Hydrogenation of 2-ethylanthraquinone over Pd/SiO_2 and Pd/Al_2O_3 in the fixed-bed reactor. The effect of the type of support

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The effects of the type of support and Pd concentration profile in alumina and silica supported egg-shell catalysts and their performance in the hydrogenation of 2-ethylanthraquinone (eAQ) were studied in 'Anthra' (AQ) and 'All-Tetra' systems. The activity and deactivation of catalysts were determined in the fixed-bed reactor. Solution saturated with hydrogen, (concentration of active quinones 60 g/dm^3, eAQ in the AQ system, 30% of eAQ and 70% of H_4eAQ–2-ethlytetrahydroanthraquinone, in the All-Tetra system) was circulated through the catalyst bed at temperature 50 °C and pressure 5 bar. The contents of eAQ, active quinones, H_4eAQ and degradation products were determined in the course of hydrogenation by GC method. The egg-shell palladium catalysts (1–2 wt% Pd) prepared by the precipitation of palladium hydroxide onto alumina and silica supports pre-impregnated with various alkaline ($NaHCO_3$, NaH_2PO_4, Na_2SiO_3) solutions were used in the hydrogenation experiments. Pd concentration profile inside the grains of catalysts was characterized by scanning electron microscopy. A difference between alumina and silica carriers with respect to the course of side reactions producing degradation products was found. Degradation of quinones in the hydrogenolytic reactions predominated on alumina supported catalysts, while the catalysts with silica favoured the hydrogenation of aromatic rings resulting in H_4eAQ-active quinone. As a crucial factor for the decrease in the activity during the hydrogenation run, the reactivity of catalyst in the hydrogenolytic reactions was established. Alumina supported catalysts exhibited much higher deactivation than those of silica supported ones. Silica carrier as well as silica species introduced onto alumina under pre-impregnation with Na_2SiO_3 exhibited an advantageous role in the catalyst performance, in terms of activity and deactivation.

KEY WORDS: 2-ethylanthraquinone; hydrogenation; egg-shell catalysts.

ABBREVIATIONS: eAQ, 2-ethyl-9,10-anthraquinone; $eAQH_2$, 2-ethyl-9,10-anthrahydroquinone; H_4eAQ, 2-ethyl-tetrahydro-9,10-anthraquinone; H_4eAQH_2, 2-ethyl-tetrahydro9,10-anthrahydroquinone; H_8eAQ, 2-ethyl-octahydro-9,10-anthraquinone; H_8eAQH_2, 2-ethyl-octahydro-9,10-anthrahydroquinone.

1. Introduction

Catalytic hydrogenation of 2-ethylanthraquinone (eAQ) is the key reaction in the anthraquinone method of H_2O_2 production [1,2]. In the cyclic process eAQ is hydrogenated (scheme 1) to yield 2-ethylanthrahydroquinone ($eAQH_2$). Oxidation of the latter results in hydrogen peroxide and regeneration of the starting eAQ. However, together with a desired very fast eAQ reduction, a slow hydrogenation of the primary and desirable product $eAQH_2$ occurs to various side products. As scheme 2 shows the consumption of $eAQH_2$ can be considered as occurring along the parallel reactions I and II. A consecutive process of aromatic ring saturation $eAQH_2 \rightarrow H_4eAQH_2 \rightarrow H_8eAQH_2$ is considered as the pathway I of the $eAQH_2$ consumption. The product of the first ring hydrogenation H_4eAQH_2, is the only compound among all of side products given in scheme 2 which is desirable because it can participate in the oxidation leading to the H_2O_2 in a similar way as $eAQH_2$. eAQ and H_4eAQ are therefore termed 'active quinones' [1–5]. The hydrogenation of second aromatic ring with formation of H_8eAQH_2 was observed only after complete transformation of quinone system in eAQ to the hydroquinone one [3]. Hence, the presence of eAQ prevented the formation of H_8eAQH_2. The reaction pathway (II) comprises the hydrogenolysis reactions of C—O bonds (formation of 2-ethylanthrone, 2-ethylanthracene, dimers etc.) preceded by the tautomerization of $eAQH_2$ to oxanthrone. All compounds formed in the reaction route II are termed 'degradation products' because they are not capable to form H_2O_2 upon oxidation and thus represent a loss of the starting eAQ. Although oxanthrone can be regenerated to active quinone, further hydrogenation leads to anthrone and, subsequently, dianthrones, products, which cannot be regenerated [1,6]. Degradation products obtained *via* tautomerization of $eAQH_2$ are not well defined, as for example dianthrone. They determine the loss of about 5% of eAQ [3]. From a technological point of view a low amount of degradation products is acceptable. The anthraquinone process can be realized as 'Anthra' (AQ) or 'All-Tetra' systems. In the former case the concentration of H_4eAQ is kept low and eAQ is the only

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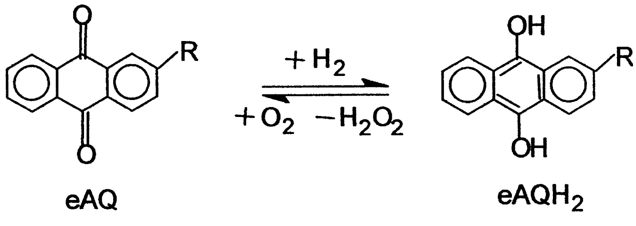


Scheme 1.

quinone taking part in cyclic reduction-oxidation process (scheme 1). In the 'All-Tetra' system the solution contains 70% of H_4eAQ and 30% of eAQ but H_4eAQ is the only quinone participating in the production cycle [5]. In the hydrogenation stage performed as a slurry operation Raney – Ni, Pd-black or Pd supported catalysts are widely used. Several papers have already reported the kinetics of fluid-bed hydrogenation [3,4,7–10]. Pd supported catalysts are also used in the hydrogenation carried out in the fixed-bed operation. This technique avoids the problem of filtration and recirculation of catalyst back into the reactor, which is required in the slurry operation. The catalyst applied in fixed-bed operation must fulfil a number of requirements, the most important is a long working life, as replacing a fixed-bed catalyst is more complicated than replacing a suspended one. Hydrogenation of eAQ as a fixed-bed operation has been studied in the past, but the available literature consists mostly of patents [11–16] reporting a profitable performance of catalysts with an egg-shell Pd concentration profile. The thickness of Pd shell has been most frequently considered as a variable essentially affecting the activity and life time of the catalysts [13,15]. A superior performance has been reported for the spherically shaped alumina supported egg-shell Pd catalysts with palladium penetration limited to only 40–50 μm [11].

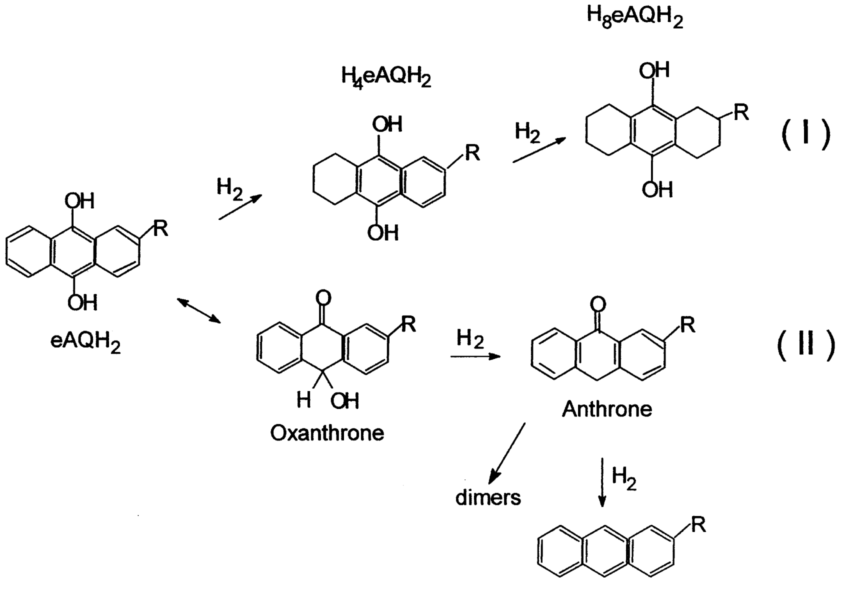
In the present work, the hydrogenation of eAQ was carried out in the fixed-bed reactor. Silica and alumina supported egg-shell catalysts having uniformly distributed Pd on the outer surface of supports and Pd penetration within the range 10–200 μm were applied. The catalysts were prepared by precipitation of palladium hydroxide onto the support grains pre-impregnated with alkaline reagents, namely $NaHCO_3$, NaH_2PO_4, Na_2SiO_3. This pre-impregnation not only facilitates the hydrolysis of palladium compounds, but also partially fills the pores of the support. It is possible, however, that the alkaline reagent modifies also the surface properties. The role of this modification in directing the course of $eAQH_2$ consumption (scheme 2) is reported. It is shown that decrease in the catalyst activity that occurs during the hydrogenation run can be correlated with high ability towards the hydrogenolytic reactions (pathway II of scheme 2). The advantageous role in deactivation behaviour exhibited silica as the support or silica species introduced onto alumina carrier. The list of chemical substances mentioned in this paper and their formulas are given at the end of publication.

2. Experimental

2.1. Materials

The reagents: 2-ethylanthraquinone, 2-ethyltetrahydroanthraquinone, organic solvents, silica and alumina supports and $PdCl_2$ were supplied by Kemira Chemicals.

Industrially manufactured materials: silica SiO_2 (1) and SiO_2 (2) (synthetic amorphous silica, Grace Davison) and alumina (activated alumina oxide, containing



Scheme 2.

partially hydrated alumina) were used as the supports. Their characteristics are summarized in table 1. Both silica carriers were in the form of irregular particles, whereas alumina was in the form of spherically shaped grains.

The catalysts with an egg-shell Pd concentration profile were prepared by precipitation of palladium hydroxide or hydrated oxide onto the grains of support. The metal loading was routinely 1 or 2 wt% Pd in the catalysts. The preparations were done as one- or two-step procedures. In the former, palladium hydroxide was precipitated onto the grains of pristine alumina (catalysts Nos. 1 and 2, table 2), while in the latter, deposition of palladium was preceded by pre-impregnation of supports with alkaline solutions 0.1 M $NaHCO_3$, 0.2 M NaH_2PO_4, 0.007 M Na_2SiO_3. The latter operation was carried out as follows: the support (dried for 16 h at 120 °C) was contacted with an excess of alkaline solution (20 cm^3 solution/1 g of support) and the mixture was gently and continuously mixed for 2 h at room temperature. The samples were then decanted off and washed with distilled water to obtain pH ~ 7–8, and dried. Palladium hydroxide (or hydrated oxide) was then precipitated onto their surface using $PdCl_2$ solution (0.8 g/dm^3) of pH = 3–3.5 adjusted with 0.1 M HCl. The support was introduced into $PdCl_2$ solution and occasionally mixed for 2 h at room temperature. The grains were then filtered off and kept under excess of 0.1 M NaOH solution to hydrolyze Pd^{2+} aquachloro-complexes. To obtain the same loading of Pd the impregnation and hydrolysis were routinely repeated 2–3 times to precipitate all the Pd onto the support. The catalysts were then washed with distilled water to remove the Cl^- ions and dried for 4 h at 120 °C. All silica supported catalysts were prepared by two-step method because Pd^{2+} complexes were not appreciably adsorbed by the silica in the conditions used (pH of $PdCl_2$ solution 3–3.5).

Table 1
Physicochemical properties of the silica and alumina supports

	Support		
	SiO_2 (1)	SiO_2 (2)	Al_2O_3
Particles shape	Irregular	Irregular	Spherical
Particles size [mm]	1.0–3.0	1.0–3.0	1.4–2.8
Density [g/cm^3]	0.4	0.4	0.76
Specific surface area [m^2/g]	396	342	395
Pores volume [cm^3/g]	1.05	1.14	0.525
Average pore diameter [nm]	10.6	13.3	5.32

The catalyst was reduced in the reactor, immediately before the hydrogenation test. The catalyst wetted with the quinone solution was reduced in flowing hydrogen for 10 min at temperature 50 °C.

Table 2 summarizes the series of alumina and silica supported catalysts together with a notation of the alkaline reagents used in the pre-impregnation stage.

2.2. Characterization of catalysts

BET specific surface area, the distribution of pores and the mean pore radius of the samples were measured and evaluated by nitrogen adsorption isotherms using a Sorptomatic 1990 apparatus. The sample (0.3–0.4 g) was evacuated at 25 °C for 16 h before the measurement. The BET surface area was calculated from the amount of nitrogen adsorbed at 77.35 K. Cumulative pore volume of pores between 1.7 and 300 nm diameter was determined.

The Pd and Si concentration profiles inside the catalyst grains were studied over their cross-section by means of scanning electron microscope Philips XL-30 with a resolution of 20 nm. The microscope used was equipped with a Kevex energy-dispersive X-ray analyser. The catalyst grains were resin-bounded, polished and finally coated with gold before the microscopic measurements.

Table 2
The initial activity (AQ-I, 1 h) expressed as the number of H_2O_2 moles formed after 1 h or reaction in the intial AQ-I stage and the selectivity factor N_S calculated at various conversion (%R) of eAQ to $eAQH_2$

No.	Support	Catalyst	AQ-I, 1 h	N_S	
				%R ~ 40–60	%R ~ 80–90
1	Al_2O_3	2%Pd/Al_2O_3	0.259	0.1	0.47
2	Al_2O_3	1%Pd/Al_2O_3	0.165	0.21	0.39
3	Al_2O_3	2%$Pd/Al_2O_3(SiO_3^{2-})$[a]	0.247	0.25	0.95
4	Al_2O_3	1%$Pd/Al_2O_3(SiO_3^{2-})$	0.341	1.11	1.20
5	Al_2O_3	2%$Pd/Al_2O_3(CO_3^{2-})$	0.259	0.45	0.67
6	Al_2O_3	2%$Pd/Al_2O_3(PO_4^{3-})$	0.283	0.12	0.93
7	SiO_2 (1)	2%$Pd/SiO_2(CO_3^{2-})$	0.352	1.2	1.48
8	SiO_2 (1)	1.5%$Pd/SiO_2(PO_4^{3-})$	0.174	1.6	1.70
9	SiO_2 (2)	2% $Pd/SiO_2(CO_3^{2-})$	0.506	~10	9.90
10	SiO_2 (2)	2%$Pd/SiO_2(SiO_3^{2-})$	0.283	~10	12.0

[a] In bracket the reagent used for pre-impregnation of support is given.

The colorimetric method (based on the reaction between palladium ions and KI leading to the formation of $[PdI_4]^{2-}$ [17]) was used to control the completeness of palladium ions reduction in the recovered catalysts, after the hydrogenation test. In a typical procedure the sample of catalyst was treated with 10% KI in 0.1 M HCl and the presence of $[PdI_4]^{2-}$ ions extracted from the catalyst was colorimetrically controlled.

2.3. Hydrogenation experiments

In hydrogenation experiments two solutions were used in which the concentration of quinones was equal to 60 g/dm^3. The first solution consisted only eAQ while the composition of second one corresponded to that applied in 'All-Tetra' system: 18 g/dm^3 eAQ and 42 g/dm^3 H_4eAQ (70% of H_4eAQ). As the solvent for anthraquinone reagents a mixture containing 70% of non-polar component (a commonly used mixture of aromatic hydrocarbons) and 30% of polar ones (tetrabutylurea and alkyl phosphates type compounds) was applied.

The quinone solution was saturated with hydrogen at the same pressure as in hydrogenation tests (5 bar) before introducing into fixed-bed reactor. The reactor (cylinder: diameter 54.4 mm, height 10.8 mm, area 23.23 cm^2, volume 25 cm^3) was charged with 25 cm^3 of catalyst and a quinone solution (4 kg) was circulated through the reactor with the flow rate 170 kg/h. Solution was passed into the top of the catalyst bed. During the catalytic run the solution was continuously saturated with hydrogen in order to maintain the constant concentration of hydrogen in the solution.

Each catalytic run comprised three subsequent stages AQ-I, AQ-II and TETRA-III.

Stage AQ-I: In the first stage fresh catalyst and fresh solution containing eAQ (60 g/dm^3) were used. The hydrogenation was carried out for 5 h at temperature 50 °C and pressure 5 bar. Although the reduction of eAQ to eAQH$_2$ was almost complete ($\%R$ ~90) after 5 h of reaction, the hydrogenation was continued for 18 h at the hydrogen pressure 1 bar. The samples of solution taken from the reactor after 1, 2, 3.5, 5 and 23 h of reaction were oxidized with O_2 and analysed. The concentration of eAQ and H_4eAQ was determined with a gas chromatograph (Hewlett Packard model 5890) equipped with a FID detector in conditions: column DB-1701. 30 m × 0.32 mm × 0.25 μm, isothermal run 230 °C, flow rate of He gas 1.3 cm^3/min. GC analysis also showed that no essential change in the composition of solvents occurred during the whole hydrogenation experiment. Reproducibility of the chromatographic analysis was ≈5%.

The presence of products other than active quinones (eAQ, H_4eAQ) produced in definitely lower content was analysed with gas chromatography–mass spectrometry (GC–MS). Most of them although detected by much more sensitive thin layer chromatography (TLC) was not detected by GC or HPLC, probably because they remain already on the top of chromatographic columns. Thus, cumulative content of these compounds termed as the degradation products was calculated from the mass balance similarly as it has been done by other authors [3].

The content of H_2O_2 produced upon oxidation of the anthraquinone reagents was analysed by titration with $KMnO_4$ solution. The number of H_2O_2 moles formed during the first hour of the hydrogenation presents (AQ-I, 1 h) value, while (AQ-I, 2 h) corresponds to the second hour of test. From the number of H_2O_2 moles determined in the first AQ-I stage, the conversion ($\%R$) of quinone (eAQ) to hydroquinone (eAQH$_2$) has been calculated.

Stage AQ-II: The new solution of eAQ (4 kg) was introduced into reactor without contacting the catalyst with air. The hydrogenation was carried out for 2 h at 50 °C and 5 bar with circulation of the eAQ solution with rate 170 kg/h. The samples of liquid were taken in every hour and the number of H_2O_2 moles (AQ-II, 1h) and (AQ-II, 2h) was determined.

Stage TETRA-III: Solution has the composition corresponding to that in the 'All-Tetra' system: H_4eAQ (70%) and eAQ (30%), total concentration of quinones 60 g/dm^3. The hydrogenation was carried out for 1 h in the same conditions as in stage AQ-II. In the solution taken after 1 h of reaction the number of H_2O_2 moles (TETRA-III, 1 h) was determined.

The performance of catalyst was characterized by the initial activity and deactivation occurring during the hydrogenation run. As the measure of the initial activity the number of H_2O_2 moles (AQ-I, 1 h) formed during the first hour of the initial AQ-I stage has been assumed. As the measure of catalysts deactivation the drop in the catalysts activity after the initial AQ-I (Deact-1 and Deact-2) and second AQ-II (Deact-3) stages of hydrogenation run have been assumed. From the number of H_2O_2 moles formed during the first and second hours of reactions in AQ-I and AQ-II stages the decrease in the activity characterized by Deact-1 and Deact-2 respectively, were calculated as follows:

$$\text{Deact-1} = (\text{AQ-II}, 1\,\text{h})/(\text{AQ-I}, 1\,\text{h})$$

$$\text{Deact-2} = (\text{AQ-II}, 2\,\text{h})/(\text{AQ-I}, 2\,\text{h})$$

Deact-3 presents the drop in the activity during both AQ-I and AQ-II stages. Deact-3 was calculated from the number of H_2O_2 moles determined after the first hour of reactions in the TETRA-III stage and the initial AQ-I stage:

$$\text{Deact-3} = (\text{TETRA-III}, 1\,\text{h})/(\text{AQ-I}, 1\,\text{h})$$

The hydrogenation experiments were reproducible with ≈5% over 2–3 catalyst batches. After the hydrogenation experiment, the catalyst was removed and treated with several portion of organic solvents such as toluene, acetone. The resulting solution was examined by GC–MS. In order to control the completeness of palladium ions reduction, the sample of catalyst was analysed with colorimetric method. In all the catalysts recovered from the hydrogenation experiment only metallic palladium was determined.

3. Results and discussion

3.1. Characterization of alumina and silica supported catalysts

Figure 1 illustrates the SEM micrograph of the cross-section of catalysts obtained by deposition of Pd onto the not-pre-impregnated-pristine alumina (2%Pd/Al$_2$O$_3$, No. 1 in table 2). Palladium layer as broad as about 200 μm is visible. This micrograph can be compared with the one in figure 2 for catalyst supported on alumina pre-impregnated with Na$_2$SiO$_3$ solution (No. 4 in table 2). Silica species in the whole volume of the alumina particles appear but their level is especially high near to the outer surface of the grain. The thickness of Pd shell as small as only 60 μm is then reached thus confirming very effective blockage of pore structure due to Na$_2$SiO$_3$ pre-treatment. The blockage of pore in the alumina is also confirmed by the decrease in the specific surface area and pore volume (table 3) accompanied by an increase in the mass of sample occurring under pre-impregnation stage.

Pd concentration profiles in the silica supported Nos. 9 and 10 catalysts (table 2) are presented in figures 3 and 4 respectively. In the former (figure 3) silica was pre-impregnated with NaHCO$_3$, in the latter (figure 4) with Na$_2$SiO$_3$ solution. As in the case of alumina, pre-impregnation of silica with alkaline reagents has the advantageous effect on the Pd concentration profile. Pd shell as thin as only 10 μm was obtained under NaHCO$_3$ pre-treatment (figure 3) whereas Na$_2$SiO$_3$ (and NaH$_2$PO$_4$) resulted in slightly deeper, 30–80 μm, palladium penetration (figure 4).

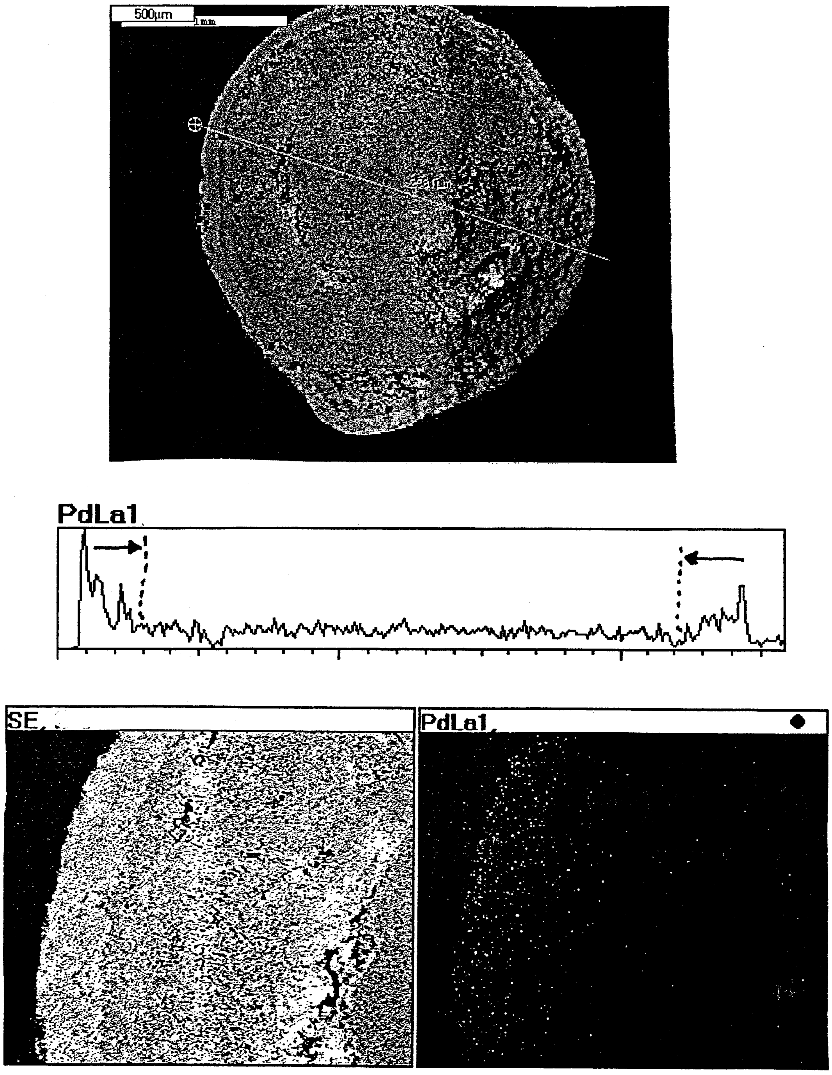


Figure 1. X-ray microprobe analysis of Pd distribution over the cross-section of catalyst grain supported on the pristine alumina (No. 1).

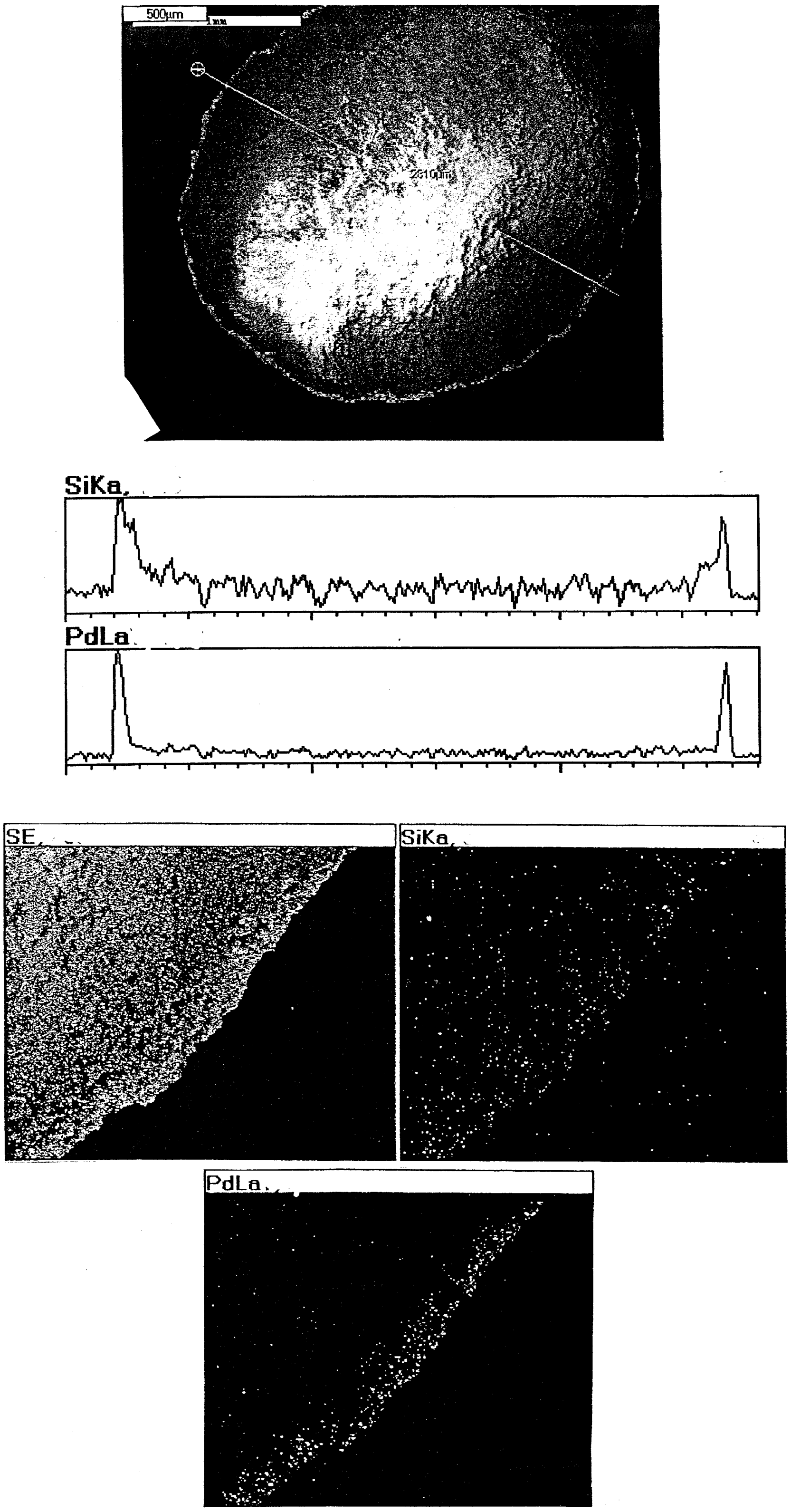


Figure 2. X-ray microprobe analysis of Pd and Si distribution over the cross-section of catalyst grain supported on alumina pre-impregnated with Na_2SiO_3 (No. 4).

Using X-ray microprobe analysis the presence of Na in the catalysts was also studied. In all alumina and silica supported catalysts very strong Na signals were detected, independently of the type of alkaline reagent used for the pre-impregnation. No evident difference in the content of Na between silica and alumina

Table 3
The influence of pre-impregnation procedure on the properties of alumina support

	Increase in mass (%)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)
Support	–	395	0.525	5.32
Support pre-impregnated with Na_2SiO_3	3	345.5	0.47	5.46
Catalyst, 2% Pd on support pre-impregnated with Na_2SiO_3	–	377	0.487	5.17

supported catalysts was also observed. Maybe, because the catalysts were washed up to elimination of Cl$^-$ ions only.

In conclusion, in the catalysts prepared by two-step procedure palladium hydroxide was precipitated mostly onto the outer surface of support grains. Very thin Pd shell (10–80 μm) appeared in these catalysts independently of the type of alkaline reagent and support materials. On the other hand, palladium penetrated distinctly deeper ($\approx$ 200 μm) when not-pre-impregnated pristine alumina was used as the support.

3.2. Hydrogenation experiments

The hydrogenation of eAQH$_2$ leading to its consumption (scheme 2) can be considered as proceeding *via* the aromatic ring hydrogenation (pathway I) and the hydrogenolytic reactions (pathway II) (scheme 2). As already described, the presence of eAQ prevents the hydrogenation of second aromatic ring resulting in the formation of H$_8$eAQH$_2$ [3]. In the present work eAQ has usually been present in the hydrogenated solution. It has been therefore assumed that the degradation products found before the complete conversion of quinone system in eAQ to hydroquinone one are the only products formed in pathway II of scheme 2. Such an assumption was also experimentally confirmed by GC–MS analysis carried out for the hydrogenated solutions as well as for the liquids obtained by treatment the recovered catalysts with several portion of organic solvents (toluene, acetone). In the chromatograms of these solutions only several peaks at m/z of 220–222 characteristic of anthrone type compounds appeared, whereas the ion molecular peak at $m/z = 244$ characteristic of H$_8$eAQ was not observed. Thus, even if this non-reactive H$_8$eAQ compound is formed before 100% conversion of eAQ, its content is definitely lower compared to those of hydrogenolytic products easily detected in the present conditions. More detailed identification of particular compounds termed in the present work as degradation products is under investigation.

Both processes along pathways I and II usually proceed simultaneously. In order to clarify which dominates, the coefficient N_S defined as the ratio of the number of H$_4$eAQH$_2$ moles N (H$_4$eAQH$_2$) to the number of moles of degradation products N (D) was introduced

$$N_S = n(H_4eAQH_2)/n(D)$$

The value of N_S below 1 indicates that the hydrogenolytic reactions (pathway II) producing degradation products exclusively proceeded. In contrast, the value of N$_S$ higher than 1 indicates that the hydrogenation of phenyl rings in eAQH$_2$ (pathway I) is favoured over the hydrogenolytic processes.

The course of eAQH$_2$ consumption in the initial AQ-I stage carried out over fresh catalysts was studied. The general pattern of this process can be described as follows. If we consider an ‘ideal case’ that desired reaction i.e. the reduction of eAQ to eAQH$_2$ proceeds as the only reaction, the sum of both eAQ + eAQH$_2$ does not decrease in the whole process. However, in actual conditions, with the increase in eAQ to eAQH$_2$ reduction (%R) there is the slow decrease in the eAQH$_2$ content due to its consumption along pathways I and II. If the hydrogenation of aromatic ring is the only process (pathway I), the content of active quinones (ACQ) calculated as the sum of eAQ + H$_4$eAQ is constant. On the other hand, a slow decrease in the ACQ content shows the consumption of eAQH$_2$ in the hydrogenolytic reactions (pathway II).

3.2.1. Alumina supported palladium catalysts

Pre-impregnation of alumina with alkaline reagents did not essentially affect the initial activity of catalysts with 2% Pd (table 2). Comparable number of H$_2$O$_2$ moles (0.247–0.283) was formed after the first hour of the AQ-I stage. The effect of pre-impregnation was much stronger when only 1 wt% of Pd was introduced. Activity increased then from 0.165 for the pristine alumina supported catalyst (No. 2) to 0.341 for the alumina pre-impregnated with Na_2SiO_3 (No. 4). In view of the present data it seems difficult to explain the effect of Pd loading on the initial activity. It is possible, however, that the diffusion limitation plays some role during the hydrogenation reaction. Additional hydrogenation tests are therefore needed with regard to the role of mass-transfer limitation in the present hydrogenation conditions, before we can explain the effect of Pd loading in the catalysts.

Pre-impregnation of supports has an essential role in directing the course of eAQH$_2$ consumption producing H$_4$eAQH$_2$ and degradation products. This effect can clearly be seen if we compare figures 5 and 6 showing the

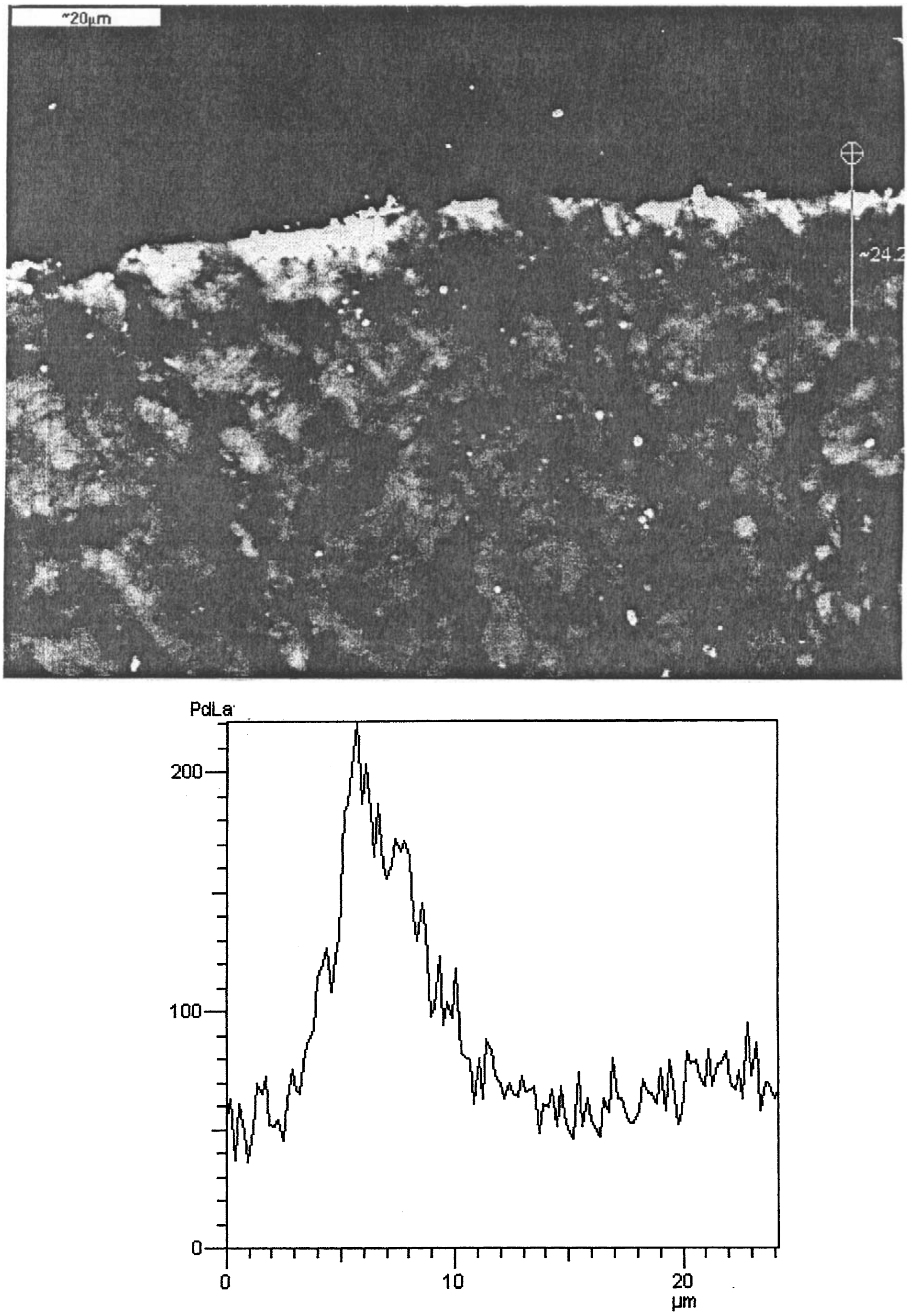


Figure 3. X-ray microprobe analysis of Pd distribution over the cross-section of catalysts grain supported on silica pre-impregnated with $NaHCO_3$ (No. 9, 2% Pd/SiO_2(CO_3^{2-})).

content of H_4eAQH_2 (curve T) and degradation products (curve D) (expressed as mol%) as a function of eAQ to $eAQH_2$ conversion (%R). The results in figure 5 present performance of catalysts on pristine alumina (1% and 2% of Pd) and in figure 6 of alumina pre-impregnated with NaH_2PO_4 and Na_2SiO_3. In the presence of pristine alumina supported catalysts the content of degradation products (pathway II) increased from the very beginning of the hydrogenation (figure 5) whereas an appreciable content of H_4eAQH_2 was detected only when more than 30% of eAQ was reacted to $eAQH_2$ (%$R > 30$). Because the content of degradation products exceeded that of H_4eAQH_2 during the whole process (up to%$R \sim 90$%), the N_S coefficient below 1 was attained (table 2). The identical course of $eAQH_2$ consumption resulting in the $N_S < 1$ was observed on alumina pre-impregnated with $NaHCO_3$ and NaH_2PO_4 (figure 6c). For all of these catalysts the

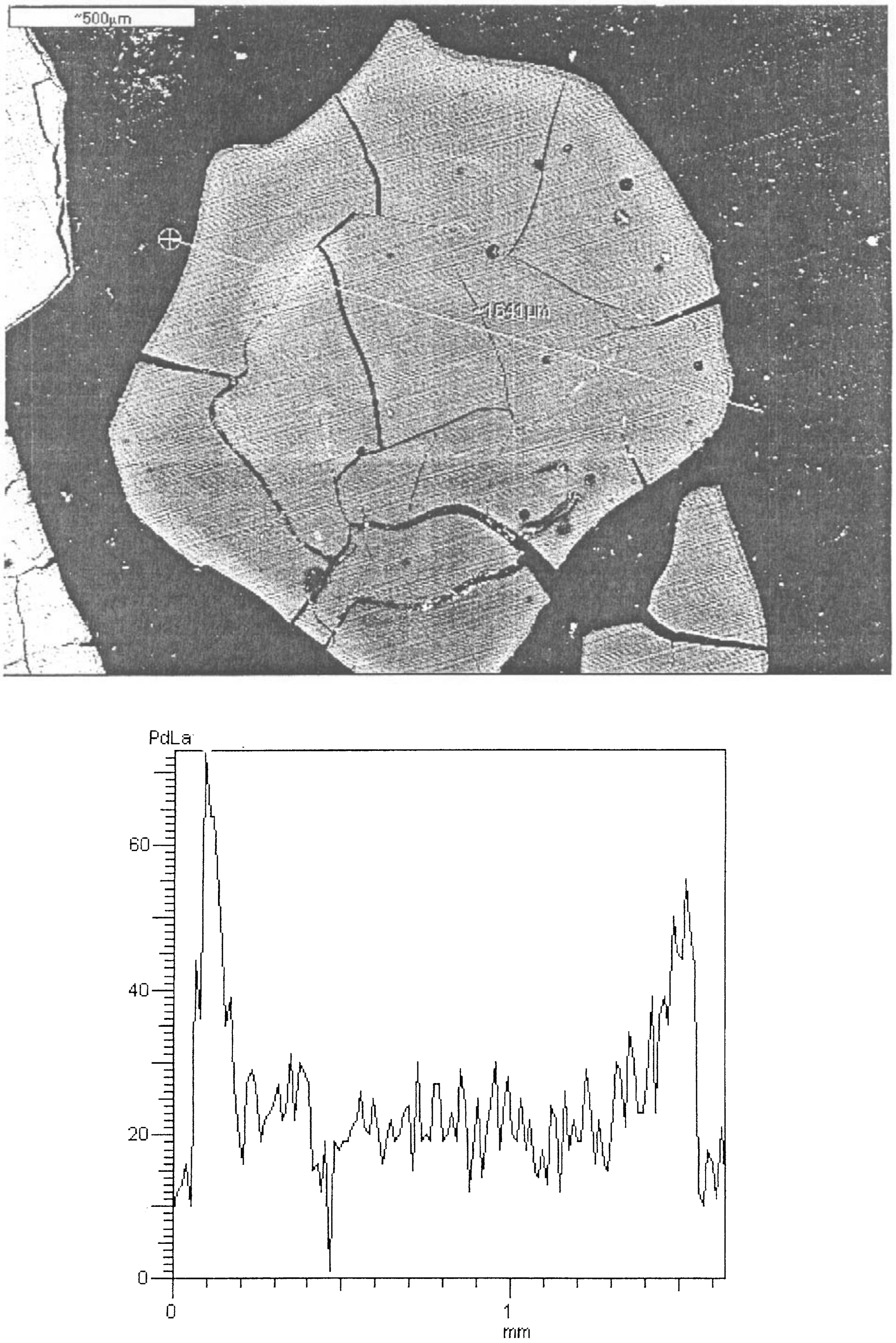


Figure 4. X-ray microprobe analysis of Pd distribution over the cross-section of catalysts grain supported on silica pre-impregnated with Na_2SiO_3 (No. 10, 2% $Pd/SiO_2(SiO_3^{2-})$).

pathway II comprising tautomerization and hydrogenolysis, predominated over the hydrogenation of aromatic ring in $eAQH_2$. Such a predomination resulted in a slow decrease in the content of active quinones (ACQ) occurring from the very beginning of the AQ-I stage (figure 5). The opposite relation between pathways I and II was found on Na_2SiO_3 pre-impregnated alumina (figure 6a and b). The N_S coefficient very close or even higher than 1 was then reached showing that the hydrogenation of phenyl ring in $eAQH_2$ predominated over the hydrogenolytic reactions. Thus, a profitable role of Na_2SiO_3 in directing the consumption of $eAQH_2$ along pathway l as well as in weakening the reactivity in hydrogenolytic reactions is observed.

3.2.2. Silica supported palladium catalysts

The type of alkaline reagents did not evidently affect the initial activity of silica supported catalysts. Some-

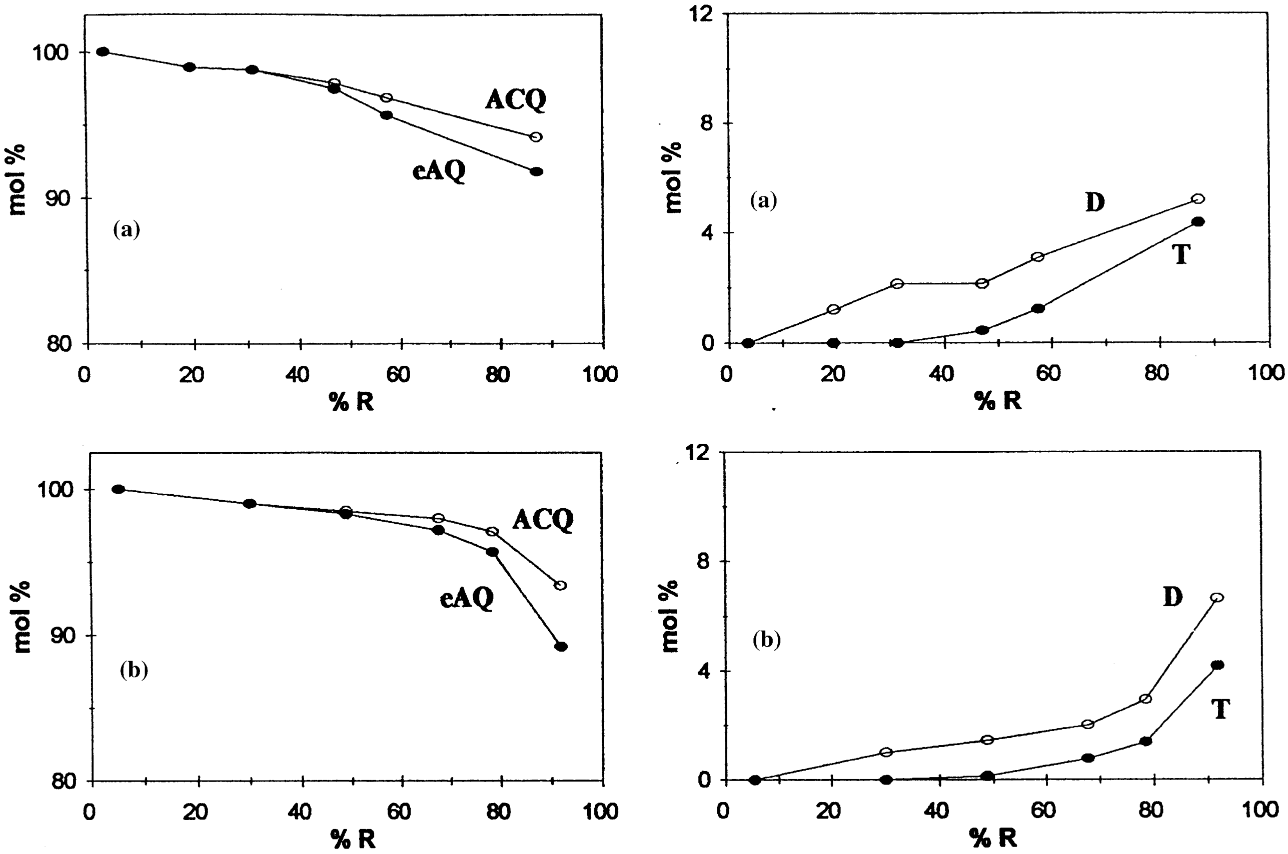


Figure 5. The change of the concentration (mol%) of eAQ, active quinones (ACQ), H_4eAQ (T) and degradation products (D) in the course of AQ-I stage, pristine alumina supported catalysts with 1% Pd (a) and 2% Pd (b).

what higher activity was exhibited only by the catalysts pre-treated with $NaHCO_3$ solution (table 2). However, the initial activity of SiO_2 (2) supported catalysts was much higher than those of SiO_2 (1) based ones. The reduction of eAQ to $eAQH_2$ – desired reaction – was the only reaction from the very beginning of the AQ-I stage on all the silica supported catalysts. In contrast to the alumina support, the consumption of $eAQH_2$ started only when nearly 30% of eAQ was reacted to $eAQH_2$ ($\%R \sim 30\%$) (figure 7). The course of $eAQH_2$ consumption also differed from that on alumina supported catalysts. The content of H_4eAQH_2 (curves T) evidently exceeded that of degradation products (curves D) during the whole hydrogenation reaction on catalysts with silica carrier. The N_S coefficient higher than 1 is then calculated thus showing the hydrogenation of aromatic ring (pathway I) as the preferential route of $eAQH_2$ consumption. Such a predomination appeared on all the silica based catalysts, independently of the nature of alkaline reagents used in the pre-impregnation stage. As a consequence of the preferential hydrogenation of phenyl ring, a very high content (98%) of active quinines (ACQ) was reached on all the silica supported catalysts (figure 7).

However, the predomination of pathway I to some degree depended on silica SiO_2 (1) or SiO_2 (2) supports. The N_S as high as 9.2–11 for catalysts No. 9 and 10 but distinctly smaller, equal to only 1.5–1.7, for catalysts No. 7 and 8 (table 2) can be seen. In the former case SiO_2 (2) while in the latter SiO_2 (1) supports were used. It is difficult to explain the observed effect of SiO_2 carrier as both silica supports exhibited very similar density, specific surface area and porosity (table 1). More detailed characterizations of particular SiO_2 (1) or SiO_2 (2) supports and final catalysts are required. The reported data are insufficient at this time to justify a reason of substantial difference in the performance of SiO_2 (1) and SiO_2 (2) supported catalysts. More data with regard to the dispersion of palladium in the catalysts as well as acidity of particular silica supports is needed, before we can speculate further.

3.3. The effect of catalysts deactivation

In the initial AQ-I stage of the hydrogenation run, the fresh catalyst and fresh eAQ solution were used whereas stage AQ-II corresponded to the reaction in a new eAQ solution on the catalyst partially deactivated during the AQ-I stage. Deact-1 and Deact-2 are the measure of catalyst deactivation. They show decline in the activity compared to those determined after the first and second hour of reaction in initial AQ-I stage (table 4).

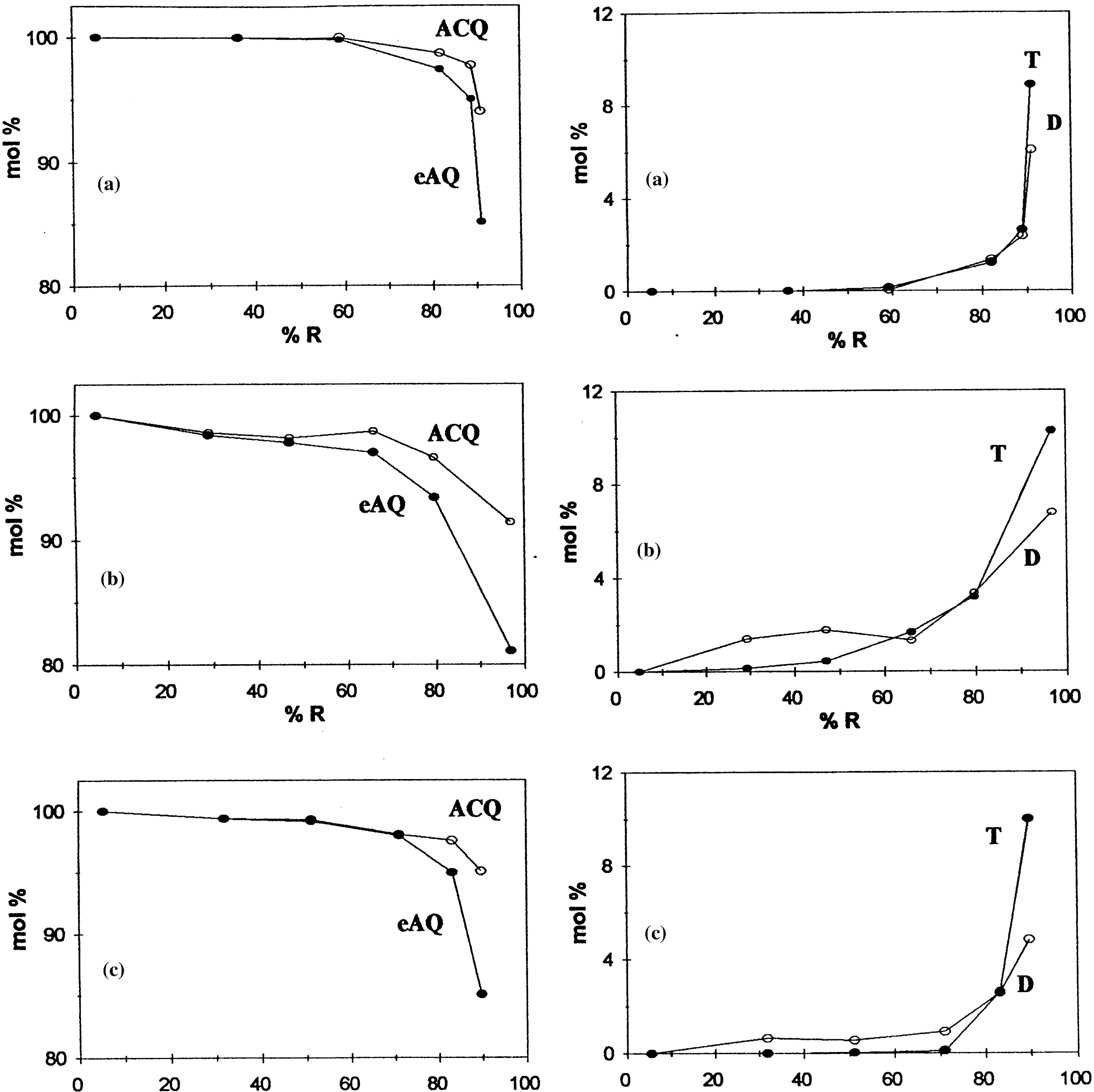


Figure 6. The change of the concentration (mol%) of eAQ, active quinones (ACQ), H_4eAQ (T) and degradation products (D) in the course of AQ-I stage on catalysts with alumina pre-impregnated by Na_2SiO_3 and NaH_2PO_4. (a) 1% Pd/Al_2O_3 (SiO_3^{2-}) (No. 4), (b) 2% Pd/Al_2O_3 (SiO_3^{2-}) (No. 3), (c) 2% Pd/Al_2O_3 (PO_4^{3-}) (No. 6).

For all the catalysts except 2% $Pd/SiO_2(SiO_3^{2-})$, the values of Deact-1 below 1 are seen (table 4) thus showing a partial deactivation of catalysts during the AQ-I stage, when fresh catalysts was used. Very similar values of Deact-1 and Deact-2 suggest that no further deactivation occurred during the AQ-II stage. Activities seem to stabilize after the first hour of the AQ-II stage, but on slightly lower level compared to the one determined in the AQ-I stage. Deactivation of the individual catalysts differed each other, the strongest (Deact-1 = 0.67) being for pristine alumina supported 2% Pd/Al_2O_3 (No. 1). In the latter catalyst the Pd shell as broad as ~200 μm (figure 1) was observed. Although, pre-treatment of alumina with $NaHCO_3$ and NaH_2PO_4 resulted in a very thin Pd shell in No. 5 and 6 catalysts, decrease in their activity under the initial AQ-I stage was also high and comparable to that of 2% Pd/Al_2O_3. Deactivation was slower, however, on alumina catalyst

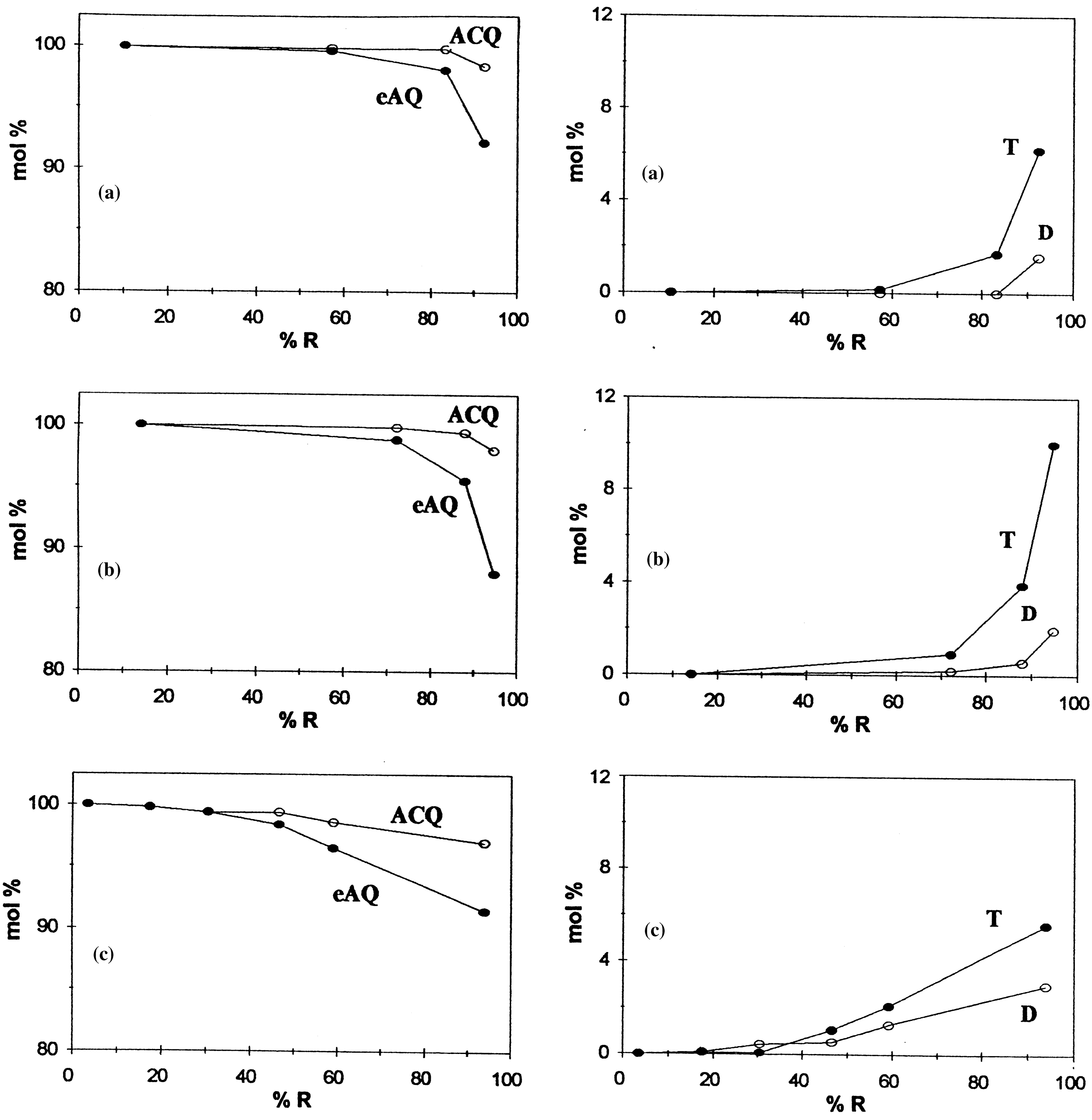


Figure 7. The change of the concentration (mol%) of eAQ, active quinones (ACQ), H$_4$eAQ (T) and degradation products (D) in the course of AQ-I stage on silica supported catalysts pre-impregnated with various reagents. (a) 2% Pd/SiO$_2$ (CO$_3^{2-}$) (No. 9), (b) 2% Pd/SiO$_2$ (SiO$_3^{2-}$) (No. 10), (c) 1.5% Pd/SiO$_2$ (PO$_4^{3-}$) (No. 8).

pre-impregnated with Na$_2$SiO$_3$ (table 4). This implies that other reasons than Pd shell thickness determines the observed deactivation.

The initial activity of silica supported catalysts also decreased during the first AQ-I stage, but their deactivation was remarkably lower (Deact-1 ~ 0.8–0.9) compared with those on alumina. Thus, a profitable role in the maintenance activity during the AQ-I stage exhibited silica. This role is more evidently ascertained by Deact-3 (table 4) showing the decrease in the initial activity during the whole hydrogenation run, AQ-I and AQ-II stages. Deact-3 presents the ratio of the activity in the TETRA-III stage carried out in ‘All-Tetra’ system (30% eAQ and 70% H$_4$eAQ) to the initial one determined in the AQ-I stage (eAQ the only quinone in the solution).

Since the composition of solution in the TETRA-III stage differed from that in the AQ-I stage, separate series of hydrogenation experiments were performed.

Table 4
The decrease in catalysts activity during the hydrogenation experiment

No.	Catalyst	Deact-1	Deact-2	Deact-3
1	2%Pd/Al_2O_3	0.67	0.76	0.82
2	1%Pd/Al_2O_3	0.82	0.82	0.91
3	2%Pd/$Al_2O_3(SiO_3^{2-})$	0.76	0.71	1
4	1%Pd/$Al_2O_3(SiO_3^{2-})$	0.93	1.05	1.06
5	2%Pd/$Al_2O_3(CO_3^{2-})$	0.73	0.69	0.91
6	2%Pd/$Al_2O_3(PO_4^{3-})$	0.74	0.83	0.96
7	2%Pd/$SiO_2(CO_3^{2-})$	0.83	0.94	1.21
8	1.5%Pd/$SiO_2(PO_4^{3-})$	0.84	0.84	1.54
9	2% Pd/$SiO_2(CO_3^{2-})$	0.86	0.87	1.14
10	2%Pd/$SiO_2(SiO_3^{2-})$	1	1.28	1.14

In these experiments the activities of fresh catalysts in the fresh solution of 'All-Tetra' composition (30% eAQ and 70% H_4eAQ) were determined. All the fresh catalysts exhibited 1.1–1.2 times higher initial activity in the solution of 'All-Tetra' composition compared to those when eAQ is the only quinone like in the AQ-I stage. These results are in agreement with the literature data reporting a slightly higher reactivity of H_4eAQ compared to that of eAQ. Hence, if deactivation of catalyst is reversible during the whole hydrogenation test, Deact-3 higher than 1 should be observed.

When comparing the values of Deact-3 (table 4) the evident difference between silica and alumina supports can be seen. The values of Deact-3 are below 1 for all the catalysts with alumina carrier except the ones pre-impregnated with Na_2SiO_3. On the other hand, Deact-3 higher than 1 is attained on all silica supported catalysts. Thus, deactivation of catalysts with silica is not so much irreversible as is that of alumina-based ones. The observed difference in deactivation between alumina and silica seems quite well correlated with the course of eAQH_2 consumption characterized by the N_S coefficient (table 2). For the catalysts having N_S coefficient below 1 as in the case of alumina support, the consumption of eAQH_2 in the hydrogenolytic reactions predominated over the phenyl ring hydrogenation and these catalysts irreversibly deactivated (Deact-3 < 1). On the other hand, if silica is the support or silica species are introduced onto alumina, the hydrogenolytic reactions become strongly limited and N_S higher than 1 are attained. Even, as initial activity of the latter catalysts slightly decreases during the AQ-I stage, it almost returns to the starting level after subsequent use of new eAQ (AQ-II stage) and TETRA solutions.

A partial blockage of palladium by bulky molecules – the products of quinone molecules condensation has been suggested [7] as a very probable reason of slow decrease in the Pd/Al_2O_3 activity during the anthraquinone process. In the literature [6] it is reported that a high ability to dimerization is a property very characteristic of anthrone type compounds [6]. Formation of dimeric products can be therefore expected in the conditions favouring the hydrogenolytic processes presented as the pathway II of scheme 2. The probability of dimerization may also be greater when the concentration of anthrone type compounds increased on the catalyst surface. Indeed, a greater tendency to hydrogenolytic reactions (pathway II) was exhibited by catalyst on pristine alumina as well as alumina pre-impregnated with $NaHCO_3$, NaH_2PO_4. Although, Pd shell was broad in the former 2% Pd/Al_2O_3 and a very thin in both latter catalysts, the hydrogenolytic products were formed in the presence of all three catalysts from the very beginning of the AQ-I stage and they deactivated irreversibly during the hydrogenation run.

It is interesting to note that two-step procedure resulted in a very thin Pd shell in the catalysts independently of the type of alkaline reagents ($NaHCO_3$, NaH_2PO_4, Na_2SiO_3) used for the support pre-impregnation. However, only silica carrier or pre-impregnation of alumina with Na_2SiO_3 resulted in the markedly decreased tendency towards the hydrogenolytic reactions and better activity maintenance during the hydrogenation experiments. Hence, there is no direct relation between the thickness of Pd shell in the catalysts and its effect on the catalyst deactivation. On the other hand, an important conclusion is that the catalyst ability to directing the course of eAQH_2 consumption is independently of other factors influenced by chemical nature of the support, alumina or silica.

It cannot be excluded that silica species modify the sorption properties and reactivity of catalyst surface towards the quinones. It may be also thought that silica species influenced the course of palladium hydroxide reduction (the precursor of palladium) carried out in the presence of anthraquinone. Such assumptions, although they seem very probable, need additional studies.

A parameter that can, in principle, influence performance of catalyst is the shape of grains as well as the particle size distribution. As already described, alumina grains were spherical while the particles of silica were of irregular form. Although no change in the shape of spherical alumina appeared under pre-impregnation with Na_2SiO_3, this pre-impregnation resulted in substantial change in the reactivity of alumina supported catalysts (catalysts No. 3, 4, tables 2 and 4). At the present stage of the investigation, no further explanation can be given with respect to effect of the shape of catalyst particles.

4. Conclusions

The egg-shell Pd catalysts (1 and 2 wt% Pd) were prepared by the precipitation of palladium hydroxide onto the silica and alumina supports pre-impregnated with various alkaline $NaHCO_3$, NaH_2PO_4 and Na_2SiO_3 solutions. The effects of support, nature of alkaline reagent and Pd concentration profile in the fixed-bed hydrogenation of eAQ were examined over such catalysts. The hydrogenation tests carried out in the AQ and All-Tetra systems provided information about the initial activity and partial deactivation of catalysts. Substantial differences of the reactivity in side reactions producing degradation products between alumina and silica supported catalysts were found. All the catalysts with silica carrier favoured the hydrogenation of aromatic rings resulting in the formation of H$_4$eAQ-active quinone. On the other hand, degradation of quinones in the hydrogenolytic reactions predominated on all the catalysts with alumina, independently of both the thickness of Pd shell and nature of alkaline reagent used in the pre-impregnation stage. All these catalysts deactivated irreversibly during the hydrogenation run. The only exception was pre-impregnation of alumina with Na$_2$SiO$_3$ giving properties of catalyst similar to those of silica supported ones. They exhibited much better activity maintenance during the hydrogenation run than alumina supported catalysts. The latter effect was attributed to the lower reactivity in the hydrogenolytic reactions observed for the catalysts with silica carrier and Na$_2$SiO$_3$ pre-impregnated alumina.

References

[1] *Ulmans Encyclopedia of Industrial Chemistry* (VCH, Weinheim, 1989) Vol. A 13, p. 443.

[2] C.S. Cronan, Chem. Eng. (1959) 118.

[3] E. Santacesaria, M. Di Serio, R. Velotti, U. Leone, J. Mol. Cat. 94 (1994) 37.

[4] A. Drelinkiewicz, J. Mol. Catal. 101 (1995) 61.

[5] T. Berglin, N.H. Shon, Ind. Eng. Chem. Process, Des. Dev. 22 (1983) 150.

[6] J. Houben, *Das Antracen und die Antrachinone* (Georg Thieme Verlag, Leipzieg, 1929).

[7] E. Santacesaria, M. Di Seri, R. Velotti, U. Leone, Ind. Eng. Chem. Res. 33(2) (1994) 277.

[8] E. Santacesaria, P. Wilkinson, P. Babini, S. Carra, Ind. Eng. Chem. Res. 27 (1988) 780.

[9] T. Berglin, N.H. Shon, Ind. Eng. Chem. Process Des. Dev. 20 (1981) 615.

[10] A. Drelinkiewicz, J. Mol. Catal. 75 (1992) 321.

[11] UK patent 876 459 (1961).

[12] UK patent 858 035 (1961).

[13] US patent 3 615 207 (1971).

[14] US patent 4 061 598 (1977).

[15] US patent 4 800 075 (1989).

[16] UK patent 746 385 (1954).

[17] J.G. Fraser, F.E. Beamish, W.A. McBryde, Anal. Chem. 26 (1954) 495.