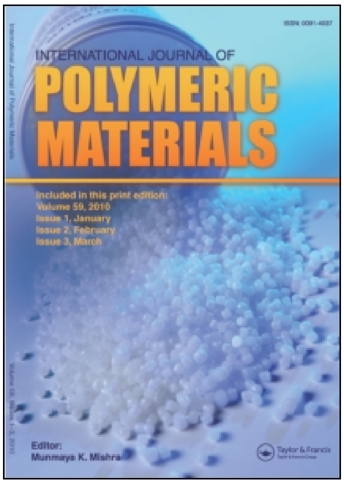

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Influence of Swelling of the Palladium Containing Polymers on their Catalytical Activity in Hydrogenation

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Influence of Swelling of the Palladium Containing Polymers on their Catalytical Activity in Hydrogenation

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Hydrogenation of nitrobenzene in the presence of palladium containing polymer are investigated. Found quantitative link between the catalyzed reaction rate constants and the swelling values of the polymer macroligand in solvents is discussed.

Keywords: Swelling; polymers; palladium; hydrogenation

RESULTS AND DISCUSSION

Metal containing ionites are widely used as catalysts of the organic synthesis reactions [1] including hydrogenation [2]. This polymers are accessible and it is easy to synthesize metallopolymers on their base (Scheme (I)):

$$P - X + ML_n \underset{-mL}{\rightarrow} P - XML_{n-m} \underset{-L}{\overset{[H]}{\rightarrow}} P - XM^{(0)} \qquad \text{(I)},$$

where P – the polymer matrix of the ionite, X – functional groups of the polymer matrix of the ionite, L – ligand of salt or of the transitional metal complex.

Complexes of transitional metal immobilized in the polymer matrix are forming with reaction of the ligand or ion exchange at first. Then they are reducing with $NaBH_4$, molecular hydrogen or other reducers.

As a result particles of zerovalent metal (clasters with 5 – 7 atoms of palladium [2]) binding with the polymer matrix because of partial transfer of the electron density from atoms of functional groups onto metal are forming.

When studying catalytic reactions including hydrogenation influence of solvent onto rate and selectivity of the process is noted frequently. But attempts to determine "the solvent effect" quantitatively *i.e.*, to find correlations between dielectric permeability or donor (acceptor) properties or other characteristics of the solvents and parameters of the catalytic reaction are undertaken very seldom. In case of the metal containing polymers specific influence of the solvents onto the hydrogenation rate should be expected because of possible swelling of the polymer matrix in the reaction mixture. Detailed analysis of the literature data was made in [2, 3]. It should be noted that in literature there are no quantitative values of influence of the solvents onto rate of reactions catalyzed with the metal containing polymers. So investigating of the influence of the solvent onto catalytical properties of the palladium containing anionites became the goal of the present work. The nitrobenzene hydrogenation was chosen as a model reaction in most cases.

Studied anionites are three-dimensional polymers. Accessibility of their functional groups is unequal because of steric difficulties. Swelling of the anionite when the solvent molecules penetrate into the polymer matrix changes accessibility of the functional groups and metallocentres of the palladium containing anionites. The swelling degree (n) depends on molar volume, polarity and other physicochemical parameters of the solvent moelcules and in our opinion over this reason it can be considered as the general characteristic of the solvent in the solvent – the metal containing polymer system.

We investigated swelling of the palladium containing anionites in 17 organic solvents and determined that the hydrogenation rate changes similar to the polymer matrix swelling changing (Fig. 1). Equation taking into account influence of the anionite swelling onto observed rate of the process (W_{obs}) was concluded [4, 5]. For hydrogenation of aromatic nitrocompounds on such catalysts this equation may be written as:

$$W_{obs} = k_0\, e^{-(\beta n_\infty / RT)}\, [C_{cat}][H_2], \tag{1}$$

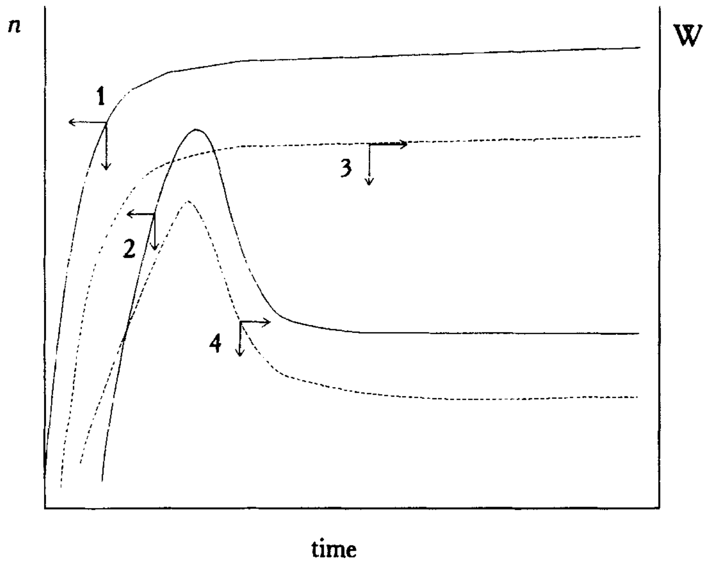

FIGURE 1 Types of kinetic curves of swelling (1, 2) and of the hydrogenation rate (3, 4). 1, 3 – for normal alcohols and hydrocarbons, 2, 4 – for alcohols with the branch hydrocarbon skeleton.

where k_0–the rate constant on "dry" catalyst: n_∞–the limiting swelling degree of the anionite in the solvent; β–characteristic of changing of properties of the polymer matrix chain when passing from non-stretch to stretch state; $[C_{cat}]$–total concentration of active metallocentres of the catalyst; $[H_2]$–concentration of hydrogen with account of changing of it's partial pressure because of the solvent vapour pressure.

W_{obs} values calculated according proposed equation are in good consent with obtained experimental data. Difference of the calculated and experimental values of W_{obs} is not exceeded 5% and is quite satisfactory.

When using anionites with different concentrations of the sewing agent sections of chains between knots of the polymer net will have diverse flexibility so supported metallocentres will have diverse activity. To test the supposition hydrogenation of nitrobenzene on the palladium containing anionite *AH*-108-*θ* (lowbased anionite of the ethylenediamine type) sewing with divinyl ether of ethyleneglycol added in 3, 7 and 10 mass% was studied (Tab. I). As it was to be expected n_∞ increases with a decrease of the sewing degree of the anionite. In case of alcohols n_∞ is 2–3 times as much (depending on the polymer matrix rigidity) than for hydrocarbons. Analogous results were obtained when investigating swelling of anionite *AB*-17-8. The *AB*-17-8 anionite is aminated chloromethylated copolymer of styrene with 8% divinylbenzene.

The catalytic properties of patterns of *AH*-108-θ-Pd completely swelled in corresponding solvents were studied. Taking into account the same nature of functional groups of the anionite patterns with the different sewing degree, equal concentration of palladium, the same mode of it's immobilization and penetrability of all the patterns for the nitrobenzene molecules it may be thought that every experimental point (Fig. 2) corresponds to the metal-polymer distinguishing from the other one only with strain of elementary cell of the polymer matrix. Then the n_∞ value is measure of work strain of the polymer net and characterizes flexibility of sections of chains between knots of sewing.

The same dependence of effective constant of rate of hydrogenation of nitrobenzene from n_∞ is observed for of all series of the investigated patterns (Fig. 2). Besides that, severing at the ordinate axis lgk_0 value which characterizes the rate constant of hydrogenation on non-swelled polymer (see Eq. (1)) is equal for all series. This may be considered as confirmation of identity of nature of active metallocentres in *AH*-108-θ-Pd with the sewing degree equal 3, 7 and 10%.

When studying catalytic properties of porous anionites on the base of aminated chloromethylated polystyrene with the sewing agent content (divinylbenzene) equal 12, 25 and 50 mass% correspondingly (*APA*-12*n*-Pd; *APA*-25*n*-Pd; *APA*-50*n*-Pd) the linear dependence

TABLE I Swelling of *AH*-108-θ anionite in organic solvents

Solvent	*The limiting swelling degree* $(n)_\infty$ *The swelling agent content*, %		
	3	7	10
Hexane	0.47	0.42	0.14
Toluene	0.54	0.50	0.22
Pentanol	0.82	0.73	0.30
Butanol	0.86	0.78	0.37
Propanol-2	0.90	0.82	0.43
Ethanol	1.02	0.85	0.50

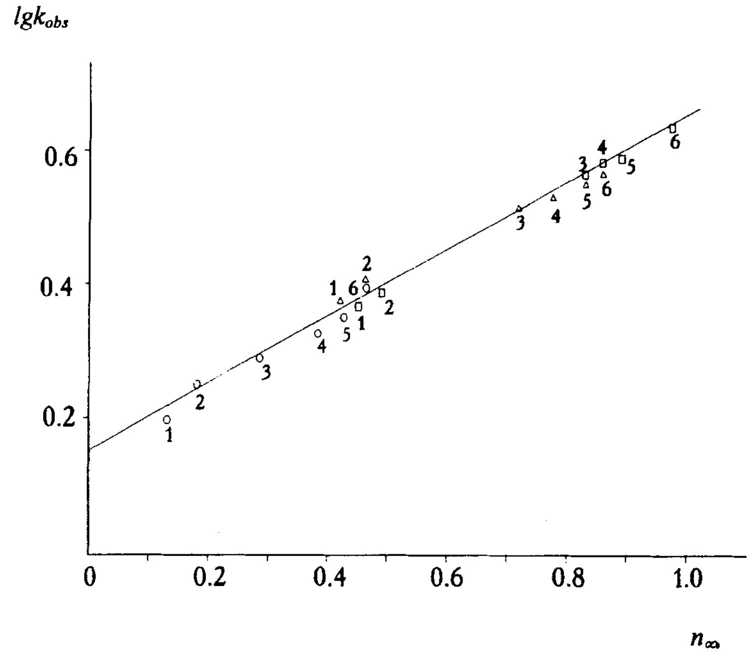

FIGURE 2 Influence of swelling of *AH*-108-θ-Pd with different sewing degree onto the hydrogenation rate of nitrobenzene. Solvents; 1-hexane, 2-toluene, 3-pentanol, 4-butanol, 5-propanol-2, 6-ethanol. The sewing degree: 3% (☐), 7% (△), 10% (○).

$lgk_{\mathrm{obs}} = f(\eta_\infty)$ [6] was obtained too. This also confirms identity of the active metallocentres of catalysts differ only with the sewing degree of the polymer matrix.

As it can be seen from Table II the hydrogenation rate in case of alcohols is 5 (for *APA*-12*n*) or 2 (for *APA*-25*n*) times as much than for hydrocarbons. When using *APA*-50*n* the reaction in hydrocarbons is not observed, in alcohols it's rate is constant in limits of error of measurement. The reaction rate on Pd/C which can not swell at all is practically independent from the solvent nature (Tab. II). Hence, the solvent influence can be stipulated with the polymer matrix flexibility solely, exactly with influence of it's strain because of swelling onto activity of the metallocentres binding with the polymer. Indeed, judging by Eq. (1), the reaction does not occur when one of factors is equal zero. Only the observed rate constant may be equal zero because other factors are not equal zero in the conditions of the experiment.

TABLE II The nitrobenzene hydrogenation rate on the palladium containing catalysts*

Solvent	k_{obs}, *mole/(min g-at Pd)* ± 6%			
	APA-12n-Pd	*APA-25n-Pd*	*APA-50n-Pd*	*Pd/C*
Methanol	5.0	2.5	1.2	–
Ethanol	4.6	2.0	1.2	25
Propanol	3.8	1.7	1.2	21
Propanol-2	2.4	1.4	1.2	20
Butanol	2.5	1.3	1.1	20
Heptane	1.2	1.2	0.0	–
Toluene	1.2	1.1	0.0	20

*The hydrogenation conditions: 1atm H_2; 45°C; the nitrobenzene concentration 0.1 mole/l; catalyst contains 1 mass% of Pd (*APA*-50*n*-Pd contains 0.1 mass.% of Pd).

At the same time when strain in the polymer matrix net increase (in case of *APA*-50*n*) the reaction has place though it's rate is very small. Appearance of the catalytic activity of the metal polymer when reaching the definite value of swelling (strain) of the polymer matrix was fixed obviously in hydrogenation of *o*-nitrotoluene and 1-nitronaphtalene on *AB*-17-8-Pd [2].

In whole it may be stated that the lesser sewed matrix experiences the larger strain because of penetrating of the solvent molecules into it. As far as the active metallocentres are supported on the polymer net the net strain (so the surplus energy) is passing to them. Namely this determines the total hydrogenation rate.

The larger the net strain the higher the catalyzed reaction rate. It can be supposed that the active metallocentre lowers the strain during the catalytic act, taking away part of the surplus energy of the polymer net to proper hydrogenation of the substrate and this is expressed in increasing of the reaction rate as compared with non-swelling, *i.e.*, non-strained analog. As far as the reaction takes place in solution the net strain is reducing instantly and the hydrogenation rate remains constant till to total conversion of the substrate. To ascertain the validity of the supposition further investigations are necessary.

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