**D-Glucose Hydrogenation over Ru Nanoparticles Embedded in Mesoporous Hypercrosslinked Polystyrene**

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**ABSTRACT:** The kinetics of D-glucose hydrogenation on the catalyst containing Ru nanoparticles in the matrix of hypercrosslinked polystyrene was studied. Two routes of the hydrogenation reaction were revealed; their rates differ by several digits. The first route includes the interaction of D-glucose with the spilled-over hydrogen supplied by the catalyst; the second one includes classical interaction of the sorbed substrate with incident hydrogen from the reaction medium. A mathematical description of D-glucose conversion and the change of the catalyst activity by the first method of D-glucose hydrogenation were obtained. The most probable scheme of the process flow was suggested. The main kinetic parameters were calculated. The role of hydrogen spillover phenomenon in the kinetics of the processes is discussed.

**1. INTRODUCTION**

Catalytic hydrogenation of D-glucose to D-sorbitol is widely used in the technology of several chemical pharmaceutical preparations and food production (biologically active compounds, vitamins, medicines, and others). The catalytic method of D-sorbitol production is a complex process (Scheme 1) providing several reaction routes. The use of heterogeneous systems for selective hydrogenation of D-glucose is of great practical importance considering its high ecological safety.3—5 Now the industrial catalyst for D-glucose hydrogenation is Raney Ni catalyst.6—8 However, the drawback of Ni catalysts is their tendency to Ni outwashing that results not only in the loss of catalytic activity (after five recycles the activity decreases by 40%)9 but also in the necessity of introducing the additional stage of the product purification. The use of active and stable catalysts on the base of ruthenium6,10 which hypercrosslinked polystyrene is a carrier, will help solve this problem.

Besides the nature of the metal, the catalyst effectiveness is determined by physical chemical properties of the carrier, the true role of which was revealed after the detection of spillover effect.12,13 As a rule the oxides of metals M₂O₃ capable of taking hydrogen from metal-catalyst and accumulating it on their surface and in their volume are chosen as a carrier. Now the choice of a carrier is not limited to various oxides. Carbon materials, carbon nanotubes in particular,14—16 are widely spread. Besson and Gallezot17 used 1.8% (wt) Ru/C, which provided the yield of sorbitol of up to 99.5%. Hoffer et al.9 on similar catalysts Ru/C obtained high selectivity of the target product formation (>98%). The effectiveness of carbon materials as carriers for the hydrogenation catalysts is explained by the ability to accumulate hydrogen atoms on cyclic C₆ fragments. Providing a high concentration of chemibounding hydrogen in the catalyst solid phase and near the reaction center hydrogen spillover increases sharply the effectiveness of catalytic systems. Quantum mechanical calculations18—20 showed that the migration of hydrogen atoms from the metal to the carbon layers of nanotubes, graphene, or graphite—coronene model takes place exothermally. The atomic hydrogen then spills over to the aromatic unit as the receptor via surface diffusion of sp² structures and defect sites and can migrate further across the carrier surface.15

The idea of using polymeric carriers on the basis of hypercrosslinked polystyrene (HPS)21 seems rather prospective. HPS with the specific surface from 1223 m²/g adsorbs 2.13% (wt) of hydrogen. Other hypercrosslinked nanoporous polymers22 can accumulate hydrogen in a similar way. The calculations23 show that the aromatic ring can hold 6 atoms of hydrogen and the gravimetric analysis confirms that the carrier can store up to 5.5% (wt) of hydrogen. Unfortunately, there are not enough literature data which show how hydrogen spillover influences the hydrogenation kinetics. We hope that the study of the kinetics of the hydrogenation reaction on the catalyst, in which hypercrosslinked polystyrene is a carrier, will help solve this problem.

The present paper is devoted to the study of the kinetics of D-glucose to D-sorbitol hydrogenation on Ru-containing heterogeneous catalyst. Mesoporous hypercrosslinked polystyr-
ene with sharp pore size distribution with a maximum of 4 nm was used as a carrier. The unique property of HPS is its ability to swell in different solvents even in water and accumulate hydrogen.\textsuperscript{24-26} The presence on nanosized pores provides the control of catalytically active particles formation. In this case the particle size is limited to the pore size.\textsuperscript{27-29}

2. EXPERIMENTAL SECTION

2.1. Synthesis and Analysis of the Catalyst. Ruthenium-containing catalysts on the basis of HPS (MN-270 Purolite Ltd. production) were synthesized by impregnating HPS with ruthenium(IV) hydroxochloride (Ru(OH)Cl\textsubscript{3}) from a complex solvent (tetrahydrofuran + methanol + water at a ratio of 4:1:1). In a typical experiment 3 g of pretreated and dried HPS (MN270, size of granules = 60 to 400 \(\mu\)m) was impregnated with 6 mL of complex solvent (4 mL of THF, 1 mL of MeOH, and 1 mL of water) containing dissolved precursor Ru(OH)Cl\textsubscript{3} (0.24 g) during 10 min. After the impregnation of Ru(OH)Cl\textsubscript{3} dissolved in the complex solvent, the resulting system was dried at 75 \(\pm\) 2 °C during 1 h and boiled about 2 h in 21 mL of 0.1 M NaOH solution with the addition of 2 mL of hydrogen peroxide (30%). Such a treatment allows the formation of RuO\textsubscript{2} particles and oxidation of Ru(III), which can be present in negligible amounts in the precursor, to Ru(IV). After that the Ru-containing polymer was washed with water until pH 6.4–7.0 and the absence of reaction on chloride ions, then dried again at \(t = 75 \pm 2 \) °C.

The precatalyst obtained in such a way \{Ru/HPS\} was reduced by gaseous hydrogen at atmospheric pressure and a temperature of 300 °C for 2 h then it was cooled to ambient temperature in a nitrogen atmosphere. The catalyst reduced by hydrogen was designated as \{Ru/HPS (H\textsubscript{2})\}. According to X-ray fluorescence analysis data the ruthenium content is 3% (wt). The Ru content was obtained by X-ray fluorescence (XRF) measurements performed with a Spectroscan–Maks–GF1E (Spectron, St-Petersburg, Russia) spectrometer (Mo anode, LiF crystal analyzer, and SZ detector).

TEM of HPS-based catalysts was performed with a JEOL JEM1010 electron microscope operated at accelerating voltage of 80 kV (Department of Chemistry, Indiana University). Metal-containing HPS powders were embedded in epoxy resin and subsequently microtomed at ambient temperature. Images of the resulting thin sections (ca. 50 nm thick) were collected with the Gatan digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit.

X-ray photoelectron spectra were obtained by using Mg K\(\alpha\) (\(h\nu = 1253.6\) eV) monochromatized radiation with a modified ES-2403 spectrometer (provided by the Institute for Analytic Instrumentation of the Russian Academy of Sciences, St. Petersburg, Russia). All data were acquired at an X-ray power of 200 W and an energy step of 0.1 eV. The electron flood gun accessory was used to obtain the total emitted electron flux current from the flood gun. Samples were allowed to outgas for 30 min before analysis and were sufficiently stable during examination. Data analysis was performed with use of a standard XPS-set with a Resolver program.

2.2. Hydrogenation Process Procedure and the Reaction Mixture Analysis. D-Glucose hydrogenation was carried out in a steel temperature-controlled shaker-type autoclave bath reactor of 120 mL volume. The reactor is equipped with a special loading chamber (volume 16 mL), which allows introducing the substrate solution into the reactor at preselected pressure and temperature. The suspension of a heterogeneous catalyst with the solvent was introduced into the autoclave through the side fitting and the substance under study dissolved in 15 mL of solvent into the loading chamber. The total volume of the liquid fraction was 50 mL. Before the reaction the catalyst was saturated with hydrogen at a preselected temperature for 30 min, and then the substrate was introduced. The process of hydrogenation was carried out at constant shaking of the autoclave.

The kinetic experiments were performed by changing the initial concentrations of D-glucose (\([C]_0\), mol/L) and the catalyst (\([cat]_0\) mol Ru(L)\textsuperscript{2+}). For the convenience of calculations the catalyst concentration in a reaction volume was determined by scaling the amount of ruthenium in the catalyst introduced on the volume of the reaction mixture in the

![Scheme 1. The D-Glucose Hydrogenation Process](Image)
The reaction was performed at various temperatures (T) and pressures (P).

The reaction flow was tested by sampling the catalyst for the analysis. The analysis was carried out by the method of HPLC, using a refractometric detector. Reproreg-H column: 500 × 10 mm, the number of theoretical plates 160 000; conditions of separation: eluent consumption (9 Mmol solution H₂SO₄) 0.5 mL/min; temperature of the column 25 °C; eluent pressure 6.5 MPa; time of analysis 30 min. The qualitative identification was carried out with use of pure reference substances.

3. RESULTS AND DISCUSSION

3.1. Physical Chemical Study of the Catalyst. One of the reasons for using HPS as a carrier is that the size of catalytically active particles while forming is “controlled” by the diameter of a polymer mesopores.²⁷–²⁹ The next step in obtaining the finished catalyst {Ru/HPS (H₂)} is the reduction of the form obtained {Ru/HPS} under hydrogen at an increased temperature. It is known that under the influence of hydrogen the enlargement of metal ruthenium grains takes place.² To determine the stability of the synthesized catalyst active phase we compared Ru particles distribution in the precatalyst {Ru/HPS} and in the finished catalyst {Ru/HPS (H₂)}. According to TEM study results the images of the catalysts ultrathin sections were analyzed, on the basis of which the particles size distribution was calculated (Figure 1).

![TEM images of Ru-containing particles for catalysts](image)

Thus it was revealed that the treatment of the catalysts with hydrogen does not result in the aggregation of Ru-containing nanoparticles. Their mean diameter for the unreduced (Figure 1a) and reduced (Figure 1b) catalyst was 1.4 ± 0.3 nm.

To determine the qualitative and quantitative composition of the surface of Ru-containing nanoparticles, stabilized in HPS matrix, the study of the catalysts samples was performed by the method of X-ray photoelectron spectroscopy. In Table 1 XPS data on qualitative and quantitative composition (atom %) of Ru-containing nanoparticles formed are of mixed nature and contain both Ru(0) and Ru(IV) species.

3.2. Study of Kinetics of D-Glucose to D-Sorbitol Hydrogenation. Preliminary Investigation. Before a systematic study of the heterogeneous catalytic process the area of the reaction flow and the stability of the catalyst should be determined. To define the area of the reaction flow preliminary series of experiments at changing the intensity of shaking of the reaction mixture were done and the influence of the catalyst fractional composition was determined. The process was performed under the following conditions: D-glucose initial concentration [C]₀ = 1.6 mol·L⁻¹, the catalyst concentration [cat]₀ = 2.32 × 10⁻³ mol Ru·L⁻¹, hydrogen partial pressure was 4 MPa, temperature was 140 °C, and the catalyst fraction was varied according to sizes from 60 to 400 μm.

The effect of the intensity of shaking of the reaction mixture and the influence of the catalyst dispersity (i.e., the change of its external surface) were determined according to the estimation of the reaction apparent rate (W_app) at the 80th minute. The apparent reaction rate was defined as the amount of the substrate reacted at a chosen time related to the mol Ru a second.

\[
W_{\text{app}} = \frac{\left( [C]_0 - [C]_f \right)}{[\text{Ru}]_f \cdot (\text{mol} \times \text{mol} \cdot \text{Ru}^{-1} \cdot \text{s}^{-1})
\]

where [C]₀ and [C]ₙ are the initial and final concentration of D-glucose (mol·L⁻¹), [Ru] is the amount of ruthenium introduced into the reaction (mol Ru·L⁻¹), and r is the time of the process (s).

The experiments showed that at increasing the intensity of shaking by accelerating the reactor shaking frequency D-glucose conversion increases and becomes constant if the intensity of shaking exceeds 480 shakings/min. The use of catalyst granules less than 60 μm in size does not result in the change of the process rate. The independence of the degree of D-glucose conversion on the intensity of shaking and the sizes of the catalyst external surface proves that the process flows in the kinetic area. For further study catalyst granules of less than 60 μm in size and intensity of shaking 500 shakings/min were used.

To study the stability of {Ru/HPS (H₂)} we determined the conversion and selectivity of the hydrogenation reaction using the catalyst repeatedly. The conditions of the reaction in this series of experiments were constant. The Ru leaching was not noticed in 10 repeated cycles. The results obtained are presented in Table 2.

<table>
<thead>
<tr>
<th>Table 1. Qualitative and Quantitative Composition of the Surface of Ru-Containing Nanoparticles, Stabilized in HPS Matrix, According to XPS Data and the Bond Energy for Ru 3p₁/₂ (in parentheses)</th>
<th>composition (atom %)/(bond energy for Ru 3p₁/₂ eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>compd</td>
<td>[Ru/HPS]</td>
</tr>
<tr>
<td>Ru</td>
<td>9.55 / (462.5)</td>
</tr>
<tr>
<td>RuO₂</td>
<td>0.00</td>
</tr>
<tr>
<td>RuO₂·H₂O</td>
<td>46.78</td>
</tr>
<tr>
<td>[RuO₄(OH)₃]⁺</td>
<td>43.63</td>
</tr>
</tbody>
</table>
Table 2. Dependence of the Catalyst Activity on the Number of the Repeated Cycles for \([C]_0 = 1.6 \text{ mol}(L)^{-1}, [\text{cat}] = 2.32 \times 10^{-3} \text{ mol Ru}(L)^{-1}, P = 4 \text{ MPa}, \text{ and } T = 100 \degree \text{C} \)

<table>
<thead>
<tr>
<th>no. of repeated cycles</th>
<th>conversion (%)</th>
<th>selectivity (%)</th>
<th>(W_{\text{Ru}}) mol/(mol Ru-s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>40.9</td>
<td>98.5</td>
<td>0.059</td>
</tr>
<tr>
<td>1</td>
<td>41.1</td>
<td>98.4</td>
<td>0.060</td>
</tr>
<tr>
<td>5</td>
<td>41.7</td>
<td>98.1</td>
<td>0.060</td>
</tr>
<tr>
<td>10</td>
<td>42.8</td>
<td>97.9</td>
<td>0.062</td>
</tr>
</tbody>
</table>

On the basis of the data presented in Table 2 the catalyst \{Ru/CITEC (H2)\} can be considered stable for 10 repeated cycles.

Kinetic Regularities of the Reaction, Route 1. The detailed study of the process kinetics was carried out by four series of single factor experiments changing the concentration of D-glucose, the catalyst, the reaction temperature, and hydrogen pressure (series 1, 2, 3, and 4 accordingly). In each series of experiments only one factor was changed: D-glucose initial concentration (series 1) \([C]_0 = 3.2, 1.6, 0.8, 0.4, \text{ and } 0.2 \text{ mol}(L)^{-1}\), at constant values of the other parameters—[cat] = 2.32 \times 10^{-3} \text{ mol Ru}(L)^{-1}, T = 100 \degree \text{C}, \text{ and } P = 4.0 \text{ MPa} (series 1); catalyst concentration (series 2) \([\text{cat}] = 1.16 \times 10^{-3}, 1.74 \times 10^{-3}, 2.32 \times 10^{-3}, 2.87 \times 10^{-3}, \text{ and } 3.44 \times 10^{-3} \text{ mol Ru}(L)^{-1}\), at constant values of the other parameters—\([C]_0 = 1.6 \text{ mol}(L)^{-1}, T = 100 \degree \text{C}, \text{ and } P = 4.0 \text{ MPa}\); reaction temperature (series 3) \(T = 90, 100, 110, 120, 130, \text{ and } 140 \degree \text{C}\), at constant values of the other parameters—\([C]_0 = 1.6 \text{ mol}(L)^{-1}, [\text{cat}] = 2.32 \times 10^{-3} \text{ mol Ru}(L)^{-1}, \text{ and } P = 4.0 \text{ MPa}\); pressure (series 4) \(P = 2.0, 3.0, 4.0, 6.0, \text{ and } 8.0 \text{ MPa}\), at constant values of the other parameters—\([C]_0 = 1.6 \text{ mol}(L)^{-1}, [\text{cat}] = 2.32 \times 10^{-3} \text{ mol Ru}(L)^{-1}, \text{ and } T = 140 \degree \text{C}\). During the reaction the pressure was maintained constant.

It should be noted that in all the series performed the reaction of D-glucose hydrogenation flows with high selectivity (≥97%). Only at a high temperature (140 °C) and pressure increase up to 10 MPa does selectivity begin to decrease (up to 95%) due, apparently, to D-glucose hydrolytic hydrogenation as its conversion is 100% under these conditions. The results of the experimental series discussed above are presented in Figures 2–5 accordingly.

At first glance the kinetic curves of the series of single factor experiments show that the reaction of D-glucose hydrogenation under the conditions studied follows according to two routes: “fast” and “slow”. This conclusion can be made on the basis that the reaction rates according to the routes indicated decrease with increasing hydrogen pressure (series 3) \(P = 2.0, 3.0, 4.0, 6.0, \text{ and } 8.0 \text{ MPa}\), at constant values of the other parameters—\([C]_0 = 1.6 \text{ mol}(L)^{-1}, [\text{cat}] = 2.32 \times 10^{-3} \text{ mol Ru}(L)^{-1}, \text{ and } T = 140 \degree \text{C}\). During the reaction the pressure was maintained constant.

The polynomial in substrate concentration, in the case considered, is \(f([\text{C}]_0, [\text{C}]_i)\), where \(f\) is the so-called catalyst “complexation” function. The appearance of the term containing the value \([\text{C}]_i\) is conditioned by the material balance ratio, i.e., \([\text{product}] = ([\text{C}]_0 - [\text{C}]_i)\).

Such dependence is conditioned by equilibrium formation of the complexes of the catalyst with reagents and the reaction products. The degree of polynomial \(f([\text{C}]_0, [\text{C}]_i)\) depends on the number of molecules sorbed on the catalyst active sites. For the preliminary estimation of constants and finding the functions of the catalyst complexity the method of the initial rates is usually used. During this period the influence of the reaction products is almost not noticeable because of low
degree of reagents conversion. But in our case this method cannot be applied and we used the differential method of the analysis for all the kinetic curves of the first series of single factor experiments shown in Figure 2.

For the differential method of the kinetic curves processing eq 2 can be transformed into eq 3.

\[
\frac{[C]_i}{W_i} = \frac{1}{k_{eff}} f([C]_0, [C]_i)
\]

\[
= \alpha + \beta([C]_0 + \gamma[C]_i) + \delta([C]_0)^2 + \eta([C]_i)^2 + ...
\]

\[
\equiv F([C]_0, [C]_i)
\]

(3)

where \(W_i\) is the reaction rate calculated for the current concentration of the substrate (\(\text{D-glucose}\)) at some time and \([C]_0\) and \([C]_i\) are the initial and current concentration of \(\text{D-glucose}\) (mol L\(^{-1}\)).

After calculating the current rates of the reaction \(W_i\) and \(([C]_0)/[W_i]\) ratio the data obtained \([([C]_0)/[W_i])\) for the corresponding values \([C]_0\) and \([C]_i\) were processed by the method of linear multiple regression. Terms coefficients \([C]_0^*\), \([C]_i^*\), or \([C]_0^*[C]_i^*\) turned out to be insignificant. On the basis of the results obtained we made a conclusion that function \(F([C]_0, [C]_i)\) in the kinetic eq 2 is linear with respect to values \([C]_0\) and \([C]_i\) (eq 4):

\[
F([C]_0, [C]_i) = \alpha + \beta([C]_0 + \gamma[C]_i)
\]

(4)

For the series of experiments on the change of the initial concentration of \(\text{D-glucose}\) (series 1, see above), the parameters \(\alpha, \beta, \gamma\) of the correlation function eq 2, or \([C]_0\) accordingly were calculated. The estimated and experimental values of the substrate concentrations in the discussed series of experiments for the second route of the hydrogenation reaction agreed well (Figure 2). The validity of approximation was \(R^2 = 0.99\).

Then we studied the second series of experiments (series 2) in which the catalyst concentration was changed. Integrating was performed by using the equilibrium constants obtained—\(K_i\) and \(K_p\). Varying the numerical value of constant \(k^*\) we obtained the maximum validity of approximation. The calculation curves are presented in Figure 3. For different concentrations of the catalyst value \(R^2\) of the correlation between the experimental and estimated values \([C]_i\) was \(R^2 = 0.99\), and the dependence of the rate constant on the catalyst concentration was in the form of

\[
\frac{d[C]_i}{dt} = \frac{k^*[K_i][C]_i}{1 + K_i[Pr] + K_p[C]_i}
\]

(6)

From comparison of eqs 5 and 6, taking into account the numerical values of parameters \(\alpha, \beta, \gamma\), the constants of the rate and equilibrium (sorption) of the system of reactions I and II \((k^* = 0.000175 \text{ mol (L s)}^{-1}, K_i =5.1 \text{ L (mol)}^{-1}, K_p =3.0 \text{ L (mol)}^{-1}\) accordingly) were calculated. The estimated and experimental values of the substrate concentrations in the discussed series of experiments for the second route of the hydrogenation reaction agreed well (Figure 2). The validity of approximation was \(R^2 = 0.99\).

\[
\text{Figure 3. Experimental points and calculated curves of D-glucose conversion depending on the change of the initial concentration of the catalyst (series 2): } [\text{cat}]_0 = 1.16 \times 10^{-3} \text{ (line 1), } 1.74 \times 10^{-3} \text{ (line 2), } 2.32 \times 10^{-3} \text{ (line 3), } 2.87 \times 10^{-3} \text{ (line 4), and } 3.44 \times 10^{-3} \text{ (line 5) at constant values of the other parameters: } [C]_0 = 1.6 \text{ mol (L)}^{-1}, T = 100 ^\circ\text{C, and } P = 4.0 \text{ MPa.}
\]
at \( k_0^\circ = (32.5 \pm 0.5) \text{ mol} \cdot \text{L}^{-1} \cdot (\text{mol Ru})^{-2} \cdot \text{s}^{-1} \).

The quadratic dependence of the reaction rate on Ru concentration (formally — the second order of the reaction on the catalyst) was the sum of two effects: the first order of the reaction of the substrate hydrogenation according to Scheme 1 (see above) and the rate constant that includes the phases ratio (the phase where the reaction flows and the phase where the substrate is). In the kinetic eq 6 the reaction rate is expressed as the change of the substrate amount in the volume of all the reaction mixture \( [(d[C])/(dt)] \) while the reaction itself flows either on the surface or in the volume of the catalyst (we designate as \( \theta \), the numerical value of which is in proportion to the value [cat]) and should be expressed as \( [(dn)/(\theta dt)] \). From the expression

\[
\frac{dn}{\theta dt} = \frac{dn}{V dt} \cdot \frac{V}{\theta} = \frac{d[C]}{dt} \cdot \frac{V}{\theta}
\]

in the right-hand side of kinetic eqs 2, 5, or 6 multiplier \( (\theta/V) \) is to appear. This multiplier implicitly entered the rate constant \( k_0^\circ \) and, as \( \theta \) is in proportion to [cat], appeared in the form of quadratic dependence \( k_0^\circ \) on the catalyst concentration.

It is clear from the graphs of Figure 4 that the temperature change does not make significant differences to the process presenting the functional dependences of the constants on the temperature in the following form:

\[
k_0^\circ = \exp \left( \ln(k_0^\circ(373)) - \frac{\Delta H_0}{R} \left( \frac{1}{373} - \frac{1}{T_K} \right) \right)
\]

mol·L⁻¹·(mol Ru)⁻²·s⁻¹

(8)

\[
K_i = \exp \left( \ln(K_i(373)) - \frac{\Delta H_i}{R} \left( \frac{1}{373} - \frac{1}{T_K} \right) \right) \text{L}^{-1} \cdot (\text{mol})^1
\]

(9)

\[
K_p = \exp \left( \ln(K_p(373)) - \frac{\Delta H_p}{R} \left( \frac{1}{373} - \frac{1}{T_K} \right) \right) \text{L}^{-1} \cdot (\text{mol})^1
\]

(10)

where \( \Delta H_0, \Delta H_i \), and \( \Delta H_p \) are the enthalpies of activation and sorption of the reaction product and the substrate, accordingly; \( R \) is the gas constant; and \( T_K \) is the Kelvin temperature.

The unknown parameters \( \Delta H_0, \Delta H_i \), and \( \Delta H_p \) were found by comparing the experimental data \([C]_i\) of the third series of experiments (Figure 4) and estimated by eq 6, in which instead of constant values \( k_0^\circ, K_i \), and \( K_p \), their functional dependences eqs 8, 9, and 10 were used. Varying the values of activation and sorption enthalpies we obtained minimal discrepancy between estimated and experimental values of D-glucose concentration.

Within high validity of approximation \((R^2 = 0.985)\) the numerical values were obtained: \( \Delta H_0/R = -4440 \pm 50 \text{ K} \), \( \Delta H_i/R = +2000 \pm 100 \text{ K} \), and \( \Delta H_p/R = +4000 \pm 100 \text{ K} \). The estimated and experimental values \([C]_i\) are in good agreement (Figure 4).

Thus as a result of the analysis of the kinetic data of the first three series of experiments (see above) it was revealed that the kinetic curves are described well by kinetic eq 6. The constancy of hydrogen pressure during the reaction allows supposing that the functional dependence of the reaction rate on pressure can be expressed as a multiplier in kinetic eq 6. Really, changing only the value of constant \( k_0^\circ \) in eq 6 we described all the kinetic curves of this series of experiments of series 4. The estimated curves and the experimental points are presented in Figure 5. For different hydrogen pressures the value of correlation of experimental and estimated curves \([C]_i\) was high and made \( R^2 = 0.985 \). The correlation of the rate constant with hydrogen pressure \((P, \text{MPa})\) in the reactor presented in Figure 6 can be formally described by the following:

\[
k_0^\circ = (1 \times 10^{-4})P^2 - (2 \times 10^{-4})P \text{ at } R^2 = 0.9963.
\]

The polynomial form of the obtained dependence \( k_0^\circ \) on hydrogen pressure and the fact that before \( P \leq 1.5 \text{ MPa} \) hydrogenation does not practically flow does not agree with any “classical” schemes of heterogeneous catalytic hydrogenation.\(^{35}\) Most data obtained in studying carbons hydrogenation on the catalysts of platinum group metals,\(^{33}\) on Ru/C in particular, show that such dependences are of the form of the curves “with saturation”. Only in some cases a nonproportionally big increase of the rate constant on pressure was observed. The authors explain this effect by the sharp increase of hydrogen solubility in saccharides aqueous solutions at high temperature and pressure. This conclusion raises a
doubt as the change of gas solubility in liquid for a three-phase system gas—liquid—adsorbent can influence only the kinetics of gas adsorption but cannot affect the thermodynamic values of the Langmuir equation, i.e., cannot change the adsorbent sorption properties.

All the facts showing unusual regularities of the kinetics of D-glucose hydrogenation on the catalyst [Ru/mesoporous hypercrosslinked polystyrene] can be explained with the assistance of the regularities of hydrogen spillover on the carrier and its ability for hydrogen storage.

As we noted before, the compositions of platinum group metals with the carriers on the basis of hypercrosslinked mesoporous polymers, polystyrene in particular, can store hydrogen in much bigger quantity than the possibility of chemisorption of the metals themselves. Numerous research of the accumulating capacity of such compositions showed that sorption and desorption isotherms are practically linear but reveal hysteresis. The desorption isotherm shows the residual quantity of the adsorbed hydrogen, which corresponds to the portion adsorbed at $P \approx 1.0\text{–}1.5$ MPa. The hysteresis on sorption isotherms is evidence of the existence of at least two types of sorbed hydrogen with more or less strong bonds between hydrogen and the catalyst. It is logical to suppose that chemisorption on the metal and on the carrier which appeared as a result of spillover shows different reaction capacity. At low pressure hydrogen chemisorption on the surface of the catalyst metal takes place. The hydrogenation reaction with chemisorbed hydrogen flows slowly. Only while increasing the pressure beginning with $P \approx 1.5 \div 2.0$ MPa when the saturation of the catalyst metal with hydrogen is achieved does the migration (spillover) of hydrogen atoms on the surface or in the volume of the carrier occur. As the activity of hydrogen migrating across the catalyst surface is higher than that of the sorbed on metal of the catalyst system we should get the very correlation of the rate constant on hydrogen pressure that is presented in Figure 6. In fact the presented model of the process of hydrogen sorption—desorption is similar to the mechanism described by the curves of Dubinin—Radushkevich sorption isotherms. The part of capillary condensation is performed by hydrogen spillover. It is clear that in this case the hydrogenation scheme is to include the modified mechanism of Rideal—Eley when hydrogen impinges from the reaction medium onto the adsorbed molecule of D-glucose. In our case the attack is performed by a loosely bound hydrogen rather atomic which migrates across the carrier surface.

**Kinetic Regularities of the Reaction, Route 2.** The discussed scheme of the second (“slow”) route of D-glucose hydrogenation allows explaining the nature of the first (“fast”) route of hydrogenation. As was mentioned, before the beginning of the reaction the catalyst was saturated with hydrogen at a predetermined time for 30 min before the substrate was introduced. During this time the thermodynamic equilibrium was established in scheme III above. Accumulated this way active hydrogen provides the first (“fast”) route of D-glucose hydrogenation. High pressure and high temperature contribute to the additional accumulation of hydrogen due to its spillover from Ru to the carrier (hydrogen storage by hydrogen spillover) and appropriately increase the share of the first route of hydrogenation (Figures 4 and 5).

The high rate of the reaction flow did not allow us to get the kinetic curves of D-glucose conversion. But this very fact allows determining precisely the share of the first route of hydrogenation in various series of experiments. The initial concentration jump discontinuity $[C]$ in Figures 2—5 corresponds to the amount of D-glucose consumed by the first reaction route. The starting decrease of D-glucose concentration depends on the initial conditions of the reaction as is seen from Figures 7—10.

If our assumption on the flow of the first route of hydrogenation reaction is correct then the amount of D-glucose reacted must depend only on the amount of hydrogen accumulated on the catalyst during the preparation of the latter. Really, the jump of D-glucose conversion observed agrees with the change of the process conditions contributing to hydrogen spillover onto the carrier. These conditions are such parameters of the process as the catalyst amount, the increase

Figure 5. Experimental points and calculated curves of D-glucose conversion depending on the change of hydrogen pressure (series 4): $P = 2.0$ (line 1), 3.0 (line 2), 4.0 (line 3), 6.0 (line 4), and 8.0 MPa (line 5) at constant values of the other parameters: $C_0 = 1.6 \text{ mol} \cdot \text{L}^{-1}$, $[\text{cat}]_0 = 2.32 \times 10^{-3} \text{ mol Ru} \cdot \text{L}^{-1}$, and $T = 140$ °C. During the reaction the pressure was maintained constant.

Figure 6. Dependence of the constant of hydrogenation rate $k^*_h$ on hydrogen pressure in the reaction system.

...
of temperature, and pressure of hydrogen. The amount of the D-glucose reacted turned out to be dependent on D-glucose initial concentrations (Figure 7) although it should have remained constant. This suggests that the share of the first route is determined not so much by the amount of active hydrogen accumulated as by the rate of its interaction with D-glucose. The assumption was made that the first reaction route is determined by the primary activity of the initial catalyst \([\text{cat}]^*\). During the reaction the catalyst for some reason loses activity turning into the catalyst leading the second reaction route although the amount of active hydrogen accumulated is not exhausted.

To go into the details of the scheme of the first reaction route and the nature of the catalyst we simulated the process with the system of two differential equations which describe the reactions of the first route.

\[
\frac{d[\text{cat}^*]}{dt} = -k(\text{I})[\text{cat}^*][\text{C}]
\]  (11)

\[
\frac{d[C]}{dt} = -k(\text{II})[\text{cat}^*][\text{C}]
\]  (12)

consumption of the active catalyst ([cat*]) with constant \(k(\text{I})\), \(L^{-1} \text{(mol·s)}^{-1}\) (eq 11) and consumption of D-glucose ([C]) with constant \(k(\text{II})\), \(L^{-1} \text{(mol·Ru·s)}^{-1}\) (eq 12). It is clear that the rate constants should be functions of the initial conditions of the process. The determination of parametric dependences \(k(\text{I})\) and \(k(\text{II})\) on the initial concentrations \([\text{cat}]_0\), \([\text{C}]_0\) and pressure \(P\) will allow giving a detailed mathematical description of the reactions of the first route and the idea of the flowing physical processes.

To achieve the aim set for each experiment in three series of single factor experiments such numerical values of constants were chosen that the final D-glucose concentration corresponded to its conversion on the first route. We chose such absolute values of rate constants so that the process did not exceed 60 s. It is clear that the real rate constants should be equal or less in magnitude but their ratio should remain constant.
The processing of the series of experiments with the change of \([\text{cat}]_0\) (Figure 8) and pressure (Figure 10) turned out to be the most simple. Varying of numerical values \(k(I)\) at constant \(k(II)\) resulted in the negative result, i.e., the rate constant \(k(I)\) should have decreased with the increase of the catalyst and pressure. We got the appropriate description of \(\delta\)-glucose primary conversion \((\Delta C)\) at constant \(k(I) = 0.2\;\text{L·mol}^{-1}·\text{s}^{-1}\) and the following functional dependences of the other constant:

\[
k(II) = 10^4[\text{cat}]_0\;\text{L·mol}^{-1}·\text{Ru·s}^{-1}
\]

\[
k(II) = 25·[P]\;\text{L·mol}^{-1}·\text{Ru·s}^{-1}
\]

The validity of approximation \((R^2)\) in these cases was 0.90 and 0.98 accordingly. The simulation of the series of experiments at changing \([C]_0\) was the most complicated. We obtained similar validity of approximation \((R^2) \approx 0.96\) in two cases: (1) at constant \(k(I) = 0.2\;\text{L·mol}^{-1}·\text{s}^{-1}\), the second rate constant had the form of:

\[
k(II) = (7.0 + 11.3[C]_0)\;\text{L·mol}^{-1}·\text{Ru·s}^{-1}
\]

(2) at constant \(k(II) = 23.0\;\text{L·mol}^{-1}·\text{Ru·s}^{-1}\), the first constant was a function of \([C]_0\):

\[
k(I) = 1/([1.5 + 2.6[C]_0])\;\text{L·mol}^{-1}·\text{Ru·s}^{-1}
\]

The last variant of simulation seems the most appropriate as it can answer the questions about the nature of the active catalyst and the reason for the change of its reaction capacity. After substituting for the dependences found into the system of eqs 11 and 12 we obtain a more informative mathematical model of the process (eqs 11a and 12a):

\[
d[\text{cat}^*]/dt = -[\text{cat}^*]/([C]/(1.5 + 2.6[C]_0))
\]

(11a)

\[
d[C]/dt = -k(I)·[\text{cat}^*]·[\text{cat}]_0/[C]·[P]
\]

(12a)

The right-hand side of eq 11a is in proportion to the linear fractional function, which is characteristic of expressing the concentration of the substrate sorbed on a heterogeneous catalyst (see Scheme 1). This fact allows assuming that the inactivation of the initial catalyst \([\text{cat}^*]\) flows through the stage of the substrate sorption. In this case using the evaluated constants of equilibria (of sorption) \(K_i\) and \(K_p\) (eqs 9 and 10) we get a more precise equation of the active catalyst consumption:

\[
d[\text{cat}^*]/dt = -k(I)^*·K_i·[\text{cat}]_0/[1 + K_i[C]_0 + (K_p - K_i)[C]_0]
\]

(11b)

If our assumptions are correct, the first route of \(\delta\)-glucose hydrogenation should be described with a system of differential eqs 11b and 12a. Integrating of this system allows determining \(\delta\)-glucose conversion in each series of experiments.

Trying to achieve minimum descrepancy between calculated and experimental values of glucose at varying values \(k(I)^*\) and \(k(II)\) we evaluated them. For all the experiments conducted at a temperature of \(T = 373\;\text{K}\) the rates constants \(k(I)^*\) and \(k(II)\) were the same, equal to \(-0.2\;\text{s}^{-1}\) and 125 \(\text{L}^2·(\text{mol Ru})^{-2}·(\text{MPa})^{-1}·(\text{s})^{-1}\) accordingly. While processing the series of experiments performed at different temperatures, within high validity of approximation \((R^2 = 0.989)\), we obtained the temperature dependences of the reaction constants:

\[
k(I)^* = \exp\left(\ln(0.2) - \frac{\Delta H_1}{R} \left(\frac{1}{373} - \frac{1}{T_k}\right)\right)\;\text{s}^{-1}
\]

(13)

\[
k(II) = \exp\left(\ln(125) - \frac{\Delta H_2}{R} \left(\frac{1}{373} - \frac{1}{T_k}\right)\right)\;\text{L}^2·(\text{mol Ru})^{-2}·(\text{MPa})^{-1}·(\text{s})^{-1}
\]

(14)

where \(\Delta H_1\) and \(\Delta H_2\) are the enthalpies of activation of the active catalyst and \(\delta\)-glucose conversion in the first route of the process; \(R\) is the gas constant; and \(T_k\) is the Kelvin temperature.

Thus mathematical modeling of the reactions allowed obtaining the parameters of the kinetic model of the first route of hydrogenation. The validity of approximation of the linear correlation between the experimental and calculated values \((\Delta[C]\text{exp})\) and \((\Delta[C]\text{cal})\) of \(\delta\)-glucose conversion for all the experimental data was \(R^2 = 0.990\) (Figure 11).

![Figure 11. Correlation between the calculated \((\Delta[C]\text{cal})\) and experimental values \((\Delta[C]\text{exp})\) of \(\delta\)-glucose conversion by the first route for all the series of experiments under study.](dx.doi.org/10.1021/jp312703j)
substrate sharply decreases the catalyst metal capacity to activate hydrogen that limits the reaction flow by the first route.

4. CONCLUSIONS

The analysis of numerous literature data on mathematical description of D-glucose hydrogenation shows the existence of different, sometimes mutually exclusive, models of the process even if one and the same metal is used in a catalytic system. It is especially noticeable in the case of using the carriers capable of storing hydrogen by hydrogen spillover. Apparently, one of the conditions of spillover effect emerging is the use of metal nanoparticles.

During the study of the regularities of D-glucose hydrogenation on the catalyst containing Ru nanoparticles on hypercrosslinked polystyrene we revealed two routes of the process. The change of the catalyst catalytic activity at the beginning of the reaction is probably explained by a slowdown of hydrogen spillover from Ru onto the carrier if the metal coordinates the reaction products. With the change of the ratio of hydrogen sorbed on the metal and the substrate (or product) the scheme (routes) of the hydrogenation processes changes.

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