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Cyclization and Dehydrocyclization of C_5 Hydrocarbons over Platinum Nanocatalysts and in the Presence of Hydrogen Sulfide

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Transformation of aliphatic C_6–C_8 hydrocarbons into cyclic ones (mainly benzene and its homologues) is well studied for a long time due to works by N.D. Zelinskii and his school [1]. In the case of C_6 hydrocarbons, such as *n*-hexane and *n*-hexenes (and higher linear hydrocarbons), the use of platinum dehydrocyclization catalysts affords aromatic hydrocarbons in reasonable yields and the corresponding technological process ("platforming") was accomplished in industry long ago.

However, the yields of dehydrocyclization products from C_5 hydrocarbons are very low when common platinum catalysts are used. Nonetheless, the cyclization of C_5 hydrocarbons is a rather new field of research of practical interest. Indeed, C_5 cyclic products, such as cyclopentadiene (CPD), its dimer (dicyclopentadiene, DCPD), cyclopentene (CPE), and cyclopentane (CPA) are used for synthesizing various products with valuable properties [2]. One of the interesting fields in the application of CPD and DCPD is the synthesis of strained hydrocarbons [3, 4]. Recently, an interest is shown in the epoxidation of DCPD for further preparation of synthetic resins, additives to petroleum products, etc. [5].

At present, CPD and DCPD are isolated from the by-products of gasoline pyrolysis and coal carbonization. The extension of sources is possible only using synthetic methods. In this context, the synthesis of cyclic C_5 hydrocarbons by the cyclization of linear precursors becomes urgent.

In this work, we have studied the dehydrocyclization of C_5 hydrocarbons—piperylene (pentadiene-1,3), pentenes, and pentane—with the use of (i) nanodisperse platinum catalyst on Al_2O_3 or SiO_2 and (ii) hydrogen sulfide as an initiator [6].

RESULTS AND DISCUSSION

Dehydrocyclization of piperylene over heterogeneous platinum nanocatalysts. We developed a procedure for the preparation of a new supported platinum catalyst under conditions providing a high degree of dispersion of deposited platinum. The choice of the method agrees with the recent studies on nanocatalyst preparation [7]. In particular, the preparation of 2.2-nm platinum nanoparticles by reduction of platinum salts with alcohols and their use as hydrogenation catalysts has been reported [8]. To obtain platinum nanoparticles, we used the reduction or thermal decomposition of metal complexes [9, 10]. The platinum-on-alumina catalyst (2% Pt on Al_2O_3) was prepared by impregnation of calcined Al_2O_3 grains with an aqueous solution of chloroplatinic acid $H_2[PtCl_6]$ followed by drying at 100°C and activation in a hydrogen flow at 400–500°C. Samples of the platinum-on-silica catalyst (2% Pt on SiO_2) were obtained by our procedure via impregnation of calcined silica gel grains with a benzene solution of tetrakis(triphenylphosphine)platinum(0) $Pt[(C_6H_5)_3P]_4$ and tetrakis(triphenyl phosphite)platinum(0) $Pt[(C_6H_5O)_3P]_4$ in a carefully purified nitrogen atmosphere followed by removal of benzene in vacuo and thermal activation at 150–200°C in a nitrogen flow.

Under these conditions, we obtained a highly dispersed platinum catalyst with the expected increased activity. The control analyzes[1] of the samples of platinum on silica gel prepared by the above procedure showed that the samples contain nanoparticles with sizes in the range 3–7 nm. This corresponds to nanosized Pt_n clusters ($1 \leq n \leq 20$) containing valence-unsaturated platinum atoms. These nanocatalysts stabilized

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Table 1. Dehydrocyclization of C_5 hydrocarbons over platinum catalysts (2% Pt on support, contact time is 15 min at 600°C, dwell time in the reactor is 0.8 s, dilution with nitrogen is 1 : 6 by volume)

Catalyst type*	Solvent	Support	Conversion of raw materials, %	Yields of products**, %		
				CPD	CPE	CPA
Dehydrocyclization of piperylene						
A	Benzene	SiO_2	88.3	53.6	4.7	0.1
B	Benzene	SiO_2	83.2	58.1	2.2	–
C	Water	Al_2O_3	32.1	11.3	1.3	0.4
C	Water	SiO_2	36.9	36.8	5.6	1.8
Dehydrocyclization of *n*-pentenes						
A	Benzene	SiO_2	85.9	35.8	0.7	0.2
B	Benzene	SiO_2	76.9	29.1	3.8	–
C	Water	Al_2O_3	33.4	3.9	–	0.1
C	Water	SiO_2	41.7	6.7	1.3	0.2
Dehydrocyclization of *n*-pentane						
A	Benzene	SiO_2	73.9	21.4	2.7	0.3
B	Benzene	SiO_2	79.0	6.0	1.2	2.1
C	Water	Al_2O_3	17.6	1.4	0.1	0.1
C	Water	SiO_2	21.1	0.7	–	–

* A, $Pt[(C_6H_5)_3P]_4$; B, $Pt[(C_6H_5O)_3P]_4$; C, $H_2[PtCl_6]$.
** The rest is C_1–C_4 hydrocarbons and tars.

in part with residual phosphine or phosphite ligands should be very sensitive to water and oxidation by traces of oxygen. To prevent catalyst degradation, we operated in an atmosphere of specially purified nitrogen.

The results of dehydrocyclization experiments are given in Table 1. The results show that the samples of the platinum catalysts of types A and B prepared by the above procedure provide a sharp (up to 53–58%) increase in the yield of CPD in the dehydrocyclization of piperylene. Moreover, *n*-pentenes and, unexpectedly, even *n*-pentane over a highly dispersed platinum catalyst form dehydrocyclization products in 35 and 21% yield, respectively. Unfortunately, the revealed high activity of the platinum nanocatalyst in the dehydrocyclization of C_5 hydrocarbons retains only within first minutes of operation (most often not longer than 15 min). Even the first oxidative–reductive regeneration to remove tar and coke destroys active centers. It is clear that aggregation of particles occurs resulting in a metal crystal lattice with a much lower content of valence-unsaturated platinum atoms, which is typical of nonstabilized nanosystems. If an appropriate method for the high-temperature stabilization of hyperactive platinum nanocatalyst is found in the future, this will open new interesting possibilities for practice.

Table 2. Cyclization of piperylene in the presence of hydrogen sulfide (molar ratio $C_3H_8 : H_2S = 1 : 1$)

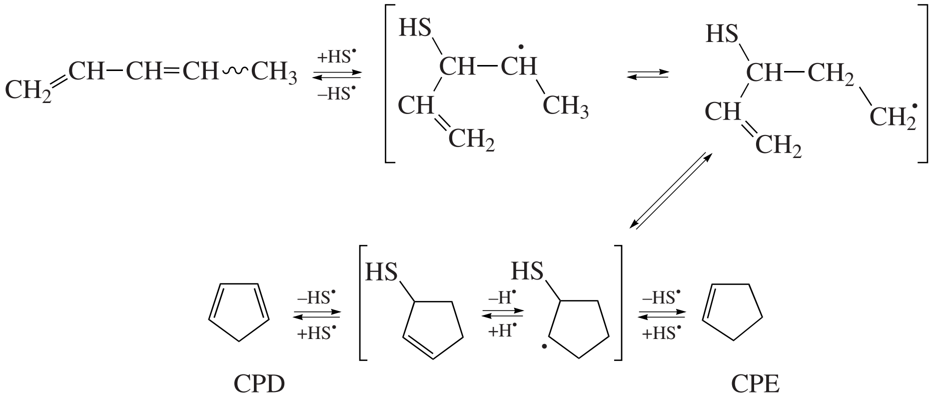
Temperature, °C	Dwell time in the reaction zone, s	Piperylene conversion, %	Yield*, %	
			CPD	CPE
550	4.0	10.9	9	57
600	2.0	23.8	12	59
650	0.7	35.0	25	50
700	0.3	45.1	45	28

* The rest is *n*-butenes, *n*-butane, C_1–C_3 hydrocarbons, and tars.

Dehydrocyclization of piperylene in the presence of hydrogen sulfide. It was found earlier that the gas-phase thermocatalytic cyclization of 1,3-pentadiene (piperylene) in the presence of hydrogen sulfide made it possible to simultaneously obtain CPD and CPE [6], although the scope and mechanism of these reactions remained unclear. We studied the reaction of piperylene (a mixture of *cis* and *trans* isomers) in the presence of H_2S. All experiments for comparison with the previous results were carried out in the same reactor under the same conditions (but in the absence of the solid catalyst). The results are presented in Table 2.

These data show that, at 550–650°C, the piperylene conversion is low (about 10–35%) and CPE is the main product. Thus, piperylene cyclization preferably takes place under these conditions. When temperature was elevated to 700–750°C, the conversion level rose and the yield of CPD increased, while the yield of CPE correspondingly decreased. Thus, the growth in reaction temperature leads to the domination of piperylene dehydrocyclization.

At temperatures about 500°C, hydrogen sulfide undergoes thermal dissociation to form thiyl free radicals $HS^{\cdot}$. The cyclization of piperylene results from primary, probably reversible, attack of the thiyl free radical at the double bond followed by the transformations of the nascent intermediate free radicals. It is obvious that only cisoid conformations of intermediates with closely spaced terminal carbon atoms can be responsible for the cyclization. Under this assumption, the cyclization may be considered as the ultimate result of a series of sequential transformations of intermediate free radicals exemplified in Scheme 1.



Scheme 1.

In this work, we proceeded from the working hypothesis on the similarity of mechanisms of action for the above fundamentally different catalysts in the thermocatalytic transformations of C_5 hydrocarbons. Thus, in spite of the difference between the thermocatalytic cyclization of piperylene in the presence of hydrogen sulfide and its dehydrocyclization over the platinum catalyst, one can note an important similarity in reaction mechanisms at the initial key stage: both thiyl radicals and platinum atom have a common feature, an unpaired electron, which can attack the C=C double bond. The attack can occur by the 3*p* unpaired electron of the sulfur atom in the first case and by the unpaired 6*s* electron of the platinum atom in the second case. If this assumption is correct, the mechanism of initiation of piperylene cyclization over valence-unsaturated platinum atoms under comparable conditions should not differ fundamentally from that of initiation of cyclization with thiyl radicals. Based on this assumption, we developed the above procedure for the preparation of the platinum-on-silica catalyst under conditions that provide a high degree of dispersion of deposited platinum.

EXPERIMENTAL

Nitrogen was purified from traces of oxygen (with activated copper shavings) and water (with freshly calcined Al_2O_3). Benzene used as a solvent for the above platinum complexes was deoxygenated and dried by refluxing with 5% of triethylaluminum followed by distillation in a purified nitrogen flow. Initial C_5 hydrocarbons were purified prior to use from traces of oxygen and water by treatment with a 5% triethylaluminum solution in benzene. The preparation of the platinum catalysts is described above.

The dehydrocyclization was carried out in a quartz tubular reactor by passing raw materials through a fixed bed of a catalyst activated by heating immediately prior to feeding the raw material. The experiments were conducted at 500–750°C and upon dilution of raw materials with purified nitrogen in volume ratio of 1 : 6.

Both the initial C_5 hydrocarbons and reaction products were analyzed by GLC (triethylene glycol *n*-butyrate on Chromosorb as the stationary phase, capillary column, column temperature 20–30°C, flame ionization detector, nitrogen carrier gas).

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