

ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Selective Hydrogenation with the Use of Nanocatalysts

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Abstract—Process of single-stage hydrogenation of phenol to cyclohexanone with industrial (domestic and imported) palladium catalysts, and also with nanocatalysts synthesized in laboratory, was studied. The activation energies and rate constants were determined for various nanocatalyst samples. A comparative analysis of the hydrogenation results for the industrial and laboratory samples was made.

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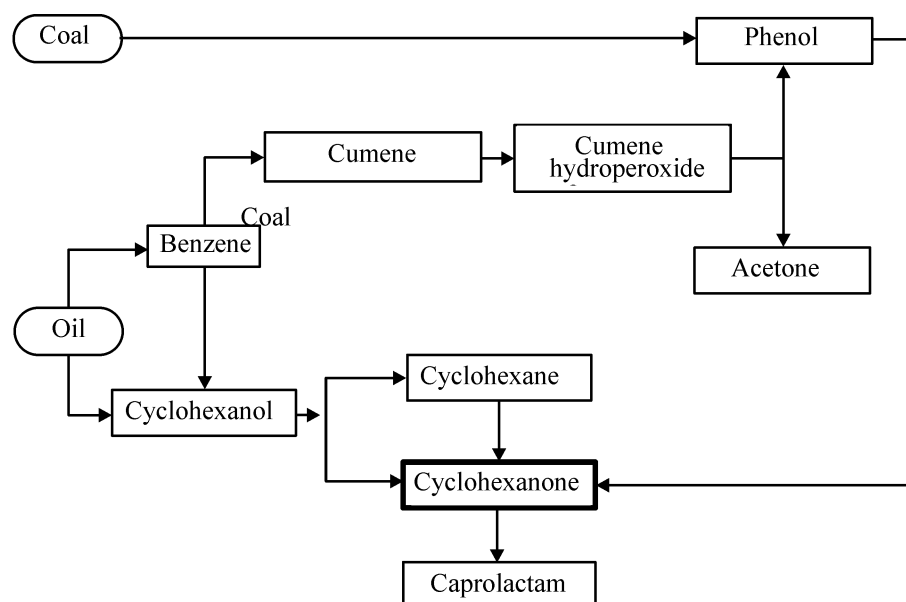
There exist two nearly equally efficient ways to synthesize caprolactam: via cyclohexane and via phenol (60 and 40% of world's manufacture, respectively) (see Scheme)

In Russia, the caprolactam production facilities were created in the mid-1960s. On the whole, they are based on the outdated cyclohexane method (85% of the total output capacity in Russia).

The main disadvantage of this method is its low selectivity: the conversion of benzene to the target product is lower than 70%, and the amount of organic by-products is as large as 0.3 ton per ton of caprolactam.

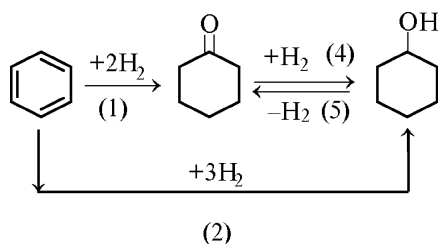
The phenol scheme for synthesis of cyclohexanone as the main intermediate product in manufacture of caprolactam has a substantially higher selectivity but involves a larger number of stages. In the case of the

Schemes of existing methods for manufacture of caprolactam



cumene process, a necessity arises for distribution of acetone.

Use of commercial phenol makes substantially lower the capital expenditure for production of caprolactam, and the expenses associated with the higher (almost twice) cost of phenol, compared with benzene [1] can be covered by introduction of a novel single-stage technology for phenol hydrogenation to cyclohexanone:



Phenol is hydrogenated in the industry by using Group-VIII metals (Ni, Co, Pt, Pd, etc.) as catalysts, but this involves a number of difficulties. Use of nickel as catalyst provides a cyclohexanone yield not exceeding 45%, with the rest constituted by cyclohexanol, which should be dehydrogenated and thereby makes larger the expenditure for synthesis of caprolactam [2].

The most efficient catalyst for hydrogenation of phenol to cyclohexanone is palladium [3, 4].

It was found that two successive reactions occur on palladium catalysts: the initially formed cyclohexanone is further hydrogenated to cyclohexanol. Because the second reaction occurs at a lower rate, compared with the main process, it is possible to select conditions in which the selectivity with respect to cyclohexanone is as high as 95–99%. Both the reactions are strongly exothermic (ΔH_r 400 and 150 kJ mol⁻¹), and, therefore, when the reaction is performed in a fivefold excess of hydrogen, the temperature of adiabatic heating-up may be as high as 300°C at a phenol conversion exceeding 80%; upon an increase in the temperature in the reaction zone from 120 to 140°C, the process selectivity falls to 85–90%.

During the recent 20–25 years, extensive studies have been carried out in order to find an efficient Pd-containing catalyst for single-stage hydrogenation of phenol to cyclohexanone [5–8].

The studies were performed under the following conditions: wide range of concentrations of Pd deposited onto a support (0.1–3 wt %); temperature range 120–200°C, liquid or gas phase, atmospheric or somewhat higher pressure; 4–5-fold molar excess of hydrogen; and volumetric flow rate of the raw material of 0.1–1.2 h⁻¹.

Table 1. Conversion of phenol at various temperatures. Volumetric flow rate of phenol 0.8 h⁻¹, hydrogen : phenol molar ratio 4 : 1

<i>T</i> , °C	Conversion, wt %, for indicated sample				
	no. 1	no. 2	no. 3	no. 4	no. 5
150	6.7	44.5	86.2	30.2	99.3
160	8.9	75.5	94.9	50.2	99.6
170	10.5	88.7	97.9	68.1	99.7
180	13.1	95.8	96.6	75.2	99.7

Table 2. Conversion *X* of phenol at various temperatures and volumetric flow rates *V* of the raw material. Catalyst sample no. 5. hydrogen : phenol molar ratio 4 : 1

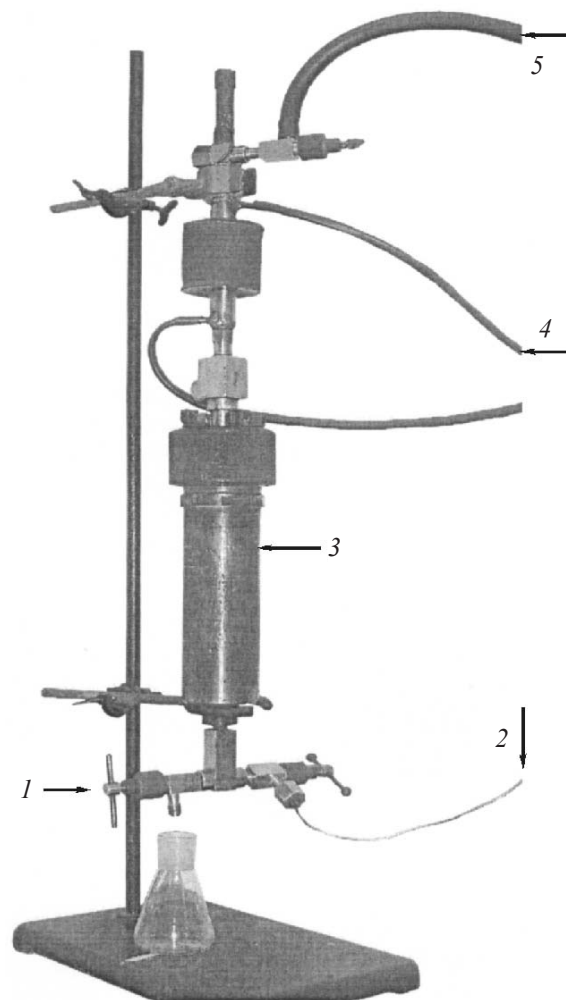
<i>T</i> = 150°C		<i>T</i> = 160°C		<i>T</i> = 170°C		<i>T</i> = 180°C	
<i>V</i> , h ⁻¹	<i>X</i> , %	<i>V</i> , h ⁻¹	<i>X</i> , %	<i>V</i> , h ⁻¹	<i>X</i> , %	<i>V</i> , h ⁻¹	<i>X</i> , %
1.1	99.3	0.8	99.6	0.5	98.4	0.8	99.7
1.1	97.3	1.0	99.4	1.2	99.7	1.3	99.6
2.0	59.6	2.6	52.5	3.3	73.9	3.2	78.0

The results of hydrogenation (in comparable modes) depended on the type of a support, method used to deposit the metal onto the support surface, and promoting additives. These results were as follows: degree of phenol conversion in the range from 10 to 100%, and the selectivity with respect to cyclohexanone, from 20 to 96%. The following most important issues can be distinguished:

(1) The process selectivity decreases if the support itself has catalytic properties; e.g., aluminum oxide or zeolites accelerate alkylation, dehydration, and polymerization.

(2) To control (suppress) the exothermicity of the process, it is necessary to use a palladium catalyst whose larger part is inactive. This is possible if the size of the inlet windows is smaller than the critical diameter of the molecule of phenol (6 Å); in this case, the reaction can occur on the secondary surface, whose area does not exceeds 10% of the total surface area of the catalyst. The second variant is a layer-by-layer dilution of the catalyst with an inert material.

(3) A considerable influence on the activity and selectivity of Pd catalysts in the reaction of phenol hydrogenation is exerted by the method of their preparation; differences in activity are due to the resulting distribution and size of palladium particles. Studies of



Setup for phenol hydrogenation to cyclohexanone. (1) Sampling valve, (2) hydrogen supply, (3) reactor body (catalyst + inert medium + phenol) heated by a clamshell jacket with electric heating, (4) feed from a liquid thermostat to preclude crystallization of the phenol vapor, and (5) hydrogen outlet. Temperature is monitored with a thermocouple inserted into the reactor cover.

recent years have placed a special emphasis on the effect of the main parameters of catalytic systems: dispersity of the metal (%) and specific surface area of the catalyst ($\text{mm}^2 \text{g}^{-1}$). It was found that the conversion and selectivity increase at palladium dispersities of 55–70% and a specific surface of no less $400 \text{ mm}^2 \text{g}^{-1}$.

(4) The main technological parameters of the process under consideration are the conversion of phenol, selectivity with respect to cyclohexanone, and stability (service life) of the catalyst.

(5) The process can be performed if the conversion

Table 3. Ratio between the products of the reaction of phenol hydrogenation (cyclohexanone/cyclohexanol) N at various conversions X and volumetric flow rates V of the raw material. Catalyst sample no. 5. hydrogen : phenol molar ratio 4 : 1

$T, ^\circ\text{C}$	$V = 0.8 \text{ h}^{-1}$		$V = 1.2 \text{ h}^{-1}$	
	$X, \%$	N	$X, \%$	N
150	99.3	8.77	97.3	12.00
160	99.6	9.16	99.4	15.57
170	99.7	9.49	99.7	9.49
180	99.7	9.1	99.6	10.33

of phenol is no less than 98–99% to avoid its recycling and the selectivity with respect to cyclohexanone is no less than 90%; the resulting cyclohexanone–cyclohexanol mixture is easily separated by rectification.

EXPERIMENTAL

The study was carried out with nanocatalyst samples synthesized by deposition of palladium onto hyper-cross-linked polystyrene (HCLPS)^a. The HCLPS matrix used to form Pd nanoparticles had the following characteristics: formal degree of cross-linking 200%, internal surface area $\sim 1000 \text{ m}^2 \text{g}^{-1}$, narrow pore size distribution peaked at around 2 nm, and polymer grain size 40–60 μm .

Pd was introduced into the HCLPS matrix from solutions of H_2PdCl_6 in methanol and tetrahydrofuran (THF). The use of solvents provides the maximum “opening” of pores and the strongest swelling of HCLPS.

The prepared nanocatalyst samples were analyzed using modern physicochemical analytical techniques: the particle size was determined by analysis of TEM micrographs, and the metal content of polymeric samples, by X-ray fluorescence analysis.

Five nanocatalyst samples were obtained. Sample nos. 1–3 were prepared by the same method and contained different amounts of palladium (0.1, 0.3, 0.5 wt %). The content of Pd in sample nos. 3–5 was the same (0.5 wt %), but the samples differed in the method of metal deposition onto the support surface.

In hydrogenation of phenol on palladium catalysts, a special requirement is imposed upon the content of sulfur compounds in the raw material. Phenol of

^a Samples synthesized at Tver State Technical University.

Table 4. Comparative kinetic parameters of phenol hydrogenation on various catalysts

Catalyst		$T, ^\circ\text{C}$	Apparent activation energy, kJ mol^{-1}	Rate constant $k_{\text{obs}}, \text{mol g}^{-1} \text{h}^{-1}$	Optimal parameters	
no.	type				$X, \%$	selectivity with respect to cyclohexanone, %
6	Industrial domestic	136–177	39 ± 15	0.06	92–96	86–88
8	Industrial imported	141–170	36 ± 10	0.056	92–93	90–92
5	Laboratory nanocatalyst	150–180	36.1 ± 4.9	0.055	99–100	90–95

analytically pure grade, additionally purified on Ni/Re at 120–140°C, was used in the experiments. The content of sulfur compounds was lowered from 0.1 to 0.005 wt %.

The reaction mixture was analyzed by GLC on a 20-m-long strongly polar PEG-20M capillary column (polyethylene glycol as stationary phase), which effectively separated closely boiling components of the mixture (phenol, benzene, cyclohexanone) at a flame ionization detector temperature of 250°C.

Preliminary tests of sample nos. 1–5 were performed in a flow-through glass reactor with a volume of 2 ml. The charged amounts of all catalyst samples were the same (0.9 g). The results obtained in the temperature range 150–180°C are listed in Table 1.

The highest activity and stability under the experimental conditions was observed for sample no. 5 {0.5% Pd[PdCl₂(CH₃CN)₂]}. Further studies of the effect of temperature and volumetric flow rate of the raw material were performed with this sample (Tables 2, 3).

The results obtained demonstrate that, on sample no. 5 in the temperature range 160–180°C and volumetric flow rates of phenol of 0.8–1.3 h⁻¹, the conversion of phenol is 99.4–99.6% at a selectivity of 90.5–94% with respect to cyclohexanone.

Stand tests were carried out with sample no. 5 in the optimal modes (see figure). For comparison, industrial palladium catalysts of domestic (sample no. 6) and foreign make (sample nos. 7, 8), in which palladium is deposited in amounts of 0.3–0.6 wt % onto aluminum oxide promoted with alkali metals, were tested in the same modes.

The process conditions were as follows: temperature

range 110–200°C, pressure 1–10 atm, hydrogen : phenol molar ratio (10–50) : 1, hydrogenation time 0.5–3 h. Cyclohexanone was isolated from the reaction mass by rectification.

The main results obtained for industrial samples (nos. 6–8) and nanocatalyst sample no. 5 are listed in Table 4. The experimental data were used to estimate the activation energy and the kinetic parameter that takes into account the catalyst concentration and the flow rate at the reactor inlet [10]:

$$m = (F/kP) \ln [1/(1 - X_a)],$$

where m is the catalyst mass (g); F , flow rate of phenol (h⁻¹); k , kinetic factor; P , pressure (atm); and X_a , conversion of phenol.

Analysis of the data in Table 4 shows that the kinetic parameters of all the samples have close values. However, the required technological parameters of the process, i.e., the conversion of phenol (99–100%) and the ratio between the target products, cyclohexanone and cyclohexanol (not lower than 9–10, which corresponds to a selectivity of 90–95% with respect to cyclohexanone), were obtained only with the nanocatalyst sample no. 5 {0.5% Pd[PdCl₂(CH₃CN)₂]}.

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