

New Organic Synthesis Processes

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New Organic Synthesis Processes

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Preface

The latest trends in the world's science and industry of organic synthesis are the production of novel more effective chemical compounds and the creation of progressive technologies for the production of already known and widely used products. The new technologies must meet high requirements, especially as regards the selectivity of chemical reactions and the absence of production wastes.

Scientists and specialists of a number of Soviet research institutes have developed or radically improved scores of production processes distinguished by their high technical level. They employ new chemical reactions, progressive engineering and technological solutions, and are noted for their diminished consumption of materials and energy. These processes make it possible to expand the starting material resources by drawing in less scarce kinds of hydrocarbons, making a better use of the by-products, and improving the ecological conditions of production. Owing to the enumerated advantages, most of these processes differ from the traditional ones in a substantial reduction of the capital outlay and operating costs, and also in a higher labor productivity.

The novel processes presented in this book include primarily the catalytic pyrolysis of hydrocarbons, the production of propylene oxide, methylethylketone, allyl acetate, acetopropyl acetate, allyl alcohol, pentan-2-ol, unsaturated higher alcohols, 2-methoxypropene, and the oxidizing methylation of various compounds.

A description is given of the radical improvements introduced in the technology of industrially important processes such as the production of higher 1-alkenes, acetaldehyde, isobutylmethylketone and isobutylmethylcarbinol, glycidol, some oligomers of the lower alkenes, and alkylaromatic hydrocarbons.

Also treated are new developments in the technology of producing some comparatively novel compounds including allene, methylacetylene, and oxygen-containing compounds of the cyclobutane series.

The aim of the present book is to acquaint a broad circle of specialists of the chemical and petrochemical industry with new developments. It sets out information that is practically absent in scientific monographs and textbooks. The slight information on these pro-

cesses contained in periodical publications, reports, and patent literature is scant and incomplete.

The book considers the scientific fundamentals of processes, presents brief, but the most important information on the chemism and kinetics of the reactions, the technology and equipment, the technical and economical aspects of production processes, and on the fields of application and the significance for the national economy of the obtained organic synthesis products.

The processes described in the book have been developed at the leading Soviet institutes in the field of industrial organic synthesis and petrochemistry. The specialists who supervised this work or took an active part in it were invited to participate in writing the book.

Sergei P. Chernykh

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Chapter 1. Hydrocarbon Starting Materials

1.1. Pyrolysis

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1.1.2. Pyrolysis of Heavy Petroleum Fractions

1.1.3. High-Temperature Pyrolysis of Fuel Oil

1.2. Separation and Recovery of Pyrolysis By-Products

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1.1. Pyrolysis

The petrochemical potential of the industrially developed countries is determined by their production of the lower alkenes—ethylene and propylene. These alkenes together with aromatics, primarily benzene, are the starting materials for the organic synthesis industry. At present, the lower alkenes in the world's petrochemical industry are produced by the pyrolysis of gaseous and liquid hydrocarbon feedstock in pipe furnaces or stills characterized by virtually extreme yields of the target products. This has been facilitated by continuous improvements in the pyrolysis process. A fundamental improvement consisted in the development and introduction of pyrolysis furnaces with a vertically arranged pyrolysis coil enabling the process to be conducted in the region of low contact times and high temperatures. Another improvement consisted in the inclusion in the furnace units of hardening and vaporizing apparatus. The latter utilizes the heat of the pyrolysis products with the generation of high-pressure steam used to drive the pyrolysis gas compressors [1].

Notwithstanding the appreciable improvement in the technical and economical indices of pyrolysis in pipe furnaces, the latter have a number of shortcomings. For instance, the more rigorous pyrolysis conditions in the processing of heavy petroleum fractions increase the thermal stresses in the reactor surface and require the use of more heat-resistant materials for fabricating the pyrolysis tubes.

The fundamentally novel process of pyrolysis on heterogeneous cat-

alysts improves the selectivity of pyrolysis and, accordingly, lowers the consumption of the starting materials, which are the basic criteria for appraising the technical and economical indices of ethylene production. Catalytic pyrolysis proceeds at lower temperatures than pyrolysis in pipe furnaces, and no heat-resistant materials are needed for its embodiment.

The prevailing difficulties in supplying large plants with a homogeneous feedstock (e.g., gasoline or naphtha fractions) necessitate the creation of flexible pyrolysis flow diagrams that make it possible to employ a wider range of hydrocarbon feedstock, including atmospheric and vacuum gas oils. Preliminary hydrofining allows these kinds of feedstock to be used in ethylene plants outfitted with pipe furnace pyrolysis units.

A very important way of economizing in light petroleum products and in petroleum as a whole is the processing of the heavy petroleum residues (fuel oil, tar). The use of these products as a pyrolysis feedstock, which will extend the range of petrochemical starting materials, requires the development of special pyrolysis processes and the design of the relevant reactors.

1.1.1. Catalytic Pyrolysis of Hydrocarbons

The search for pyrolysis catalysts was begun many years ago. Initially metals such as nickel, molybdenum, tungsten, aluminium, iron, and copper were studied. They were not effective because they chiefly catalyzed the deep decomposition of hydrocarbons with the formation of hydrogen, methane, and coke. The oxide catalysts studied at that time were also ineffective.

The first publications showing the possibility of employing heterogeneous catalytic systems based on metals for intensifying the pyrolysis of hydrocarbon raw materials appeared in the second half of the 1960's [2]. But even in the middle of the 1970's, some scientists refuted the very possibility of catalysis at temperatures close to 800 °C, notwithstanding the fact that by this time data had been obtained confirming the higher yield of ethylene in the presence of oxide heterogeneous catalysts.

To date, much information has been accumulated concerning the catalytic pyrolysis of various kinds of hydrocarbon starting materials that convincingly confirms the effectiveness and catalytic nature of the process [3, 4]. The notion of high-temperature catalysis has also changed.

Among the catalysts used in the pyrolysis of hydrocarbons and proposed by various investigators, a vanadium catalyst (potassium metavanadate KVO_3) on a support modified with boron oxide has been developed the most completely [5-8].

Studies of catalytic hydrocarbon pyrolysis with the use of the

above catalyst [9, 10] have revealed that in the processing of liquid and gaseous hydrocarbons (from ethane to vacuum gas oil), the ethylene yield grows by 20-30% in comparison with that in thermal pyrolysis, the temperature of catalytic pyrolysis being 40-80 K lower than in the thermal process.

The development of pyrolysis catalysts suitable for commercial use required the carrying out of a large volume of theoretical and technological research. Studies of the catalytic pyrolysis of individual hydrocarbons and their mixtures gave birth to the basic notions on the mechanism of the process and brought to light its features and fundamental laws. The problems of coke formation have been studied, the demands to pyrolysis catalysts have been determined, and the flow diagrams and equipment for the process have been developed.

Catalysts. Pyrolysis catalysts must have a high activity and selectivity. They must ensure higher yields of ethylene and other lower unsaturated compounds and lower yields of methane and liquid products than in thermal pyrolysis. Catalysts must also have a high stability and strength and a low carbon deposit.

Pyrolysis catalysts are a complicated system whose main components are an active substance and a support. The latter, having a certain catalytic activity, imparts the required mechanical properties (strength) to the catalyst and improves its stability. The active component in most of the proposed pyrolysis catalysts mainly consists of oxides of variable valence metals such as vanadium, niobium, indium, and iron. The catalytic activity of such oxides in pyrolysis seems to be associated with a change in their valence in a catalytic process. For example, it has been shown that an oxidized vanadium pyrolysis catalyst containing pentavalent vanadium as its active component has (without preliminary activation) a low activity. It acquires its maximal activity only after the vanadium is reduced by hydrogen (e.g., by the hydrogen contained in the pyrolysis products) to a lower valence. A highly reduced catalyst specimen exhibiting a high activity from the very first moments of supplying the feedstock evidently contains vanadium reduced to $\text{VO}_{0.5}$ (a monovalent state), which has been detected on its diffraction patterns. The time needed to reduce vanadium to its active state depends on the temperature—at 300 °C this requires 15 min, and at 750 °C, less than 1 min. Oxidation-reduction reactions can also be assumed to proceed in catalytic pyrolysis for other catalysts.

The support plays an exceedingly great role in forming the properties of a catalytic system for pyrolysis. The chemical nature of the support and the structure of its pores substantially affect the stability and activity of the supported catalysts and their likelihood of depositing carbon during pyrolysis. This is why supports must have definite properties such as a comparatively small specific

surface area [10] and sufficiently large pores. The supports used when studying catalytic systems included pumice, which meets the above requirements, but has an inadequate mechanical strength, corundum, which consists mainly of alpha aluminium oxide prepared from the gamma oxide by calcination at 1400-1600°C, and mullite-corundum. These supports are characterized below [11]:

	Pumice	Corundum	Mullite-corundum
Bulk mass, kg/m ³	350	[1200]	2400
Specific surface area, m ² /g	6	1	1
Average pore radius, μm	7	—	7
Mechanical crushing strength, MPa	20	70]	100

The tested supports have a certain catalytic activity. A definite relation can be traced between the activity and the carbon deposit of catalysts and supports: the carbon deposit of catalysts depends on that of the supports, but is about half of the latter value. The specific surface area of a support, like that of a catalyst as a whole, must never exceed 1-5 m²/g [11].

Recent years saw the synthesis of a ceramic support—mullite-corundum, which in its properties is not inferior to synthetic corundum, while in some properties is superior to it [12]. Mullite-corundum includes fractions of electrocorundum of a various granulometric composition and kaolin.

The results of studying specimens of supports varying in their composition and pore structure have shown that a decrease in the content of the fine fraction (kaolin) in the supports is attended by a higher yield of ethylene from straight-run gasoline (petrol) and by less carbon deposition. For compositions with a constant ratio of the large and medium fractions, these properties change especially sharply at a kaolin content below 25%. This is why it is good to use mullite-corundum supports with a kaolin content not over 20-25%.

The following steps are used to prepare pyrolysis catalysts: application of the active substance onto the support, drying, calcination, cooling of the catalyst, and activation thereof by hydrogen [10]. The active component is applied by impregnating the support with its aqueous solution, e.g. potassium vanadate, whose concentration corresponds to the required content of the active component on the support, and evaporation of the solution until dry. Vanadium catalysts on various supports prepared in this way generally contained 15-20% of the active substance. A lower content of the latter detracted from the catalyst activity. Another way of impregnation consists in holding the support in a solution of the active component containing its excess amount in comparison with that needed to prepare an active catalyst under definite (standard) conditions. When preparing a potassium vanadate catalyst, the concentration of the

impregnating solution should be 9.8% of KVO_3 at an impregnation temperature and duration of 80 °C and one hour, respectively. Catalysts prepared by impregnation without evaporation (CVI) and containing 2.8-4.5% of potassium vanadate are not inferior in their activity to a catalyst prepared by impregnation with evaporation (CVE) and containing 15% of KVO_3 . After impregnation, the catalyst is dried for two or three hours at 90-120 °C. The next step is calcination. The activity of a catalyst grows with elevation of the temperature and more prolonged calcination, as well as with slow cooling (Table 1.1). The conditions under which a catalyst is dried, on the other hand, do not affect its activity.

Table 1.1. Yield of Main Products in the Catalytic Pyrolysis of Gasoline (Catalyst calcination temperature = 750 °C, drying temperature and duration 90 °C and 2 h, rapid cooling)

Catalyst*	Yield, %					
	CH_4	C_2H_4	C_3H_6	C_4H_{10}	Total gas	Carbon deposit
<i>Calcination during 6 h</i>						
Support (corundum)	11.2	32.3	13.2	4.5	69.0	0.40
CVI-2.8**	13.4	42.6	14.8	5.6	85.2	0.13
CVI-2.8	13.8	39.6	12.8	4.0	79.4	0.13
CVI-2.8	12.3	40.3	13.2	5.1	79.0	0.13
<i>Calcination during 2 h</i>						
CVE-5	12.1	33.2	14.4	4.9	72.1	0.10
CVE-15	14.6	40.3	13.8	6.3	86.3	0.20

* The catalysts CVI and CVE have been prepared by impregnation and evaporation, respectively. The figures indicate the content of the active component (in %).

** Slow cooling.

Electron-microscope studies of a catalyst in different steps of its preparation have revealed [12] an increase in the dispersion of the active component, which on a prepared catalyst consists of octahedral and hexagonal crystallites with various shape defects. The phase composition of a vanadium catalyst in the course of its preparation also changes. X-ray diffraction analysis suggests that the phases KVO_3 and $V_2O_4 \cdot 6V_2O_5 \cdot nH_2O$ are present on uncalcined specimens. After calcination, these phases vanish and the phase $VO_{0.5}$ appears, while sometimes vanadium bronze of the composition $K_4V_{10}O_{27}$ is present. After the reduction step, the content of the $VO_{0.5}$ phase increases quite noticeably. Consequently, during the synthesis of a vanadium catalyst, the valence of the vanadium diminishes.

The electron-microscope studies have shown that the crystallites of the active component on the surface of CVE catalysts have an edge length of 10 μm , are stratified, and form islet clusters; part of the active component is not effective. On CVI catalysts, the dispersion of the active component crystallites is greater, and their size is 0.1–1.0 μm [10]. Hence, by choosing an appropriate way of synthesizing a catalyst and its characteristics, one can lower the content of the active substance four or five times without changing the activity of CVI catalysts [10].

The deposition of carbon on catalysts, which is one of the most important practical problems when developing them, can be diminished by adding suitable modifiers. For a vanadium catalyst, boric acid was found to be the best of the studied modifiers (K_2SO_4 , K_2CO_3 , Fe_2O_3 , H_3BO_3 , etc.). An addition of boric acid in a concentration of 1.9% to a catalyst lowers the carbon deposit several times [13]. Boron oxide forms on the catalyst after calcination. Its inhibiting effect consists chiefly in retarding the reaction of carbon deposition on the surface of the catalyst and, to a much smaller extent, in accelerating the reaction of carbon gasification with the formation of carbon oxides. When the pure active component KVO_3 and KVO_3 together with H_3BO_3 are deposited on a support, crystallites varying in structure form. In the latter case, the dispersion of the catalytic system increases substantially and the size of the crystallites diminishes by an order of magnitude. Amorphous globular formations are discovered on the surface of a catalyst (the globules are 0.7–2.0 μm in size). They block part of the catalyst surface and prevent the deposition of carbon on it. Moreover, an increase in the dispersion of the active substance as a result of introduction of a modifier leads to more complete coverage of the support surface. This affords better protection of the latter, which without such protection is more prone to carbon deposition than the active component. The introduction of boric acid into a vanadium catalyst being tested in a pilot plant increased the duration of the continuous operation of the plant several times (without regeneration—the removal of the carbon from the catalyst).

Of the proposed and studied pyrolysis catalysts, the vanadium and indium ones have the highest activity (Table 1.2). It should be noted that the deposition of carbon on an indium and iron-chromium catalysts is significantly (two and more times) higher than on a vanadium catalyst.

Fundamental Laws. The results of catalytic pyrolysis of various feedstock on a vanadium catalyst under laboratory conditions are presented in Table 1.3 on p. 17 [4].

The high carbon yields in the processing of vacuum gas oil hamper its use in catalytic pyrolysis, therefore it is good practice to preliminarily subject it to hydrogenation. Here the lower deposition of

Table 1.2. Results of Pyrolysis of Straight-Run Gasoline on Various Catalysts

Parameter	Catalytic pyrolysis*					Thermal pyrolysis
	1	2	3	4	5	
Temperature, °C	780	780	750	850	780	840-850
Duration of contact, s	0.1	0.1	0.4	0.68	0.1	0.5-0.6
Steam:feedstock ratio	1:1	1:1	2:1	1:1	1:1	0.5:1
Product yield, %:						
H ₂	1.8	1.4	1.0	2.5	1.2	0.9
CO	1.0	0.4	2.9	2.5	0.4	0.2
CO ₂	0.3			13.8		
CH ₄	14.5	20.4	10.0	17.3	14.5	15.5
C ₂ H ₆	1.7	7.5	—	1.8	—	4.2
C ₂ H ₄	39.9	39.3	30.5	36.3	39.1	28.7
C ₃ H ₈	0.5	0.3	—	0.9	—	0.3
C ₃ H ₆	14.1	16.3	16.3	13.4	16.8	14.8
C ₄ H ₁₀	0.3	—	—	—	—	0.5
C ₄ H ₈	3.4	0.6	4.1	1.0	—	5.1
C ₄ H ₆	6.0	1.9	1.3	4.8	5.4	4.3
unsaturated hydrocarbons C ₂ —C ₄	63.4	58.1	52.2	55.5	61.3	52.9
Degree of gas formation, %	83.8	88.1	75.9	80.1	86.9	75.2

* 1—20% of potassium vanadate on corundum [11]; 2—20% of indium oxide on pumice [14]; 3—iron-chromium catalyst (88% Fe₂O₃, 7% Cr₂O₃, and 5% Al₂O₃ + CaO) [15]; 4—calcium and aluminium oxides [16]; 5—20% of potassium chloride on pumice.

carbon will be attended by a substantial increase in the ethylene yield.

The temperature is a very important parameter of catalytic pyrolysis. When the temperature is raised from 700 to 780 °C, the yield of ethylene and butadiene continuously grows, while the yield of propylene reaches a maximum at about 760 °C. In the presence of a vanadium catalyst on corundum, the optimal pyrolysis temperature is about 780 °C (Fig. 1.1a). The highest yields of ethylene and propylene are observed at a contact time of 0.1 to 0.2 s (Fig. 1.1b) [17].

Consequently, the optimal conditions of catalytic pyrolysis are displaced appreciably in the direction of more moderate parameters than in thermal pyrolysis (the optimal temperature is lower by 40-60 K).

Catalytic pyrolysis, like the thermal process, is conducted in the presence of steam that lowers carbon deposition and usually increases the yield of lower alkenes. For instance, in the pyrolysis of pro-

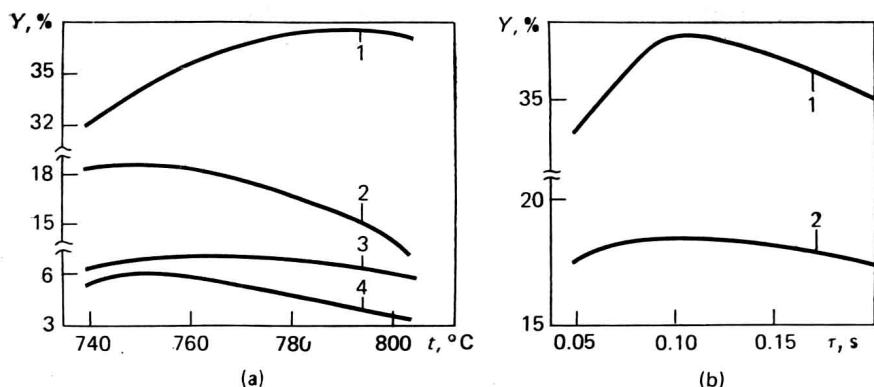
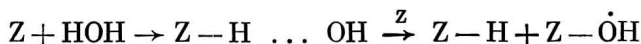


Fig. 1.1.

Yield Y of unsaturated C_2-C_4 hydrocarbons with respect to the processed feedstock versus the temperature t at a contact time of 0.1 s (a) and versus the contact time τ at 780 °C (b) (a steam:feedstock ratio of 1:1)

1— C_2H_4 2— C_3H_6 3— C_4H_6 4— C_4H_8

pane in the presence of a vanadium catalyst, steam lowers the deposition of carbon at least two times, noticeably increases the yields of ethylene, propylene, C_4 alkenes, and butadiene, and also increases somewhat the conversion of the initial hydrocarbon. Steam has a still more appreciable effect when other catalysts are employed (e.g., indium oxide). The water is apparently chemisorbed on the active centers formed as a result of the interaction of the support with the active component and dissociates by the reaction



forming active radicals (Z is an active center on the support surface).

The influence of the diluent on the catalyst activity depends on the nature of the support. The degree of dilution and the nature of the diluent when using pure supports does not affect their activity.

The optimal steam:feedstock ratio for the catalytic pyrolysis of n -hexane in a laboratory plant was 1:1. It has been shown in an experimental plant, however, that the lowering of this ratio to 0.7 diminishes the yield of lower alkenes negligibly.

In the catalytic pyrolysis of a mixture of hydrocarbons of various classes, their mutual influence has been noted. For instance, the experimental data obtained in the pyrolysis of a mixture of n -octane and isooctane (1:1) in the presence of a vanadium catalyst on corundum differ from the values calculated by the additivity rule in the direction of an increase in the degree of gas formation and in the yields of ethylene, propylene, and butylene. The deviations reach