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Catalysis: 2000 AD[1]

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Abstract—A review of achievements in the science of catalysis that have seen use in industry is presented. Special attention is given to homogeneous catalysis and prospects for the use of methane and relevant raw materials in large-scale organic syntheses.

INTRODUCTION

An attempt to survey the state of the art in such a field of science as catalysis, which has been rapidly growing for the last two centuries, inevitably comes across various obstacles. The most serious of them is the limited space of a journal article, which is too small to analyze the main achievements, not even list them. The only way to surmount this obstacle is to focus on the main elements and ignore minor, although notable, details. Of course, any selection of this sort is subjective. Thus, a bird's eye view of the earth distinguishes only sizeable objects, although smaller constructions may be competitive in artistry and historical importance.

Of the three divisions of physical chemistry, catalysis fills a special place because it is most closely related to chemical industry. In addition to problems that are common to any field of basic science, catalysis is involved to a greater degree in solving industrial problems that society sets than thermodynamics and chemical structure theory. Therefore, here I focus on achievements that found use in industry. The first section of this paper provides their summary.

Starting from the 1960s, homogeneous catalysis by metal complexes has been growing very rapidly. The main achievements in this field are discussed in the second section.

Other sections consider the role of catalysis in the development of raw materials for basic organic syntheses and its role in solving the problems of energy and environment in modern chemistry.

The relationships between catalysis and material science (the syntheses of new materials from bakelite in the beginning of the 20th century to Ziegler–Natta syntheses of polyolefin and polyketone syntheses, the use of zeolites and zeotypes in oil refining and organic synthesis, etc.), and the problems of kinetics and the mathematical modeling of catalytic processes [1] are outside the scope of this review.

MAIN ACHIEVEMENTS IN CATALYSIS

The beginning of the deliberate use of catalysis refers to 1746–1749 when the first large-scale manufacture of tower sulfuric acid [2–4] was commercialized in England, although long before this process mankind used enzymatic catalysis to make cheese and brew beer and acid–base catalysis to make paper [5].

The discovery of the English chemical engineers was ahead of the development of theoretical chemistry. Only half a century later, Lavoisier devised his oxygen theory of oxidation when scientists refuted phlogiston theory and discovered oxygen. Twenty-five years later, Desormes and Clement explained chemical transformations in a lead chamber, where sulfurous anhydride was oxidized to sulfuric anhydride.

The principles of heterogeneous catalysis and the history of catalysis with reference to heterogeneous and enzymatic catalysis were described in a number of recent papers [6–10]. The most detailed record of commercial catalytic processes can be found in [4, 9, 10]. Table 1 summarizes these data with minor changes.

Table 1 does not include a number of important reactions, such as the Friedel–Crafts reaction, because I failed to determine the accurate date for the commercialization of the first process. The Gomberg synthesis of epoxides (alkene chlorohydrin synthesis followed by dehydrochlorination) and Prilezhaev epoxidation, which is widely used in laboratory and industrial practices, were not included. In other words, Table 1 gives an approximate picture.

Another feature of this list is that it points to the time when a process was commercialized rather than to laboratory discovery. Thus, acetylene hydration (Kucherov's reaction) was discovered in 1881. However, almost forty years elapsed before engineers learned to remove acetaldehyde from a reaction solution using a flow of unreacted acetylene (Consortium für Electrochemische Industrie

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[1] Plenary Lecture presented at the XVI Mendeleev Congress of the Russian Chemical Society dedicated to the 250th anniversary of Russian chemical science.

Table 1. Development of industrial catalysis

Year	Process	Catalyst
1746	Lead-chamber process of H_2SO_4 manufacture	NO/NO_2
1870	SO_2 oxidation	Pt
1880	Deacon process (Cl_2 manufacture from HCl)	$ZnCl_2/CuCl_2$
1885	Klauss process (sulfur manufacture from H_2S and SO_2)	Bauxites
1888	Desulfurization of petrochemicals	Cu
1889	Methanol-to-formaldehyde conversion	Cu
1900	Fat hydrogenation	Ni
	Methane synthesis from syngas	Ni
1910	Coal liquefaction	Fe
	Improved coal liquefaction	WS_2
	Haber–Bosch process (ammonia synthesis)	Fe/K
	NH_3 oxidation to nitric acid	Pt
	Kucherov reaction (acetylene-to-acetaldehyde conversion)*	Hg^{2+}/H_2SO_4
1920	High-pressure process of methanol synthesis	Zn and Cr oxides
	SO_2 oxidation	V_2O_5
	Vinyl acetate synthesis from acetylene	Zn(II)/C
	ε-Caprolactam synthesis from phenol via the Beckmann rearrangement	Zn or Cu, H^+
1930	Catalytic cracking (fixed-bed catalyst, the Houdry process)	Clay
	High-temperature H_2O/CO conversion	$Fe_2O_3/Cr_2O_3/MgO$
	Vinyl chloride synthesis from acetylene	Hg(II)/C
	Ethylene epoxidation	Ag
	Synthetic rubber from ethanol (Lebedev’s reaction)	ZnO, MgO/Al_2O_3, Na
	Fischer–Tropsch syntheses	Promoted Fe and Co
	Polyvinyl chloride*	Peroxides
	Low-density polyethylene (ICI)*	Peroxides
	Indirect hydration of ethylene to ethanol*	H^+
	Hydrogen cyanide synthesis from CH_4 and NH_3 (Andrusov’s reaction)	Pt, Rh
	Benzene oxidation to maleic anhydride	V
	Alkene alkylation*	HF/H_2SO_4
1940	Alkene hydroformylation to aldehydes (Roelen’s reaction)*	Co
	Catalytic reforming (gasoline manufacturing)	Pt
	Cyclohexane oxidation (nylon-66 synthesis)	Co
	Benzene hydrogenation to cyclohexane	Ni, Pt
	Direct hydration of ethylene to ethanol	H^+
	Synthetic butadiene rubber*	Li, peroxides
	Butyl-acrylonitrile rubber*	Peroxides
	Butyl rubber*	$AlCl_3$
	Synthesis of phenol and acetone from propylene and benzene*	$AlCl_3/H^+$
1950	High-density polyethylene (Ziegler–Natta process)	Ti
	Ethylene polymerization (Phillips)	Cr
	High-density polypropylene (Ziegler–Natta process)	Ti
	High-density polybutadiene (Ziegler–Natta process)	Ti
	Hydrodesulfurization	Co and Mo sulfides
	Naphthalene oxidation to phthalic anhydride	V and Mo oxides
	Ethylene oxidation to acetaldehyde (Wacker–Hoechst process)*	Pd, Cu

Table 1. (Contd.)

Year	Process	Catalyst
	p-Xylene oxidation to methyl terephthalate*	Co, Mn
	Ethylene oligomerization*	Co
	Oil hydrotreatment	Co–Mo/Al_2O_3
	Alkane oxidation to secondary alkanols (Bashkirov's reaction)*	B, $RO_2^{\bullet}$
1960	Butylene oxidation to maleic anhydride	V and P oxides
	Acrylonitrile synthesis by propylene oxidative ammonolysis	Bi and Mo oxides
	Propylene oxidation to acrolein and acrylic acid	Bi and Mo oxides
	Xylene hydroisomerization	Pt
	Propylene metathesis	W, Mo, Re
	Adiponitrile synthesis by butadiene hydrocyanation*	Ni
	Improved catalysts for reforming	Pt, Re/Al_2O_3
	Acetic acid synthesis by methanol carbonylation*	Co
	Vinyl chloride synthesis by the oxidative chlorination of ethylene	Cu chlorides
	Fumaric acid hydration to L-hydroxysuccinic acid	Fumarase
	Fumaric acid amination to L-aspartic acid	Aspartase
	Ethylene oxidation to vinyl acetate*	Pd/Au, KOAc
	o-Xylene oxidation to phthalic anhydride	V and Ti oxides
	Propylene oxidation to propylene oxide*	Mo
	Hydrocarbon cracking on zeolites	Faujasite
	Hydrocracking	Ni–W/Al_2O_3
	Steam reforming of methane	Ni
	Low-temperature H_2O/CO conversion	CuO/ZnO/Al_2O_3
1970	Methanol synthesis (low pressure, ICI)	Cu–Zn–Al oxides
	Acetic acid synthesis from methanol by carbonylation (low pressure, Monsanto)*	Rh
	Xylene isomerization improved	Zeolites
	Toluene metathesis to benzene and *p*-xylene	HZSM-5
	Benzylpenicillin conversion into 6-aminopenicillinic acid	Immobilized penicillinacylase
	L-Methionine synthesis by *N*-acetylmethionine hydrolysis	Penicillinamidase
	CBZ-aspartame synthesis from *N*-CBZ-*L*-aspartic acid and methyl ester of *D,L*- phenylalanine	Thermolysine
	Stereoselective hydrolysis of enantiomers of esters and diltiazem synthesis	Esterase
	Esterification of myristic acid by isopropanol	Lipase
	Glucose isomerization to fructose	Immobilized glucosoisomerase
	α-Alkene synthesis (SHOP) involving the steps of oligomerization, isomerization, and metathesis of ethylene*	Ni, Mo
	Improved hydroformylation*	Rh
	Catalytic afterburning of exhaust gases	Pt/Rh
	L-Dioxyphenylalanine synthesis (*L*-DOPA, Monsanto)*	Rh
	Ring-opening cyclooctene polymerization (metathesis)*	W
	Hydroisomerization	Pt/zeolite
	Selective NO reduction by NH_3	V_2O_5/TiO_2
	Methyl *t*-butyl ether synthesis from methanol and isobutylene	Acidic ion-exchange resins

Table 1. (Contd.)

Year	Process	Catalyst
	Concentrated fructose synthesis from glucose	Immobilized *Arthrobacter*
	Raffinose synthesis	Immobilized *Mortierella vinacea*
1980	Gasoline synthesis from methanol (Mobil)	Zeolites
	Benzene alkylation to ethylbenzene by ethylene	HZSM-5
	Vinyl acetate synthesis from methanol and CO*	Rh, Pd
	Acetic anhydride synthesis from methyl acetate (carbonylation)*	Rh
	Oil tar hydrocracking	Pt/zeolite, Ni/zeolite
	NO_x reduction	Pt/Rh, V/Ti
	Methacrylic acid synthesis by *tert*-butanol oxidation	Mo oxides
	Acrylonitrile hydration to acrylamide	Nitrylhydratase
	Improved coal liquefaction	Co and Mo sulfides
	Diesel fuel from syngas	Co
	K_4 vitamin synthesis	Pd/membrane
	Alkane dehydrocyclization (Cyclar)	Ga/ZSM-5
	Light alkane aromatization	Ga/ZSM-5
	Metacrolein oxidation	Heteropoly acids (Mo–V–P)
	Isobutylene hydration	Acidic ion-exchange resins
	Tetrahydrofurane polymerization	Phase-transfer catalysis
	Propene hydroformylation in a two-phase (water/fat) system in the presence of sulfonated triphenylphosphine*	Rh/TPPS
	Beckmann rearrangement	HZSM-5
1990	Dimethylcarbonate synthesis from Co and methanol*	$CuCl/CuCl_2$
	Hydroperoxide (H_2O_2) oxidation of phenol to hydroquinone and catechol	Ti/silicalite
	Butene-1 isomerization to isobutylene	Acidic zeolites, H^+-ferrierite, H^+-theta-1
	Cyclohexanone oxime isomerization to ε-caprolactam	Silica-alumina-phosphate molecular sieves (SAPO-11)
	Hydrolysis *R*,*S*-racemate of 2-chloropropionic acid to form optically pure *S*-2-chloropropionic and *L*-lactonic acids	Dehalogenase
	Oxidative (H_2O_2) amination of cyclohexanone to cyclohexanone oxime	Ti/silicalite
	Dimethyl ether synthesis	Cu–Zn–Al oxides, H^+
	Acylation of aromatic compounds by acetic anhydride	H-β zeolite
	Direct hydrogenation of aromatic and aliphatic carboxylic acids to aldehydes	Ru/Sn, Zr/Cr
	Stereoselective reduction of octyl ester of γ-chloroacetoacetic acid, *L*-carnitine synthesis	Reductase
	Stereoselective hydroxylation of γ-butyrobetaine to *L*-carnitine	Hydroxylase
	Microbiological hydroxylation of aromatic hydrocarbons and side-chain oxidation in heterocyclic compounds	Bacteria
	Polyketone synthesis from CO and ethylene*	Pd
	Methyl methacrylate synthesis from methylacetylene*	Pd
2000	Benzene hydroxylation to phenol under the action of N_2O (Institute of Catalysis and Solutia)	Fe/ZSM-5

* Homogeneous catalytic system.

GmbH, later Wacker–Chemie). This expedient enabled process commercialization in Germany in 1916.

The methods of industrial catalysis have been improving. Not just new engineering methods were introduced, which led to a decrease in energy consumption, but the main improvements concerned catalyst improvement. The first silver catalysts for ethylene epoxidation enabled a selectivity of 60%. Now the selectivity is as high as ~90%.

New processes and methods were developed during the whole period considered here. Russian chemists contributed greatly to this development.

The Russian chemist L. Andrusov discovered the reaction of oxidative ammonolysis—hydrogen cyanide synthesis by ammonia and methane oxidation—after he had emigrated from Soviet Russia to the West. This process was first reported in 1925 in *Angewandte Chemie*. However, the first commercial plant for hydrogen cyanide syntheses using this method was constructed in Dzerzhinsk shortly before World War II. Only after the war, analogous plants appeared in industrialized countries in the West.

V.N. Ipatieff is well known for his pioneering studies of hydrocarbon conversions, specifically catalytic reforming. The process was commercialized in 1940 by UOP, which sponsored Ipatieff's studies. Ipatieff's closest co-worker, who was also an emigrant from Russia, Kh. Pines developed the process of acid-catalyzed alkylation of alkanes for the first time.

S.V. Lebedev proposed the first industrial process for synthetic rubber manufacture based on I.I. Ostromyslenskii and I.L. Kondakov's achievements. For many years, the Soviet Union kept the synthesis of Lebedev's catalyst a secret. Nowadays, this method is not used. However, taking into account that ethanol was produced in Lebedev's time and will be produced in the future from renewable vegetable sources, Lebedev's chemistry should not be disregarded.

The contribution made by V.V. Markovnikov and N.D. Zelinskii's schools to alkane petrochemistry is well known. In 1911, N.D. Zelinskii discovered the conversion of six-membered alkanes into aromatic hydrocarbons. In the 1930s, B.A. Kazanskii and B.L. Moldavskii simultaneously and independently obtained aromatic hydrocarbons from naphthenes at almost the same time. A short review of Russian studies along these lines and relevant references can be found in [5].

In the West, the method of phenol and acetone synthesis from propylene and benzene is known as Hock's method [2]. Indeed, Hock and Lang were the first to publish a paper that described cumyl hydroperoxide decomposition under the action of acids to yield phenol and acetone [11]. However, it would be justly to mention that two years before that publication, R.Yu. Udris in P.G. Sergeev's laboratory carried out the same reaction [12, 13]. Udris and Sergeev were unable to publish their work because of the secrecy related to its practical importance and because they were in prison in 1937. Other prisoners—A.A. Vinogradov, B.D. Kruzhalov, and M.S. Nemtsov—implemented Udris' discovery "in metal." As early as in 1950, in Dzerzhinsk near Nizhni Novgorod (at that time Gorky), the first industrial plant was put into service. More recently, it has been copied many times at other places. Thus, in Russia, this method became a practice at least six years earlier than in the West, although Russian scientists worked under difficult conditions in prison during wartime.

A.N. Bashkirov, an outstanding specialist in the field of syntheses from CO and hydrogen, went down in the history of catalysis for his studies of alkane and alkylaromatics oxidation. He was the first to use a stop-reagent that prevented target products (secondary alcohols in the case of alkanes) from being oxidized. Bashkirov's oxidation of alicyclic alkanes in the presence of boric acid or its anhydride was first put into service in the 1960s in Shebekino.

In 1957, I started a new work in Ya.K. Syrkin's laboratory on the design of a catalytic system that would enable direct ethylene conversion into acetic aldehyde rather than conversion via ethanol. The idea was based on the well-known reaction of Pd(II) salt reduction by ethylene in aqueous solutions discovered by Phillips in 1894 [14]. I realized very quickly that Phillips's reaction, which was used as an analytical test for ethylene in gaseous mixtures, is indeed very selective toward acetic aldehyde:

$$PdCl_2 + C_2H_4 + H_2O \longrightarrow Pd^0 + CH_3CHO + 2HCl. \quad (I)$$

The task was reduced to a search for conditions for efficient metallic palladium oxidation by oxygen. Reaction (I) was supposed to be an element of a catalytic cycle.

At that time, an idea that a catalytic reaction (and a "catalytic cycle," which is now an accepted term) can be composed of stoichiometric macrokinetic steps, sounded new, and many researchers did not accept it. It sounded unusual that an oxidant (ideally, oxygen), which is consumed by the reaction, does not react directly with a substrate. However, it is this feature that attracted our attention—the absence of steps where the substrate was oxidized by oxygen—promised a high selectivity.

Together with M.N. Vargaftik, who joined me a bit later, I managed to show that hydrogen peroxide, *p*-benzoquinone, and oxygen with Cu(II) compounds [15, 16] can be used as oxidants. In the latter case, the catalytic reaction is a combination of three steps:

$$PdCl_2 + C_2H_4 + H_2O \longrightarrow Pd^0 + CH_3CHO + 2HCl \quad (I)$$

$$Pd^0 + 2HCl + 2CuCl_2 \longrightarrow PdCl_2 + 2CuCl + H_2O \quad (II)$$

$$2CuCl + 2HCl + 1/2O_2 \longrightarrow 2CuCl_2 + H_2O \quad (III)$$

$$C_2H_4 + 1/2O_2 \longrightarrow CH_3CHO + 52.26 \text{ kcal/mol.}$$

The system was literally designed on the basis of thermodynamic and kinetic data. It had another useful feature: the steps of olefin oxidation (reactions (I) and (II)) and catalytic solution reoxidation (reaction (III)) can be separated and carried out in different apparatus, which was a common practice [17].

Publication of these results was delayed for two years due to a wait-and-see attitude of the Ministry of Chemical Industry and the excessive caution of Laboratory Chief Ya.K. Syrkin, who endured and remembered the discussion on resonance theory and other attributes of the totalitarian regime. Only after the appearance of a paper published by German researchers [18], who had begun similar research at the same time with us and arrived at the same catalytic system, did Ya.K. Syrkin bring himself to publish our findings.

To our delight, German chemists, who developed an elegant industrial process, failed to carry out alkene oxidation both in the medium of acetic acid and in alcohol solutions. Palladium chloride and ethylene do not react in glacial acetic acid. The solvent nucleophilicity was too low, and polymeric palladium chloride did not dissolve. Taking this into account, M.N. Vargaftik and I carried out experiments where alkene contacted a solution of $PdCl_2$ in acetic acid containing sodium acetate, which is a strong nucleophile. Under these conditions, we managed to carry out ethylene acetoxylation to form vinyl acetate for the first time. In this reaction, a hydrogen atom from alkene is substituted for an acetoxy group:

$$C_2H_4 + PdCl_2 + 2NaOAc$$

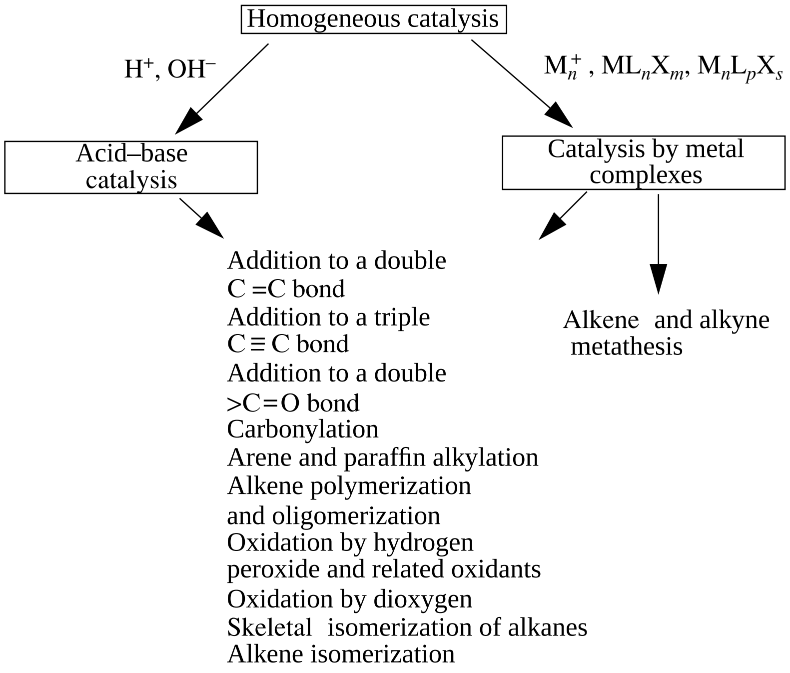
$$\longrightarrow CH_2{=}CHOAc + Pd^0 + 2NaCl + AcOH.$$

Also, as in the case of aqueous solutions, reduced palladium can be returned into the solution using an oxidant. However, this homogeneous system appeared to be too corrosive. Besides, if oxygen is used as an oxidant, special procedures are needed to remove water from the solution. These circumstances impelled first Bayer and later Hoechst to search for a heterogeneous catalyst. A new $Pd,Au/SiO_2$ catalyst is very selective and stable. Nevertheless, the heterogeneous process is named after one of the Russian authors, who was the first to carry out oxidative acetoxylation [2, pp. 3, 59, 386].

HOMOGENEOUS CATALYSIS BY METAL COMPLEXES

The ability of metal complexes to accelerate chemical reactions has been known from the time of M.G. Kucherov (1881, acetylene hydration), C. Friedel, and J.M. Crafts (1877, alkylation and acylation of aromatic compounds in the presence of $AlCl_3$). The works of H.J.H. Fenton appeared somewhat later (1894, the oxidation of hydroxyl groups in α-oxyacids and α-glycols and the hydroxylation of aromatic compounds by the $FeSO_4/H_2O_2$ system). Late in the 1930s, Roelen hydroformylation was reported. After World War II, Reppe syntheses saw the light of the day. Nevertheless, until studies at Wacker–Chemie, homogeneous catalysis was thought to be a subfield of acid–base catalysis.

Kinetic and mechanistic studies of alkene reactions catalyzed by palladium shed light on the role of organopalladium compounds formed in a catalytic system by alkene oxypalladadation [15, 19, 20]. This idea initially sounded unusual (σ-organopalladium compounds were thought to exist only as complexes with tricoordinated organic phosphines), but later it attracted considerable attention and formed the basis for many reac-



Scheme 1. Homogeneous catalysis: general structure.

Table 2. Commercially important liquid-phase catalytic systems

Process	Catalyst
Friedel–Crafts process	$AlCl_3$
Acetaldehyde synthesis from acetylene (Kucherov's reaction)	Hg^{2+}/H_2SO_4
Vinyl acetate synthesis from acetylene	Zn(II)/C
Prilezhaev's epoxidation	RCOOOH
ε-Caprolactam synthesis from phenol via the Beckmann rearrangement	H^+
Vinyl chloride synthesis from acetylene	Hg(II)/C
Alkane alkylation	HF/H_2SO_4
Alkene hydroformylation to aldehydes (Roelen reaction)	Co
Cyclohexane oxidation (nylon-66 synthesis)	Co
Direct hydration of ethylene to ethanol	H^+
Ethylene oxidation to acetaldehyde	Pd, Cu
p-Xylene oxidation to methyl terephthalate	Co, Mn
Ethylene oligomerization	Co
Ring-opening polymerization of cycloalkenes (metathesis). Synthesis of cyclooctenamers	W, Mo, Re
Adiponitrile synthesis by butadiene hydrocyanation	Ni
MeOH carbonylation to acetic acid	Co
MeOH carbonylation to acetic acid (low pressure, Monsanto process)	Rh
MeOH carbonylation to acetic acid (BP process)	Ir + In
Ethylene oxidation to vinyl acetate	Pd, Au, $KOAc/SiO_2$
o-Xylene oxidation to methyl terephthalate	Co, Br^-
Propylene oxidation to propylene oxide	Mo
Alkene hydroformylation	Rh
L-Dioxyphenylalanine synthesis (*L*-DOPA, Monsanto)	Rh
Vinyl acetate synthesis from methanol and acetic acid	Rh, Pd
Synthesis of polyketones from CO and ethylene	Pd
Dimethyl carbonate synthesis from CO and methanol	$CuCl/CuCl_2$
α-Alkene synthesis from ethylene (SHOP), oligomerization/isomerization/metathesis	Ni, Mo
Alkane oxidation to secondary alkanols (Bashkirov's oxidation)	$RO_2^{\bullet}$, B
Methyl methacrylate synthesis from methylacetylene and CO	Pd

tions catalyzed by palladium and other transition metal compounds [21, 22].

Today homogeneous catalysis covers two subfields: acid–base catalysis and catalysis by metal complexes (Scheme 1).

In both subfields, there are examples of reactions catalyzed by the H^+ or OH^- ions and metal complexes or clusters. Scheme 1 provides a list of these reactions. Of course, both substrates and reaction mechanisms in catalysis by metal complexes and acid–base catalysis are different. Nevertheless, some steps of metal-complex catalysis can be modeled by allied steps from acid–base catalysis in many cases. The only exception is alkene metathesis [23], a reaction that has no analogs in acid–base catalysis:

$$2C_3H_6 \xrightarrow{\text{Cat}} C_2H_4 + C_4H_8,$$

where Cat is a compound of W, Mo, Re, Ru, or other metals.

It is difficult to mention all of the reactions of acid–base catalysis that found use in industrial syntheses. There are numerous examples of hydrolysis and etherification, transformations of alkenes, peroxides, aromatic compounds, etc. Almost everything known as the synthesis of fine chemicals is a field of acid–base catalysis. Along with acids and bases, many industrial pro-

Table 3. Advantages and shortcomings of homogeneous and heterogeneous catalysis [27, 28]

Characteristics	Homogeneous catalysis	Heterogeneous catalysis
Activity per metal content	High	Depends on conditions
Selectivity	High	Depends on conditions
Service life	Depends on conditions	Long
Sensitivity to catalytic poisons	Low	High
Diffusion problems	Absent	Can be important
Catalyst recovery	Expensive	Not required
Possibility for changing the steric and electron properties of a catalyst	Possible	Impossible
Understanding of the operating mechanism	Rarely possible	Impossible (unless it is a model system)

cesses are catalyzed by metal complexes in solutions (Table 2).

Some fields of industrial organic synthesis, such as the manufacture of acetic acid, from carbohydrate fermentation to the modern methods by Monsanto (Rh, CH_3I, CO, and CH_3OH) and British Petroleum (Ir, In, CH_3I, CO, and CH_3OH), are in a territory occupied by liquid-phase catalysis.

From times immemorial acetic acid (wine vinegar) was produced by fermentation of wine and other alcohol-containing aqueous solutions. For a short period, a method based on the destructive distillation of wood was applied. However, starting from 1916, acetaldehyde was produced in Germany and Canada by Kucherov's method, and acetic acid was manufactured by acetaldegyde oxidation. In the mid-1950s, the method of acetaldehyde oxidation in the presence of copper and manganese salts was developed. This method enabled acetaldehyde transformation into a mixture of acetic acid and its anhydride in a liquid phase. The method of acetic acid manufacture by the liquid-phase oxidation of butane was developed at the same time, but it was used on a relatively small scale. In Russia, this method was put forward by N.M. Emanuel' and co-workers [24]. Starting from the 1970s, acetic acid has been produced by the liquid-phase carbonylation of methanol [25]. All industrial methods except the destructive distillation of wood are based on exothermic reactions in a liquid phase.

The commercial production of acetaldehyde, butyraldehyde, propionic acid, and formic acid from CO and water, as well as methyl formate from CO and methanol, adipic acid, and adiponitrile, are also based on liquid-phase reactions. The Beckman rearrangement, which is used to produce ε-caprolactam, was carried out in concentrated solutions of H_2SO_4 until recently. The liquid-phase oxidation of toluene and *p*-xylene [26] yields terephthalic acid, benzoic acid, and their esters.

Homogeneous liquid-phase catalysis produces millions of tons of materials every year.

The principles and problems of homogeneous catalysis, as well as the advantages and shortcomings of liquid-phase systems have recently been discussed in the literature [27, 28]. A typical example of such analysis borrowed from [27, 28] is shown in Table 3.

Everything in Table 3, except the last row, is rather questionable. For instance, such characteristics as activity, selectivity, and others can be discussed only in the context of a specific process for which both types of catalysts are available. It would be completely incorrect to believe that there is no diffusion in homogeneous systems. In industrial apparatus, gaseous feedstock usually reacts with a liquid phase, which contains a catalyst and where the reaction occurs. Systems where two liquid phases react with each other have recently become more frequent. For these systems, phase-transfer catalysts are important. Everybody who has experience in the kinetic studies of liquid-phase processes knows that it is sometimes difficult to overcome constraints associated with the transfer through a gas–liquid or liquid–liquid phase boundary and find reliable evidence for the absence of diffusion constraints.

The possibility of the fine control of steric and electron properties of active sites in heterogeneous catalysts cannot be excluded either.

The most important advantage of homogeneous catalysis is mentioned in the last row of Table 3. In the last two decades, physicochemical methods for solid surface studies have been rapidly developing and intensively used. These methods were applied in catalysis (Table 4). Despite evident progress in understanding the nature of solid catalysts, surface structure, and the structure of active sites, the available information on heterogeneous catalysts does not allow one to judge important details such as the stoichiometric composition of an active site. As a rule, we can only conjecture the stoichiometry of an active site, the nature of ligands and their geometric arrangement around a metal atom responsible for the substrate activation.

Without going into further details of other estimated advantages and shortcomings of homogeneous liquid-phase catalysis listed in Table 3, I only wish to note that

Table 4. Modern physical methods for catalyst studies

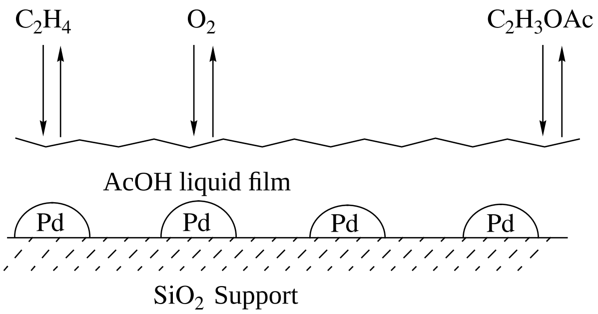
Radiation	Energy (vibration frequency, cm^{-1})	Method
Radio	10^{-2} 10^{-1}	NMR
Microwave	1	ESR
Infrared	10^{2} 10^{3}	Vibrational and electron spectroscopy
Ultraviolet	10^{4} 10^{5}	
X-ray	10^{6} 10^{7}	XPS, EXAFS
Electron diffraction	10^{8} 10^{9}	Electron spectroscopy
γ-radiation		Moessbauer spectroscopy

Abbreviation	Method
AES	Auger Electron Spectroscopy
AFM	Atomic Force Microscopy
ED	Electron Diffraction
EELS	Electron Energy Loss Spectroscopy
ESCA	Electron Spectroscopy for Chemical Analysis
EXAFS	Extended X-ray Absorption Fine Structure Spectroscopy
HREELS	High Resolution Electron Energy Loss Spectroscopy
HREM, HRTEM	High Resolution Transmission Electron Microscopy
FAB–MS	Fast Atom Bombardment Mass Spectroscopy
FTIR	Fourier-Transform IR Spectroscopy
GC/MS	Gas Chromatography–Mass Spectroscopy
LEED	Low Energy Electron Diffraction
LEELS	Low Energy Electron Loss Spectroscopy
LIDS	Lase-Induced Desorption Spectroscopy
MALDI MS	Matrix–Laser Desorption Ionization Mass Spectroscopy
MAS NMR	Magic Angle Spinning Nuclear Magnetic Resonance
NEXAFS	Near Extended X-ray Absorption Fine-Structure Spectroscopy
SAXS	Small–Angle X-ray Scattering
SEM	Scanning Electron Microscopy
SERS	Surface–Enlarged Raman Spectroscopy
SEXAFS	Surface-sensitive Extended X-ray Absorption Fine-Structure Spectroscopy
SIMS	Secondary Ion Mass Spectroscopy
STM	Scanning Tunnel Microscopy
TEM	Transmission Electron Microscopy
XANES	X-ray Absorption Near-Edge Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction

the main technological advantages of liquid-phase systems and the main achievements of metal-complex catalysis in organic synthesis are not mentioned there.

When heterogeneous catalysts are used, the problems of reaction heat removal constrain the capacity of a contact apparatus. In the history of industrial heterogeneous catalysis, chemical engineers always worked on methods for heat removal from the reaction zone and mass-transfer intensification [1]. In the early 1930s, G.K. Boreskov proposed to carry out exothermic reactions in a fluidized bed of a catalyst. Starting from the late 1940s and early 1950s, this idea found practical use. Numerous constructions were proposed, such as multiple-section apparatus with built-in heat exchangers. All these engineering solutions were rather complex from the construction standpoint. They led to an increase in capital investment and running costs.

In liquid-phase systems, constraints associated with heat removal are absent. The heat of reaction is consumed for the partial evaporation of a solvent and can be removed in a condenser attached to the contact apparatus. Reaction exothermicity sometimes plays a positive role: it serves to remove a volatile target product (for instance, acetaldehyde in Kucherov's reaction or when ethylene is oxidized in the presence of palladium catalysts).



Scheme 2. Ethylene oxidation to vinyl acetate in the acetic acid film.

This fact played a decisive role in several exothermic processes, such as reactions of addition to triple bonds (Kucherov's reaction (IV)), various oxidation reactions (e.g., reaction (V)), and olefin polymerization (VI):

$$C_2H_{2(gas)} + H_2O_{(liquid)} \xrightarrow[100°C]{Hg(II),\ H_2SO_4} CH_3CHO_{(gas)} + 25.5\ \text{kcal/mol}, \quad \text{(IV)}$$

$$C_2H_{4(gas)} + 1/2O_2 \xrightarrow[100°C]{Pd(II),\ Cu(II),\ Cl^-} CH_3CHO_{(gas)} + 52.26\ \text{kcal/mol}, \quad \text{(V)}$$

$$nC_3H_{6(gas)} \longrightarrow (C_3H_6)_{n(solid)} + 20.7\ \text{kcal/mol}. \quad \text{(VI)}$$

Only when a reaction product has to be removed rapidly from a reaction zone or when an active oxidation catalyst capable of working under the conditions of a preserved liquid phase cannot be found, is the reaction carried out in a contact apparatus where substrate vapor and an oxidant react with a solid catalyst (Table 5). In many cases, gas-phase processes in fact occur in a liquid film of the contact solution distributed over the surface of a solid support. A striking example of such a reaction is the oxidative acetoxylation of ethylene to yield vinyl acetate:

$$C_2H_4 + AcOH + 1/2O_2 \xrightarrow[175\text{–}200°C,\ 10\ bar]{Pd,\ Au,\ KOAc/SiO_2} CH_2CH{=}OAc + H_2O.$$

Under the conditions of this reaction, a thin film of acetic acid, whose saturated vapor pressure is ~5 bar at 180°C, covers the support. Clusters with a core of palladium and gold atoms are distributed over this film [29]. The simplest model of such clusters is a compound with the idealized formula $Pd_{561}(Phen)_{60}OAc_{180}$ [30]. Ethylene and oxygen diffuse into a catalyst film, from which vinyl acetate is evaporated and removed in the flow of unreacted reagents (Scheme 2). An idea of film catalysis was formulated in a conceptual paper by N.M. Chirkov and V.I. Gol'danskii [31].

An advantage of liquid-phase systems for exothermic processes when the capacity of a contact apparatus is limited by effective transfer and reaction heat removal can also find use in welldeveloped traditionally heterogeneous processes, such as methanol synthe-

Table 5. Examples of catalytic oxidation in industry [4, 26]

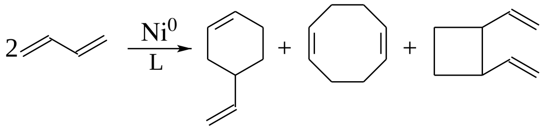
Product	Starting material	Production capacity (USA, 1989), 10^6 ton	Oxidant/Process
Terephthalic acid	*p*-Xylene	4.0	O_2/L*
Formaldehyde	Methanol	3.0	O_2/G
Ethylene oxide	Ethylene	2.8	O_2/G
Cumyl hydroperoxide	Cumene	1.6	O_2/L
Acetic acid	Ethylene or *n*-butane	1.6	O_2/L
Propylene oxide	Propylene	1.3	RO_2H/L
Acrylonitrile	Propylene, NH_3	1.3	O_2; G
Vinyl acetate	Ethylene	1.2	O_2/L**
Acetone	Propylene	1.1	O_2/L; G
Benzoic acid	Toluene	1.0	O_2/L
Adipic acid	Benzene	0.9	O_2/L
Phthalic anhydride	*o*-Xylene	0.7	O_2/G
Methyl methacrylate	Isobutylene	0.5	O_2/G
Acrylic acid	Propylene	0.5	O_2/G
Methyl ethyl ketone	1-Butylene	0.3	O_2/G; L
Maleic anhydride	*n*-Butylene	0.25	O_2/G
Methacrylic acid	*tert*-Butanol	–	O_2/G
Acetaldehyde	Ethylene	1	O_2/L
Dimethyl carbonate	Methanol, CO	0.5	O_2/L
Hydrogen cyanide	Methane, ammonia	0.7	O_2/G

* L is for a liquid phase and G is for a gas phase.

** Film catalysis

sis. Research is underway on distributing a solid catalyst suspension in an inert liquid phase [32], as well as on homogeneous catalytic systems with, for insrance, nickel complexes as catalysts [33].

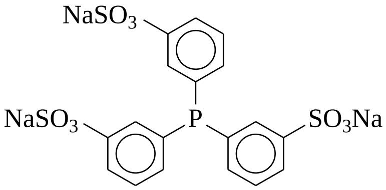
Ideas and methods of catalysis by metal complexes played an important role in syntheses of fine chemicals. After Ziegler's discovery and studies at Wacker–Chemie, it became evident that substrate molecules that become ligands of metal complexes acquire new properties. The ability of olefin π-complexes to transform into the σ-bonded organic derivatives of transition metals opened a door for a synthetic chemist into a room of new and important highly reactive fragments and new organic syntheses. One- or two-stage syntheses of many complex organic compounds became possible and replaced multiple-stage ones, which required costly reagents, labor expenses, and procedures for waste treatment when a process was carried out on a relatively large scale. An example of such a reaction is Wilke's synthesis:



The first of the products mentioned here (vinylcyclohexene) can be obtained by the thermal Diels–Alder synthesis. The other two (cycloocta-1,5-diene and 1,2-divinylcyclobutane) would require truly Herculean efforts if it were not for the Wilke catalyst [34]. New approaches to the formation of C–C and C–element bonds can be found in the papers of I.P. Beletskaya, G.A. Tolstikov, U.M. Dzemilev, and others [35–38].

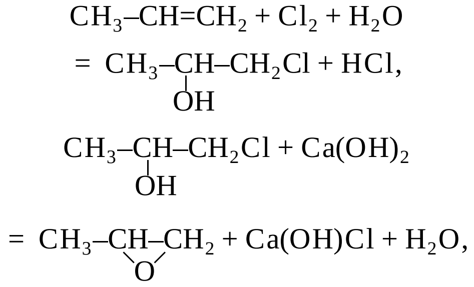
Complexes with chiral ligands opened new ways to asymmetric syntheses. Along with heterogeneous catalysts, soluble complexes and chiral acids and bases became widespread [39, 40]. In addition to enantioselective hydrogenation, various asymmetric reactions became possible: isomerization, epoxidation, cyclopropanation, co-dimerization, and cyclodimerization. An enatioselectivity close to 100% became usual for the organic synthesis of bioactive compounds.

The main shortcoming of homogeneous catalytic systems, which is commonly considered, is the difficult product separation from a contact solution. However, as mentioned above, when the product is rather volatile, its separation is no problem. Recently, a new method was developed that enables the removal of a reaction product from a catalyst solution by extraction. A striking example is propylene hydroformylation in the synthesis of *n*-butanal and butanol-1. Ruhrchemie and Rhône Pulenc used rhodium complexes with a new sodium triphenylphosphine-tris(*meta*-sulfonate) ligand in this process:



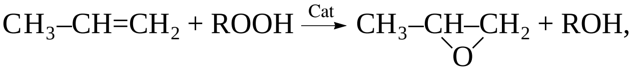
This compound forms water-soluble complexes with several transition metals, including Rh(I). In the hydroformylation process, a rhodium catalyst remains in an aqueous phase, and products form an organic phase. A new method (the replacement of distillation by separation in an aliquation apparatus) led to energy saving: in the old process with a rhodium triphenylphosphine catalyst, energy and reagents were consumed for phase separation. In the new process, a reactor generates medium-pressure steam, which is then utilized [27, 28].

Catalysis by metal complexes (both heterogeneous and homogeneous) played an important role in solving environmental problems during the whole 20th century. Thus, Gomberg's propylene epoxide synthesis



$$CH_3{-}CH{=}CH_2 + Cl_2 + H_2O$$
$$= CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_2Cl + HCl,$$
$$CH_3{-}\underset{OH}{\underset{|}{CH}}{-}CH_2Cl + Ca(OH)_2$$
$$= CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2} + Ca(OH)Cl + H_2O,$$

accompanied by the formation of nonutilizable calcium chloride was replaced by propylene epoxidation with alkyl hydroperoxides in the presence of titanium silicalite (Shell) or molybdenum complexes in ethylbenzene (Arco):

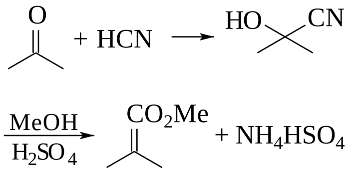


$$CH_3{-}CH{=}CH_2 + ROOH \xrightarrow{Cat} CH_3{-}\underset{\diagdown O \diagup}{CH{-}CH_2} + ROH,$$

where R = $PhCH{-}CH_3$ or *tert*-butyl.

For a long time, researchers looked for a new method of methyl methacrylate synthesis to replace a traditional process for producing this monomer, which is a raw material for the manufacture of organic glass.

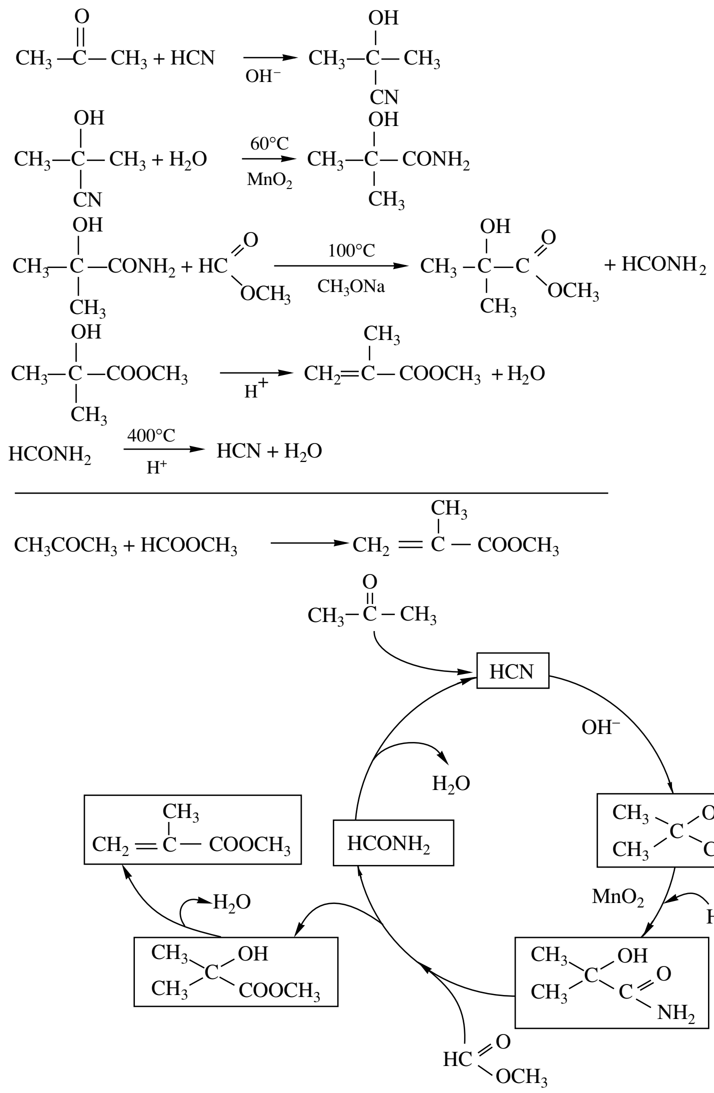
The traditional technology was based on the reactions



(VII)

and accompanied by the formation of useless ammonium bisulfate. For the past 50 years, numerous attempts were made to remove this drawback. For instance, a process based on acetone and methyl formate (Scheme 3) was proposed.

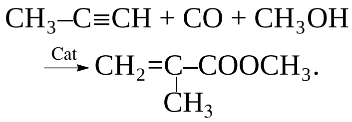
As can be seen from reactions in Scheme 3, hydrogen cyanide plays the role of an intermediate product consumed at the stage of cyanohydrin synthesis and regenerated at the stage of formamide dehydration. However, multiple stages prevented this method from being competitive with the conventional one.



Scheme 3. Methyl methacrylate synthesis from acetone and methyl formiate.

Chemists' efforts bend to the search of syntheses based on alkenes, syngas, and formaldehyde (Scheme 4).

The most promising method of synthesis was recently developed by Shell (E. Drent) [41]. According to this method, methylacetylene, which is an unusable product of kerosene pyrolysis, undergoes methoxycarbonylation in the presence of a palladium catalyst (a palladium complex with 2-piridylphosphine containing a weakly coordinated anion)



$$CH_3{-}C{\equiv}CH + CO + CH_3OH \xrightarrow{Cat} CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}{-}COOCH_3. \qquad \text{(VIII)}$$

A high rate of the reaction (50 000 mol (g-atom Pd)$^{-1}$) h^{-1}), a high selectivity (99%), and mild conditions (50°C, 1 MPa) make this process very attractive.

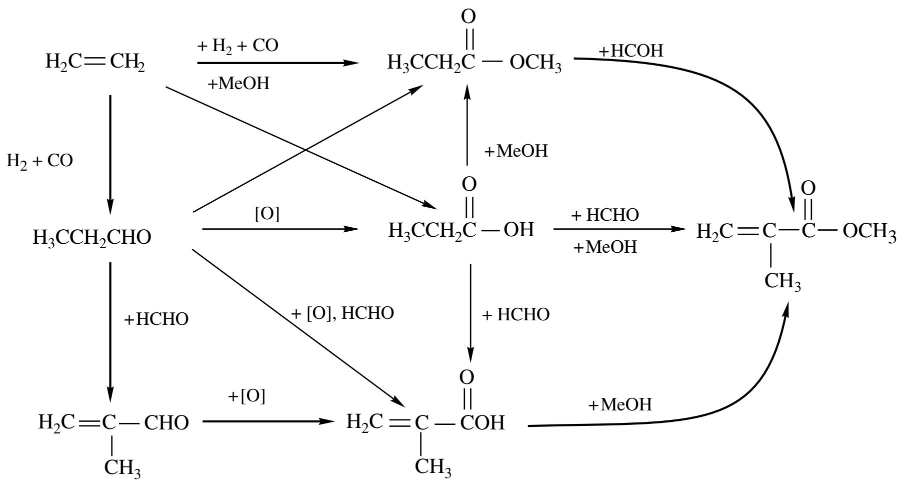
The history of methyl methacrylate synthesis is an example of the evolution of methods for basic organic synthesis where homogeneous catalysis by metal complexes played an important role.

Notable recent achievements in the basic research of homogeneous catalysis are reactions in superacid solutions (G. Olah), alkane activation by platinum complexes (A.E. Shilov), and nitrogen fixation under mild conditions (M.E. Vol'pin, V.B. Shur, A.E. Shilov).

EVOLUTION OF RAW MATERIALS FOR BASIC LARGE-SCALE ORGANIC SYNTHESIS

The main task of chemical engineering has always been exergy loss reduction (E_{loss}) [42]:

$$\Sigma E_{in} - \Sigma E_{out} = E_{loss} = T_0 \Delta S. \qquad (1)$$



Scheme 4. Methyl methacrylate synthesis from ethylene and products of C_1 chemistry.

By definition, exergy is the maximal work obtained from the streams of materials and energy in the course of attaining equilibrium with a medium. Equation (1) shows that E_{loss} is lower when less energy is needed for manufacturing and when the feedstock is energetically cheaper, all other conditions being the same (that is, when ΣE_{in} is lower and ΣE_{out} is higher).

Soviet chemical industry consumed ~15% of all energy produced in the country, being one of the most energy-consuming sectors of the national economy. The low efficiency of chemical technology of that time (Scheme 5) was the main reason for energy loss in chemical industry. The lower the catalyst activity, the stricter the reaction conditions (higher temperature and pressure) and the greater the expenses to heat starting materials and compress them. Moreover, more energy is required to cool final products if a technological scheme requires doing that.

The technological scheme often does not contain units for recuperating energy, but rather requires more energy to cool the streams to the temperature required by the next technological operation or synthetic step.

Milder conditions of a reaction are favorable for lower energy consumption: a decrease in temperature and pressure (a decrease in ΣE_{in}) became one of the main directions for the development of technological processes. For that purpose, new-generation highly active catalysts were required. However, this is not the only role of catalysis in reducing energy consumption, which was observed during the whole period of chemical technology evolution.

Technological operations in chemistry are characterized by low coefficients of efficiency (Table 6).

Low energy efficiency in separation processes issues the challenge of decreasing the number of operations in the product manufacturing process. To solve this problem, the reduction in the number of stages in the synthesis and the replacement of multiple-stage processes with single-stage ones are required. The history of organic catalysis knows many examples of this sort.

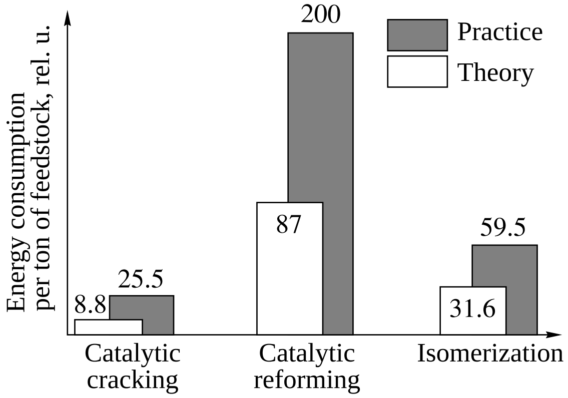
Energy efficiency was often characterized in the 1980s by an oil equivalent (OE) equal to the sum of energy and material expenses corresponding to the calorific value of oil (the heat capacity of oil was assumed to be equal to 10500 kcal/kg). Thus, the manufacturing of 1 ton of product was measured in OE: ethylene, 2.9 OE; polyethylene, 3.88 OE, polyethylene tubes, 4.29 OE; divinyl, 7.18 OE; isoprene, 8.51 OE [43]. Of 2.89 OE needed for ethylene manufacture, 0.7 OE was energy consumption.

Catalysis played an important role in reducing energy consumption through diminishing the number of synthetic stages (savings due to the partial removal of separation stages), an increase in selectivity (savings due to the removal of separation stages and feedstock cost reduction, i.e., a decrease in ΣE_{in}, and a decrease in the expenses for the utilization of by-products), and making reaction conditions milder (savings due to reduction in heat-exchange and compression expenses, i.e., a decrease in ΣE_{in}).

A trend toward the use of feedstock that requires less energy for its processing, which was observed from the beginning of this century, dominates the search for a means to reduce energy expenses. The replacement of coal (in fact, acetylene) by oil and its refining products and the current trend toward replacing oil by natural gas

Table 6. Efficiency of operations in chemical technology [43]

Operation	Efficiency, %
Compression	60
Heat exchange	40
Distillation	10
Chemical reaction	70



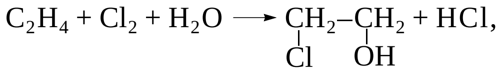
Scheme 5. Theoretical and real energy consumption in oil refining [43]

correlates with a switch from feedstock characterized by lower values of the Gibbs energy to feedstock with higher values (lowering the contribution to ΣE_{in}). All changes in the raw materials for basic organic synthesis became possible due to advances in the science of catalysis, which turn into an engine for solving this task of chemical technology.

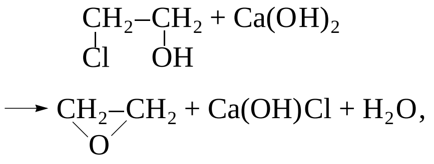
During the 20th century, the raw materials for basic organic synthesis changed many times (Table 7). In the beginning of the century, the raw materials were coal and carbohydrates (potato and grains). The thermal treatment of coal was used to manufacture coke, aromatic hydrocarbons, ammonia in the form of ammonium sulfate, and many other products and intermediates, which formed the ground for the syntheses of dyes, polymers, varnish, etc. Carbohydrate raw materials were used to manufacture ethanol by fermentation.

Ethanol was used as a feedstock for a number of syntheses and ethylene in large-scale manufacture. For instance, in the 1950s in China, ethylene glycol was produced from ethanol and chlorine:

$$C_2H_5OH \xrightarrow[Al_2O_3]{\sim 300°C} C_2H_4 + H_2O,$$

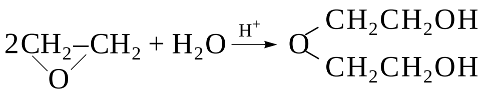


$$C_2H_4 + Cl_2 + H_2O \longrightarrow \underset{Cl}{CH_2}–\underset{OH}{CH_2} + HCl,$$



$$\underset{Cl}{CH_2}–\underset{OH}{CH_2} + Ca(OH)_2$$

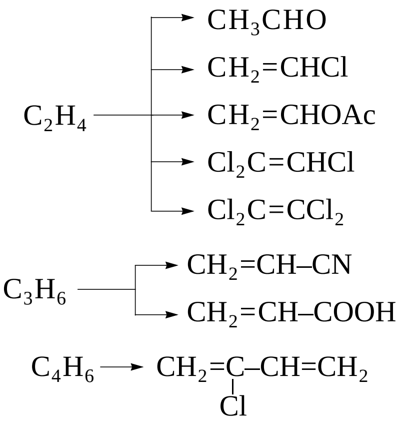
$$\longrightarrow \underset{O}{CH_2–CH_2} + Ca(OH)Cl + H_2O,$$



$$2\underset{O}{CH_2–CH_2} + H_2O \xrightarrow{H^+} O\begin{matrix} CH_2CH_2OH \\ CH_2CH_2OH \end{matrix}$$

Late in the 1920s, young Soviet Russia faced the problem of synthetic rubber production, and S.V. Lebedev chose potatoes as a base raw material rather than kerosene for butadiene rubber manufacture. Nowadays, this sounds surprising, but at that time industry chiefs proceeded from the fact that only one percent of domestic potato production covered the whole Russia's demand in synthetic rubber. To produce the same amount of butadiene from oil, large amounts of kerosene were needed because the yield of butadiene from kerosene pyrolysis is rather small.

Based on coke produced from coal, acetylene manufacture was developed. Acetylene seemed to be the unit that would cover the demands of rapidly developing basic organic synthesis. In the 1960s and 1970s, the epoch of acetylene and coal ended when the methods for manufacturing acetaldehyde, vinyl chloride, other chloroethylenes, and vinyl acetate from ethylene, acrylonitrile and acrylic acid from propylene, and butadiene from chloroprene were developed:



$$C_2H_4 \longrightarrow \begin{cases} CH_3CHO \\ CH_2{=}CHCl \\ CH_2{=}CHOAc \\ Cl_2C{=}CHCl \\ Cl_2C{=}CCl_2 \end{cases}$$

$$C_3H_6 \longrightarrow \begin{cases} CH_2{=}CH–CN \\ CH_2{=}CH–COOH \end{cases}$$

$$C_4H_6 \longrightarrow CH_2{=}\underset{Cl}{C}–CH{=}CH_2$$

Before 1960, all these products were produced from acetylene.

The main incitement for the replacement of coal by oil feedstock was the discovery of palladium catalysts. Palladium made it possible to oxidize ethylene to acetaldehyde and vinyl acetate. More recently Monsanto and Halcon introduced new processes for methanol and dimethyl ether carbonylation to acetic acid, methyl acetate carbonylation to acetic anhydride, and vinyl acetate synthesis from methanol. Palladium and rhodium started to dominate in catalysis by transition metal compounds. Before the 1960s, palladium was very cheap and directive bodies looked for the use of this

Table 7. Raw materials for basic organic synthesis in the 20th century

Beginning of the century	Coal, hydrocarbons
1920s and 1930s	Coal → acetylene; hydrocarbons → ethanol → alkenes, butadiene
1950s, 1960s, and to the end of the century	Alkenes from oil, carbon monoxide from methane; alkanes

metal. Nowadays, palladium is more expensive than gold. Russia is a monopolist on the market of palladium.

Another factor that played an important role in the replacement of acetylene by alkenes was the discovery of catalysts based on bismuth and molybdenum oxides that enabled one-stage acrylonitrile manufacturing to replace a chain involving Andrusov's synthesis of hydrogen cyanide and acetylene hydrocyanation. The new method was more profitable because it had only one stage and because cheap propylene was used instead of expensive acetylene. In addition to acrylonitrile from propylene, acrolein was produced in the presence of copper catalysts, and acrolein was a starting material in acrylic acid manufacture.

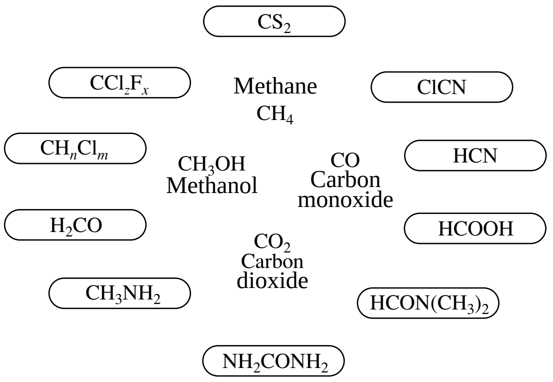
In parallel to the development of modern petrochemistry, the position of C_1 chemistry also strengthened. An example is the evolution of methods of methyl methacrylate synthesis from the method based on acetone and hydrogen cyanide (1930s, reaction (VII)) to syntheses using formaldehyde, CO, methylacetylene, and other products as starting materials (see Schemes 4 and 5 and reaction (VIII)).

Today's industry consumes a number of C_1 molecules, and this field of industrial chemistry is now known as C_1 chemistry (Scheme 6). Scheme 6 shows all compounds containing one carbon atom whose production and demand is over 100000 ton/year. The production and demand of four substances shown in the center of Scheme 6 is over 10^6 ton/year. These four substances—methane, carbon monoxide, carbon dioxide, and methanol—form the basis for more than 70% of the production of basic organic and petrochemical synthesis. In the subsequent discussion, I will focus on the use of methane.

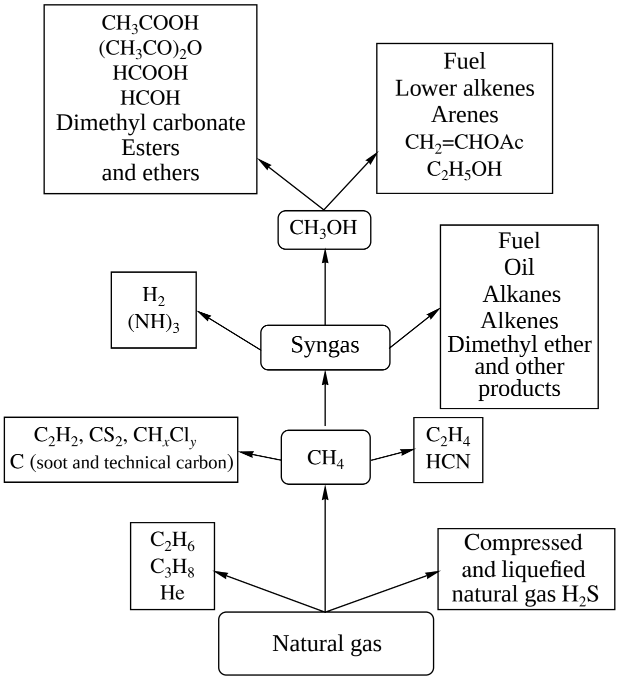
Currently, natural gas and its main component (methane) are primarily used as fuel. Twenty to twenty-five percent is consumed for direct energy production, about 40% is consumed as fuel in industry, and 40% is used for domestic needs. Thus, methane is primarily consumed as fuel, and it accounts for 20% of all energy sources. In 2050, its contribution is expected to reach 30%. Only ~5% is consumed for the manufacture of chemicals, although methane is a valuable source of carbon and can be used in the syntheses of many products and intermediates in chemical and petrochemical sectors.

Scheme 7 shows a chemical tree of natural gas. As can be seen methane is a prospective source of fuel, lower alkanes, alkenes, carboxylic acids, alcohols, esters, and ethers (including methyl *tert*-butyl ether, which is currently used as a fuel additive that replaced environmentally harmful tetraethyl lead).

A trend toward the direct use of methane and its closest homologs instead of conventional raw materials is seen in the search for alternative methods of synthesis: formaldehyde synthesis from methane to replace synthesis from methanol, ethylene synthesis by the oxidative coupling of methane to replace ethane pyrolysis, and vinyl chloride synthesis by the oxidative chlorination of methane instead of methods based on ethylene and HCl. Analogously, ethane and HCl are expected to be used instead of ethylene and HCl in the synthesis of 1,2-dichloroethane, ethane and air (O_2) are expected to replace CO and methanol in the synthesis of acetic acid, propane could replace propylene in the direct synthesis of acrylic acid and acrylonitrile, and isobutene could replace metacrolein in methacrylic acid synthesis.



Scheme 6. Structure of C_1 chemistry.



Scheme 7. Natural gas as a feedstock for basic organic synthesis.

Let us now turn to the processes where methane is used. As mentioned above, hydrogen cyanide manufacture by the oxidative ammonolysis of methane or by the pyrolysis of methane and ammonia have been used since the late 1930s:

$$CH_4 + NH_3 + 3/2O_2 \xrightarrow[\text{Ph/Pt}]{>1100°\text{C}} HCN + 3H_2O$$

(Rulon plant in Dzerzhinsk, ~1938;
the selectivity based on CH_4 is 90%,
the selectivity based on NH_3 is 90%),

$$CH_4 + NH_3 \xrightarrow[\text{corundum, Pt, Ru}]{1300°\text{C}} HCN + 3H_2$$

(Degussa; the selectivity based on CH_4
is 90%; the selectivity based on NH_3 is 83%).

The manufacture of chloromethanes—carbon tetrachloride, methyl chloride, chloroform, and methylene chloride—are based on methane or carbon disulfide chlorination:

$$2CS_2 + 5Cl_2 \xrightarrow[\text{FeCl}_3]{30°\text{C}} 2CCl_4 + 2S + S_2Cl_2$$

(The selectivity to CCl_4 is 90%,

the selectivity based on Cl_2 is 80%),

$$CH_4 + Cl_2 \xrightarrow[-\text{HCl}]{300°\text{C}} \left\{\begin{array}{ll} CH_3Cl & 37\% \\ CH_2Cl_2 & 41\%, \\ CHCl_3 & 19\% \end{array}\right.$$

$$CH_3OH + HCl \xrightarrow[\text{ZnCl}_2]{100–150°\text{C}} CH_3Cl + H_2O$$

(Lummus, the selectivity is >97%),

$$CH_4 + HCl + 1/2O_2 \xrightarrow[\text{CuCl}_2,\ \text{KCl}]{} CH_3Cl + H_2O.$$

Table 8. Performance characteristics of methanol synthesis process

Output:		
nominal	ton/year	60000
real	ton/year	66670
	ton/day	200
Full costs	$ million	24.1
Cost per unit	$/ton	362
Capital outlays	$ million	21.3
Earnings from sales (assuming a methanol price of $247 per ton)	$ million/year	17.0
Operating costs	$ million/year	8.8
Specific operating costs	$/ton	132
Maintenance staff	persons	429
Annual profit	$ million/year	5.9
Pay-back period	years	20
Prime cost of methanol:		
Texaco/Lurgi (syngas from coal)	$/ton	145
ICI (syngas from natural gas)	——〃——	98

These are large-scale manufactures, especially methyl chloride, chloroform, and methylene chloride syntheses, which were successfully developed in the 1960s and 1970s.

However, most of methane is consumed for syngas production:

Steam reforming: $CH_4 + H_2O \rightleftarrows 3H_2 + CO$,

Carbon dioxide reforming:

$$CH_4 + CO_2 \rightleftarrows 2H_2 + 2CO,$$

Methane oxidation: $CH_4 + 1/2O_2 \rightleftarrows 2H_2 + CO$,

$$H_2 + 1/2O_2 \rightleftarrows H_2O.$$

By combining these three methods, one can achieve different $H_2 : CO$ ratios depending on consumers' requirements. Catalysts for methane reforming are nickel salts supported on various supports. Side reactions accompanying steam conversion are coking. Because the rate of coking increases with an increase in pressure, syngas manufacturing at elevated pressures was impossible. Radical changes in this field happened in the 1960s, when promoters proposed to catalyze the reaction of coke with steam. This led to intensifying syngas and hydrogen production, and to changes in the syntheses of methanol and ammonia.

Methanol is one of the most important products in the chemical industry. The most common method is based on methane, which is converted into methanol via syngas:

$$CO + 2H_2 \longrightarrow CH_3OH$$

$$(\text{or } CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O).$$

According to the theory developed at the Institute of Petrochemical Synthesis of the Russian Academy of Sciences by A.N. Bashkirov, A. Ya. Rozovskii, and others, carbon monoxide, which is a component of syngas, reacts with water to form CO_2 and H_2 on industrial catalysts, and then these compounds react to form methanol [44, 45].

This is one of the most advanced technologies and one of the best sample pieces of modern chemical engineering. The process is characterized by a high degree of energy recuperation (Table 8).

For many years, research has been underway toward direct methane conversion into methanol

$$CH_4 + 1/2O_2 \xrightarrow{430°\text{C, 100 atm}} CH_3OH.$$

As shown by V.I. Vedeneev and V.S. Arutyunov at the Institute of Chemical Physics of the Russian Academy of Sciences [46], methane can be oxidized to methanol under relatively mild conditions with a yield of 86% and a rate of 1.3 kg l^{-1} h^{-1}. A shortcoming of this method and its analogs is that the acceptable selectivity to methanol (55%) is achieved only if the single-pass conversion is 3%. The higher the conversion, the lower the selectivity. Therefore, the process should be carried out in steps. In the case of four-step methane oxidation with methanol removal after each step, acceptable characteristics of the process are achievable. Of course, the quality of methanol synthesized by direct oxidation is lower than that from syngas. The economical characteristics of the process are also somewhat worse compared with the conventional method. However, an important advantage of the new method is that it does not require costly equipment. It remains profitable even if the capacity is low, whereas the profitability of syngas process is optimal only if the throughput is at least 60000 ton/year. Direct oxidation allows methanol on-mine manufacturing. Without fine purification, it can be used as an agent that prevents hydrate formation, as a solvent or motor fuel at the same gas mine or nearby.

Another important direction of methane processing is its conversion into acetylene. Starting in the 1950s, the methods for acetylene synthesis from methane were developed in Germany, Russia, and other countries. There are variants: one is based on electrocracking, and others are based on cracking with heat carriers, such as overheated steam from the combustion of hydrogen and methane, and on thermal oxidative cracking:

$$2CH_4 \xrightarrow{>1400°C} HC{\equiv}CH + 3H_2$$

$$(\Delta H^\circ_{298} = +89.78\ \text{kcal/mol})$$

$$(\Delta G^\circ_{298} = +74.12\ \text{kcal/mol})$$

$$[C_2H_2] = 5\text{–}20\%,$$

$$2CH_{4(\text{gas})} + 3/2O_{2(\text{gas})} \longrightarrow C_2H_{2(\text{gas})} + 3H_2O_{(\text{gas})}$$

$$(\Delta H^\circ_{298} = -83.61\ \text{kcal/mol})$$

$$(\Delta G^\circ_{298} = -89.78\ \text{kcal/mol}).$$

In several countries technical soot is produced from methane:

$$CH_4 \longrightarrow C_{(\text{solid})} + H_{2(\text{gas})}$$

$$(\Delta H^\circ_{298} = +17.88\ \text{kcal/mol})$$

$$(\Delta G^\circ_{298} = +12.146\ \text{kcal/mol}).$$

Rather exotic methods appeared for acetylene synthesis. For example, a method was proposed according to which hydrogen is oxidized in a preliminary camera to generate hydrogen atoms. Then, they react in the main camera with methane to form acetylene [47]:

$$\begin{array}{c} 4.5H_2 + 1.5O_2 \longrightarrow 3H_2O + 3H^\bullet \\ 3H^\bullet + 2CH_4 \longrightarrow C_2H_2 + 4.5H_2 \\ \hline 2CH_4 + 1.5O_2 \xrightarrow{4.5\,H_2} C_2H_2 + 3H_2O. \end{array}$$

In this method, hydrogen is a catalyst for methane oxidation to acetylene.

A new potential industrial use of methane is its oxidative coupling to form ethylene. Of course, this was preceded by the thermal oxidative cracking of methane, Khcheyan's reaction, which was developed in 1979–1981 at the All-Union Research Institute of Organic Synthesis, and the oxidative coupling of toluene in the presence of tin oxide and metallic tin:

Thermal oxidative cracking (BASF) [48]

$$3CH_4 + 1/2O_2 \longrightarrow C_2H_2 + 5H_2 + CO$$

(The conversion into C_2H_2 ~30%),

Khcheyan's reaction (1979–1981) [49]

$$PhCH_3 + CH_4 + O_2 \longrightarrow Ph\text{–}CH{=}CH_2 + 2H_2O$$

$$PhCH_3 + CH_4 + 1/2O_2 \longrightarrow Ph\text{–}CH_2\text{–}CH_3 + H_2O,$$

$$NCCH_3 + CH_4 + O_2 \longrightarrow NCCH{=}CH_2 + 2H_2O,$$

Oxidative coupling of toluene in the presence of PbO/Pb [50]

$$2PhCH_3 + 2PbO \xrightarrow{540\text{–}650°C} PhCH{=}CHPh + 2H_2O + 2Pb$$

$$Pb + 1/2O_2 \xrightarrow{\sim 500°C} PbO$$

$$PhCH{=}CHPh + CH_2{=}CH_2 \xrightarrow{Mo^n} 2PhCH{=}CH_2.$$

Today many research papers are devoted to the oxidative coupling of methane. Intensive studies of this reaction were initiated by a paper [51], which was published early in the 1980s:

$$CH_4 + O_2 \xrightarrow[\text{Cat}]{700\text{–}800°C} \begin{cases} \longrightarrow CH_2{=}CH_2 + 2H_2O \\ \longrightarrow CH_3\text{–}CH_3 + H_2O \\ \longrightarrow CO \\ \longrightarrow CO_2 \end{cases}$$

Oxides of different metals, sometimes with the addition of alkali metals are the most frequent catalysts used for this reaction [46]. The studies of ethylene synthesis from natural gas by the oxidative coupling of methane are carried out in several research centers in Russia.

Lead melt containing lead oxide can probably be recognized as the most selective catalyst for the oxidative coupling of methane [52]. In the presence of lithium oxide, lithium hydroxide, and potassium hydroxide, the main pathway of the reaction is methane conversion into a mixture of ethylene and ethane. At 750°C, the ethane-to-ethylene ratio is 2 : 1, and the selectivity to the sum of C_2 hydrocarbons reaches 99%. A serious shortcoming of the method is the low capacity of the catalyst melt (6 g $(\text{l cat})^{-1}$ h^{-1}). This value is at the boundary, beyond which industry cannot afford a process.

Systems based on rare-earth element oxides are very efficient catalysts for the oxidative coupling of methane [53, 54].

However, a high selectivity is usually achieved at a low conversion of methane. Thus, the task of catalyst design and the choice of conditions for the oxidative coupling of methane that would combine a high selectivity and an acceptable activity is still topical.

For several years, the growth of publications devoted to the oxidative coupling of methane somewhat decelerated. At the same time, in the countries possessing large sources of natural gas or cheap access to them, an interest is still rather strong. This is primarily due to the fact that the prices for natural gas in Europe and America are rather high, and the process of ethylene synthesis from it is currently unable to compete with ethane pyrolysis, which is used now. Russia possesses substantial resources of natural gas and mines rather expensive oil; therefore, it sees a radically different situation.

A distinctive feature of the oxidative coupling of methane is that the main and side reactions are highly isothermic. Technological flowcharts enable utilizing this heat to generate steam with a pressure of 30–110 atm. The amount of steam thus produced covers all the needs of process technology and can even be supplied to other plants. Therefore, the economical efficiency of this process is determined by the cheapness of feedstock and the extra amount of steam.

Technical and economic assessment shows that the prime cost depends linearly on the price of natural gas. When the price is \$10 per 1000 m^3, the cost of ethylene is \$85 per 1 ton (in 1999). Thus, ethylene manufacturing by the oxidative coupling of methane can currently be profitable in Russia.

A number of studies are devoted to the direct functionalization of methane, that is, to the synthesis of valuable products, such as acetic acid, directly from methane:

$$CH_4 + CO + 1/2O_2 \longrightarrow CH_3COOH.$$

The catalysts for this process are

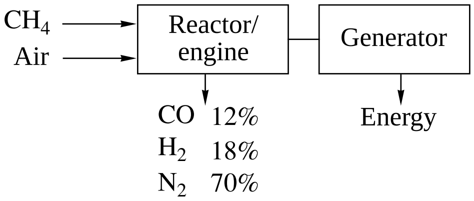
$$RhCl_3/NaCl/KI–H_2O \ [55],$$

$$PdX_2–CF_3COOH \ [56],$$

$$RhCl_3/NaCl/KI–CF_3COOH/H_2O \ [57],$$

$$\text{and } VO_3^-/C_4N_2H_2(COOH)(CH_3CN(H_2O)) \ [58].$$

One of the promising methane applications is a combination of a chemical process and energy production—a so-called energochemical process. Yu.A. Kolbanovskii, N.A. Plate, and others [59] proposed a method for gas-phase methane oxidation by air to produce syngas and energy. For this process, a modified diesel or a compression engine is used, which also plays the role of a chemical reactor. The process was implemented in 1998 at a plant with a capacity of 10 000 m^3 of syngas per hour. It is characterized by a high unit-volume reactor capacity. A schematic diagram for such a process is shown in Scheme 8.



Scheme 8. Combined production of syngas and energy [44].

Low-pressure natural gas, possibly right from an out-of-service mine, can be used in this process. Air is an oxidant of natural gas to improve economics (oxygen manufacture is not needed), although this lowers the quality of target syngas because of a high nitrogen concentration (about 70%). Nevertheless, experiments demonstrated that this syngas can be used for the manufacture of gasoline and dimethyl ether, which is a prospective diesel fuel [44].

Another energochemical process based on methane is methane conversion into carbon dioxide in a fuel cell. This process is being developed by V.A. Sobyanin and co-workers [60, 61] (Table 9).

Energochemical studies also concern methane homologs. Nowadays, propane is pyrolyzed to obtain ethylene, and research is underway to find catalysts for the oxidative dehydrogenation of propane to propylene and the oxidation of propane to acrylonitrile [62].

Carbon monoxide is traditionally viewed as a bridge between methane and industrial chemicals [63]. Today's industry uses many processes based on carbon monoxide:

- Hydrogen manufacture,
- Methanol synthesis,
- Fischer–Tropsch syntheses,
- Roelen hydroformylation and relevant processes,
- Acetic acid synthesis,
- Gatterman–Koch synthesis (synthesis of carboxylic acid halides) and related processes,
- Formic acid synthesis,
- Phosgene synthesis,
- Dimethyl carbonate synthesis,
- Polyketone synthesis, and
- Methyl methacrylate synthesis.

The situation with the use of carbon dioxide is much worse. In the 1980s, V.A. Legasov tried using heat from a nuclear reactor to cleave carbon dioxide into carbon monoxide and oxygen:

$$CO_{2(gas)} = CO_{(gas)} + 1/2O_{2(gas)}$$

$$(\Delta H^\circ_{298} = +68.63 \text{ kcal/mol})$$

$$(\Delta G^\circ_{298} = +61.45 \text{ kcal/mol}),$$

$$CO_{2(gas)} = CO_{(gas)} + O_{(gas)} \ (\Delta H^\circ_{298} = +127.2 \text{ kcal/mol}).$$

The prospects of this interesting method are limited by the fact that a mixture of CO and oxygen is explosive.

Carbon dioxide reduction is equally unsuitable for technology. The reduction of CO_2 by hydrogen to form formic acid is thermodynamically unfavorable. It becomes possible only in alkali solutions:

$$CO_{2(gas)} + H_{2(gas)} = HCOOH_{(liquid)}$$

$$(\Delta G^\circ_{298} = +11.55 \text{ kcal/mol}),$$

$$CO_{2(gas)} + H_{2(gas)} = HCOOH_{(aq)}$$

$$(\Delta G^{\circ}_{298} = +9.15 \text{ kcal/mol}),$$

$$CO_{2(gas)} + H_{2(gas)} + OH^{-}_{(aq)} = HCOO^{-}_{(aq)} + H_2O_{(liguid)}$$

$$(\Delta G^{\circ}_{298} = -4.83 \text{ kcal/mol}).$$

However, in alkali solutions, the products are formic acid salts. To isolate formic acid from this solution, neutralization with mineral acid is needed. This is uneconomical (alkali and acid consumption) and environmentally unacceptable (salt waste).

Recent data show that a base is important for the activation of carbon dioxide even under supercritical conditions, that is, at pressures above 80 atm and a moderate temperature, when thermodynamic limitations are surmounted [64, 65]:

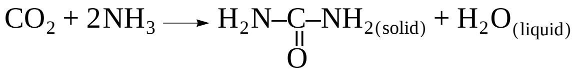
$$CO_2 + H_2 \xrightarrow[50°C,\ 210\ atm]{RuH_2[P(CH_3)_3]_4,\ NEt_3} HCOOH$$

$$CO_2 + H_2 + CH_3OH \xrightarrow[80°C,\ 210\ atm]{RuCl_2[P(CH_3)_3]_4,\ NEt_3} HCOOCH_3 + H_2O$$

$$CO_2 + H_2 + HNMe_2 \xrightarrow[80°C,\ 210\ atm]{RuCl_2[P(CH_3)_3]_4,\ NEt_3} HCON(CH_3)_2 + H_2O.$$

It is likely that ammonia or other bases, including those that react with formic acid, are needed for carbon dioxide reduction whichever catalyst is used. Probably, a base (amine, ammonia, or OH^-) is also needed for CO_2 activation.

Carbon dioxide remains one of the most difficult objects in industrial C_1 chemistry. By now, the only large-scale process that uses carbon dioxide from both natural and human-caused origins is urea synthesis:



$$CO_2 + 2NH_3 \longrightarrow H_2N{-}\underset{\underset{O}{\|}}{C}{-}NH_{2(solid)} + H_2O_{(liquid)}$$

$$\Delta G^{\circ}_{298} = -3.42 \text{ kcal/mol}.$$

At the same time, environmental problems require CO_2 utilization. Although chemists posses a number of methods for CO_2 conversion, all reactions occur at rather strict conditions and require substantial hydrogen consumption [66]:

$$2CO_2 + 6H_2 \xrightarrow[Fe,Co/SiO_2]{1\ atm,\ 670\ K} CH_2{=}CH_2 + 4H_2O,$$

$$3CO_2 + 9H_2 \xrightarrow[Fe,Co/SiO_2]{1\ atm,\ 670\ K} CH_3CH{=}CH_2 + 6H_2O,$$

$$(CO_2 : H_2 = 2 : 1).$$

These reactions require much energy. Correspondingly, this energy is obtained by burning fuel accompanied by CO_2 emission that diminishes the gain in CO_2 conversion into useful products. Nevertheless, studies of catalytic CO_2 conversion should be continued with the hope that alternative sources of energy will be found that are not associated with burning hydrocarbon fuel.

CONCLUSION

The modern industry of petrochemical and basic organic synthesis is a giant sector of chemical industry with an infrastructure and market developed for the past century. Obviously, such sectors of industry as car manufacturing, building construction, varnish-and-paint industry, textile industry, and other sectors of economy depending on chemical commodity products will not radically change the structure of their consumption in the near future. Therefore, chemists should find the methods to convert nonconventional carbon-containing raw materials (natural gas) into conventional commodity products without substantial changes in the prices for these products to maintain sustainable development of the world economy. Such methods primarily include the above-mentioned processes for natural gas conversion into such products as alkenes to substitute for their oil-dependent sources. A search for methods for carbon dioxide activation using traditional catalysts, as well as photocatalytic and electrocatalytic methods, is one of the primary tasks.

A search for direct synthetic methods to replace multiple-stage syntheses of important products and intermediates are still topical (e.g., direct propylene-to-propylene oxide, benzene-to-phenol, and hydrogen-to-hydrogen peroxide oxidation and direct alkene hydration, especially regioselective anti-Markovnikov hydration of higher alkenes). Some of these reactions are actively studied in laboratories today.

An important problem is the design of catalysts and processes that help to carry out thermodynamically hindered reactions as coupled conversions. For instance, ~40% of methanol is consumed for formaldehyde synthesis. Therefore, it sounds topical to find a method for direct syngas conversion into formaldehyde. However, the thermodynamics is not favorable for this conversion. Neither is it in the case of acetylene synthesis from CO and hydrogen or acetaldehyde synthesis from methane and CO:

$$2CO_{(gas)} + 3H_{2(gas)} \longrightarrow HC{\equiv}CH + 2H_2O_{(liquid)} \quad (\Delta G^{\circ}_{298} = +6.34 \text{ kcal/mol}), \tag{IX}$$

Table 9. Methane conversion to carbon monoxide in a fuel cell

Electrode/Catalyst

CH_4 ⫽ $0.9\,ZrO_2 + 0.1\,Y_2O_3$, Pt ⫽ Air

Electrode	*T*, °C	CO conversion, %	CO yield, %
Ag	800	19	~0
Pt/2% CeO_2	800	28	~1
Pt	800	75	69
Pt	1100	~100	97
Ni	800–850	93	82–88
Fe	950	74.5	73

$$CH_{4(gas)} + CO_{(gas)} \longrightarrow CH_3CHO_{(gas)} \quad (\Delta G^\circ_{298} = +13.1 \text{ kcal/mol}), \tag{X}$$

$$CO_{(gas)} + H_{2(gas)} \longrightarrow H_2C{=}O_{(gas)} \quad (\Delta G^\circ_{298} = +6.54 \text{ kcal/mol}), \tag{XI}$$

$$CO_{(gas)} + H_2O_{(liquid)} \longrightarrow HCOOH_{(liquid)} \quad (\Delta G^\circ_{298} = +1.06 \text{ kcal/mol}). \tag{XII}$$

A slightly positive value of ΔG°_{298} in CO hydration makes the one-stage conversion (XII) of CO and H_2O into formic acid impossible. In industry, formic acid is produced in two stages: CO and methanol react to yield methyl formate in the presence of sodium methoxide. Then, methyl formate is hydrolyzed. Expensive energy-consuming separation operations usually follow each synthetic stage. This is our fee for the inability to overcome thermodynamic limitations. The coupling of reactions could be a method to solve this problem.

Two important CO-consuming reactions below are thermodynamically favorable:

$$CO_{(gas)} + 2H_{2(gas)} \longrightarrow CH_3OH_{(liquid)} \quad (\Delta G^\circ_{298} = -6.92 \text{ kcal/mol}), \tag{XIII}$$

$$CO_{(gas)} + H_2O_{(gas)} \longrightarrow H_{2(gas)} + CO_{2(gas)} \quad (\Delta G^\circ_{298} = -6.82 \text{ kcal/mol}). \tag{XIV}$$

Acetylene synthesis (reaction (IX)) coupling with water-gas shift reaction (XIV) could make one-stage acetylene synthesis from CO and hydrogen (reaction (XV)) possible. An analogous coupling of reaction (XI) with water-gas shift (XIV) or methanol synthesis (XIII) could provide the possibility for formaldehyde synthesis from CO and hydrogen (reactions (XVI) and (XVII)):

$$4CO_{(gas)} + H_{2(gas)} \longrightarrow C_2H_{2(gas)} + 2CO_{2(gas)} \quad (\Delta G^\circ_{298} = -7.28 \text{ kcal/mol}), \tag{XV}$$

$$2CO_{(gas)} + 3H_{2(gas)} \longrightarrow CH_2O_{(gas)} + CH_3OH_{(liquid)} \quad (\Delta G^\circ_{298} = -0.36 \text{ kcal/mol}), \tag{XVI}$$

$$2CO_{(gas)} + H_2O_{(gas)} \longrightarrow CH_2O_{(gas)} + CO_{2(gas)} \quad (\Delta G^\circ_{298} = -0.27 \text{ kcal/mol}). \tag{XVII}$$

Reaction coupling requires searching for new catalytic systems and compositions, such as the membrane catalysts of V.M. Gryaznov [67, 68], cluster systems [69], and others.

Catalysis will undoubtedly fill an important place in the systems for storing energy obtained from nuclear stations and nontraditional sources (tidal power stations, solar energy, etc.) [70].

As mentioned above, the product market of organic synthesis does not need extending the assortment. In this sector, studies are toward the search for more active catalysts and making reaction conditions milder. For instance, a catalyst that would allow decreasing the temperature of water-gas shift reaction would see great commercial success. V.A. Likholobov, Yu.I. Ermakov, and others, who discovered the ability of palladium complexes to catalyze the reaction of CO and water in thrifluoroacetic acid solutions [71] made the first attempts along these lines. More recently, the rhodium complex $RhI_2(CO)_2^-$ was shown to be more efficient. The liquid-phase conversion of CO, which actively occurs in the presence of this complex, is an undesirable process under the conditions of methanol carbonylation to acetic acid [72].

Most commercial processes have selectivities ranging from 90 to 95%, but the task of increasing the selectivity of many processes remains topical.

Unlike the products of basic organic synthesis, the fine chemicals market will constantly need new products. New medicines, bioactive additives, and active vitamin forms will always be needed to support life. New technologies will require compounds capable of existing in a liquid-crystal state, new dyes, composite components, and other materials. The field of chemistry needs new catalysts that would reduce a number of synthetic stages and provide high regio- and stereoselectivity. Lessons learned from nature and data borrowed from enzymatic catalysis should play an important role [73].

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