05% Pd^0), 3B (3.32% Pd^0), 4B (4.63% Pd^0), 5B (8.32% Pd^0).

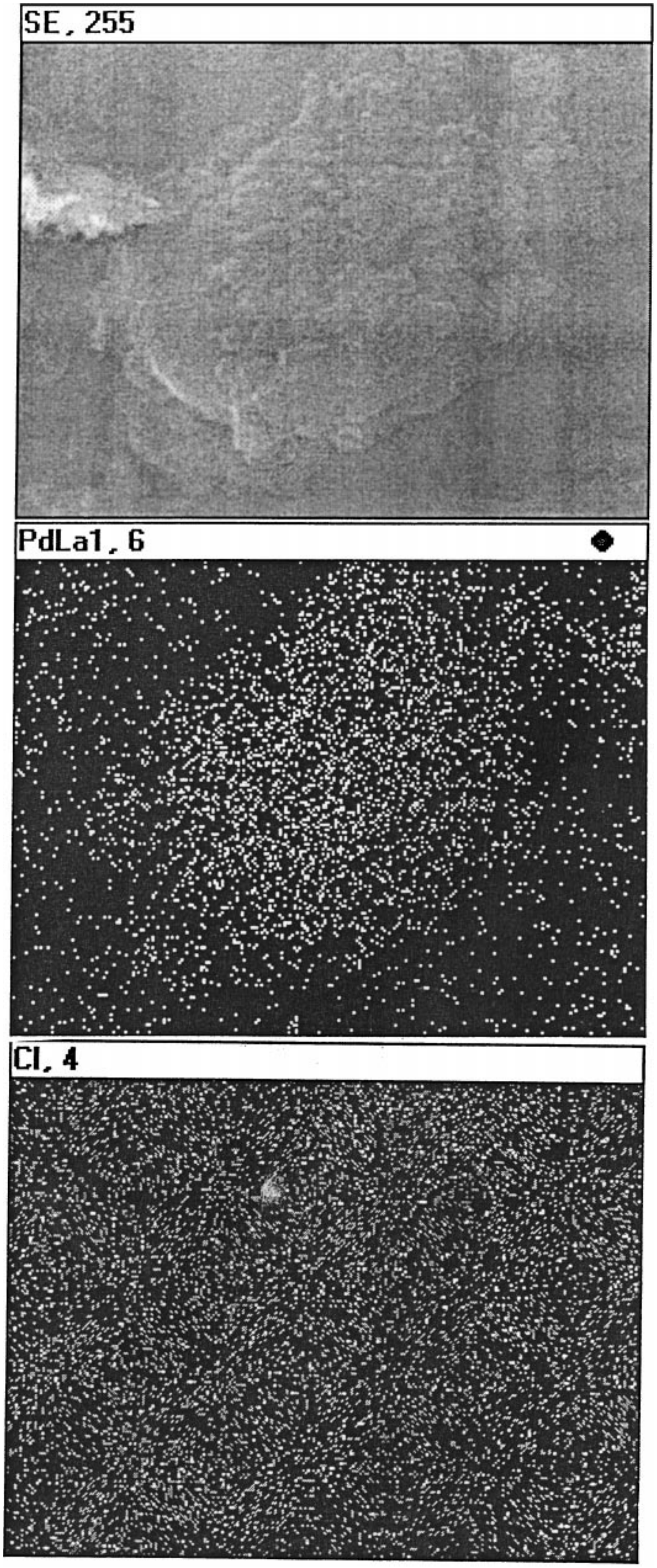


FIG. 4. Scanning electron micrographs of catalyst of series B. (a) 1B (original magnification, ×2000), (b) 2B, (c) 3B, (d) 5B (b, c, and d original magnification, ×8000).

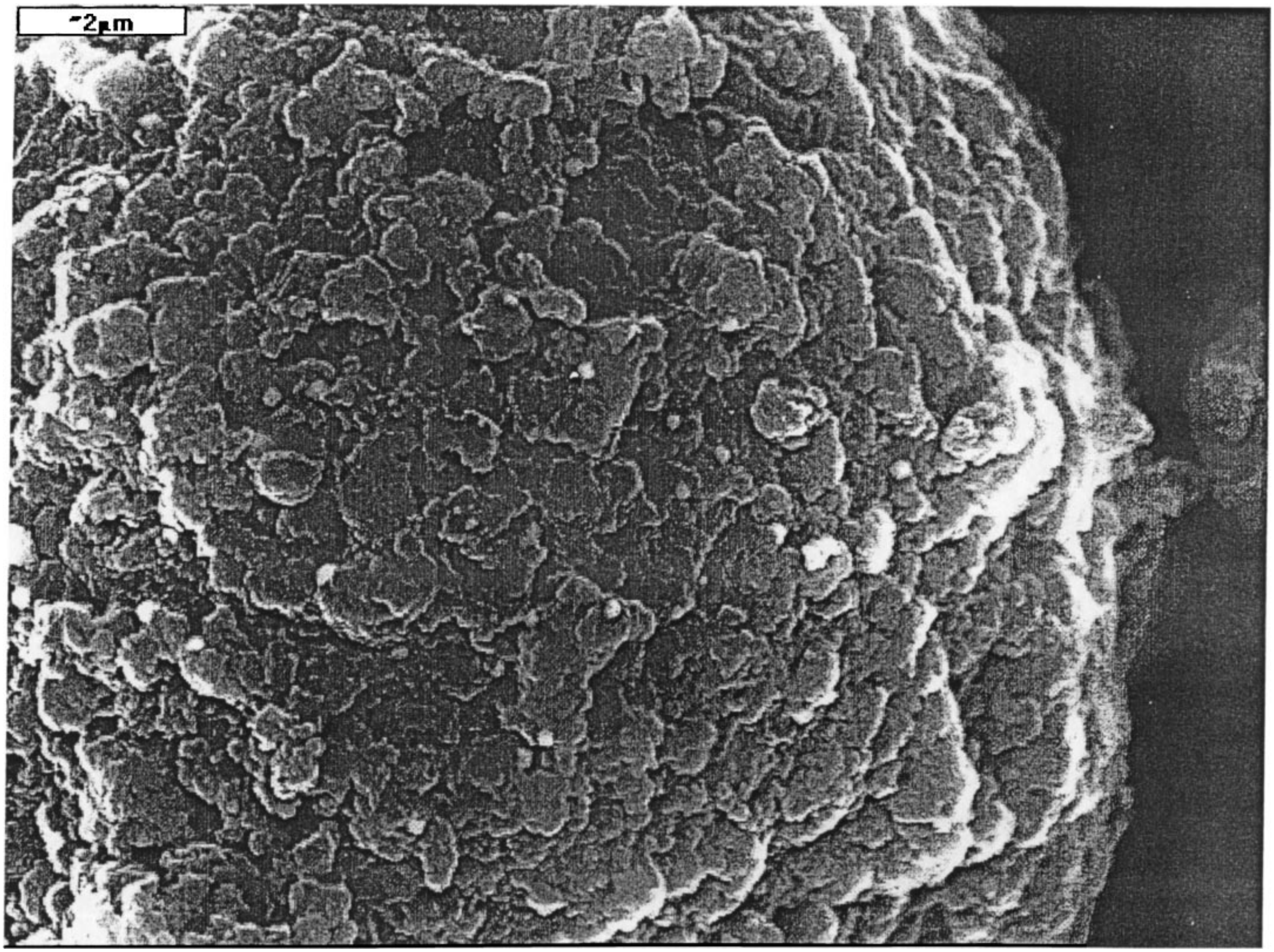


FIG. 4—*Continued*

in the doping solution. However, the mechanism of doping was different and so were the physicochemical and catalytic properties of the catalysts. In procedure A, the hydrochloric acid concentration was high and the anionic complexes $[PdCl_4]^{2-}$ were introduced into PANI in an acid–base type reaction. When series B catalysts were prepared, the electrically neutral $[PdCl_2(H_2O)_2]$ complexes were the main palladium-containing species in the solution, and a redox reaction was involved in the doping process, resulting in partial reduction of Pd^{2+} to Pd^0. Such doping mechanisms were earlier confirmed by XPS and Raman examination (6, 8). Pd 3*d* XPS spectra unequivocally show that upon PANI treatment with $PdCl_2$ solution type A, palladium is incorporated into the polymer at the Pd^{2+} oxidation level (BE Pd 3*d* $5/2 = 337.7$ eV). In catalysts prepared using solution B, both Pd^{2+} and Pd^0 (BE Pd 3*d* $5/2 = 335.4$ eV) were present and Pd^0 predominated (80%). The Raman spectra of series B catalysts indicate the oxidation of PANI chain observed as the partial transformation of –NH– to =N– groups (8).

Figure 1 presents the SEM and a map of the Pd distribution for the series A catalyst with the highest content of Pd^0, which was equal to 9.4 wt%. Uniform dispersion of palladium is observed, but no distinct palladium aggregates are visible. Similar distributions were also observed for other series A catalysts. In XRD spectra of catalysts of series A (Fig. 2), only a broad “halo” centered around $2\theta = 20^\circ$, characteristic of PANI, is present. The position of this halo does not interfere with the Pd diffraction pattern as it is shown in Fig. 3. In an X-ray spectrum of catalyst 1A containing the lowest level of Pd (0.93 wt% Pd^0), no peaks characteristic of Pd are seen, while in the spectra of catalysts 5A and 4A (5.80 wt% Pd^0) a small perturbation in the background line at a position corresponding to the Pd peak is visible, which may indicate that very small Pd crystals are present, the size of which is at the limit of detectability. The

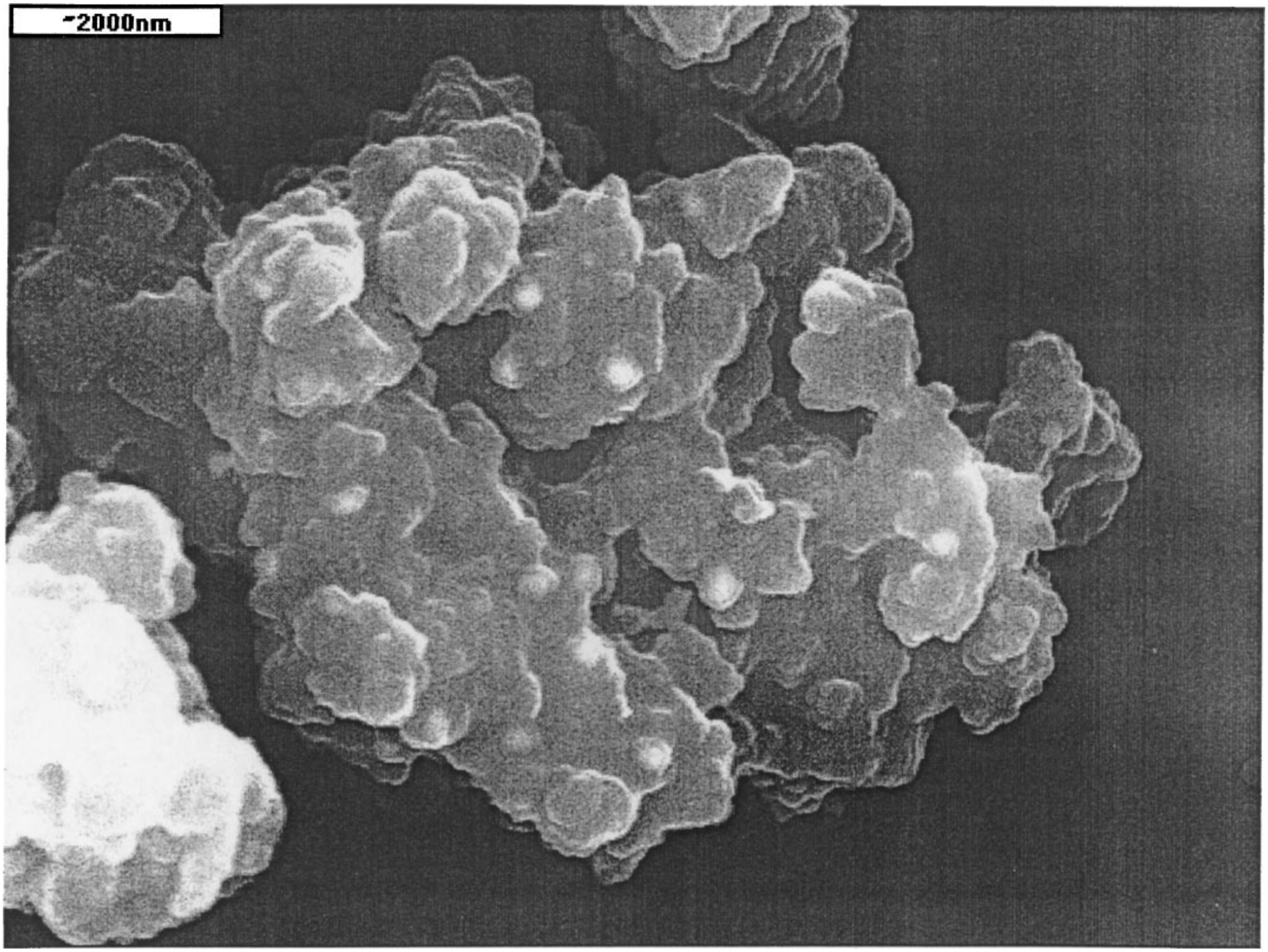


FIG. 4—*Continued*

absence of Pd peaks in catalysts with lower amounts of Pd indicates that the dispersion of palladium is high and the size of Pd crystals is in fact smaller than the limit of XRD measurement.

In series A catalysts, Pd^{2+} ions were present in the form of counterions $[HPdCl_4]^-$ or as coordinatively bonded Pd^{2+} ions (Pd–N) (6). After reduction, catalysts of highly and uniformly dispersed palladium crystals were obtained. It can be therefore concluded that this type of Pd^{2+} bonding in PANI prevented the formation (in reduction process) of X-ray-detectable palladium crystallites.

Series B catalysts, in which Pd^0 was created as the result of reduction–oxidation between PANI and $[PdCl_2(H_2O_2)]$, show significantly different morphology. Pd^0 appears in the crystalline form, observed in XRD patterns as sharp and narrow peaks at $2\theta = 40.1^\circ$ and 46.6° (Fig. 3). Only for the sample of the lowest content of Pd^0 (0.93%) was the presence of Pd crystalline peak not so evident. As Fig. 3 shows, the intensity of the Pd^0 peaks increased with increasing Pd content in the catalyst, while that characteristic of PANI decreased. This effect indicates that the change in the ordering of the polymer structure occurred during the reduction–oxidation process between PANI and Pd^{2+} ions. IR spectra show that this change does not result in polymer degradation (6). The shape of the XRD peaks of Pd^0, sharp and narrow, proves the existence of large Pd particles.

Figure 4 shows SEMs of series B catalysts (1B–5B). Only in the micrograph of the catalyst with the lowest Pd content (1B) is dispersion of palladium uniform, and no palladium agglomerates are seen. In the micrographs of all other catalysts (2B–5B) containing higher amounts of palladium, distinct Pd particles in the form of white spots exhibiting high contrast against the support are seen. The density of such particles grows distinctly with increasing amounts of palladium. Independent of the amount of palladium, the shapes of all palladium particles are similar. The particles are regular and spherical. X-ray microprobe analysis of the Pd element, carried out at different surface points,

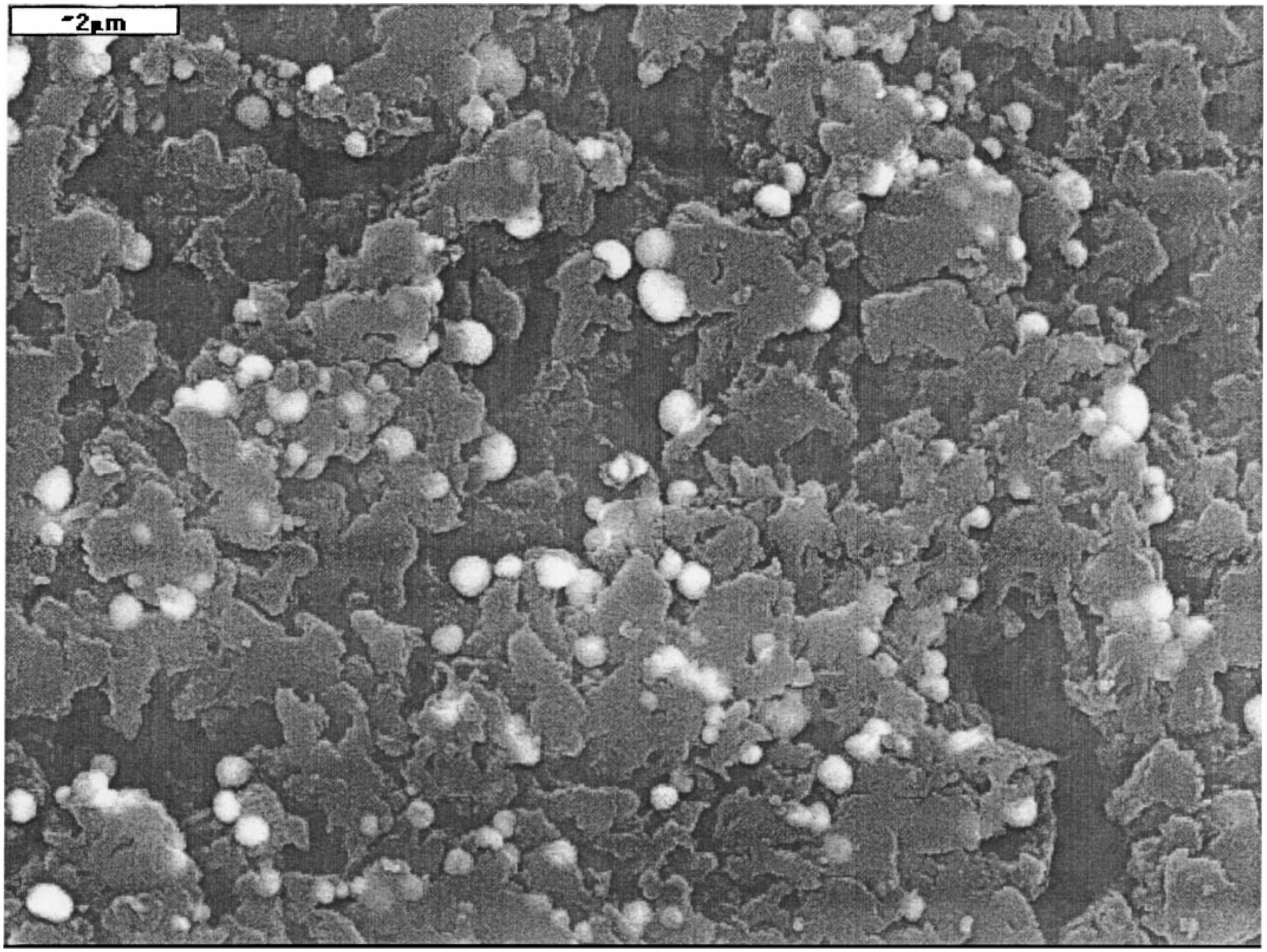


FIG. 4—*Continued*

indicated that the content of Pd is in fact the highest in white spots. On the other hand, in all other analyzed points located beyond the limits of white spots, Pd was practically absent. A typical X-ray line profile for Pd analysis is presented in Fig. 5. It shows very high Pd content in the areas corresponding to white spots, while at other surface points dark in the photograph Pd is not evident.

Thus, the SEM and XRD observations are very consistent; the white spots in SEM micrographs correspond to the crystalline palladium particles. However, it is difficult to decide whether the particular spots are the individual crystal particles or are composed of the smaller crystalline particles.

The size distribution of the Pd particles was determined (by counting all visible particles for the individual catalysts (132 particles for 2B, 126 for 3B, 321 for 4B, and 248 for 5B catalyst)) assuming spherical shape for all particles. The percentage contribution of the Pd^0 particles depending on their size is presented in Fig. 6. In all samples (2–10 wt% Pd), particles as large 100–300 nm are present, and the maximum contribution corresponds to particles of 200 nm. With increasing Pd content in the catalysts the maximal contribution becomes somewhat lower but increases that of larger particles. As a consequence, in catalysts with the highest Pd^0 content (9.3%) particles as large as 500 nm are apparent (Fig. 6).

Catalytic Activity

In the discussion of the results of catalytic investigations it has been assumed that SEMs are representative for the entire surface of the catalysts (especially series B) and that the total amount of Pd acting in hydrogenation is Pd detected by SEM in the form of distinct metallic particles.

As already noted, the course of eAQ hydrogenation was followed by measuring the volume of hydrogen consumed as a function of reaction time. From this correlation the rate of hydrogenation expressed as the number of H_2 mol/min

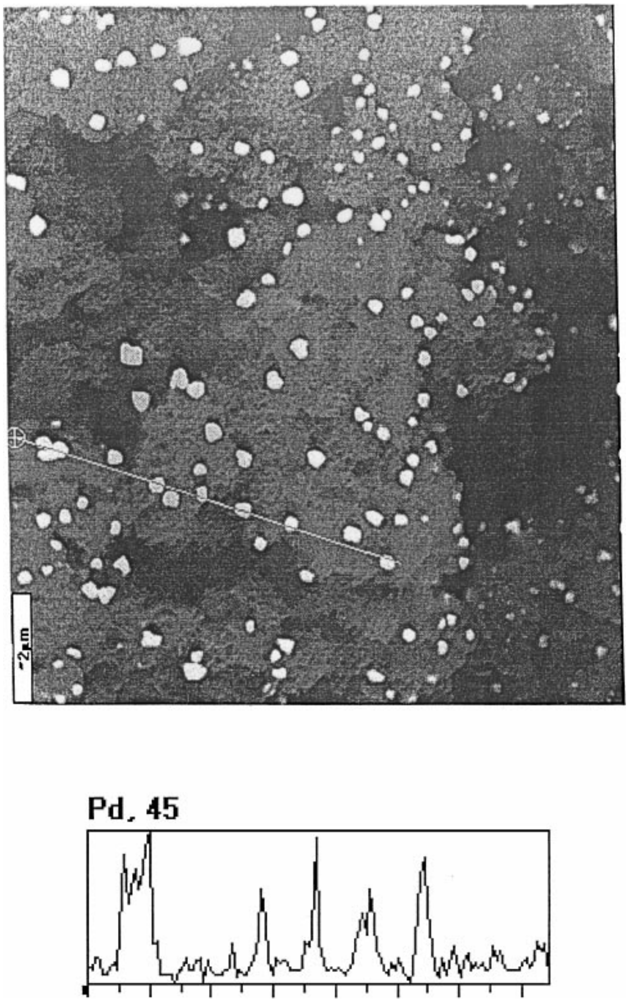


FIG. 5. X-ray line profile of Pd, catalyst 4B, containing 4.63% Pd^0.

per gram of catalyst was calculated. This correlation between the initial rate of hydrogenation (mol H_2/min g of catalyst 10^{-5}) and the content of Pd^0 in catalyst for series A and B is presented in Fig. 7. Although at the lowest Pd content the rate is similar for both series, above 3% Pd it is definitely lower for the series B catalysts.

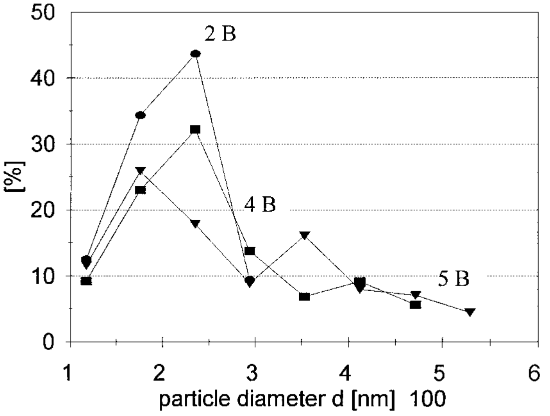


FIG. 6. Palladium particles size distribution in the catalysts of series B.

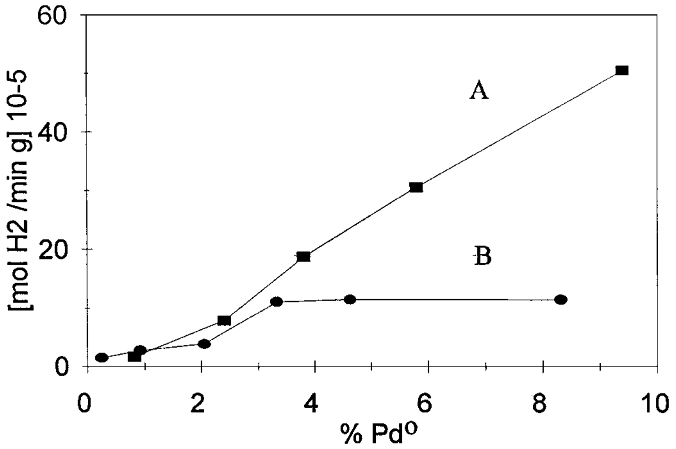


FIG. 7. The rate of hydrogenation (mol H_2/min g catalyst 10^{-5}) as a function of % Pd^0.

For series A and B catalysts in which the palladium content is very low (1A and 1B, about 1 wt% Pd) the rates of hydrogenation were comparable. This is in accordance with SEM and XRD results showing that in fact at such low palladium level in catalyst 1B no distinct metallic particles exist.

In the presence of series A catalysts, the rate of hydrogenation increases linearly with the increasing wt% of Pd^0 within the whole range of palladium content (Fig. 7). This linear correlation indicates that in series A catalysts the amount of catalytically active palladium (number of Pd^0 catalytic centers) increases in proportion to the palladium content. SEM investigation indicates uniform distribution of this metal. It may be present in the form of such small particles that they cannot be unequivocally detected by XRD.

The differences in activity between series A and B catalysts are especially apparent at higher Pd^0 content when in series B catalysts large Pd^0 particles appear. In series B catalysts, the percentage contribution of larger palladium particles increases with increasing Pd content, resulting in the approximate constancy of the metal surface taking part in hydrogenation.

However, it seems interesting to determine whether the size of Pd^0 particles influences the selectivity of eAQ hydrogenation. In the considerations of the selectivity of the process, data from HPLC analyses, including the concentrations of $eAQH_2$ and H_4eAQH_2, were used. As Scheme 2 shows the reaction pattern of eAQ hydrogenation is complicated. From the large number of different products, only two $eAQH_2$ and H_4eAQH_2 (active quinones) are desired because only these two take part in oxidation reactions leading to H_2O_2 formation (Scheme 3). It should be noted that H_4eAQH_2 can be also degraded (formation of 2-ethyloctahydroanthrahydroquinone), but the rate of its

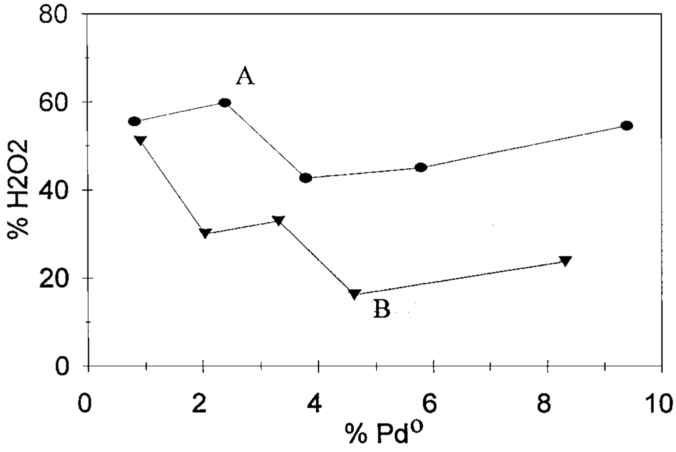


FIG. 8. The % H_2O_2 as a function of the Pd^0 content in catalysts (determined after absorption of 1.8 mol of H_2 per 1 mol of eAQ initially present in the reactor).

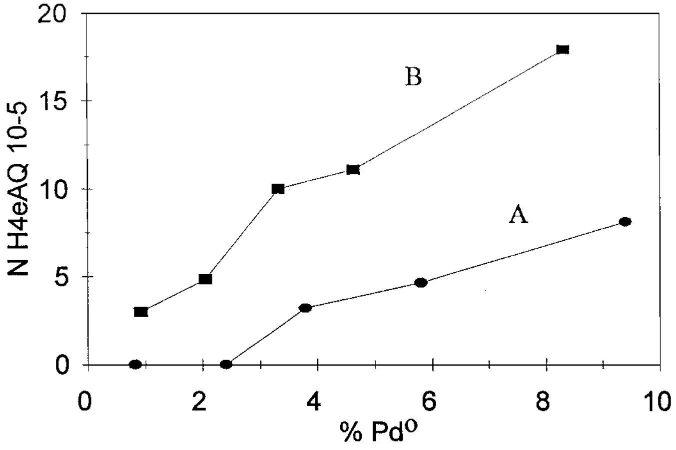


FIG. 9. The number of H_4eAQ moles formed as a function of the Pd^0 content in catalysts (determined after absorption of 1.8 mol of H_2 per 1 mol of eAQ initially present in the reactor).

degradation is distinctly slower than the rate of reactions 2 and 3 (Scheme 2) (9, 12, 13) and therefore this process is not presented in Scheme 2.

The maximum number of moles of H_2O_2 which can be obtained in reaction carried out in the present batch type reactor is equal to the initial number of eAQ moles present in the reactor. This number was assumed to be 100%. When the reduction of $eAQH_2$ is selective and only H_4eAQH_2 is formed (Scheme 2, reaction 2), the number of moles of H_2O_2 is still equal to 100%, because 1 mol of H_4eAQH_2 is formed from 1 mol of $eAQH_2$. On the other hand, when $eAQH_2$ is hydrogenated to H_4eAQH_2 and also other degradation products, the number of H_2O_2 moles becomes lower than 100%. Hence percentage of H_2O_2 has been assumed as the measure of the degradation process of $eAQH_2$.

As Fig. 8 shows, after consumption of 1.8 mol of H_2 per mole of eAQ initially present in the reactor, the percentage of H_2O_2 formed is distinctly lower over a catalyst of series B. The correlation presented in Fig. 9 shows that the course of aromatic ring hydrogenation over catalysts of both series was also different. The number of H_4eAQH_2 moles formed increased with increasing Pd^0 content in both series of catalysts. However, it was lower over catalysts of series A, and in this case H_4eAQH_2 was formed in a detectable amount only when the percentage of Pd^0 in the catalysts was higher than ca. 4 wt%. On the other side, the process of aromatic ring hydrogenation in $eAQH_2$ was always observed in the presence of series B catalysts (Fig. 9). The higher amount of H_4eAQH_2 formed, as well as the higher number of moles of degraded $eAQH_2$ observed in the presence of catalysts of series B, suggests that the size of Pd^0 particles significantly affects the course of $eAQH_2$ hydrogenation. This is also illustrated in Fig. 10, showing the change in degradation factor D (number of $eAQH_2$ moles consumed per mole of H_2O_2 formed) as a function of the percentage of Pd^0 in the catalyst. The value of this degradation factor is very low (0.5) and practically independent of the percentage of Pd^0 for catalysts of series A. Its value becomes distinctly higher for catalysts of series B. In addition, the value of D increases when Pd^0 content in series B catalysts increases, reaching a value as high as about 3 (Fig. 10). In the discussion of the differences in the activity and selectivity of series A and B catalysts, the effect of the reducing agent (NaH_2PO_2) should also be considered. In the catalytic reaction the series A catalysts reduced exclusively with NaH_2PO_2 were used, because reduction with other agents was unsatisfactory. Therefore, the influence of NaH_2PO_2 on the catalytic properties of series A samples could not be determined. However, to control the effect of this reducing agent on catalytic properties, selected samples of series B were treated with NaH_2PO_2 solution under the same conditions as those used for catalysts of series A.

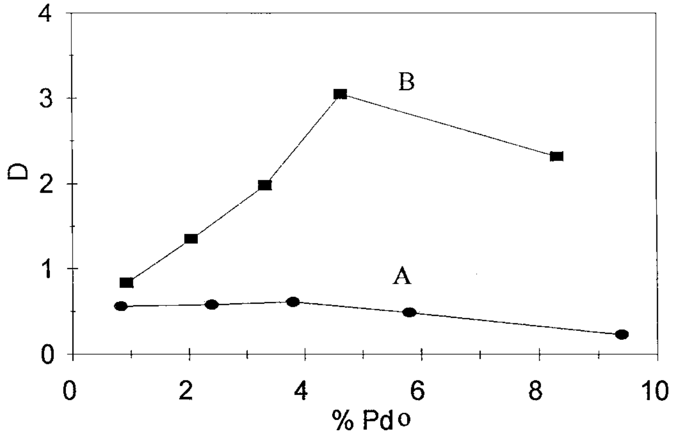


FIG. 10. The change in degradation parameter D depending on the wt% Pd^0.

After this treatment, no changes in the Pd^{2+} content or the surface morphology (SEM) were observed. This treatment also did not influence the catalytic properties of investigated samples.

Therefore, the effect presented in Fig. 10 confirms the earlier suggestion that the presence of large Pd^0 particles favors hydrogenation processes in which aromatic ring hydrogenation as well as other degradation processes proceeded. In fact, in solutions after hydrogenation experiments over catalyst of series B, the presence of 2-ethylanthrone and 2-ethylanthracene was detected using mass spectroscopic analysis.

The dispersion of palladium seems to be the main factor controlling the catalytic behavior of our catalysts. However, whether the electroactive support can play a chemical role in the catalytic process cannot be determined on the basis of the present results.

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