Effect of the Polymeric Matrix of a Catalyst on Its Activity in Hydrogenation

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Abstract—The swelling degree of ion-exchange resin AB-17-8-OH and palladium-containing catalysts based on this resin were studied. The effects of the diameter of polymeric support grains and temperature on the activity of the catalysts in model reactions of nitrobenzene and α-nitronaphthalene hydrogenation were investigated. It was found that the catalyst preparation procedure and the particle size appreciably affect the rates of these reactions.

INTRODUCTION

Metal-containing polymers are used as catalysts for many reactions in organic synthesis, including hydrogenation reactions [1, 2]. Among these catalysts, palladium-containing anionites such as AB-17-8-Pd have been well studied. In the presence of this catalyst, multiple bonds and unsaturated functional groups can be efficiently reduced [3–5].

In studies on AB-17-8-Pd, it was repeatedly noted [2, 6–8] that a polymeric matrix (copolymer of aminated chloromethylstyrene and divinylbenzene (8 wt %)) significantly affected the rate and, in some cases, the selectivity of catalytic reactions.

Usually, metal-containing ionites are synthesized by placing a polymer in a solution of a metal compound. In this case, the process of polymer swelling and the fixation of the metal in the matrix take place simultaneously. It is believed that a change in the swelling degree (that is, in the cell stress) of a polymeric matrix can control catalyst activity and selectivity in a catalytic reaction even at the stage of catalyst synthesis.

In this work, we studied the effect of AB-17-8-Pd catalyst preparation procedure on catalyst activity in nitrobenzene and α-nitronaphthalene hydrogenation.

EXPERIMENTAL

In this work, commercial anionite AB-17-8 (Russia) in Cl form was used. It was transformed into OH form according to a published procedure [9]. AB-17-8-Pd catalysts (containing 1 wt % Pd) were prepared in the following way: 1 g of anionite AB-17-8 in OH form was introduced into a 50-ml flask, and a solution of 0.0302 g of potassium tetrachloropalladate in distilled water was added. The contents were stirred for 1 h at 20–25°C using a magnetic stirring rod. Then, the catalyst was filtered off, washed with 100 ml of water and 50 ml of acetone, and dried in air to constant weight.

The palladium content of the catalyst was 0.99 ± 0.01 wt %. Two types of catalysts were prepared. First, air-dry AB-17-8-OH was used for the immobilization of K_2PdCl_4 (Cat1). Second, the same anionite swelled for 1 h in a solvent (ethanol) immediately before palladium immobilization was used (Cat2). Then, the catalysts were activated using the same procedure for both Cat1 and Cat2. The sample of an air-dried catalyst was placed in a glass reactor equipped with a stirrer and thermostatted at 45°C, 10 ml of ethanol was added, and 0.05 g of sodium borohydride was then introduced in a hydrogen flow. Thereafter, the contents of the reactor were stirred for 1 h; the catalyst was filtered off, washed with distilled water and acetone in air, and dried to constant weight.

The swelling degrees (n) of AB-17-8 in OH form and of initial and activated Cat1 and Cat2 samples prepared using this anionite were determined by gravimetry [10] in a thermostat at 20, 40, and 50°C. The swelling degree was calculated using the equation

$$n = (m - m_0)/m_0, \qquad (1)$$

where m is the mass of a swollen polymer, and m_0 is the mass of the polymer dried at 110°C.

The catalytic activity was studied by the example of model reactions of liquid-phase nitrobenzene and α-nitronaphthalene hydrogenation. In these reactions, electrolytic hydrogen (without additional purification) and chemically pure nitrobenzene and α-nitronaphthalene were used.

Ethanol (10 ml), 0.2 g of a catalyst (in this case, both Cat1 and Cat2 were swollen in ethanol for 1 h before use in hydrogenation), and 1 mmol of a substrate were introduced into a thermostatted glass reactor with a magnetic stirrer. Then, the reactor was purged with hydrogen, and the hydrogenation was carried out at 0.1 MPa of H_2 until the hydrogen was completely consumed. The reaction mixtures were analyzed by gas–

liquid chromatography (GLC) [11]. The reaction rate was determined using both volumetric and GLC data. The apparent rate constant was calculated using the equation

$$k = w/([H_2][Cat]P), \qquad (2)$$

where w is the apparent reaction rate, $[H_2]$ is the hydrogen concentration, $[Cat]$ is the catalyst concentration, and P is a correction for the influence of the partial pressure of solvent vapor, which was calculated by the equation

$$P = (P_{atm} - P_p)/760, \qquad (3)$$

where P_{atm} is the atmospheric pressure during the experiment (torr), and P_p is the pressure of ethanol vapor at the temperature of the experiment (torr).

Preliminary experiments showed that under the chosen conditions the hydrogenation of both substrates takes place in a kinetic region. This was confirmed by the Thiele modulus (0.06–0.4 depending on the substrate and the catalyst particle size). In all experiments, zero order of reaction with respect to a substrate and first order with respect to a catalyst or hydrogen were observed.

RESULTS AND DISCUSSION

Earlier [6], it was concluded using experimental and published data that the active sites in the AB-17-8-Pd catalyst are palladium clusters immobilized in a polymeric matrix. As Cat1 and Cat2 were prepared and activated using identical procedures, the expected difference in their catalytic activity can be due to the fact that palladium clusters were bound to differently stressed polymer chains of a three-dimensional polymer network. Indeed, Cat1 was obtained by the immobilization of initial potassium tetrachloropalladate on an air-dry anionite; that is, the immobilization was combined with the swelling of a polymeric matrix in water. In the case of Cat2, a swollen anionite was used for immobilization. If our assumption is correct, Cat1 and Cat2 must have similar polymeric matrix characteristics (for example, swelling degree) and different catalytic properties (for example, rate of catalytic reaction or activation energy).

Experimental data presented in the table show that in the entire temperature range the swelling degrees of Cat1 and Cat2 are practically identical; however, they are lower than the swelling degree of the parent anionite. This can be explained by a decrease in the volume of elementary cells of a polymeric matrix due to the immobilized palladate (or palladium clusters after the activation) or by an increase in the anionite rigidity because palladate (or palladium clusters) can act as an additional cross-linking agent. It is likely that both of these factors occur simultaneously.

The activity of Cat1 and Cat2 in a model reaction of nitrobenzene hydrogenation was studied at the same temperatures at which the swelling degree was determined. The Arrhenius function (Fig. 1) is valid for both catalysts in the entire temperature range. The reaction rate increases with temperature. The apparent activation energy (E_a) is equal to 63 or 42 kJ/mol for Cat1 or Cat2, respectively. The error of the determination of E_a is equal to 10%. This fact allows us to consider a significant difference between catalysts prepared by different procedures. The rate of reduction on Cat2 is lower than that on Cat1 at all tested temperatures.

The different activities of Cat1 and Cat2 can be explained in the following way. The palladate ion is much smaller than the nitrobenzene molecule. Therefore, in the immobilization under conditions of swelling, a portion of the palladium penetrates into pores that are inaccessible to nitrobenzene in the course of hydrogenation. Therefore, hydrogenation on Cat2 takes place on a knowingly smaller number of active sites than in the case of Cat1, and the activity of Cat2 calculated on a total palladium basis must be lower. Therefore, catalyst size reduction, which causes the destruction of pores, will result in equal numbers of available active sites in Cat1 and Cat2 at a certain particle size. In this case, if the nature of active sites in both catalysts is the same, the specific activities should be equal, and the ratio between the apparent rate constants of hydrogenation $k(Cat1)/k(Cat2)$ must be equal to unity.

Earlier [2, 6], it was found that the particle size of the AB-17-8-Pd catalyst significantly affects the rate of hydrogenation. In some cases, the reaction begins only at a certain size of catalyst particles. This fact was explained by the influence of the polymeric support on the active sites of AB-17-8-Pd.

The experiments described below were carried out to determine the reasons for this difference in activities

Swelling degrees (n) of anionite AB-17-8-OH and catalysts based on this anionite in ethanol

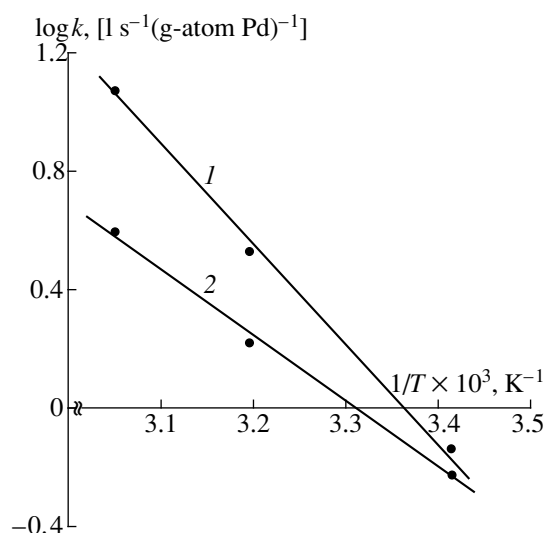| T, K	n				
	AB-17-8-OH	Cat1	Cat1 after activation	Cat2	Cat2 after activation
293	0.376 ± 0.079	0.228 ± 0.016	0.229 ± 0.009	0.230 ± 0.029	0.269 ± 0.004
313	0.359 ± 0.032	0.207 ± 0.002	0.292 ± 0.058	0.234 ± 0.003	0.233 ± 0.022
328	0.365 ± 0.015	0.226 ± 0.012	0.228 ± 0.013	0.229 ± 0.086	0.263 ± 0.007

Fig. 1. Rate constant of nitrobenzene hydrogenation on (*1*) Cat1 or (*2*) Cat2 as a function of temperature. Experimental conditions: solvent, ethanol (10 ml); 0.1 MPa of H_2; [nitrobenzene] = 0.1 mol/l; catalyst weight, 0.2 g; palladium content, 1 wt %.

Fig. 2. Rate constant k of α-nitronaphthalene hydrogenation as a function of particle size of the catalyst AB-17-8-Pd (the catalyst was crushed after Pd immobilization). (*1*) Cat2 (Pd was immobilized in a swollen matrix), (*2*) Cat1 (Pd was immobilized in an unswollen anionite). Experimental conditions: 45°C; solvent, ethanol (10 ml); catalyst weight, 0.2 g; palladium content, 1 wt %; [α-nitronaphthalene] = 0.1 mol/l; 0.1 MPa of H_2.

of the catalyst samples. Catalysts Cat1 and Cat2 were crushed and separated into fractions. Then, using these samples completely swollen in ethanol, we hydrogenated α-nitronaphthalene (Fig. 2). We found that the reaction rate is a complex function of the average particle diameter (d_{av}) of both catalysts. These functions for Cat1 and Cat2 are similar, but Cat1 was always more active. A decrease in d_{av} from 6.5×10^{-4} to 2.5×10^{-4} m led to a decrease in $k(\text{Cat1})/k(\text{Cat2})$ from 2.3 to 1.3, and this ratio remained constant after a further decrease in d_{av} (Fig. 3). Thus, different activities of Cat1 and Cat2 can be explained by the simultaneous action of two factors: on the one hand, different numbers of available active sites and, on the other hand, the influence of the polymeric matrix on the activity. The data of Fig. 3 show that the former factor dominates under the test conditions.

Let us consider in more detail the rate constants of catalytic reactions on Cat1 and Cat2 as a function of particle size (Fig. 2). The reaction rate increases initially with a decrease in particle size and then decreases. It is believed that, owing to steric factors, not every active site participates in the catalysis. Size reduction increases the number of available active sites and the reaction rate. After reaching a certain particle size, all active sites become available, and no further increase in the reaction rate due to this factor takes place. Such functions were obtained in the hydrogenation of nitrobenzene on AB-17-8-Pd [6] and in the oxidation of tetrahydronaphthalene on Co^{2+}/SiO_2[12]. The type of this function was different in the hydrogenation of more complex substrates on AB-17-8-Pd. Thus, for α-nitronaphthalene, the rate of the reaction decreased by a factor of 1.8 rather than remained constant (Fig. 2)
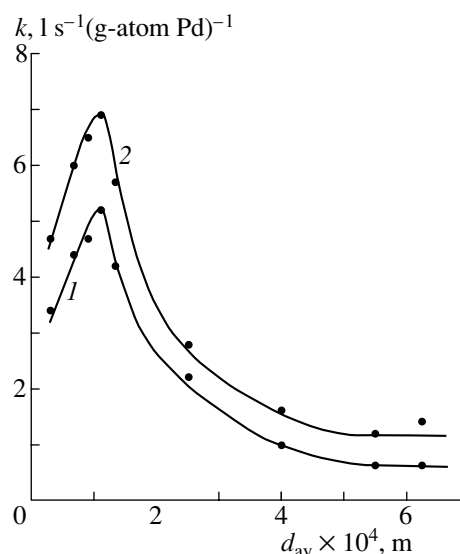
as the particle diameter decreased from 1.02×10^{-4}–1.2×10^{-4} m to 0.3×10^{-4} m. The same type of function was also observed in the hydrogenation of 2-methyl-3-nitro-4-methoxymethyl-4-cyano-6-chloropyridine on AB-17-8-Pd [5, 6].

For the explanation of the curves presented in Fig. 2, it is possible to suppose that, in a catalytic process in the presence of metal-polymeric catalysts, a change in the free energy (ΔG) of the system on going from an initial to a transition state consists of at least three terms:

$$\Delta G = \Delta G_{\text{chem}} + \Delta G_{\text{pol}} + \Delta G_{\text{surf}}, \qquad (4)$$

where ΔG_{chem} is the term corresponding to a chemical process without taking into account structural changes of the whole chain of a polymeric matrix, ΔG_{pol} is the term corresponding to a change in the structure of the polymeric matrix, and ΔG_{surf} is the term corresponding to a change in the free energy of formation of a unit surface.

If the nature of active sites in catalysts Cat1 and Cat2 with different particle sizes is identical, the contribution ΔG_{chem} to the total change in free energy of the system is constant in every case for the dependence under consideration.

If the particle size reduction of the sample does not result in detectable destruction and hydrogenation takes place at a constant temperature, the contribution ΔG_{pol} to the total free-energy change of the system is also constant for catalysts with different average particle sizes.
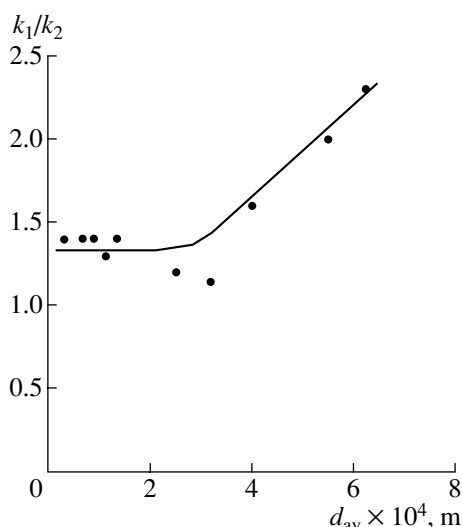
Fig. 3. The ratio k_1/k_2 (where k_2 and k_1 are the rate constants of α-nitronaphthalene hydrogenation on Cat2 and Cat1, respectively) as a function of catalyst particle size. Experimental conditions are specified in Fig. 2.

In our opinion, the experimental changes in activity cannot be explained by the destruction of a polymeric matrix or, for example, by a change in its swelling degree for this reason. The destruction of a three-dimensional polymer must lead to a change in its cross-linking and, therefore, to a change in its swelling degree. The dependence of an apparent reaction rate constant on the swelling degree of anionites that differ only in the degree of cross-linking was described [2, 6, 13, 14]. Polymers of the same chemical nature but with different degrees of cross-linking have the same value of k on a "dry" catalyst.

The contribution ΔG_{surf} primarily depends on the surface tension energy of support particles (Y). This value depends on the average particle size, and it can be described by the equation

$$Y = Y_\infty(1 - 4\delta/d), \qquad (5)$$

where Y and Y_∞ are surface tensions at finite and infinitely high (flat surface) radii of curvature, respectively; d is the catalyst particle diameter; and δ is a constant equal to the thickness of a surface layer. The value of δ is approximately equal to 10^{-5} m.

As the value of δ is comparable with the molecular sizes of low-molecular-weight compounds and, especially, their solvates, it is clear that the nature and size of substrate molecules affect the value of Y. Strictly speaking, in the case of a catalytic reaction, ΔG_{surf} depends on the difference between initial and final states of the system or, in our case, on the difference between the contributions of the solvates of a nitro compound and an amine to Y: $Y = Y_{amine} - Y_{nitro}$.

Thus, for every substrate, a particular type of the function $k = f(d)$ can exist.

ACKNOWLEDGMENTS

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