Hydrogenation of 2-ethyl-9,10-anthraquinone on Pd/SiO$_2$ catalysts
The role of humidity in the transformation of hydroquinone form

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Abstract

The role of humidity in the hydrogenation of 2-ethyl-9,10-anthraquinone (eAQ) and especially in the further transformation of 2-ethylanthracen-9,10-diol (eAQH$_2$) primary and desirable product formed on eAQ hydrogenation was studied. Three 0.5% Pd/SiO$_2$ catalysts differing in the content of Na$_2$CO$_3$ and thus in alkaline properties were used. They were obtained by successive removing of Na$_2$CO$_3$ from the catalyst prepared by precipitation of palladium hydroxide onto Na$_2$CO$_3$ pre-impregnated SiO$_2$. Hydrogenation experiments were carried out in "standard" and subsequently in "wet" systems at 62 °C, atmospheric pressure of H$_2$ in mixture of 2-octanol–xylene (1:1) as the solvent. Humidity influences the whole hydrogenation process, fundamental reaction, the hydrogenation of eAQ to eAQH$_2$ (quinone–hydroquinone stage) and further transformation of eAQH$_2$. A complicated effect of humidity is observed. Humidity has an effect on consecutive reactions transforming eAQH$_2$ via OXO-tautomer to intermediate product 2-ethyl-9,10-dihydro-9,10-dihydroxyanthracene (INT), precursor of 2-ethylanthrone (eAN). The influence of humidity varies depending on the content of Na$_2$CO$_3$ in catalysts and thus their alkaline properties. The observed effects are correlated with adsorption configuration of reagents and especially eAQH$_2$ and INT. Highly alkaline medium as well as humidity facilitated adsorption in the carbonyl group—bonded configuration thus enhancing the transformation of eAQH$_2$ by hydrogenolytic reactions and especially the formation of eAN.
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*Keywords:* 2-Ethyl-9,10-anthraquinone; Palladium catalysts; Hydrogenation

1. Introduction

Catalytic hydrogenation of 2-ethyl-9,10-anthraquinone (eAQ) is the key reaction in the industrial synthesis of H$_2$O$_2$ [1,2]. Hydrogenation of quinoid system of eAQ to the aromatic hydroquinone one (2-ethylanthracen-9,10-diol, eAQH$_2$) is followed by the oxidation (Scheme 1) yielding hydrogen peroxide with regeneration of the starting eAQ. The target product, eAQH$_2$ formed in the quinone–hydroquinone stage undergoes further hydrogenation to give various products [3–6].

Hydrogenation of aromatic rings produces partially and fully saturated products, 2-ethyl-5,6,7,8-tetrahydroanthracene-9,10-diol (H$_4$eAQH$_2$) and 2-ethyl-1,2,3,4,5,6,7,8-octahydroanthracene-9,10-diol (H$_8$eAQH$_2$), respectively. The first product, H$_4$eAQH$_2$, is the only desirable compound among all of by-products formed because its oxidation produces H$_2$O$_2$. The formation of fully saturated non-active H$_8$eAQH$_2$ was observed only after the complete transformation of eAQ to eAQH$_2$ [5,7]. Hydrogenation of C–O in eAQH$_2$ produced the hydrogenolysis-deriving products. According to the mechanism proposed for the reduction of anthraquinone as well as eAQ, the hydrogenolytic process can follow the reaction pathway shown in Scheme 2 [3–5]. The hydrogenation of eAQH$_2$ (I) can proceed along two reaction pathways, both giving the same intermediate product, 2-ethyl-9,10-dihydro-9,10-dihydroxyanthracene (INT, III) [4,5]. One consists of the successive steps, tautomerization of hydroquinone to 2-ethyl-10-hydroxy-9-anthrone (OXO, II) isomer, followed by the reduction of the latter to the intermediate product INT. The second route is direct hydrogenation of eAQH$_2$
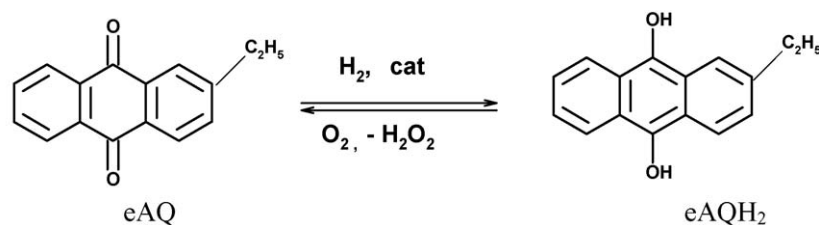
Scheme 1. Quinone–hydroquinone stage.

to give INT. Transformation of INT (III) by dehydratation yields 2-ethylanthrone (eAN, two isomers 2-ethyl-9-anthrone, 2-ethyl-10-anthrone [6]) and subsequently 2-ethylanthracene (eANT). Subsequent hydrogenation of phenyl ring in eAN and eANT produces 2-ethyltetrahydroanthrone (H$_4$eAN, two isomers) and 2-ethyltetrahydroanthracene (H$_4$eANT), respectively. All of hydrogenolysis-deriving products are termed "degradation products" because they are not oxidized to form H$_2$O$_2$ and thus represent a loss of the starting eAQ. Moreover, with degradation products a slow and irreversible deactivation of palladium catalysts in anthraquinone process is correlated [8].

Bulky molecules (dimers), products of anthraquinone molecules condensation are considered as the most probable species leading to catalysts deactivation. It has also been observed that moisture present in eAQ solution due to hydrogen peroxide extraction has an effect on deactivation of Pd/Al$_2$O$_3$ catalysts [8]. The presence of greater amount of water (water suspension) resulted in a reversible deactivation however, in opinion of authors an influence of moisture on slow and irreversible poisoning of palladium catalyst cannot also be excluded [8]. Hence, the role of humidity in the hydrogenation of eAQ and especially in degradation process is an important problem and this role is the object of the present work. It is well known that humidity has a strong effect on palladium catalysts activity in the quinone–hydroquinone stage [8–10]. The increase in activity almost proportional to the water additives was observed [9]. Much more complex effects were observed on studying the influence of humidity on the consumption of eAQH$_2$, primary and desirable product and thus on the formation of degradation products [10]. In the presence of Pd/Al$_2$O$_3$

humidity influenced the reactions concentrating on carbonyl groups but had no effect on the hydrogenation of aromatic ring in eAQH$_2$. Moreover, the effect of humidity varied depending on the type of alkaline reagent used for such Pd/Al$_2$O$_3$ catalysts preparation. Pd/Al$_2$O$_3$ were synthesised with a well-established procedure commonly used to prepare the catalysts for anthraquinone process [11–13]. In this procedure palladium hydroxide is precipitated onto support pre-impregnated with alkaline reagent, NaH$_2$PO$_4$ and Na$_2$SiO$_3$ in previous studies [10]. However, high complexity of the observed effects makes difficult the explanation of the role of humidity. It has also been previously established that water and NaOH when introduced to these Pd/Al$_2$O$_3$ catalysts markedly enhanced their deactivation during the hydrogenation run [10]. Systematic studies of the role of humidity in eAQ hydrogenation and particularly in the formation of degradation products are therefore undertaken in the present work using silica supported catalysts (0.5% Pd/SiO$_2$). The objective is to clarify the role of humidity in individual reactions involved during the consumption of eAQH$_2$ and to correlate the effect of water with the properties of these catalysts. They were prepared with the same precipitation method as the one previously used to prepare Pd/Al$_2$O$_3$ catalysts. In the present studies, however, Na$_2$CO$_3$, most frequently applied and preferred alkaline reagent [13] is used for pre-impregnation of silica support. Three catalysts differing in the content of Na$_2$CO$_3$ and thus in the alkalinity are used in the hydrogenation of eAQ carried out in "standard" and subsequently in "wet" systems differing in the content of humidity. The influence of humidity on the first quinone–hydroquinone stage and on further transformation of eAQH$_2$, primary and desirable product is studied in these systems.
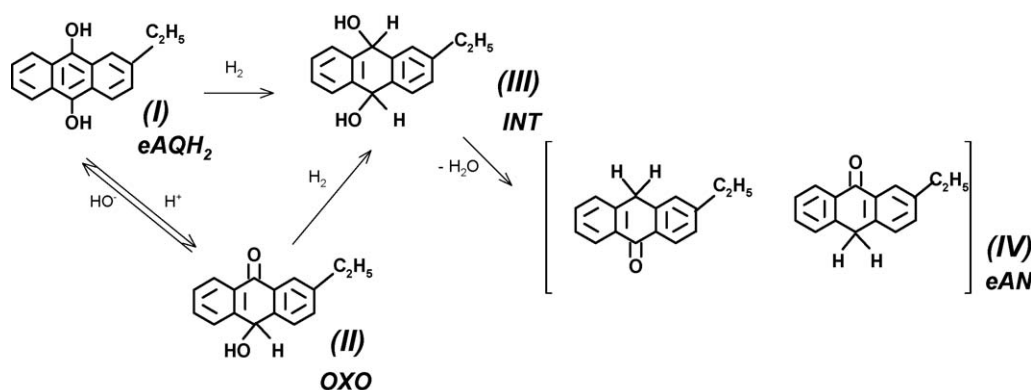

Scheme 2. Reaction pattern during the hydrogenation of hydroquinone form (eAQH$_2$).

Table 1
Properties of catalysts

Sample	Specific surface area (m^2/g)	CO_3^{2-} (wt.%)	pH of catalyst slurry	Content of water in wet catalyst (wt.%)
SiO_2	156			
Pd-1	175	0.39	9.5	13.3
Pd-2	172	0.30	7.9	11.54
Pd-3	173	0.015	7.0	7.7

2. Experimental

2.1. Preparation of catalysts

Silica support (dried for 16 at 120 °C) was at first treated with an excess of Na_2CO_3 solution (0.05 mol/dm³, 60 ml of solution per 10 g of support). Then, the obtained material was impregnated with Pd^{2+} solution (0.0408 g $PdCl_2$ and 0.162 g NaCl in 10 ml of solution, pH $\sim$ 3–4) by evaporating liquid phase at slow heating of catalyst (at 60 °C). Then, the sample was washed with water only until the Cl^- ions were removed and dried at room temperature (initial Pd-1 catalyst). The Pd-1 catalyst was treated with water to remove a portion of Na_2CO_3 introduced during the catalyst preparation (Pd-2 catalyst). Subsequent washing of Pd-2 sample with several portion of hot distilled water gives Pd-3 sample containing only a very low content of Na_2CO_3 (Table 1). Stepwise lowering of Na_2CO_3 content is also evidenced by the experiments in which pH of the catalysts slurry was measured (see characterization of catalysts).

Prior the hydrogenation test in so termed "standard conditions" the catalysts were dried for 16 h at 120 °C (Pd-1, Pd-2 and Pd-3 standard catalysts). In order to study the effect of humidity, dried catalysts were saturated with water vapour in desiccator for 48 h. Humidification resulted in the increase in samples mass. The content of moisture determined in catalysts after this treatment is given in Table 1.

Reduction of catalysts was performed in the reactor immediately before the hydrogenation test. The catalyst wetted with eAQ solution was reduced in flowing hydrogen for 30 min at temperature 62 °C.

2.2. Characterization of catalysts

Surface area measurements were carried out by Quantachrome Autosorb Gas Sorption System using sorption of nitrogen at 77 K. The content of CO_3^{2-} was determined by Elemental analyser Euro EA 300 (Euro Vector). The pH of the aqueous catalyst slurry was measured with a pH-meter, according to the procedure reported in [14]. Slurries were prepared by placing 1 g of catalyst and 25 cm³ of pre-boiled distilled water in a closed vessel (to avoid dissolution of atmospheric CO_2) and thoroughly mixed with heating and allowed to boil for 3 min. Then the solid was separated by filtering the hot slurry, and the clear liquid was allowed to cool to room temperature in a closed bottle. Finally, the pH values of liquid were measured (the error in the measurements was ca. 0.02 pH units).

2.3. Hydrogenation experiments and analytical procedure

The activity test was carried out in agitated glass reactor at atmospheric pressure of hydrogen, temperature 62 °C. The course of hydrogenation was followed by measuring hydrogen uptake as a function of reaction time. A mixture (volume ratio 1:1) 2-octanol and xylene (mixture of isomers) was used as the solvent and the concentration of eAQ was 20 g/dm³. The solvents (Aldrich) were of analytical grade. They were additionally dried over molecular sieve 4A.

In hydrogenation experiments carried out in "standard conditions", dried Pd-1, Pd-2 and Pd-3 catalysts and eAQ solution containing dried solvents were used. Hydrogenation tests, termed "wet conditions" were carried out in the presence of catalysts saturated with water vapour using eAQ solution also saturated with water. The solution of eAQ was shaken with distilled water in a separator and allowed to stay for 24 h. Then the layers were separated and organic phase was used in the hydrogenation experiments. The same content of humidity was determined by MCA 1410 Moisture Content Analyser Fibro System (Sweden) in water-saturated eAQ solution and in water saturated 2-octanol (5.05 wt.% [15]). This method showed two-times lower content of humidity in the "standard" eAQ solution containing dried solvents. A separate measurements performed for this standard solution (humidification of solution was carried out by stepwise injection of know portions of water with a microsyringe (20 μl) into 50 cm³ of this solution) showed content of humidity 2.46 wt.%, nearly equal to one half of the water solubility in 2-octanol [15].

Two series of hydrogenation experiments were performed. In the first concentrating on the quinone–hydroquinone stage the hydrogenation tests were carried out at low concentration of catalyst (0.04 g in 10 cm³ of eAQ solution) and the reaction was stopped at $\beta = 1$ ($\beta = nH_2/n^0$ (eAQ)) e.g. after the consumption of 1 equiv. of hydrogen. After catalyst filtration the solution was extracted with water and the content of H_2O_2 formed upon oxidation of eAQH$_2$ was determined by titration with $KMnO_4$ solution. From the number of H_2O_2 moles the selectivity of quinone–hydroquinone stage (eAQ to eAQH$_2$ reduction) was calculated as follows:

$$S = \frac{n(H_2O_2)}{n(H_2)} \times 100\%.$$

As a measure of catalysts activity in the quinone–hydroquinone stage the initial rate of hydrogen uptake is assumed.

In the second series, the hydrogenation of eAQH$_2$ (hydroquinone form) was studied. The experiment was performed at

high content of catalyst (0.28 g in 20 cm^3 of eAQ solution) and the reaction was carried out up to the consumption of ca. 2–3 mol H$_2$/n^0(eAQ) (β = 2–3). The samples of solution were taken from reactor at appropriate time intervals (15–20 min) and the composition of solution was analysed by HPLC and GC methods. It should be noticed that the hydroquinone forms eAQH$_2$, H$_4$eAQH$_2$ (present in the solution taken from the reactor) are not stable in contact with air because they react spontaneously and quantitatively with atmospheric oxygen, thus forming hydrogen peroxide and regenerating quinones eAQ and H$_4$eAQ respectively. In standard procedure, the reaction with oxygen was complete even before chromatographic analysis. It has been therefore assumed, that the number of eAQH$_2$ and H$_4$eAQH$_2$ moles in the hydrogenated solution was equal to the number of eAQ and H$_4$eAQ determined in the re-oxidized solution.

The contents of eAQ $\{n^t(\text{eAQ})\}$ and H$_4$eAQ $\{n^t(\text{H}_4\text{eAQ})\}$ at time t were analysed in a re-oxidized solution by HPLC. The analysis was performed using a chromatograph (Knauer) with UV detector (254 nm), column 10 cm long, SiO$_2$ fraction d_p = 5 μm, eluent: 2% isopropyl ether + 0.2% diglyme in heptane. The sum of eAQ and H$_4$eAQ moles was smaller that the initial content of eAQ. This difference was assumed as a cumulative content of degradation products (degr) given by a mass:

$$\text{degr} = n^0(\text{eAQ}) - n^t(\text{eAQ}) - n^t(\text{H}_4\,\text{eAQ}).$$

Compounds termed "degradation products" were analysed by GC–MS method using Perkin-Elmer Auto System XL, capillary column PE-5 MS, 0.25 μm × 0.25 mm × 30 m long, isothermal run 200 °C, flow rate of He gas 1 ml/min. From the GC–MS analysis the content of 2-ethylanthrone (eAN) was also determined. Reproducibility of the chromatographic analysis was ca. 5%.

3. Results and discussion

3.1. Characterization of catalysts

Table 1 lists the main properties of the catalysts. Successive rinsing of initial Pd-1 catalyst with water resulted in stepwise removing of not reacted Na$_2$CO$_3$ from 0.39 wt.% in the Pd-1 up to 0.015 wt.% in the final Pd-3 catalyst. Removing of Na$_2$CO$_3$ is also evidenced by lowering the pH value of catalyst slurry from pH 9.5 (initial Pd-1 sample) to pH 7 for the less alkaline Pd-3 catalyst. Low loading of Pd (0.5 wt.% Pd) in the used catalysts makes difficult detection of TEM images of satisfactory good quality. Nevertheless, well dispersed Pd was observed in all three catalysts thus showing that removing of Na$_2$CO$_3$ did not essentially influence dispersion of Pd in the reduced catalysts.

3.2. Hydrogenation experiments

3.2.1. Quinone–hydroquinone stage

From the hydrogenation experiments performed at low concentration of catalyst (0.04 g in 10 ml of eAQ solution) the first quinone–hydroquinone stage (eAQ to eAQH$_2$ reduction) is char-
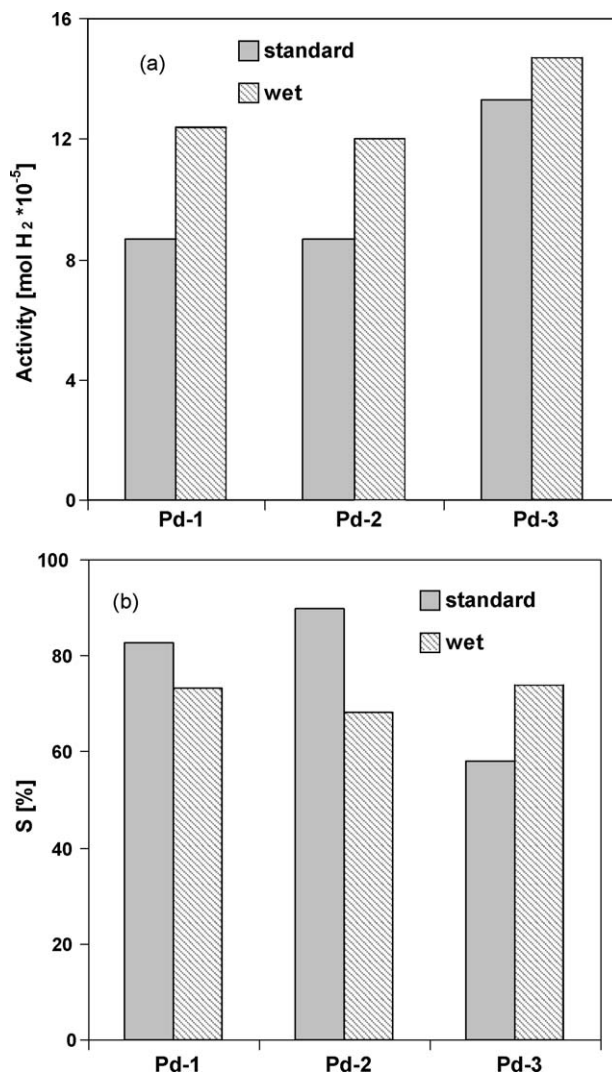

Fig. 1. Activity (mol H$_2$ × 10^{-5}/min) (a) and selectivity (%) (b) of Pd-1, Pd-2 and Pd-3 catalysts in the first quinone–hydroquinone stage.

acterized. In these experiments the hydrogenation is interrupted after the consumption of one equivalent of hydrogen (β = 1). HPLC and GC–MS analyses registered in final solutions (at β = 1) showed only slightly lower intensity of eAQ peak while in no case the peak of H$_4$eAQ was observed. Hence, H$_2$O$_2$ determined after oxidation of these solutions was formed by oxidation of eAQH$_2$ only and the content of produced H$_2$O$_2$ was used to calculate the selectivity of quinone–hydroquinone stage. The obtained data of catalysts activity and selectivity in the first quinone–hydroquinone stage are reported in Fig. 1.

In "standard conditions" the activities of more alkaline Pd-1 and Pd-2 catalysts are comparable, but both are slightly lower than that of less-alkaline Pd-3 catalyst. The selectivity of eAQ to eAQH$_2$ reduction attained higher level (83–90%) on more alkaline Pd-1 and Pd-2 catalysts. This observation is very consistent with the literature data concerning catalytic reduction of aromatic ketones [16].

Humidity leads to the increase in activity of all three catalysts and in "wet conditions" identical tendency as the one prior

the humidification is preserved (Fig. 1a). The activities of more alkaline Pd-1 and Pd-2 catalysts are again comparable and lower than that of Pd-3 sample. The role of humidity in selectivity of quinone–hydroquinone stage varies, depending on alkalinity of catalysts (Fig. 1b). In the case of more alkaline Pd-1 and Pd-2 catalysts the selectivity decreases, whereas it grows in the case of less alkaline Pd-3 catalyst. As a consequence, in "wet conditions" the selectivities of quinone–hydroquinone stage are practically the same on all three catalysts. This result indicates that alkaline properties of catalyst have no essential role in the selectivity of eAQ reduction when the system is saturated with water. The role of these properties, however, is significant when the content of humidity is lower, evidenced by observations in "standard systems".

3.2.2. Hydrogenation of hydroquinone form eAQH$_2$

In order to get more light on the role of humidity in the eAQH$_2$ consumption, hydrogenation experiments were carried out up to the consumption of 2–3 mol of H$_2$/1 eAQ mol in "standard" and subsequently in "wet" systems. The quinone–hydroquinone stage, the fundamental reaction is definitely faster process compared to all other reactions resulting in the consumption of hydroquinone. Since palladium catalysts are very active in this reaction it cannot be excluded that mass transport processes are to some extent influenced the quinone–hydroquinone stage, preceding the process of eAQH$_2$ hydrogenation. At almost full completion of the first quinone–hydroquinone stage a readily discernable break at $\beta \sim 1$ (ca. 167×10^{-5} mol H$_2$) appears (Fig. 2). Further hydrogenation occurring at relatively low rate resulted in the consumption of hydroquinone (eAQH$_2$) and studies are concentrated on this process.

The decrease in eAQH$_2$ content (mol%) against reaction time is plotted in Fig. 3 and products distribution curves are reported in Figs. 4 and 5 for hydrogenation experiments carried out up to $\beta \sim 2$–3. The cumulative content of degradation products (degr), the content of H$_4$eAQH$_2$ and eAN (sum of isomers) against conversion of hydroquinone (eAQH$_2$) are there plotted. As the consumption of eAQH$_2$ progresses the contents of H$_4$eAQH$_2$, degradation products and eAN systematically increase. It can be clearly observable in Figs. 4 and 5 that degradation products are slowly transformed to eAN and as the reaction progresses this transformation becomes almost complete. Identical effect was observed in our previous studies devoted to identification of degradation products. We observed in these studies that in the initial stage of eAQH$_2$ consumption, eAN (two isomers, identically to observation in Ref. [6]), OXO and INT products were formed as the only degradation products. Other by-products such as 2-ethyl-5,6,7,8-tetrahydro-9-anthrone and/or 2-ethyl-5,6,7,8-tetrahydro-10-anthrone (H$_4$eAN), 2-ethylanthracene (eANT) and 2-ethyl-5,6,7,8-tetrahydroanthracene (H$_4$eANT) were formed only when more than 70–80% of eAQH$_2$ was consumed.

It should be pointed out that chromatographic peaks of OXO and INT were not satisfactory separated from the peak of eAQ especially at high content of eAQ [5]. Quantitative analysis of individual reagents, OXO and INT was therefore practically impossible (although INT was prepared and chromatograph-
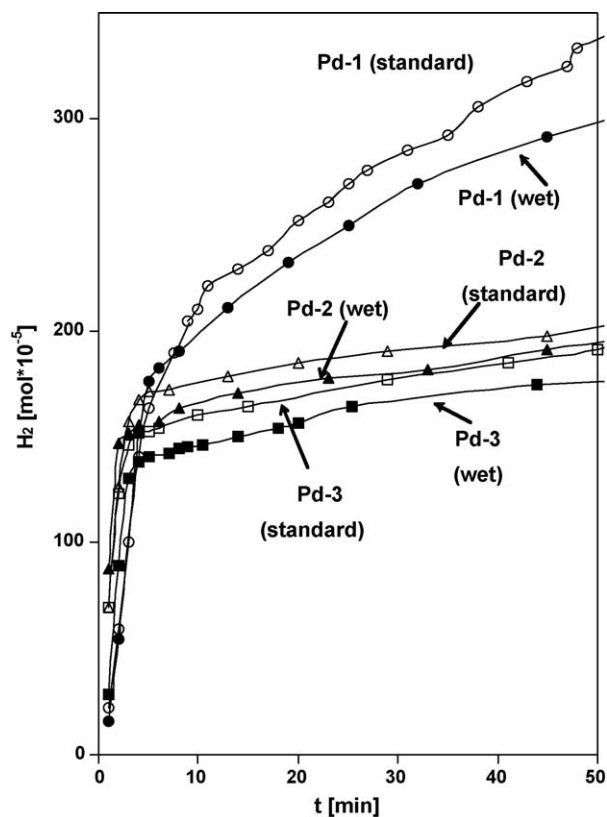

Fig. 2. The number of hydrogen moles consumed as a function of the reaction time (initial number n^0(eAQ) = 167×10^{-5} mol in the reactor). Hydrogenation carried out in conditions 20 ml of eAQ solution (20 g/dm^3), 0.28 g of catalyst, 62 °C.

ically analysed [5]). Because in the initial stage of eAQH$_2$ consumption, degradation products were composed of OXO, INT and eAN only, the sum of OXO + INT was taken into consideration. This sum was calculated as the difference between the cumulative content of degradation products (degr) and that of eAN. Identical effects are observed in the present studies. GC
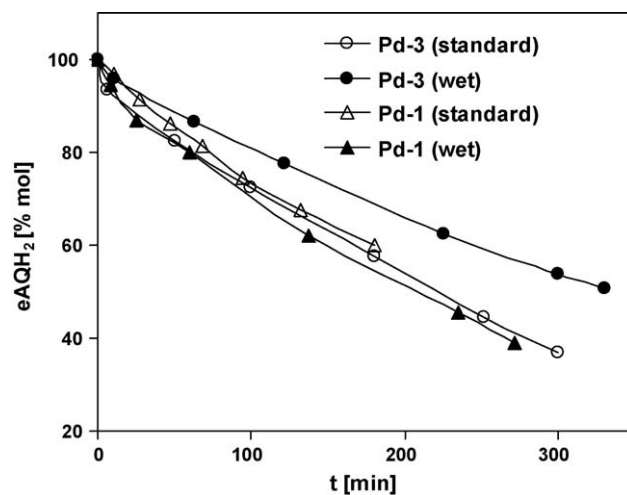

Fig. 3. Decrease in the content of hydroquinone (eAQH$_2$) against reaction time. Hydrogenation carried out on Pd-1 and Pd-3 catalysts in "standard" and "wet" systems (conditions 20 ml of eAQ solution (20 g/dm^3), 0.28 g of catalyst, 62 °C).
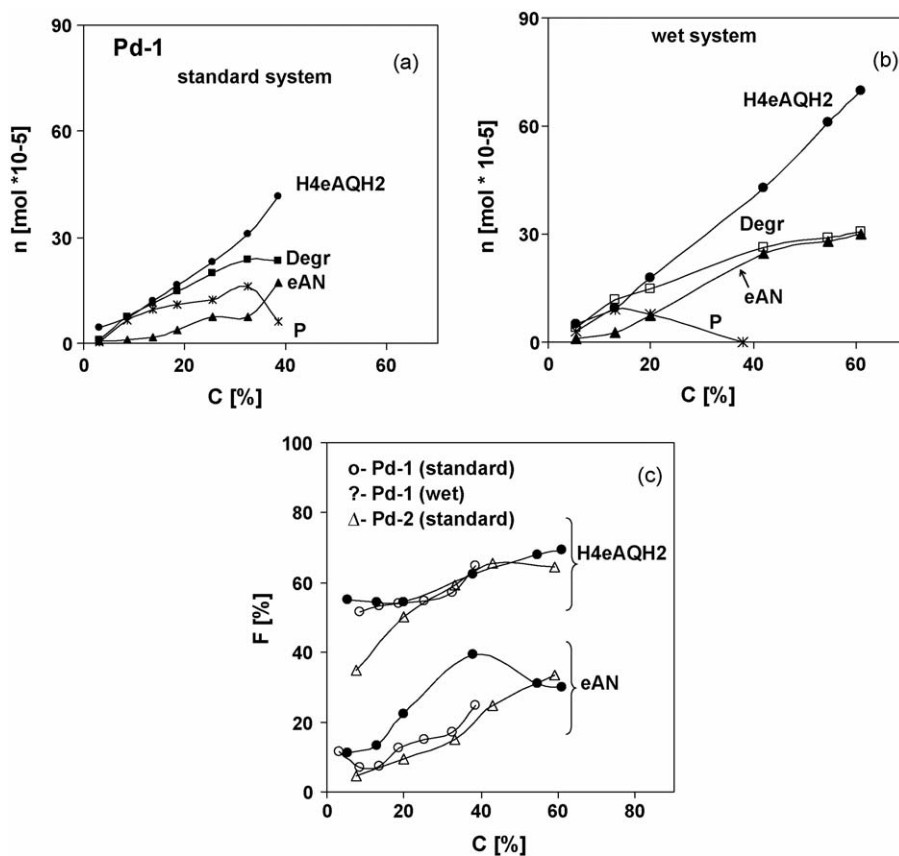
Fig. 4. Hydrogenation of eAQH$_2$ over Pd-1 catalyst. The content of H$_4$eAQH$_2$, degradation products (degr), 2-ethylanthrone (eAN) and intermediate product (P) against hydroquinone (eAQH$_2$) conversion (a) "standard" and (b) "wet" conditions. (c) Fractions of hydroquinone (eAQH$_2$) transformed to H$_4$eAQH$_2$ (F-H$_4$) and to eAN (F-eAN) in "standard" and "wet" conditions.

analysis registered in the initial stage of eAQH$_2$ consumption (up to ca. 40% conversion) showed besides the peak of not-reacted eAQH$_2$, the peaks of eAN and H$_4$eAQH$_2$ only.

However, in view of Scheme 2 and previous results [5,6] the presence of OXO tautomer and intermediate product INT should be taken into account, because the cumulative content of degradation products excided that of eAN. The sum of their contents (OXO + INT) termed P, is calculated with the same method as used in our previous studies [5].

Figs. 4 and 5 show that the content of intermediate P (INT + OXO) is high in the beginning of eAQH$_2$ consumption and this content slowly decreases during the reaction. At ca. 40–50% conversion of eAQH$_2$, almost all intermediate product P is transformed to eAN. Degradation products are then composed mostly of eAN. Such an effect is observed on all three catalysts in both "standard" and "wet" conditions.

In order to examine the effects of alkalinity and humidity the fraction (%) of eAQH$_2$ reacted by phenyl ring saturation to give H$_4$eAQH$_2$ (F-H$_4$) and the fraction of eAQH$_2$ reacted by hydrogenolytic reaction leading to eAN (F-eAN) against conversion of hydroquinone (II) are considered. These relationships for reaction in "standard" and "wet" systems are plotted in Figs. 4c and 5c. The fraction of eAQH$_2$ transformed to H$_4$eAQH$_2$ is calculated as the ratio of the moles of H$_4$eAQH$_2$ produced to the moles of eAQH$_2$ consumed ($\times$100%) from the very beginning of the hydrogenation experiment. From the number of eAN

moles the fraction of hydroquinone transformed to eAN is calculated.

3.2.3. Effect of alkaline properties

It is observed that reactivity of catalysts in the hydrogenation of eAQH$_2$ varies depending of their alkaline properties. The reactivities of more alkaline Pd-1 and Pd-2 catalysts are very similar but they substantially differ from that of less alkaline Pd-3 catalyst. On the former, more alkaline catalysts during the whole hydrogenation process stable and practically the same fractions of eAQH$_2$ (50–60%) are reacted to H$_4$eAQH$_2$ (Fig. 4c). On the other hand, on less-alkaline Pd-3 catalyst, only very low fraction of hydroquinone is reacted to H$_4$eAQH$_2$ (Fig. 5c) from the very beginning of eAQH$_2$ consumption. This fraction slowly grows as the reaction proceeds finally reaching as high level as 82%. It should be observed that this level is evidently higher than that offered by more alkaline Pd-1 and Pd-2 catalysts (50–60%) thus showing higher tendency to phenyl ring saturation in the case of less-alkaline Pd-3 catalyst.

On all three catalysts, degradation products are transformed to eAN, however this transformation is not complete, because the intermediate product P is observed during the whole hydrogenation experiments (Figs. 4a and 5a). Slightly higher fraction of eAQH$_2$ reacted to eAN on more alkaline catalysts (Fig. 4a) indicates that alkaline properties have also a role in reactions transforming the intermediate P to eAN.
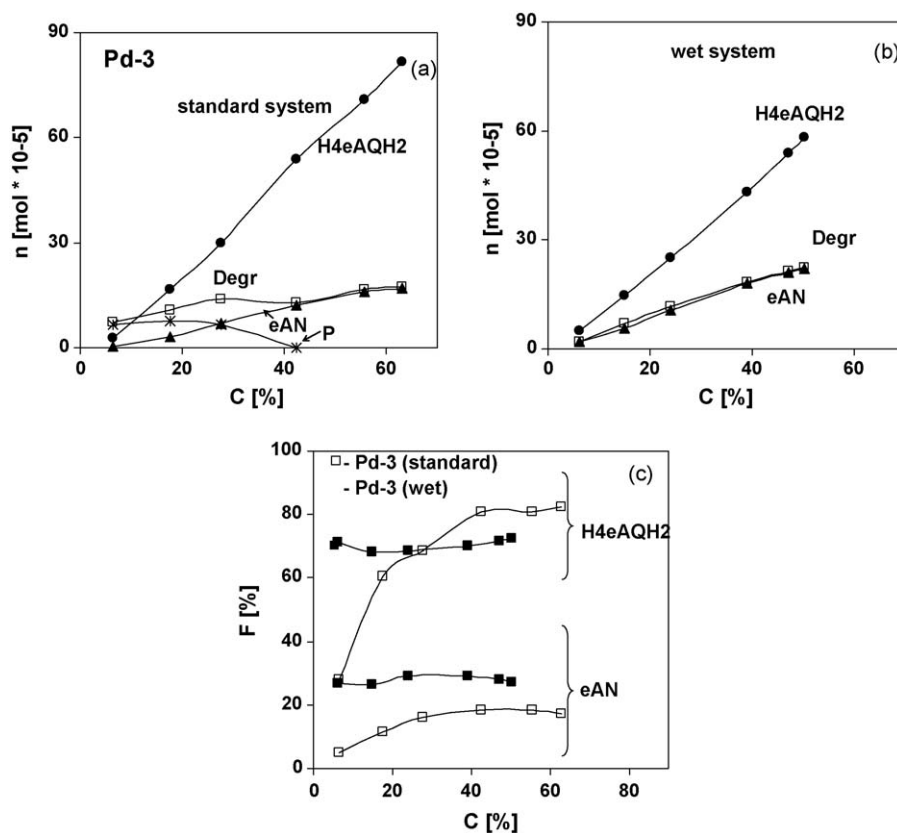
Fig. 5. Hydrogenation of eAQH$_2$ over Pd-3 catalyst. The content of H$_4$eAQH$_2$, degradation products (degr), 2-ethylanthrone (eAN) and intermediate product (P) against hydroquinone (eAQH$_2$) conversion (a) "standard " and (b) "wet" conditions. (c) Fractions of hydroquinone (eAQH$_2$) transformed to H$_4$eAQH$_2$ (F-H$_4$) and to eAN (F-eAN) in "standard" and "wet" conditions.

3.2.4. Effect of humidity

Fig. 3 shows the influence of humidity on catalysts activity in the consumption of hydroquinone (eAQH$_2$). Different effects can be recognized for more and less alkaline Pd-1 and Pd-3 catalysts, respectively. On the former, highly alkaline catalyst, the curves in "standard" and "wet" systems are almost parallel thus showing no effect of humidity on their activity in the consumption of eAQH$_2$. The curves differ only slightly in the very beginning of the eAQH$_2$ consumption. On the other hand, humidity has an effect on activity of less alkaline Pd-3 catalyst (Fig. 3). Much slower decrease in the content of eAQH$_2$ (hydroquinone) observed in "wet system" proves that humidity has a profitable effect on the consumption of desirable product, eAQH$_2$.

The role of humidity in directing the consumption of eAQH$_2$ also varies depending on alkaline properties of catalyst. On more alkaline Pd-1 and Pd-2 catalysts, humidity did not influence the transformation of eAQH$_2$ by phenyl ring saturation and thus did not affect the total content of degradation products. As Fig. 4c shows the F-H$_4$ curves in "standard" and "wet" systems are closed. Identical effect has been previously observed on Pd/Al$_2$O$_3$ catalysts [10]. It can be therefore concluded that humidity has no essential influence on catalyst activity in eAQH$_2$ consumption as well as on the directing the consumption of hydroquinone eAQH$_2$ in the case of highly alkaline medium.

On the other hand, the influence of humidity can clearly be seen in the case of less alkaline Pd-3 catalyst. This influence is evidenced by a drastic change in the shape of F-H$_4$ plot invoked by humidity (Fig. 5c). Strong increase in the fraction of eAQH$_2$ reacted by phenyl ring saturation is observed from the very beginning of eAQH$_2$ consumption in "wet conditions".

As a consequence the fraction of eAQH$_2$ reacted by phenyl ring saturation is very stable during the whole hydrogenation carried out in "wet system". Although this fraction is slightly lower (70%) compared to that in "standard conditions" (82%) both are higher compared to those offered by highly alkaline Pd-1 and Pd-2 catalysts (50–60%).

Interestingly, on all three catalysts, humidity considerably enhances the formation of eAN evidenced by higher fraction of eAQH$_2$ transformed to eAN in "wet conditions" (Figs. 4b and 5b). However the effect of humidity varies depending on alkaline properties of Pd/SiO$_2$ catalysts. On less alkaline Pd-3 catalyst the complete transformation of intermediate P to eAN is observed during the whole process of eAQH$_2$ consumption (Fig. 5b). On more alkaline Pd-1 catalyst, the transformation of P to eAN is enhanced to a lower extent because this transformation is complete only when more hydroquinone (ca. 40% eAQH$_2$ conversion) is reacted (Fig. 4b).

It has been reported in number of papers describing the hydrogenation of phenols and its derivatives [17–19] that the acid–base

properties of supported Pd catalysts strongly influence the mode of reactants adsorption thus being responsible for directing the selectivity of process. Generally, adsorption is considered as occurring via the aromatic π-electron system and/or the OH hydroxyl groups. It has been observed that reagent–metal interaction via the hydroxyl substituent promotes hydrogenolysis of reactant molecules. Number of variables can be responsible for the mode of reactant molecule adsorption and among them polarity of system. Product distribution observed in hydrogenation of paracetamol (molecule with OH and acetamide substituents) suggests favoured adsorption in a non-planar mode when the polarity increases [19] with consequent facilitation of C–OH hydrogenolysis. Similar conclusions have been formulated with respect to the role of water in selectivity of acetophenone hydrogenation [20]. The authors concluded that dielectric dipole of water molecules adsorbed to the metallic surface favoured the adsorption of carbonyl groups in acetophenone while the ring adsorption was more inhibited. As a consequence, reactivity of catalyst in the hydrogenation of C=O and aromatic ring and thus the selectivity of acetophenone varied depending on the presence of water.

Recently, the catalyst based on Ni–Cr–B alloys exhibiting almost complete inhibition of $eAQH_2$ hydroganation has been reported [21]. This exclusive selectivity of quinone–hydroquinone stage has been ascribed to a suitable adsorption configuration for the activation and hydrogenation of C=O in eAQ relative to that which is required for the hydrogenation of aromatic ring. This conclusion is very consistent with the model reported by Santacesaria et al. [7] who studied the kinetics of the hydrogenation of aromatic rings of eAQ. The tautomerization stage of hydroquinone has also been taken into consideration by the authors. It has been established [7] that dual site mechanism well explains this process. In this mechanism, the molecule of hydroquinone and two hydrogen atoms bonded on two adjacent Pd-centres are reacted in the hydrogenation of aromatic ring. It can be therefore expected that adsorption configuration of individual reagents $eAQH_2$, OXO and especially INT, precursor of eAN will be an important factor for its further transformation.

It is observed that on less alkaline Pd-3 catalyst in "standard system" the selectivity of quinone–hydroquinone stage is relatively low (54%) and from the very beginning of $eAQH_2$ consumption the fraction of hydroquinone reacted by phenyl ring saturation is low whereas dominating are the hydrogenolytic reactions. This situation is dramatically changed due to humidity. Phenyl ring saturation becomes then dominating process in the whole $eAQH_2$ consumption process, as well as evidently grows the selectivity of eAQ to $eAQH_2$ reduction. These effects can be ascribed to the influence of humidity on tautomerization equilibrium in $eAQH_2$–OXO system (Scheme 2). It can be expected that on less alkaline Pd-3 catalyst, this equilibrium is more shifted to OXO tautomer compared to highly alkaline Pd-1 catalyst. When OXO is present already at the beginning of $eAQH_2$ hydrogenation, the possibility of H_4eAQH_2 formation is low. In fact, a part of hydroquinone reacted by phenyl ring saturation is very small (Fig. 5a). As the reaction progresses, the content of hydroquinone form ($eAQH_2$) gradually decreases

as well as decreases that of OXO tautomer and at high $eAQH_2$ conversion the fraction of hydroquinone reacted to H_4eAQH_2 stabilizes. This effect is not observed on more alkaline Pd-1 catalyst, maybe because in highly alkaline conditions the tautomerization to OXO isomer is considerably prevented and the hydroquinone form $eAQH_2$ (I) is exclusively present. As a consequence, on more alkaline Pd-1 catalyst direct transformation of $eAQH_2$ to the intermediate product INT can be dominating from the very beginning of reaction resulting in almost stable fraction of $eAQH_2$ reacted by phenyl ring saturation during the whole process (Fig. 4c). This stable fraction however, is only slightly higher (50–60%) or even comparable to that reacted by hydrogenolytic reactions yielding degradation products. Hence, no preferential reaction path in the hydrogenation of $eAQH_2$ is observed in highly alkaline medium. Relatively high content of $eAQH_2$ reacted by hydrogenolytic reactions on Pd-1 catalyst suggests that adsorption of $eAQH_2$ in the carbonyl group configuration is more preferred in these conditions than in the case of less alkaline Pd-3 catalyst. This observation is proved by higher ability of the latter Pd-3 catalyst for phenyl ring saturation (70–82%) observed either in "standard" and "wet" systems (Fig. 5c). Moreover, in highly alkaline conditions, humidity did not essentially influence the process of $eAQH_2$ consumption. Hence, humidity did not affect mode/geometry of $eAQH_2$ adsorption in the case of highly alkaline medium when the adsorption in carbonyl group mode appears to relatively high extent.

On all three catalysts humidity enhances the formation of eAN at the expense of intermediate product P, however to various extents. Intermediate P is completely reacted to eAN on less alkaline Pd-3 catalyst, whereas more alkaline medium in Pd-1 catalyst retards to some extent this process. Besides such a difference, it can be concluded, that humidity evidently facilitated the formation of 2-ethylanthrone (eAN), the molecule exhibiting especially high ability for dimerization.

Hence, humidity has an effect on consecutive reactions transforming hydroquinone $eAQH_2$ via OXO tautomer to intermediate product INT and finally to eAN and the influence of humidity varies depending on alkaline properties of Pd/SiO_2 catalysts.

It should be noticed that changes in reactivity of Pd/SiO_2 catalysts invoked by humidity differ to some extent from those on Pd/Al_2O_3 catalysts [10]. In previous studies carried out on Pd/Al_2O_3 catalysts the role of humidity was examined during the quinone–hydroquinone stage when starting quinone form (eAQ) was present in the reaction medium. In these conditions humidity inhibited the consumption of $eAQH_2$ thus leading to more selective reduction of eAQ. Identical effect is observed in the present work, on less-alkaline Pd-3 catalyst. However, when the reduction of eAQ to $eAQH_2$ attained ca. 80%, a marked acceleration of $eAQH_2$ consuming reactions started and in consequence on water pre-treated Pd/Al_2O_3 catalysts much higher content of degradation products was formed at the completeness of the quinone–hydroquinone stage [10]. Moreover, it cannot be excluded that essential difference in acid–base properties of alumina and silica supports is also responsible for the observed effects.

4. Conclusions

The role of humidity in the consumption of eAQH$_2$, primary and desirable product varies depending on alkaline properties of 0.5% Pd/SiO$_2$ catalysts. No effect of humidity on the whole process of eAQH$_2$ hydrogenation is observed on more alkaline Pd-1 and Pd-2 catalysts. On these catalysts the fractions of eAQH$_2$ reacted by phenyl ring saturation and by hydrogenolytic reactions are not change due to humidification of the systems. Humidity influences the process of eAQH$_2$ transformation on less alkaline Pd-3 catalyst. Activity of Pd-3 catalyst for the consumption of eAQH$_2$, a desirable product decreases in "wet conditions" as well as equilibrium in eAQH$_2$–OXO tautomer is more shifted towards hydroquinone form. In the presence of all three catalysts humidity facilitates the transformation of intermediate product INT to eAN. These effects are related with adsorption configuration of reagents, eAQH$_2$, OXO tautomer and INT, precursor of eAN. Facilitated adsorption in the carbonyl group-bonded configuration makes easier the transformation of eAQH$_2$ by hydrogenolysis reactions as well as the formation of eAN.

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