1

Introduction and General Aspects

Hydrocarbon chemistry is essentially abiological organic chemistry although methane and fossil fuels and derivatives have biological origin.

1.1 Hydrocarbons and Their Classes

Hydrocarbons, as their name indicates, are molecular compounds of carbon and hydrogen. As such, they represent one of the most significant classes of *organic* compounds (i.e., of carbon compounds).[1] In methane (CH_4), the simplest saturated alkane, a single carbon atom is bonded to four hydrogen atoms. In the higher homologs of methane (of the general formula C_nH_{2n+2}), all atoms are bound to each other by single [(sigma (σ), two-electron, two-center] bonds with carbon displaying its tendency to form C–C bonds. Whereas in CH_4 the H/C ratio is 4, in C_2H_6 (ethane) it is decreased to 3, in C_3H_8 (propane) to 2.67, and so on. Alkanes can be straight chain (each carbon attached to not more than two other carbon atoms) or branched (in which at least one of the carbon is attached to either three or four other carbon atoms). Carbon atoms can be aligned in open chains (acyclic hydrocarbons) or can form rings (cyclic hydrocarbons).

Cycloalkanes are cyclic saturated hydrocarbons containing a single ring. Bridged cycloalkanes contain one (or more) pair(s) of carbon atoms common to two (or more) rings. In bicycloalkanes, there are two carbon atoms common to both rings. In tricycloalkanes, there are four carbon atoms common to three rings such as in adamantane (tricyclo[3.3.1.1^{3,7}]decane) giving a caged hydrocarbon structure.

Carbon can also form multiple bonds with other carbon atoms. This results in unsaturated hydrocarbons such as olefins (alkenes, C_nH_{2n}), specifically, hydrocarbons containing a carbon–carbon double bond or acetylenes (alkynes, C_nH_{n-2}) containing a carbon–carbon triple bond. Dienes and polyenes contain two or more unsaturated bonds.

Hydrocarbon Chemistry, Third Edition. George A. Olah, Árpád Molnár and G. K. Surya Prakash.

Aromatic hydrocarbons (arenes), a class of hydrocarbons of which benzene is parent, consist of cyclic arrangement of formally unsaturated carbons, which, however, give a stabilized (in contrast to their hypothetical cyclopolyenes) delocalized π system.

The H/C ratio in hydrocarbons is indicative of the hydrogen deficiency of the system. As mentioned, the highest theoretical H/C ratio possible for hydrocarbons is 4 (in CH_4), although in carbocationic compounds (the positive ions of carbon compound) such as $CH_5{}^+$ and even $CH_6{}^{2+}$ the ratio is further increased (to 5 and 6, respectively). On the other end of the scale, in extreme cases, such as the dihydro or methylene derivatives of C_{60} and C_{70} fullerenes discovered in the 1980s, the H/C ratio can be as low as ~0.03!

An index of unsaturation (hydrogen deficiency) i can be used in hydrocarbons, whose value indicates the number of ring and/or double bonds (a triple bond is counted as two double bonds) present (C and H = the number of carbon and hydrogen atoms); $i = 0$ for methane, for ethene $i = 1$ (one double bond), for acetylene (ethyne) $i = 2$, etc.

$$i = \frac{(2C + 2) - H}{2}$$

The International Union of Pure and Applied Chemistry (IUPAC) has established rules to name hydrocarbons. Frequently, however, trivial names are also used and will continue to be used. It is considered not very important to elaborate on the question of nomenclature. Systematic naming is mostly followed. Trivial (common) namings are, however, also well extended. *Olefins* or *aromatics* clearly are very much part of our everyday usage, although their IUPAC names are *alkenes* and *arenes*, respectively. Straight-chain saturated hydrocarbons are frequently referred to as *n*-alkanes (normal) in contrast to their branched analogs (isoalkanes). Similarly, straight-chain alkenes are frequently called *n*-alkenes as contrasted with branched isoalkenes (or olefins). What needs to be pointed out, however, is that one should not mix the systematic IUPAC and the still prevalent trivial (or common) namings. For example, $(CH_3)_2C{=}CH_2$ can be called isobutylene or 2-methylpropene but should not be called isobutene as only the common name *butylene* should be affixed by *iso*. On the other hand, isobutane is the proper common name for 2-methylpropane $[(CH_3)_3CH]$. We discuss, for example, the isobutane–isobutylene alkylation for production of isooctane (a major component of high-octane gasoline) but it should not be called isobutane–isobutene alkylation.

1.2 Energy–Hydrocarbon Relationships

Every facet of human life is affected by the need for energy. The sun is the central energy source of our solar system. The difficulty lies in converting solar energy into other energy sources and also to store them for future use.

Photovoltaic devices and other means to utilize solar energy are intensively studied and developed but at the enormous level of our energy demands, Earth-based major installations using the present day technology are inadequate. The size of collecting devices would necessitate to utilize large areas of the earth. Atmospheric conditions in most of the industrialized world are unsuitable to provide constant solar energy supply. Perhaps a space-based collecting system beaming energy back to Earth can be established at some time in the future, but except small-to-medium-scale installations, solar energy is of limited significance for the foreseeable future. Other unconventional energy sources, such as wind, ocean wave, tides of the seas, and geothermal energy as well as energy from the combustion of biomass represent a rapidly increasing yet still small fraction of our energy production. Nevertheless, search for alternate renewable energy sources to produce clean, safe, and sustainable energy is vital for the future sustenance of mankind.

Our major energy sources are fossil fuels (i.e., oil, gas, and coal) as well as atomic energy. Fossil energy sources are, however, nonrenewable (at least on our timescale) and their burning causes serious environmental problems. Increased carbon dioxide levels are considered to contribute to the "greenhouse" effect. The major limitation, however, is the limited nature of our fossil fuel resources. The world total proven coal reserves at the end of 2015 were estimated to be 892,000 M/t lasting about 114 years at the current rates of consumption.[2] (The timeframe for the United States with the largest coal reserve of 237,000 M/t is 292 years.) The corresponding data for total petroleum oil and natural gas are 1,697,600 million barrels (50.4 years) and 186.9 trillion cubic meters (52.8 years). In human history, these are short periods and we will need to find new solutions.

The United States still relies overwhelmingly on fossil energy sources, with only 8.3% coming from atomic energy and 9.6% from renewable sources (Table 1.1). Other industrialized countries utilize to a much higher degree of nuclear and hydroenergy[2] (Table 1.2). Since the 1980s, concerns about safety and difficulties in disposing fission by-products dramatically limited the growth of the otherwise clean atomic energy industry.

Table 1.1 U.S. Energy Consumption by Sources (%)[3]

Power Source	1990	2000	2005	2010	2014
Coal	22.6	22.8	19.7	21.3	17.9
Petroleum	39.6	38.8	40.4	36.7	34.8
Natural gas	23.3	24.2	22.6	25.2	27.5
Nuclear energy	7.2	7.9	8.1	8.6	8.3
Hydroenergy, geothermal, solar, wind, biomass	7.2	6.2	6.1	8.2	9.6

Table 1.2 Power Generated in Industrial Countries by Nonfossil Fuels (2010)

	Nonfossil Fuel Power (%)	
Country	**Hydroenergy**	**Nuclear Energy**
Canada	60	14
France	11	77
Germany	3.5	23.7
Japan	7.4	24.2
Italy	14	0
United Kingdom	1.4	13.8
USA	6.2	8.6

A way to extend the lifetime of our fossil fuel energy reserves is to raise the efficiency of thermal power generation. Progress has been made in this regard, but the heat efficiency even in the most modern power plants is limited. Heat efficiency increased substantially from 19% in 1951 to 38% in 1970, but for many years since then 39% appeared to be the limit. Combined-cycle thermal power generation—a combination of gas turbines and steam turbines—allowed in Japan to further increase heat efficiency from 35 to 39% to as high as 43%. Conservation efforts can also greatly contribute to moderate worldwide growth of energy consumption, but the rapidly growing population of our planet (7.2 billion today, but should reach about 10 billion by 2050) will put enormous pressure on our future needs.

Estimates of the world energy consumption till 2040 are shown graphically in Figure 1.1 in relationship with data dating back to 1970. A rise in global energy consumption of about 95% for the year 2025 is expected compared with 1990. Even in a very limited growth economic scenario, the global energy demand is estimated to reach 12 billion tons of oil equivalent (toe) by the year 2025.[4]

Mankind's long-range energy future clearly must be safe nuclear energy, which should increasingly free still remaining fossil fuels as sources for convenient transportation fuels and as raw materials for synthesis of plastics, chemicals, and other substances. Eventually, however, in the not too distant future, we will need to make synthetic hydrocarbons on a large scale.

1.3 Hydrocarbon Sources

All fossil fuels (coal, oil, gas) are basically hydrocarbons, varying, however, significantly in their H/C ratio[5] (Table 1.3). These are formed over eons by the

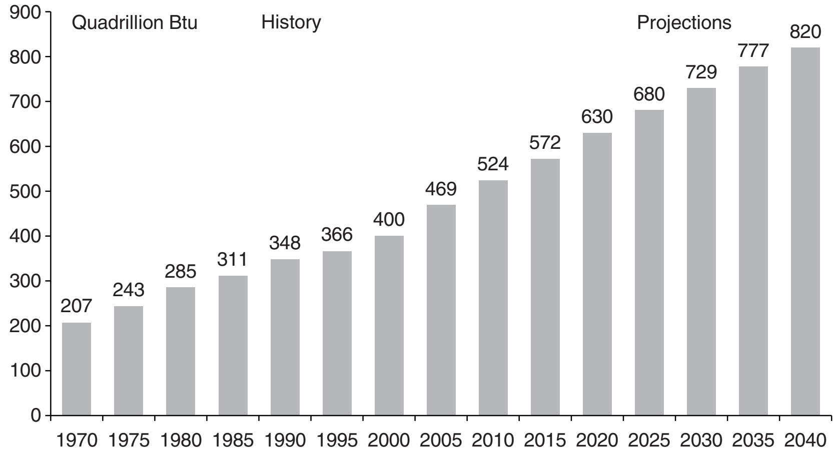


Figure 1.1 World energy consumption history and projections.

anaerobic decay of living organisms that is, they are fossilized solar energy. Consequently, all hydrocarbons available for mankind are of biological origin. Since the industrial revolution, fossil fuels have been used up rapidly. When burned they undergo oxidation to form carbon dioxide and water and, consequently, they are not renewable on a human timescale. Furthermore, their burning (oxidation) results in a large anthropogenic CO_2 emission causing harmful effect in the environment (global warming, rising sea levels, acidification of oceans, etc.).

1.3.1 Coal

Abundant coal resources can be a major source for conversion to hydrocarbons.[6] Coals (the plural is deliberately used as coal has no defined, uniform nature or structure) are fossil sources with low hydrogen content.[1b,7] The "structure" of coals means only structural models depicting major bonding

Table 1.3 H/C Ratio of Natural Hydrocarbon Sources

Methane	4.0
Natural gas	3.8
Petroleum crude	1.8
Tar sands bitumen	1.5
Shale oil (raw)	1.5
Bituminous coal	0.8

types and components, relating changes with coal rank. Coal is classified—or ranked—as lignite, subbituminous, bituminous, and anthracite. This is also the order of increased aromaticity and decreased volatile matter. The H/C ratio of bituminous coal is about 0.8, whereas anthracite has H/C ratios as low as 0.2.

From a chemical, as contrasted to a geological point of view, the coal formation (coalification) process can be grossly viewed as a continuum of chemical changes, some microbiological, some thermal involving a progression in which woody or cellulosic plant materials (the products of nature's photosynthetic recycling of CO_2) in peat swamps are converted during many millions of years and increasingly severe geological conditions to coals. Coalification is grossly a deoxygenation–aromatization process. As the "rank" or age of the coal increases, the organic oxygen content decreases and the aromaticity (defined as the ratio of aromatic carbon to total carbon) increases. Lignites are young or "brown" coals containing more organic oxygen functional groups than subbituminous coals, which in turn have a higher carbon content but fewer oxygen functionalities.

The organic chemical structural types believed to be characteristic of coals can be schematically represented as shown in Figure 1.2 showing probable structural groups and connecting bridges that are present in a typical bituminous coal.[7b]

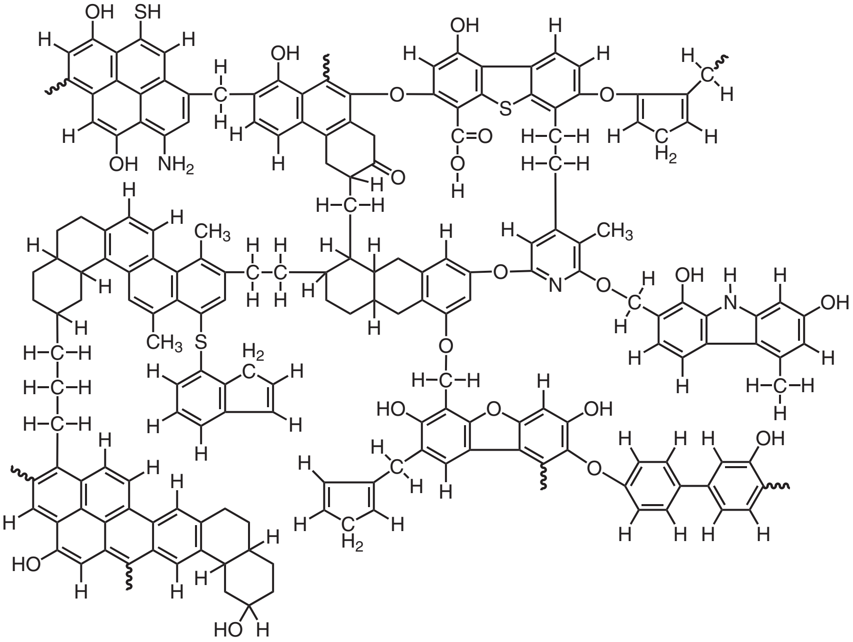


Figure 1.2 Schematic representation of structural groups and connecting bridges in bituminous coal. *Source*: Wiser 1984.[7b] Reproduced with permission of Springer. Copyright 2017.

The principle type of bridging linkages between clusters are short aliphatic groups $(CH_2)_n$ (where $n = 1–4$), different types of ether linkages, and sulfide and biphenyl bonds. All but the latter may be considered scissible bonds in that they can readily undergo thermal and chemical cleavage reactions.

The conversion of coal to hydrocarbons is discussed in Section 1.5.1

1.3.2 Petroleum Oil

Petroleum or crude oil is a complex mixture of many hydrocarbons.[1b,8] It is characterized by the virtual absence of unsaturated hydrocarbons consisting mainly of saturated, mainly straight-chain alkanes, with smaller amounts of slightly branched alkanes, cycloalkanes, and aromatics. Petroleum is generally believed to be derived from organic matter deposited in the sediments and sedimentary rocks on the floor of marine basins. The identification of biological markers such as petroporphyrins provides convincing evidence for the biological origin of our oil reserves. The question of abiological deep petroleum oil was considered, but no conclusive evidence was obtained (for abiological hydrocarbons, see Section 1.3.9). The effect of time, temperature, and pressure in the geological transformation of the bituminous coals and other heavy organics to petroleum oil is not yet clear. However, considering the low level of oxidized hydrocarbons and the presence of porphyrins, it can be surmised that organic precursors were acted upon by anaerobic microorganisms and moderate temperatures, <200 °C. By comparing the composition of typical crude oils with typical bituminous coals, it becomes clear why crude oil is a much more suitable fuel source. It is indicated by its higher H/C atomic ratio, generally lower sulfur and nitrogen contents, very low ash contents, (probably mostly attributable to some suspended mineral matter and vanadium and nickel associated with porphyrins), and essentially no water content.

It is interesting to mention that recent evidence shows that varied extraterrestrially formed abiologic hydrocarbon derivatives indeed reached earth through comets and asteroids. The earth continues to receive some 40,000 tons of interplanetary dust every year. Mass-spectrometric analysis revealed the presence of hydrocarbons attached to these dust particles including polycyclic aromatics such as phenanthrene, chrysene, pyrene, benzopyrene, and pentacene of extraterrestrial origin (indicated by anomalous isotopic ratios[9]). No petroleum oil formation from these, however, can be concluded particularly under the earth's oxygen-rich atmosphere and needed long time for their formation.

Petroleum—a natural mineral oil—was referred to as early as in the *Old Testament*. The word *petroleum* means “rock oil” [from the Greek *petros* (rock) and *elaion* (oil)]. It had been found over the centuries seeping out of the ground, for example, as in the Los Angeles basin (practically next door, where this book is written) and what are now the La Brea Tar Pits. Vast deposits were found in varied places ranging from Europe, to Asia, to the Americas, and to Africa. In the United States, the first commercial petroleum deposit was discovered in 1859 near Titusville in western Pennsylvania when Edwin Drake and Billy Smith struck oil in their first shallow (~20-m-deep) well.[10] The well yielded 400 gallons (gal) of oil a day (about 10 barrels; 1 bbl = 42 gal). The area was known before to contain petroleum that residents skimmed from a local creek's surface, which was thus called "oil creek." The first oil-producing well opened up a whole new industry. The discovery was not unexpected, but provided evidence for oil deposits in the ground that could be accessed by drilling. Oil was used for many purposes, such as in lamp illumination and even for medical remedies. The newly discovered Pennsylvania petroleum was soon also marketed to degrease wool, prepare paints, fuel steam engines, to power light railroad cars, and for many other uses. It was recognized that the well oil was highly impure and had to be refined to separate different fractions for varied uses. The first petroleum refinery, a small distillation operation, was established in Titusville in 1860. Petroleum refining was much cheaper than producing coal oil (kerosene) and soon petroleum became the predominant source for kerosene as an illuminant. In the 1910s, the popularity of automobiles spurred the production of gasoline as the major petroleum product. California, Texas, Oklahoma, and more recently Alaska provided large petroleum deposits in the United States, whereas areas of the mid-east, Asia, Russia, Africa, South America, and more recently of the North Sea became major world oil production centers. Recently discovered very large oil sources backed up in shale formations (shale oil) are in numerous locations around the world including the USA.

The forecast of daily oil consumption by the International Energy Agency for 2016 is about 96 million barrels [about 12 million tons per year (Mt)] with a daily oil output of 97.2 million bbl/d (September, 2016). This is a significant increase from 58 million barrels in 1973. The United States and China's daily oil consumption was, respectively, about 20 and 11 million barrels in 2015. Most of this is used for the generation of electricity, space heating, and as transportation fuel. About 8.5% of the petroleum and natural gas is used as feedstocks for the manufacturing of chemicals, pharmaceuticals, plastics, elastomers, paints, and a host of other products. Petrochemicals from hydrocarbons provide great many necessities of modern life, to which we have become so accustomed that we do not even notice our increasing dependence on them, and yet the consumption of petrochemicals is still growing at an annual rate of 10%. Advances in the petroleum–hydrocarbon industry, more than anything else, may be credited to the high standard of living that we have enjoyed in the past century.

1.3.3 Heavy Oils, Tar Sand, and Bituminous Deposits

Whereas light crudes are preferred in present-day refining operations, increasingly heavier petroleum sources also processed to satisfy our ever-increasing needs. These range from commercially usable *heavy oils* (California, Venezuela, etc.) to the huge bituminous formations locked up in *tar sands*.[1b,11a] These more unconventional sources of oil represent additional oil deposits in the world taken together. The largest is located in Alberta, Canada (Athabaska, Cold Lake), in the form of enormous tar sand and carbonate rock deposits containing some 2.5 trillion barrels of extremely heavy oil, called *bitumen*. It is followed by the heavy oil accumulations in the Orinoco Valley, Venezuela (over 1.2 trillion barrels) and in Siberia. The practical use of these potentially vast reserves depend on finding economical ways to extract the oil (by thermal retorting or other processes) for further processing. The peak production in the Athabaska region was 2.2 million barrels per day in 2015. Profitability of these operations requires market prices for oil to be above $40 a barrel.

The quality of petroleum varies and, according to their specific gravity and viscosity, classified loosely as light, medium, heavy, and extra heavy crude oils. Light oils of low specific gravity and viscosity are more valuable than heavy oils with higher specific gravity and viscosity. In general light oils are richer in saturated hydrocarbons, especially straight-chain alkanes, than heavy oils and contain ≤75% straight-chain alkanes and ≤95% total hydrocarbons. Extra heavy oils, the bitumens, have a high viscosity, and thus may be semisolids with high levels of heteroatoms (nitrogen, oxygen, and sulfur) and a correspondingly reduced hydrocarbon content, of the order of 30–40%.

Heavy oils and especially bitumens contain high concentrations of resins (30–40%) and asphaltenes (≤20%). Most heavy oils and bitumens are thought to be derivatives of lighter, conventional crude oils, which have lost part or all of their *n*-alkane contents along with some of their low-molecular-weight cyclic hydrocarbons through geochemical processes taking place in the oil reservoirs. Heavy oils are also abundant in molecules containing heteroatoms (N, O, S), organometallics, and colloidally dispersed clays and clay organics. The prominent metals associated with petroleum are nickel, vanadium (mainly in the form of vanadyl, VO^{2+} ions), and iron. The former two are (in part) bound to porphyrins to form metalloporphyrins.

Table 1.4 compares the difference in composition of typical light and heavy oils.

Processing of heavy oils and bitumens presents challenges for majority of the refineries, as heavy oils and bitumens can poison the metal catalysts used in the

Table 1.4 Composition (%) of Typical Light and Heavy Oils

Fraction	Light Oil	Heavy Oil
Saturates	78	17–21
Aromatics	18	36–38
Resins	4	26–28
Asphaltene	Trace–2	17

current refineries. The use of superacid catalysts,[8b] which are less sensitive to these feeds, is one of the possible solutions to this problem.

Tight sands (sandstone), shale, and other tight-rock formations lying deep underground hold large amounts of trapped natural gas and oil. These are hard to extract because of the low porosity and low permeability of the reservoir rocks. The new hydraulic fracturing (hydrofracturing, hydrofracking) technique also called "fracking," however, allows tapping the underground shale oil and shale gas and their utilization.

1.3.4 Natural and Shale Gas

Natural gas as we know it is of biological origin (not unlike petroleum oil). Large gas reservoirs were discovered and utilized in the last century. Increasingly deeper wells are drilled, and deposits under the seas are explored and tapped.

Natural gas depending on its source contains—besides methane as the main hydrocarbon component (present usually in 75–90%; Table 1.5)—some of the higher homologous alkanes. In "wet" gases the amount of C_2–C_6 alkanes is more significant.[12,13]

Homologous hydrocarbons of two to five carbon numbers (with low vapor pressures, ethane, propane, butanes, pentane) of which ethane is present in the largest amount, are called *natural-gas liquids*. These can be separated with the use of a gas-absorbing oil. A heavier hydrocarbon fraction of medium vapor pressure (pentane plus) is classified as *liquefied petroleum gas* (LPG). Natural-gas liquids, which are generally of only thermal value, are also dehydrogenated to alkenes. Their direct upgrading to gasoline-range hydrocarbons has also been developed.

Typical composition of natural gas of various origin[14] is shown in Table 1.5.

Natural gas in the early decades of oil exploitation was either vented to the atmosphere or flared. Significant improvements in pipeline technology after World War II allowed the safe, though still challenging, transportation of natural gas over pipelines over long distances (e.g., from Siberia to Central and

Table 1.5 Composition of Natural Gas [weight percent (wt%)]

Location	CH_4	C_2H_6	C_3H_8	C_4H_{10}
United States	89.5–92.5	5.1–2	2.1–0.7	1.6–0.5
Algeria	86.9	9.0	2.6	1.2
Iran	74.9	13.0	7.2	3.1
North Sea	90.8	6.1	0.7	0.1

Western Europe). Across the oceans (e.g., from the Middle East to Europe and North America), natural gas transportation is not feasible because of its gaseous voluminous nature (low boiling point of −161.5 °C). Intercontinental transportation, consequently, requires its liquefaction to liquefied natural gas (LNG). This process reduces the volume by 600 times and achieves nearly the same energy density as gasoline or ethanol. Specially designed, well-insulated, double-walled tankers are used for this purpose. LNG can be stored in cryogenic storage tanks and shipped to LNG terminal where it is regasified and distributed through pipelines. Obviously, both liquefaction and transportation of LNG are highly expensive operations. Furthermore, LNG is also potentially dangerous and blowing up of a tanker (Cleveland, Ohio, 1944) and a liquefaction facility (Algeria, 2003) had devastating effects. Similar accidents in a major port city could be highly destructive with the possible end of all LNG operations. A terrorist attack would certainly have similar consequences.

Large amounts of natural gas were found more recently in shale deposits, which can be extracted by using fracking techniques. First, a deep well is made by vertical drilling followed by horizontal drillings and then fracturing the rocks with hydraulic pressure (hydrofracking). Large amounts of fracking fluid, composed of water (90%), sand, and chemical additives are injected creating microfractures in the rock. The breaking up of rock formations results in the release of natural gas and oil trapped within. This technique, however, in some respect, is controversial because of contamination of ground and drinking water sources by exposure to harmful substances and the observed increase in seismic activity. According to the U.S. Energy Information Administration report in 2011,[15] 21 trillion cubic meters of technically recoverable shale gas and 24 billion barrels of shale oil resources have been discovered. The exploitation of shale gas has become economically viable in the last decade. In 2012, all unconventional gas sources provided 67% of the U.S. gas production with shale gas accounting for 40% (up from only 4%, 7 years before!). The U.S. daily shale gas production in 2016 was 28 million cubic meters. Countries with significant amounts of technically recoverable shale gas are China, Argentina, Algeria, Russia, and numerous others.

To avoid the use of water, Olah and Prakash have developed the concept of *dry fracking* with carbon dioxide.[16] Injecting gaseous CO_2 with inert additives (sand) at high pressures allows the extraction of shale gas without use of water. The obtained shale gas containing CO_2 can be further processed with water in a bireforming process (see discussion later) to obtain metgas for the production of methanol.

Significant amount (≤500 Mt/y) of natural methane is also released into the atmosphere from varied sources ranging from volcanic sources to marsh lands to landfills and farm animals. Significantly, large amounts of methane hydrates are deposited in Antarctica, the permafrost regions in Siberia, and over the continental shelves of the oceans (see subsequent discussion). Declining ice sheets due to global warming will increasingly release methane. Future technologies may also allow to use these resources. Microbes digesting biomass and subsequent conversion to biogas (biomethane) is another developing technology.

Although methane in the atmosphere represents only a small amount, its increase contributes to a significant greenhouse effect (23 times more greenhouse warming, compared to CO_2).

1.3.5 Other Natural Methane Sources

There exist a number of other unconventional methane sources attracting increasing attention.[13]

Natural gas can be extracted from coal beds. Since it is free from hydrogen sulfide, it is a high-quality methane. Called coalbed methane, it is adsorbed in the solid matrix of the coal as well as in cracks and fissures. In fact, it causes a significant fire risk in coal mines. Coal has six times more gas storage capacity than sandstone. Coalbed methane is extracted from coal by lowering the reservoir pressure via dewatering. Similar to other unconventional gas extractions, wells produce relatively small amounts of gas and production from a single well decreases by about 90% during the first few years. Consequently, a large number of wells are to be drilled scattered across a large area. In contrast to other methane sources, it does not contain propane, butane, and natural gas condensate. Coalbed methane, together with tight-sand gas, started to be developed in the United States in 2005.

As mentioned, vast, yet untapped reserves of natural gas (methane) are locked up as hydrates under the permafrost in Siberia. Methane gas hydrates are crystalline, ice-like, solid inclusion compounds of $CH_4 \cdot nH_2O$ composition. They have cage-like structure also called clathrates.[17] These were found as a naturally occurring constituent in Siberian gas fields. They have also been observed in oceanic and deepwater sediments as well as in polar sediments. Most methane hydrates occur in oceanic sediments hundreds of meters below the sea floor at water depths greater than 500 m. The amount of methane in gas hydrates is estimated to greatly exceed known conventional natural-gas reserves. The present estimate is about 21,000 trillion cubic meters that is about 100 times of our conventional gas reserves. The economical utilization of methane in hydrates, however, remains a challenge. Two major technical issues that need to be solved are recovery and the release of methane in an economic way. These require first significant research and development.

1.3.6 Carbon Dioxide

Mankind faces two serious challenges threatening the suitable life conditions nature provided us through coal, oil, and gas deposits. First of all, our fossil fuel resources are limited and nonrenewable and their oxidative use renders them nonrenewable on the human timescale. We thus have to find new ways to replace them. Burning (oxidative use) of coal and hydrocarbons increases the concentration of carbon dioxide in air contributing to greenhouse warming and global climate change. We have addressed these problems previously in a monograph on "Methanol Economy."[4] The concept is based on chemical carbon capture and recycling (*CCR*). Captured CO_2 can be transformed by catalytic hydrogenation or bireforming with natural gas to *metgas* (a 2:1 mixture of H_2 and CO) followed by well-established industrial methods to produce methanol. This methanol is considered regenerative methanol as contrasted to renewable methanol, which is made from continuously renewed sources and alternative energies. Needed hydrogen can be generated by reforming of methane (natural gas) as long as it is available or by electrolysis of water using any available energy sources (solar, hydro, wind, nuclear). Regenerative methanol by capture and recycling of CO_2 is thus a source of fuel and derived hydrocarbon products essentially replacing oil.[18] Further readings about assessments of methanol synthesis using captured CO_2 in varied syngas production technologies are available.[19]

The methanol economy based on CO_2 chemical recycling via methanol, would increasingly free us from our dependence on fossil fuels and, at the same time, it helps to alleviate climate change caused by excessive burning of carbon-based materials. Further discussions of the methanol economy are given in Sections 1.7, 3.2 and Chapter 14. Details of varied possibilities of chemical hydrogenerative reduction and recycling of CO_2 including transformations to hydrocarbons are given in Section 3.2.

1.3.7 Biosources

By-products from living organisms (agricultural products, animal waste, sewage, etc.) called biomass can potentially be an energy source. Biomass (natural biomass) is any source of organic carbon renewed in the natural photosynthetic carbon cycle. Biomass is used for energy production by thermolysis and can also be transformed to chemicals and fuels.[20] At the same time, it may also be utilized as a source of hydrocarbons.[21]

Biomethane (biogas, synthetic natural gas) from landfills of solid municipal waste and animal manure generated by bacteria (anaerobic digestion) has been used for heating purposes or generating electricity. Burning biogas produces CO_2. However, since the source of biogas is organic (carbon) material, biogas production can be considered carbon neutral.

Cellulosic biomass can be converted to liquid products including bio-based hydrocarbons by a number of processes.[22] Most of these, however, require multistep transformations. For example, in the Sylvan process, 2-methylfurfural derived from biomass is trimerized under acidic conditions and then hydrodeoxygenated to an alkane mixture.[23] A jet fuel feedstock of cycloalkanes can be produced by acid-catalyzed hydrolysis of hemicelluloses-derived sugars to form furfural followed by aldol condensation with acetone.[24] In the final steps, varied oligomers formed are hydrogenated over Rh/Al_2O_3 and then treated in the presence $Pt/SiO_2/Al_2O_3$ to achieve hydrodeoxygenation.

Another possibility is to use catalytic fast pyrolysis. However, the product called pyrolysis oil, also known as bio-oil,[25] cannot be directly used as a transportation fuel. It is a mixture of hydrocarbons and contains a high amount of oxygenated products (∼40%). In addition, it has high acidity, low heating value, and high water content. More importantly, it is not miscible with petroleum and cannot be fed directly into existing refineries. Additional hydrogen treatment (hydroconversion) for upgrading is difficult and expensive. Integrated hydropyrolysis and hydroconversion is a better method for the direct production of transportation fuel.[26] It is a catalytic process carried out in a fluidized bed reactor (25–30 bar hydrogen pressure, 350–480 °C) and eliminates oxygen in the form of CO_x and H_2O, and gives high-quality gasoline (called renewable gasoline) and diesel oil (renewable diesel).

Chemo-, bio-, and integrated catalytic processes for hydrocarbon production[27] and biomass-derived oil-processing technologies[28] have recently been reviewed.

1.3.8 Minerals (Carbonates) and Metal Carbides

Metal carbonates have the potential to be used as a source to manufacture hydrocarbons. Reller and coworkers studied the thermal degradation of mixed alkaline earth–transition metal carbonates (Co, Ni, Cu, 10% loading) to generate methane (>90%) under reductive conditions.[29] Similar results were reported subsequently.[30] Carbonates of varied compositions have recently been found to afford high yields of methane[31] [Eq. (1.1)]. Transformation of Ca and Mg carbonate catalyzed by Co/CoO/CaO afforded the best result (carbonate/catalyst ratio = 1:1, 100% conversion, 100% methane yield).

$$\begin{array}{lcl} \mathrm{MCa(CO_3)_2 \text{ or } M^1M^2Ca(CO_3)_2} & \xrightarrow[\text{550 °C, 5 h}]{\mathrm{H_2}\text{ flow}} & \mathrm{CH_4} + \mathrm{CO_2} \\ \text{M = Co, Ni, Fe, M/Ca = 1} & & \text{conversion 4–100\%} \\ \mathrm{M^1M^2} \text{ = CoNi, NiFe, FeCo; } \mathrm{M^1M^2Ca} \text{ = 1/1/2} & & \mathrm{CH_4} \text{ yield 80–100\%} \end{array} \qquad (1.1)$$

A few metal carbides can also be transformed to hydrocarbons. Notably, Mg_2C, Be_2C, and aluminum carbide (Al_4C_3) produce methane upon hydrolysis, whereas Mg_2C_3 forms propyne.[32] More importantly, calcium carbide (CaC_2)[33] used to have much higher significance in the manufacture of acetylene.[34] Produced from lime and coal at high temperatures, the transformation of CaC_2 to acetylene was the single most important process before the oil age and started the industrial production of hydrocarbon products first in Germany. However, after a peak production in the 1960s, the manufacture of acetylene and its products significantly decreased because it has been replaced by other, cheaper and more readily available oil-based processes.

1.3.9 Abiological Hydrocarbon Sources

An interesting but unproven concept of the possible abiogenic origin of terrestrial hydrocarbons was put forward by Gold[35] in 1981 following a similar suggestion, the so-called Russian–Ukrainian concept[36] (see also a related review of this topic[37]). It was suggested that our hydrocarbons may also be formed by slow outgassing of methane from vast abyssal deposits dating back to the origin of our planet. Besides biologically derived oil and gas, "deep" carbon compounds trapped in the Earth's crust should be subjected to intense heat, causing them to release hydrocarbons, which migrate toward the earth's surface, where they are trapped in different strata. Methane seepage is also observed at the bottom of the oceans. However, it was shown that sea bottom wells are usually do not went methane but H_2S, which subsequently may reduce CO_2 of the seas. Finds of oil during drilling into formations (such as granite) where no "biogenic" oil was expected, was cited as proof for "abiogenic" hydrocarbons. However, this evidence proved questionable because other explanations including geological origin of H_2S and CO_2 and their conversion to methane as well as oil contamination of drill bits were involved.

According to recent studies, abiogenic methane may, however, be formed in specific geologic environments. Either high-temperature magmatic processes or gas–water–rock reactions at low temperature ($<100\ °C$) are suggested to be involved.[38]

If abiogenic methane and other hydrocarbons reserves would exist (although generally geologist disagree), it was hoped that these reserves could become available when improved drilling technology is developed to reach deeper into earth's crust.[35] Increasing temperature and pressure, however, may put a limit on the feasibility of such drilling operations.

Extraterrestrial Hydrocarbons In recent years, significant observations were made by high-tech space explorations. Direct observations and studies have provided solid proof for the existence of abiogenic (extraterrestrial) hydrocarbon derivatives and their suggested astrochemistry (see Chapter 14). Astrophysical observations by advanced telescopes (including space telescopes) absorbing the light emitted by stars allowed spectroscopic analysis showing the presence of methane, methanol and many of their derivatives.

Direct observation and analysis of extraterrestrial molecular matter started with the joint NASA and European Space Agency Cassini–Huygens mission launched in 1997. The Cassini spacecraft landed the Huygens probe on the surface of Titan, one of the moons of Saturn, in 2005.[39] The probe using a range of sophisticated instrumentations [Huygens atmospheric structure instrument, Doppler wind experiment, GC–MS, descent imager/spectral radiometer (DIRS)] collected data for 69 min. Analysis of the transmitted data revealed that the atmosphere of Titan contains 1.6% methane of primordial origin with methane clouds and a surface methane humidity of ~50%. The surface temperature of −180 °C allows the existence of rivers and lakes of methane. Other hydrocarbons including ethane were also detected on the surface with cyanogen and benzene tentatively identified. It is further considered that vast deposits of methane, other organic molecules, and CO_2 may exist beneath Titan's crust.

At the same time, Cassini surveyed Titan's upper atmosphere (900–1300 km) by means of plasma spectrometer, ion neutral mass spectrometer, and ion beam and electron spectrometer. It is believed that methane and nitrogen photochemistry is initiated in this region leading to the generation of hydrocarbons and nitriles.[40] These eventually precipitate and form hydrocarbon–nitrile lakes on the moon's surface.

Another set of important data has been collected by the Rosetta spacecraft having probed the surface composition of the nucleus of comet 67P/Churyumov–Gerasimenko with the use of visible, infrared, and thermal imaging spectrometer (VIRTIS) in 2014.[41] It has provided evidence for hydrocarbon compounds based on complex aliphatic and aromatic C–H vibrations as well as OH and COOH groups (ethanol, acetic acid) inserted in a macromolecular solid. These results are in accord with the spectroscopically observed simple carbon molecules CH_4, CO, CO_2, methanol, and H_2O already observed by astrophysicists, which are precursors to the more complex hydrocarbons and their ions. These were formed upon the immense radiation in space [ultraviolet (UV) photons, proton beams, electron impact, energetic particles] on the surface of ices (space dust) or by the polymerization (polycondensation) of mixtures on ices even at more moderate temperatures.

Olah and coworkers have discussed important questions relating to these new discoveries[42] including the role of methanol and hydrocarbon derivatives to serve as carbon sources in the initial stage of biological evolution of cells leading eventually to life[43] (see further discussion in Chapter 14).

1.4 Hydrocarbon Production from Natural Sources

Whereas hydrogen was formed from energy of the Big Bang event, all other essential elements were formed subsequently in young stars and space dust by thermonuclear reactions. Nova explosions dispersed carbon (oxides) into space forming with hydrogen varied molecular matter including hydrocarbons. These were then transported to different celestial bodies and formed abiological extraterrestrial hydrocarbons as recently discussed. Earth must have also received its share, but its "goldilocks" conditions simply allowed lasting hydrocarbon formations (fossil fuels).

1.4.1 Coal Mining and Conversion

Coal played a significant role in the launching of the industrial revolution in the 18th century. The steam engine and the manufacturing of iron using coke were the two main driving forces of the so-called "coal economy." The downside, however, was environmental pollution resulting from coal burning producing smoke laden with heavy metals and other pollutants such as sulfur dioxide, nitrogen oxides, and particulates.

Coal reserves are enormous and geographically widespread estimated to last about a century.[2] However, there has been a significant switch in coal mining operations from underground to surface mining. At present, much of the coal is produced in open-pit surface mines operating with higher productivity and lower costs. As a result of advanced mining and efficient transportation technologies, the price of coal has not increased much. At the same time, strict health and environmental regulations resulted in decreasing the harmful effects of the use of coal to generate electricity. It is to be noted that China has become both the main coal producer (47.7% of global production as of 2015) and the main consumer (50% of coal produced worldwide).[2] Other countries with high output are the United States (11.9%), India (7.4%), and Australia (7.2%).

The main approaches employed in converting coal to liquid hydrocarbons revolve around breaking down the large, complex "structures" generally by hydrogenative cleavage reactions and increasing the solubility of the organic portion. Alkylation, hydrogenation, and depolymerization—as well combinations of these reactions followed by extraction of the reacted coals—are major routes taken. This can provide clean liquid fuels, for example, gasoline and heating oil.

Three types of direct *coal liquefaction processes* have emerged to convert coals to liquid hydrocarbon fuels.[7a] The first is a high-temperature solvent extraction process in which no catalyst is added. The liquids produced are those that are dissolved in the solvent or solvent mixtures. The solvent usually is a hydroaromatic hydrogen donor, while molecular hydrogen is added as a secondary source of hydrogen.

The second, catalytic liquefaction process is similar to the first except that there is a catalyst in direct contact with the coal. $ZnCl_2$ and other Friedel–Crafts catalysts, including $AlCl_3$, as well as BF_3–phenol and other complexes catalyze the depolymerization–hydrogenation of coals, but usually forceful high-temperature conditions (375–425 °C, 100–200 atm) are needed. Superacidic $HF–BF_3$-induced liquefaction of coals[7] involves depolymerization–ionic hydrogenation at relatively modest temperatures of 150–170 °C.

The third coal liquefaction approach is direct catalytic hydrogenation (pioneered by Bergius) in which a hydrogenation catalyst is intimately mixed with the pulverized coal. Little or no solvent is employed, and the primary source of hydrogen is molecular hydrogen in the latter case.

The ultimate "depolymerization" of coal occurs in Fischer–Tropsch chemistry, wherein the coal is reacted with oxygen and steam at about 1100 °C to break up, or gasify, the coal into carbon monoxide, hydrogen and carbon dioxide.[44] A water–gas shift reaction is then carried out to adjust the hydrogen/carbon monoxide ratio, after which the carbon monoxide is catalytically hydrogenated to form methanol, or to build up liquid hydrocarbons (see Sections 1.5.1 and 3.3 for detailed discussion of Fischer–Tropsch chemistry).

1.4.2 Petroleum Oil Refining and Processing

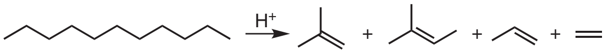
Crude oil (petroleum), a dark, viscous liquid, is a mixture of virtually hundreds of different hydrocarbons. Distillation of the crude oil yields several fractions (Table 1.6),[9,45] which then are used for different purposes.

The relative amounts of usable fractions obtainable from a crude oil do not coincide with the commercial needs. Also, the composition of the fractions obtained directly by distillation of the crude oil does not usually meet the required specifications for various applications. For example, the octane rating of the naphtha fractions must be substantially upgraded to meet the requirements of internal combustion engines in today's automobiles. These same naphtha liquids must also be treated to reduce sulfur and nitrogen contents to acceptable levels (desulfurization and denitrogenation) in order to minimize automotive emissions and pollution of the environment. Therefore, each fraction must be upgraded in the petroleum refinery to meet the requirements for its end-use application. Hydrocarbon feeds of the refining operations are further converted or upgraded to needed products, such as high-octane alkylates, oxygenates, and polymers. Major hydrocarbon refining and conversion processes include cracking, dehydrogenation (reforming), alkylation, acylation, isomerization, addition, substitution, oxidation–oxygenation, reduction–hydrogenation, metathesis, oligomerization, and polymerization. They and their uses can be schematically characterized in the followings cases:

Table 1.6 Fractions of Typical Distillation of Crude Petroleum

Boiling Point Range (°C)	Compositions	
<30	C_1–C_4	Natural gas, methane, ethane, propane, butane, LPG
30–200	C_4–C_{12}	Petroleum ether (C_5, C_6), ligroin (C_7), straight-run gasoline
200–300	C_{12}–C_{15}	Kerosene, heating oil
300–400	C_{15}–C_{25}	Gas oil, diesel fuel, lubricating oil, waxes
>400	>C_{25}	Residual oil, asphalt, tar

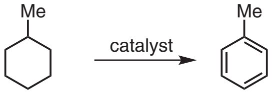
Cracking[46–49]: to form lower molecular weight products and to supply alkenes for alkylation [Eq. (1.2)].



(1.2)

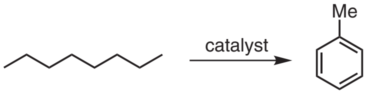
Dehydrogenation (reforming)[50–53]: to increase octane number of gasoline, to produce alkenes from alkanes [Eq. (1.3)], as well as aromatics, such as benzene, toluene, and xylenes [Eq. (1.4)].

$$CH_3CH_3 \xrightarrow{\text{catalyst}} CH_2{=}CH_2 \qquad (1.3)$$



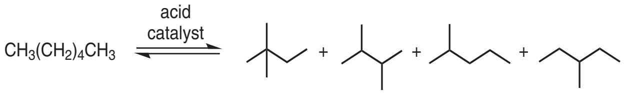
(1.4)

Dehydrocyclization[50,52]: to produce aromatics such as toluene [Eq. (1.5)].

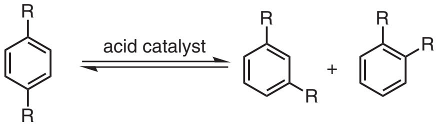


(1.5)

Isomerization [*of alkanes*, Eq. (1.6); *alkylaromatics*, Eq. (1.7)][46,52–56]: to increase octane number of gasoline, to produce xylenes and so on.

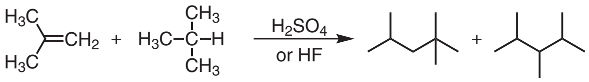


(1.6)

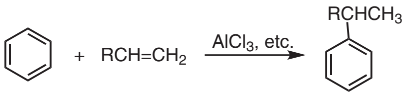


(1.7)

Alkylation [*alkenes with alkanes*, Eq. (1.8); *aromatics*, Eq. (1.9)][52,54,57,58]: to produce high-octane gasoline and jet-fuel components, detergent alkylates, plastics, intermediates, and other products.

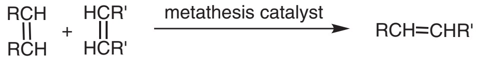


(1.8)



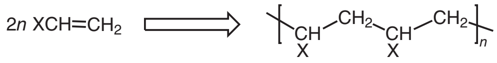
(1.9)

Metathesis[58–61] [Eq. (1.10)]:



$$\begin{matrix}RCH\\ \| \\ RCH\end{matrix} + \begin{matrix}HCR'\\ \| \\ HCR'\end{matrix} \xrightarrow{\text{metathesis catalyst}} RCH{=}CHR' \qquad (1.10)$$

Oligomerization[62,63] and *polymerization*[64–71] [Eq. (1.11)]:



(1.11)

Further transformation (functionalization) reactions include varied *additions*,[72] *carbonylative conversions*,[73] *acylations*,[74,75] *substitutions*,[74,76–80] *oxidations (oxygenations)*,[81–88] and *reductions (hydrogenations)*.[89–96]

Major petroleum refining operations are discussed in Chapter 2, whereas Chapters 4–13 discuss the chemistry of prototypical hydrocarbon transformation reactions.

1.4.3 Natural and Shale Gas Processing

Natural and shale gas as discussed are mixtures of light hydrocarbons from available natural sources. Shale formation trapped light hydrocarbons, which are generally composed mainly of methane and some ethane. Shale gas has recently gained high significance and rejuvenated the natural gas industry in the United States.

Processing of natural and shale gas is a complex industrial technology to produce clean methane by separating it from other, light hydrocarbons (ethane, propane, butanes), and even higher homologs (if methane comes from oil wells) as well as impurities. Major impurities are water, CO_2, H_2S, and mercaptans. Purified natural gas, or pure methane, may be used as a "clean" fuel [for heating, generating electricity and in compressed form (compressed natural gas) in place of gasoline]. More importantly, however, it is a feedstock to be transformed into value-added products. Any carbon-containing fuels and compounds upon oxidative use (combustion) form CO_2 a significant greenhouse gas. Consequently, without CO_2 capture and recycling (use) they cannot be considered environmentally benign.

1.5 Hydrocarbon Synthesis

1.5.1 Fischer–Tropsch Synthesis via Syngas ($CO + H_2$) from Coal or Natural Gas

Hydrocarbon synthesis is not a new challenge. Germany realizing its very limited resources in the 1920s and 1930s developed a technology for the conversion of coal into liquid hydrocarbons. The work of Bergius[97] and that of

Fischer and Tropsch[98] culminated in the development of catalytic coal liquefaction, and more significantly in an industrial process utilizing coal-derived mixtures of carbon monoxide and hydrogen gas (called *synthesis gas* or *syngas*), to catalytically produce hydrocarbons.[99–102] Syngas was obtained from the reaction of coal with steam (but can more recently also obtained by the partial burning of natural gas). The Fischer–Tropsch syngas-based synthesis was used during World War II in Germany on an industrial scale, with a peak production of around 60,000 barrels per day. For comparison, the U.S. daily domestic oil consumption was 19.1 million barrels per day. South Africa starting in the 1960s developed an updated Fischer–Tropsch synthetic fuel plant (Sasol) using improved engineering and technology. The capacity of this project is coincidentally estimated to be about the same as the peak World War II production of Germany.

In contrast, if the United States would rely overnight solely on synthetic oil for our overall needs, the United States would need some 330 Sasol-size plants. Whereas our coal reserves may last for three centuries, mining coal on the scale needed for conversion to hydrocarbons would be a gigantic task. If the United States would today convert to coal-based synthetic fuels for the 330 synthetic fuel plants mentioned above, some 10 million metric tons of coal would be needed daily. Even if our coal reserves could sustain such demand over a long period of time, not only would an enormous investment needed (in the trillions of the dollars), we would also need to recruit millions of young people to become coal miners, create an entirely new transportation system, and in general adjust our standard of living and lifestyle to pay for the enormous cost of coal-based synthetic oil—a hardly feasible scenario. Direct underground gasification of coal to methane (and subsequently pumping it out through pipelines) may also become feasible in advantageous locations. Nevertheless, many of the coal reserves would remain difficult to access. Further and very significantly, combusting coal for energy, without capturing and storing of formed CO_2, results in a major environmental greenhouse problem.

Syngas itself also cannot be piped over long distances. The Fischer–Tropsch process is also overall energetically wasteful as it burns half of the coal (or natural gas) to generate syngas in the first step, followed by an equally energetic second step in converting it into a hydrocarbon mixture of such complexity that no existing refinery could handle it. The strongest argument for Fischer–Tropsch chemistry is, of course, that it works and can produce synthetic fuels on an industrial scale. We must, however, disregard economics, labor, social, and ecological problems (for which wartime Germany and South Africa in the 1960s and 1970s were hardly acceptable models). With the relative stability of the world oil supplies for the foreseeable near future, it seems to be the right time to look for more feasible alternatives and to explore new chemistry. During the short-lived alternate fuel research boom of the 1970s and early 1980s (following the two oil crises), extensive research on updating Fischer–Tropsch chemistry was carried out in the United States, Western Europe, and Japan. Because of the proven commercial feasibility of the Fischer–Tropsch synthesis, it is still customary to refer to C_1 chemistry as the conversion of syngas into higher hydrocarbons. Its scope, however, has developed much further (C_1 chemistry is discussed in Chapter 3 where relevant references are also to be found).

1.5.2 Methane Oligocondensation

There are a number of ways to transform methane to practical products through oligocondensation.[103]

Oxidative condensation of methane can be mediated by varied metal oxides to form C_2 hydrocarbons with high selectivity (see Section 3.5.1).[104] The best catalysts are nonreducible group IIA metal oxides, alkali oxides, and carbonates as well as lanthanide sesquioxides. Many other metal cations (Sm, Ga, Bi, Mn, Re, etc.) can be used as dopants with alkali metal oxides.[105] For industrial applications, an overall yield of 35% would be required. At present, the best yields are around 30%.

High-temperature self-condensation that is direct dehydrogenation to yield C_2 hydrocarbons is favorable above 1200 °C and used for the manufacture of acetylene applying specific techniques (see Section 3.5.2). *Nonoxidative activation*, in turn, has not reached commercialization (see Section 3.5.3). Catalytic oligomerization of methane can be attained by combining catalysis and input of high energy (microwave heating, photocatalysis) to form $>C_2$ hydrocarbons. In two-step homologation, methane is adsorbed on metal surfaces at high temperature followed by hydrogenation. Methane can also be converted to aromatics called *dehydroaromatization*. The best catalysts are Mo/H-ZSM-5 preparations (see Section 3.5.4).[106] High selectivities (up to 90%) can be achieved with gallium as a promoter, albeit, at low conversions.

1.5.3 Conversion through Methanol (Mobil Process) or Methyl Halides

One of the shortcomings of the Fischer–Tropsch synthesis is its lack of selectivity giving complex product mixtures. In an attempt to improve the selectivity of syngas-based hydrocarbon synthesis, Mobil researchers developed a process consisting of converting methanol (itself, however, produced from syngas) to gasoline (or other hydrocarbons) over a shape-selective intermediate pore size zeolite catalyst (H-ZSM-5)[55, 107, 108] [Eq. (1.12)]:

$$n\ \mathrm{CH_3OH} \xrightarrow[-n\ \mathrm{H_2O}]{\text{H-ZSM-5, 350 °C}} \text{hydrocarbons} \tag{1.12}$$

The process, referred to as ***m**ethanol-**t**o-**g**asoline-conversion* (Mobil MTG process) with other variants (methanol to olefin, to aromatics, and to hydrocarbon; see Section 3.6.1), The transformation starts with dehydration of methyl alcohol to dimethyl ether. In early studies, a carbenoid-type reaction with the involvement of an oxonium ylide-type intermediate undergoing ready methylation by excess methanol (dimethyl ether) was proposed.[109] This product of crucial C_1 to C_2 conversion step then cleaves to ethylene. Once a C_1 precursor is converted into a C_2 derivative (i.e., ethylene), the further transformation to higher hydrocarbons of the gasoline range (or to aromatics) follows the well-known acid catalysis chemistry. Now there appears to be a wide consensus about the highly complex chemistry involved. Olefin methylation and cracking, aromatic methylation and dealkylation, as well as hydrogen transfer and cyclization are the major transformations.

Independent research has shown that bifunctional acid–base catalysts such as WO_3 on Al_2O_3 or tungstophosphoric acid, lacking shape-selective nature can also bring about the methanol-to-hydrocarbon conversions.[110] Shape selectivity of the catalyst thus is important in controlling product distributions and also to limit coking over the catalysts.

The Mobil process still uses syngas in its initial step. Olah has shown,[110] however, that it is possible to convert methane directly via catalytic selective electrophilic halogenation to methyl halides and through them to olefins and hydrocarbons [Eq. (1.13)]. When bromine is used, the HBr by-product of the reaction is readily reoxidized to bromine, allowing a catalytic process in which bromine acts only as a redox catalyst. Methyl halides themselves readily condense over bifunctional acid–base catalysts such as zeolite or WO_3 on Al_2O_3 to ethylene (and propylene) and subsequently to higher hydrocarbons (gasoline, aromatics) [Eq. (1.14)].

$$CH_4 + Cl_2 \text{ or } Br_2 \xrightarrow[\text{–HBr or HCl}]{\text{catalyst}} CH_3Cl \text{ or } CH_3Br \tag{1.13}$$

$$CH_3Cl \text{ or } CH_3Br \xrightarrow[\text{–HBr or HCl}]{\substack{\text{H-ZSM-5 or}\\ WO_3/Al_2O_3}} CH_2{=}CH_2 \longrightarrow\!\!\!\!\rightarrow\!\!\!\!\rightarrow \boxed{\text{hydrocarbons}} \tag{1.14}$$

1.5.4 Carbon Dioxide Conversions

C_1 hydrocarbon chemistry cannot anymore be equated mainly with syngas chemistry. Nature's own CO_2 *photosynthesis* and *bacterial methane conversion* are also C_1 conversion processes. We are far from approaching these processes for practical synthetic use efficiently. Production of methane from carbon dioxide (similarly to carbon monoxide) and hydrogen is a feasible process (methanation).[111] Similarly, reduction of carbon dioxide with hydrogen to methyl alcohol[112] is industrially developed [Eq. (1.15)] (see Section 3.2.1). Recent thorough analyses of CO_2 fixation[113] and the use of varied reductions[114] are highly advised for interested readers.

$$CO_2 + 3H_2 \xrightarrow{\text{Cu-based catalysts}} CH_3OH + H_2O \tag{1.15}$$

It has been shown by Olah et al. that transformation of methane with CO_2 and H_2O exclusively to *metgas*, a H_2/CO mixture of 2:1 ratio can be effected by metal oxides (NiO and CoO) supported on MgO (830–910 °C, 42 bar).[115] The significance of the 2:1 ratio is that it is optimal for efficient synthesis of methanol an emerging fuel and a feedstock of varied chemicals and consumer products. The process is called bireforming and, in fact, is a convenient combination of steam reforming [Eq. (1.16)] and dry reforming [Eq. (1.17)] in a single step [Eq. (1.18)].

steam reforming

$$2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2 \qquad \Delta H_{298K} = +98.2 \text{ kcal/mol} \tag{1.16}$$

dry reforming

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2 \qquad \Delta H_{298K} = +59.1 \text{ kcal/mol} \tag{1.17}$$

bireforming

$$3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 \qquad \Delta H_{298K} = +157.3 \text{ kcal/mol} \tag{1.18}$$

However, all three reactions are endothermic requiring available external heat source. A self-sufficient solution to the problem called oxidative bireforming was developed by generating heat by the combustion of one quarter of overall methane used. In addition to heat, this also provides a $H_2 + CO$ mixture in a ratio of 2:1 needed for bireforming [see Eq. (1.18)]. Accordingly, methane combustion is performed in step 1 followed by mixing the reaction product with 3 equiv of methane. Bireforming in step 2 produces again H_2+CO in the required ratio of 2:1 [Eq. (1.19)]. If the product metgas is transformed to methanol then the three-step overall process is exothermic [Eq. (1.20)]. As shown, oxidative bireforming is an efficient and economic method for the selective oxygenation of methane to methanol without any by-product formation.

oxidative bireforming

$$CH_4 + 2O_2 \xrightarrow[\text{–191.9 kcal/mol}]{\text{step 1}} \overset{\overset{3CH_4}{\downarrow}}{CO_2 + 2H_2O} \xrightarrow[\text{+157.5 kcal/mol}]{\text{step 2}} 4CO + 8H_2 \tag{1.19}$$

$$4CH_4 + 2O_2 \xrightarrow[\text{–121.2 kcal/mol}]{\text{methane oxygenation}} 4CH_3OH \tag{1.20}$$

Another transformation of carbon dioxide to hydrocarbon products is electrochemical reduction.[116] The hydrogenatively reduced CO_2 to CO is then used in Fischer–Tropsch synthesis. Silver and gold electrodes are capable of transforming CO_2 in aqueous media quite efficiently into CO and H_2 in the same reactor, which allows direct use of the mixture for further transformation to Fischer–Tropsch hydrocarbon products. Reduction by Ag and Au is characterized by relatively high-energy efficiency and high current density. The major obstacle, however, is poisoning of Ag and Au electrodes. Gold nanoparticles, in turn, show significant resistance to poisoning compared to bulk gold.

More extensive hydrogenation of CO_2 can be achieved with copper and its oxides to afford methane and higher hydrocarbon products.[116,117] The use of pyridinium ion as cocatalyst results in the formation of methanol.[118] The major products of electrochemical reduction of CO_2 in flow cells and under high pressure as well as in methods assisted by molecular catalysts are formate or CO in most cases (see Section 3.2 for further details of CO_2 reduction).

1.5.5 Additional Methane Sources, Production, and Conversion Reactions

The conversion of *methane* as a building block for higher hydrocarbons and derived products is presently the most used route for hydrocarbon synthesis (see Sections 3.4 and 3.5). Methane is still abundant on earth; it is the major component of natural (or shale) gas and methane hydrates. If we would stop burning natural gas for its energy content, our reserves as a hydrocarbon source could last for a long time. Even after our natural-gas reserves would be exhausted, the conversion and recycling of CO_2 will provide an inexhaustible source of methane as well as methanol and derived hydrocarbons. Biomass (sustained as long as there is life on our planet) can also be easily and efficiently converted by microorganisms into methane. Research work has shown the feasibility of growing algae or kelp in the vast expanses of oceans. They can be harvested and biologically converted into methane, and the gas can be pumped ashore. In some of the large U.S. cities, landfill refuse is already biologically converted into methane gas and used for energy generation. It is also known that aluminum carbide, which can be produced similarly to calcium carbide in electric arcs, upon hydrolysis gives primarily methane. Thus, atomic power plants in off-peak periods could be producing aluminum carbide and through it methane. Regardless of its source, methane and thus its conversion to higher hydrocarbons and their functionalized products will be feasible.

Biological conversion of methane to higher hydrocarbons or to methyl alcohol is clearly of great significance for the future, but it is not included in the scope of the present discussion.

The reactivity of methane to hydrocarbon products was for long mostly considered only in terms of its *free-radical* reactions. We burn large amounts of natural gas (methane) to produce energy and combustion processes are free-radical chain reactions. So is the high-temperature conversion of methane to acetylene. Other radical reactions such as chlorination, nitration, and sulfochlorination of methane also became industrial processes. These reactions show generally limited selectivity characteristics of radical reactions (e.g., the chlorination of methane under radical conditions gives all four possible chloromethanes).

Direct catalytic *oxidative condensation* of methane to ethane (with metal oxides),[85,119–121] as well as to ethylene and acetylene (via high-temperature chlorinative conversion), was also explored.[102] In all these processes, however, a significant portion of methane is lost by further oxidation and soot formation. The selectivity in obtaining ethane and ethylene (or acetylene), respectively, the first C_2 products, is low. Recently, there has, however, been much progress in metal oxide catalyzed oxidative condensation of methane to ethane.

An alternative approach of methane conversion is via *ionic electrophilic reactions*. The electrophilic conversion of methane is based on the feasibility of electrophilic reactions of single bonds and thus saturated hydrocarbons.[122] C–H and C–C bonds can act as electron donors against strongly electrophilic reagents or superacids. Olah's studies showed that even methane is readily protonated or alkylated under these conditions. Methane with SbF_5-containing superacids was also found to undergo condensation to C_2–C_6 hydrocarbons at 50–60 °C.

Condensing two methane molecules to ethane and hydrogen is, however, endothermic by some 16 kcal/mol [Eq. (1.21)].

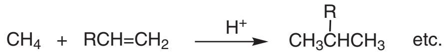
$$2\,CH_4 \xrightarrow{\qquad} C_2H_6 + H_2 \tag{1.21}$$

Any condensation of methane to ethane and subsequently to higher hydrocarbons must overcome the unfavorable thermodynamics. This can be achieved in condensation processes of oxidative nature, where hydrogen is removed by the oxidant. Superacid system containing SbF_5 or FSO_3H also act as oxidants; however, these are economically not feasible. The oxidative condensation of methane was subsequently found to take place with more economical cooxidants such as halogens, oxygen, sulfur, or selenium[123] [Eq. (1.22)].

$$CH_4 \xrightarrow[\text{superacid catalyst}]{\text{halogens, } O_2,\, S_x,\, Se} \text{hydrocarbons} \tag{1.22}$$

Significant practical problems, however, remain to carry out the condensation effectively. Conversion was so far achieved only in low yields. Because of the easy cleavage of longer chain alkanes, C_3–C_6 products predominate.

Natural gas instead of pure methane can also be used in condensation reactions.[123] When natural gas is dehydrogenated, the C_2–C_4 alkanes it contains are converted into olefins. The resulting methane–olefin mixture can then without separation be passed through a superacid catalyst, resulting in exothermic alkylative condensation [Eq. (1.23)]. Chapter 3 discusses in more detail C_1-based synthetic reactions of hydrocarbons.



$$CH_4 + RCH{=}CH_2 \xrightarrow{H^+} CH_3\overset{\displaystyle R}{\overset{|}{C}}HCH_3 \quad \text{etc.} \tag{1.23}$$

A third approach to the chemical conversion of methane involves *organometallic reactions*.[124] Extensive works with iridium complexes and other transition metal insertion reactions (rhodium, osmium, rhenium, etc.) were carried out. Even iron organometallics were studied. These reactions take place in the coordination spheres of the metal complexes, but so far the reactions are stoichiometric and noncatalytic. In terms of synthetic hydrocarbon chemistry, these conversions are thus not yet practical, but eventually it is expected that catalytic reactions will be achieved.

Fuel cells use an electrochemical process to convert the energy of a chemical reaction directly into electricity.[125] The chemical reaction is catalytically activated. In fuel cells, generally hydrogen (produced in a separate converter, e.g., from natural gas) and oxygen (from air) were reacted to produce electricity, heat, and water. Hydrocarbons (or oxygenated hydrocarbons) preferably methanol can also be used as fuels acting as hydrogen sources. The direct oxidation fuel cells use liquid oxygenated hydrocarbons (methanol[126]) or hydrocarbon fuels. They are much more convenient for transportation and other applications in view of their liquid nature. The further advantage of direct oxidation fuel cells is that they do not require any preprocessing (converter) equipment to produce hydrogen. In fact, direct oxidation methanol fuel cell (DMFC; see Section 1.9.2), where methanol reacts with air without the need of reforming, has already been used in a wide range of commercial applications (portable electronic devices, vehicles). It is expected that fuel cells will play a significant role in the future, providing cleaner and efficient propulsion systems for transportation vehicles.

1.6 Nonrenewable and Renewable Hydrocarbons

Our oil and natural gas reserves are finite and not renewable (except on a geological timescale).[5] The dire predication of the early 1970s following the first Arab oil crises that we will exhaust our oil reserves by the end of the 20th century, turned out to be overly pessimistic. Reserves have, in fact, since tripled, and our gas reserves quintupled (Table 1.7).

If we take into account less accessible petroleum and gas reserves or those locked up in the form of tar sands, oil shale, or methane hydrates, etc. our overall hydrocarbon reserves could be even three to five times higher. This would give us a century's supply, whereas our coal reserves may stretch to two or three centuries.

Despite this more favorable outlook, it is necessary to point out the existing close relationship between mankind's ever-increasing overall energy needs and hydrocarbon sources essential in a rapidly developing technological society.

Hydrocarbons are required in our modern-day life not only as energy sources (including convenient transportation fuels for our cars, tracks, airplanes) but

Table 1.7 World Oil and Natural Gas Reserves (in Billion Tons of Oil Equivalent) from 1960 to 2015[2]

Year	Oil	Natural Gas
1960	43	15
1965	50	22
1970	78	33
1975	87	55
1980	91	70
1986	95	87
1987	121	91
1990	137	108
1995	140	130
2002	160	160
2005	164	162
2006	165	163
2012	236	168.6
2015	240	168.2

also to produce commonly used products ranging from chemical products, polymers to textiles to pharmaceuticals. At the early 21st century, we can look back with substantial satisfaction at our technological and scientific achievements. We should, however, also realize that we continue to deplete the nonrenewable resources of our planet, particularly fossil fuels and hydrocarbons and at the same time create ecological and environmental problems. As mentioned earlier, dire predictions of the early exhaustion of our natural hydrocarbon sources by the end of the 20th century proved to be grossly exaggerated. Together with the discovery of new oil and gas finds we are assured of supplies, although with the inevitably higher cost to open up less accessible sources, at least through the 21st century. We must realize, however, that natural hydrocarbon supplies remaining for about half of century are not changing the basic predicament; we will need to find feasible and economical ways to synthetically produce hydrocarbons on a very large scale to satisfy our future needs. The challenge truly is a global one and we need to unite mankind's efforts to find practical solutions.[4]

In the biological carbon cycle, plants absorb carbon dioxide from the air and use sunlight to convert (through photosynthesis) the carbon dioxide and water into sugar (glucose) and oxygen. Sugar is used up in life processes and stored in tissues. Stored carbon is consumed by herbivores and, again, used up in herbivore's life processes, stored in animal tissues and given off in respiration as CO_2. This step is repeated when a herbivore is eaten by a carnivore converting it to tissue and CO_2. Decay of dead plants and animals also releases carbon dioxide into the atmosphere to be used again by plants. In a net process, carbon is taken up by photosynthesis and then released into the atmosphere. A small amount of carbon enters the oceans and the geological cycle; however, the latter operates over large timescales (millions of years).

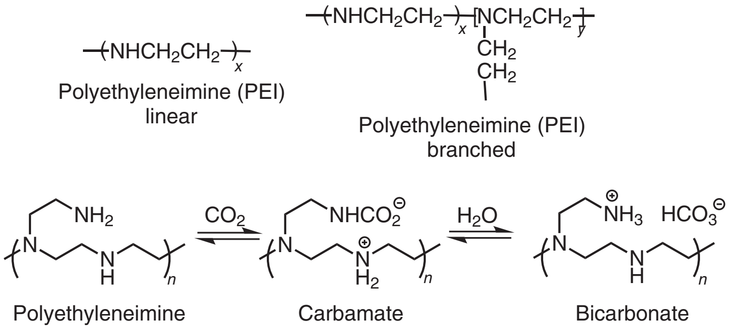
1.7 Regenerative Hydrocarbons from CO_2 Emission Capture and Recycling

We use nonrenewable (on human timescale) fossil fuels for our technology and society at an increasing rate and, consequently, we face the challenge that our fossil fuels will be depleted in the foreseeable future. In addition, excessive industrial burning of coal and hydrocarbons results in a large anthropogenic CO_2 emission. The present level of atmospheric CO_2 (~400 ppm, 0.04%) compares unfavorably with that of preindustrial level (270 ppm). Therefore, it is necessary to decrease our dependence on fossil fuels and, at the same time, alleviate the issue of CO_2 with its harmful environmental consequences.

The technique of *carbon capture and sequestration* (or storage, *CCS*) for environmental reasons is an evolving approach.[127] First, CO_2 after emission at coal- and gas-fired power plants and large industrial sources (fermentation, calcination of limestone) is captured, concentrated, pressurized, and then transported to the storage sites to be injected for geological sequestration. These are carefully selected deep underground porous geological formations located under nonporous, impermeable rock layers to prevent upward migration. Alternatively, liquid CO_2 may be injected to the bottom of the seas forming a deep-sea liquid pools. This technology, although was extensively tried at great cost, offers only a temporary solution and unpredictable events, for example, earthquakes and slides may result in sudden release of stored carbon dioxide. Additional difficulties are the leakage of CO_2 into groundwater and soil and finding of suitable sites. Furthermore, the process is economically very expensive and therefore has found no real practical application.

A more promising approach is CCR (or utilization) of carbon dioxide.[128] Capture and hydrogenative reductive recycling of CO_2 offers an economic, permanent source for regenerative carbon-based fuels and derived hydrocarbons. In a way, this is the anthropogenic version of photosynthesis, nature's carbon cycle with the aim of replacing fossil fuels by producing synthetic hydrocarbons and chemicals.

In either of the above two solutions, capture (absorption) of CO_2 is the first, essential step. Of different capturing technologies, amine solutions have been used in industry since the 1960s.[129] Typically, 25–30% aqueous solutions



Scheme 1.1

of alkanolamines (monoethanolamine, diethanolamine) are used, which react with CO_2 to form carbamates and bicarbonates. However, both absorption and regeneration are highly energy demanding. A new, more efficient, regenerable and robust CO_2 sorbent is based on nanostructured fumed silica or alumina loaded with polyethyleneimine (Scheme 1.1). With such advanced techniques in hand, CO_2 recovery is feasible and economical not only from concentrated sources (large-scale industrial emitters) but also from the air. An additional important advantage is that carbon capture from air coupled with CCR may be used to lower the concentration of atmospheric CO_2 and thus mitigating global warming.

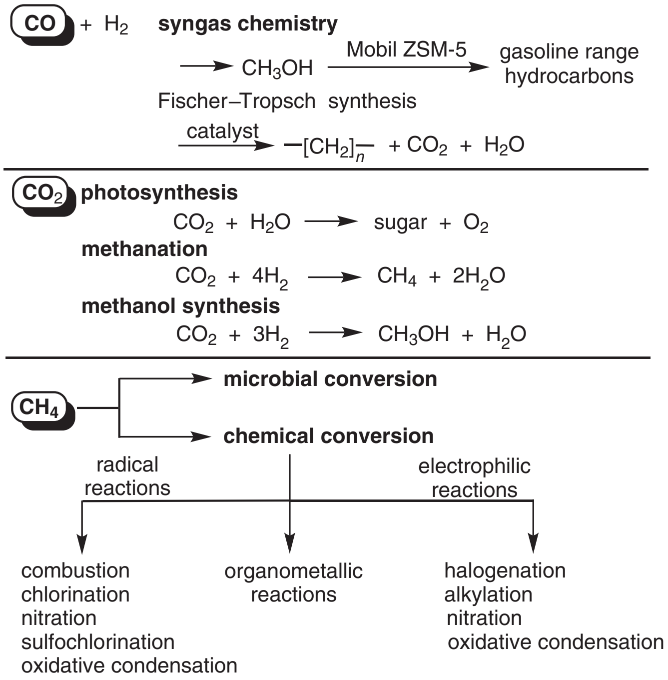
Following the pioneering development of CCR, many uses were developed to what is called carbon capture and utilization (CCU).[130] It is the use of captured CO_2 as a chemical feedstock to build it into varied carbon-containing products such as chemicals, materials, and fuel. It is a practical useful extension of CCR.

According to the methanol economy concept, carbon dioxide, once captured, can be reduced by using any available energy source (alternative energies such as solar, wind, geothermal, and atomic energy) for producing needed hydrogen and chemical conversion of CO_2 to methanol.[4] Renewable and regenerative methanol thus produced can then be further processed into simple basic chemicals (dimethyl ether, ethylene, propylene), gasoline, and all products obtained at present from natural gas and petroleum oil.

Analyses and comparison of CCS and CCU based on their significance and environmental impacts and cost-effectiveness on a life cycle basis is described.[131]

1.8 Hydrocarbon Functionalization Reactions

Using Cornforth's definition of chemical synthesis[132] as an intentional construction of molecules by means of chemical reactions, hydrocarbon synthesis



Scheme 1.2

is a systematic construction of hydrocarbons including alkanes, alkenes, aromatics, and the like. The simplest hydrocarbon, methane itself, can be practically produced from carbon monoxide (or carbon dioxide) and hydrogen (methanation). Generally, however, hydrocarbon synthesis relates to obtaining varied hydrocarbons from one-carbon (C_1) precursors, including syngas (i.e., synthesis gas: $CO + H_2$), metgas ($CO + 2H_2$), carbon dioxide, methanol, methyl halides, or methane itself.

The scope of C_1 chemistry we know it today is depicted in Scheme 1.2.

1.8.1 Homolytic (Free-Radical) Reactions

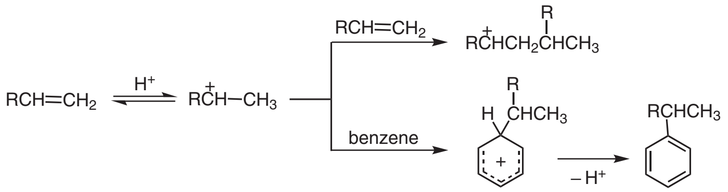
The chemistry of the high-temperature conversion and transformation processes of hydrocarbons is based on homolytic (*free-radical*) processes.[133]

The combustion of hydrocarbons for energy generation or in propulsion systems is itself a radical chain process. Thermal cracking, oxygenation, hydrogenation–dehydrogenation, cyclization, and so on proceed through free radicals. In the discussion of the transformation of hydrocarbons, the reaction chemistry as well as relevant mechanistic aspects will be treated throughout the book.

Free-radical reactions play an important role not only in high-temperature refining and processing operations (cracking, reforming, hydrocracking, dehydrogenation, etc.) but also in oxidation chemistry (Chapter 9) and in many addition and substitution reactions (Chapters 6, 10, and 11) as well as in polymerization (Chapter 13). The high-pressure polymerization of ethylene, for example, played a key role in the development of the plastic industry.

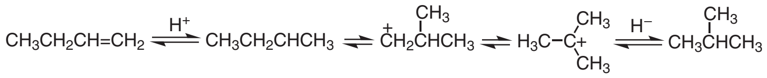
1.8.2 Heterolytic (Ionic) Reactions

In electrophilic *acid-catalyzed* reactions of unsaturated hydrocarbons (alkenes, alkynes, arenes) positive hydrocarbon ions—*carbocations*—are formed, which are then responsible for the electrophilic transformations[134] [Eqs. (1.24)–(1.26)].



(1.24)

(1.25)

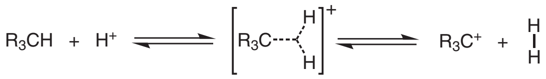


$$CH_3CH_2CH{=}CH_2 \underset{}{\overset{H^+}{\rightleftharpoons}} CH_3CH_2\overset{+}{C}HCH_3 \rightleftharpoons \overset{+}{C}H_2\underset{}{\overset{CH_3}{\overset{|}{C}}}HCH_3 \rightleftharpoons H_3C{-}\overset{+}{C}(CH_3)_2 \overset{H^-}{\rightleftharpoons} CH_3\overset{CH_3}{\overset{|}{C}}HCH_3 \qquad (1.26)$$

The carbocations involved in these reactions are trivalent carbenium ions, of which CH_3^+ is parent. It was Whitmore in the 1930s, who first generalized their importance in hydrocarbon transformations based on fundamental studies by Meerwein, Ingold, Pines, Schmerling, Nenitzescu, Bartlett, and others.

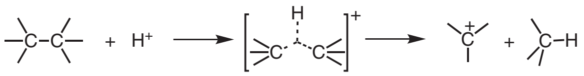
Subsequently, it was realized that hydrocarbon ions (carbocations) also encompass five (or higher) coordinate carbonium ions for which CH_5^+ is parent.[135] Alkanes having only saturated C–H and C–C bonds were found to be protonated by very strong acids, specifically, superacids, which are billions or even trillions of times stronger than concentrated sulfuric acid.[54]

Protolytic reactions of saturated hydrocarbons in superacid media[54] were interpreted by Olah as proceeding through the protonation (protolysis) of the covalent C–H and C–C single bonds. The reactivity is due to the electron donor ability of the σ bonds involving two-electron, three-center bonds. Protolysis of C–H bonds leads via five coordinate carbocations with subsequent cleavage of H_2 to trivalent ions, which then themselves can further react [Eq. (1.27)]. The reverse reaction of carbenium ions with molecular hydrogen can be considered as alkylation of H_2 through the same pentacoordinate carbonium ions that are involved in C–H bond protolysis. Indeed, this reaction is responsible for the long used (but not explained) role of H_2 in suppressing hydrocracking in acid-catalyzed reactions.



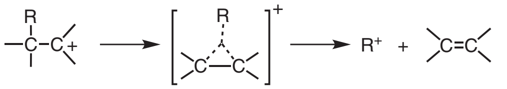
(1.27)

Protolysis can involve not only C–H but also C–C bonds [Eq. (1.28)]; this explains why alkanes can be directly cleaved protolytically by superacids, which is of significance, for example, in hydrocracking heavy oils, shale oil, tar-sand bitumens, and even coals.



(1.28)

In contrast, cracking of longer-chain alkanes with conventional acid catalysts is considered to proceed via β-scission involving initial formation of trivalent carbocations [Eq. (1.29)].

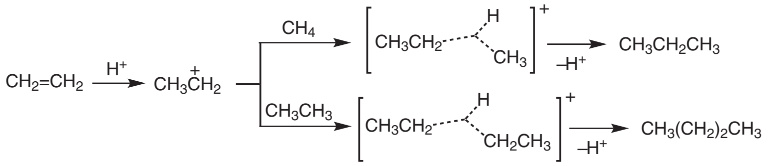


(1.29)

Acid-catalyzed alkylation and isomerization processes all proceed through carbocations. Typical is the isobutylene–isobutane alkylation giving high-octane isooctane. In this and other conventional acid-catalyzed reactions, the key is the reactivity of alkenes, giving on protonation alkyl cations that then readily react with excess alkene, giving the higher alkylate cations. These carbocations then abstract hydrogen from the isoalkane, yielding the product alkylate and forming a new alkyl cation to reenter the reaction cycle. Chapter 5 discusses acid-catalyzed alkylations and their mechanism.

In the acid-catalyzed isomerization of straight-chain alkanes to branched higher-octane ones, after initial protolytic ionization alkyl and hydrogen shifts in the formed carbocations lead to the most branched and therefore thermodynamically preferred, generally tertiary, carbocations. Intermolecular hydrogen transfer from excess alkane then produces the isomeric isoalkane with the formed new carbocation reentering the reaction cycle.

In alkane–alkene alkylation systems, it is always the π-donor alkene that is alkylated by carbocations formed in the system. In the absence of excess alkenes (i.e., under superacidic conditions), however, the σ-donor alkanes themselves are alkylated. Even methane or ethane, when used in excess, are alkylated by ethylene to give propane and *n*-butane, respectively [Eqs. (1.30) and (1.31)].



(1.30)

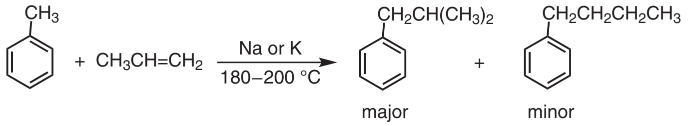
(1.31)

1.8.3 Nucleophilic Reactions

Nucleophilic *base-catalyzed* hydrocarbon conversions, although generally less common as acid-catalyzed reactions, also play a significant role in hydrocarbon chemistry. They proceed through proton abstraction giving intermediate *carbanions*[133,136] [Eq. (1.32)].

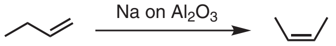
$$\text{R–H} \xrightarrow{-\text{H}^+} \text{R}^- \tag{1.32}$$

Base-catalyzed carbanionic alkylation, isomerization, and polymerization reactions are of major significance. Base-catalyzed alkylation of alkylarenes, in contrast to acid-catalyzed ring alkylation, leads to alkylation of the side chain in the benzylic position [Eq. (1.33); see also Chapter 5]; of particular interest is the alkylation of toluene to ethylbenzene (for styrene production).



(1.33)

Selective double bond migration of linear and cyclic alkenes without skeletal rearrangement is achieved by treatment with basic reagents ([Eq. (1.34)]; see also Chapter 4).



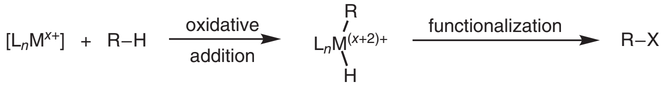
(1.34)

Base-catalyzed anionic oligomerization and polymerization are also of great significance (see Chapter 13). Styrene derivatives and conjugated dienes are the most suited for anionic polymerization. Generally good control of molecular weight distribution can be achieved, which is of great practical use. An interesting and significant characteristic of anionic polymerization is the ability to obtain "living" polymers that contain active centers for further polymerization (copolymerization) to give unique monodispersed products.

Reactions of hydrocarbons, particularly those with relatively low ionization potentials (aromatics and π systems but not necessarily alkanes) frequently proceed via *single-electron transfer* processes involving *radical ions*.[137] These reactions are particularly significant in oxidation reactions (Chapter 9).

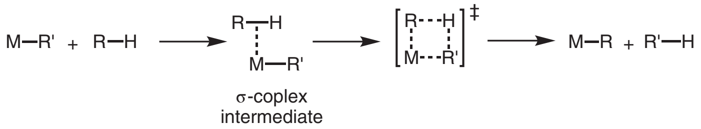
1.8.4 Organometallic Reactions

Unreactive hydrocarbon C–H bonds can also be activated through organometallic transformations.[124] Soluble metal complexes can be used in the homogeneous phase or applied as supported (heterogenized) solid catalysts.[138, 139] The two basic reactions are oxidative addition typical of electron-rich, low-valent complexes of late transition metals (Ru, Rh, Pd, Re, Os, Ir, Pt) [Eq. (1.35)] and σ-bond metathesis[140, 141] characteristic of d- and f-block metals with d^0 configuration (Zr, W, Lu, Sc) [Eq. (1.36)].



$$[L_nM^{x+}] + R{-}H \xrightarrow[\text{addition}]{\text{oxidative}} L_n\overset{R}{\underset{H}{M}}{}^{(x+2)+} \xrightarrow{\text{functionalization}} R{-}X$$

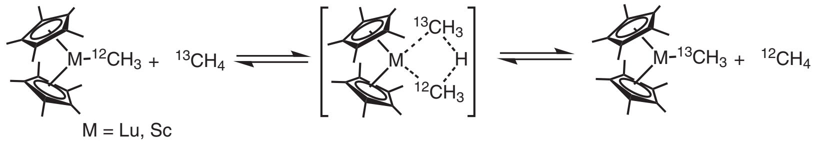
(1.35)



(1.36)

Specific early examples, respectively, are Shilov's chemistry to convert methane to methanol induced by a Pt(IV) complex [Eq. (1.37)] (see Chapter 9) and a $^{12}CH_3$–$^{13}CH_3$ exchange [Eq. (1.38)][142] and a similar CH_3–CD_3 exchange[143] first observed with the use of pentamethylcyclopentadienyl sandwich complexes.

$$CH_3{-}H + PtCl_6^{2-} + H_2O \xrightarrow[H_2O,\ 120\ ^\circ C]{} CH_3{-}OH\ (CH_3Cl) + PtCl_4^{2-} + 2\ HCl \qquad (1.37)$$



(1.38)

1.9 Use of Hydrocarbons, Petroleum Oil

Hydrocarbons are used primarily as fuels to generate and deliver energy and heating. Petroleum products provide gasoline, diesel fuel, heating oil, lubricating oil, waxes, and asphalt. A portion of petroleum oil (8.5%) is used as raw material to produce a great variety chemical products essential to our everyday life ranging from plastics to textiles to pharmaceuticals, and so on (see Section 1.9.3).

1.9.1 Energy Generation, Storage, and Delivery. Heating

The main use of natural gas is in heating, cooking, and electricity generation. The bulk amount of oil is used as heating fuel, for generating electricity, for industrial processes and predominantly as transportation fuels.

Methanol can be a convenient substitute of gasoline and diesel for efficient, reversible storage of energy.[144] Dimethyl ether, readily produced from methanol, is an excellent substitute for diesel fuel as well as a household gas for cooking and heating, replacing natural gas or LPG.

1.9.2 Transportation Fuels

A specific role is assigned to fuels to propel our cars, trucks, ships, airplanes, and other vehicles. They are generally referred to as *transportation fuels*. The impact of the internal-combustion engine on our life is fundamental. It allowed mankind to achieve mobility via easy means of transportation of persons and goods alike. In less than a century this revolution transformed and eased our life, but at the same time raised new challenges. By far the most oil-dependent sector in our modern economy is transportation accounting for about 60% of the petroleum oil consumed worldwide.

Gasoline and *diesel* fuels are used worldwide in enormous amounts and are produced by the petroleum industry by oil refining (see Chapter 2). Beside the conventional diesel engines, the recently developed spark-assisted diesel engine runs on methanol (methanol engine is gaining use and significance). Liquid transportation fuels are conveniently transported, distributed, and dispensed directly into our vehicles and aircraft. Increased environmental concerns have led to the development of cleaner burning engines. In the United States, law requires significant reduction of emissions and resulted in lead-free and more recently reformulated gasoline (RFG) containing oxygenates for cleaner burning. At the same time, they did not fundamentally change the existing technology. To find alternate fuels to supplement our oil reserves and to ensure cleaner fuels, much further effort is needed.

As long as the internal combustion engine will remain as the mainstay of our transportation technology, liquid fuels by their convenience and ease of distribution through the existing infrastructure will be preferred. LNG or methane certainly are clean-burning, high-energy content fuels, but their widespread use in transportation systems is limited by the difficulty of storing highly volatile and inflammable gases. This necessitates the use of heavy pressure vessel fuel tanks (with associated safety hazards). Nevertheless, *compressed natural gas* is widely used in large vehicles (buses, trucks), which can accommodate large pressurized tanks.

Commercial gasoline must provide sufficiently high-octane numbers for present-day engines. Organometallic additives, such as tetraethyl lead used to achieve higher octane numbers, interfere with catalytic converters (which assure cleaner exhausts) and were phased out. To maintain needed octane numbers, oxygenated additives, such as alcohols or ethers (e.g., *tert*-butyl methyl ether or *tert*-butyl ethyl ether—MTBE or ETBE) are added to gasoline. These oxygenates are produced on large scale by the petrochemical industry. In the United States about 85% of RFG contained MTBE and 8% contained ethanol in 1999.[145] In the early 2000s, however, there was growing concern about the use of MTBE following its detection in underground water in California, Maine, and other states.[146] MTBE is soluble in water, moves rapidly in groundwater, and has unpleasant taste and odor. In addition, it is difficult to remove from water and resistant to microbial degradation. Also its health effects are also of concern. Regulations have led to ban of its use, particularly in the USA. Other places have limited MTBE use.

As elaborated in the methanol economy concept,[4] methanol itself can be blended with gasoline and can directly be used in both combustion engines and, with only minimal modifications. The mentioned new diesel type engines (modified spark-assisted engines) with methanol as the preferred fuel (in methanol engines) are gaining extensive use. In addition, it can be the transportation fuel of the future in electric cars using fuel cells.

Furthermore, methanol, being a convenient energy storage medium and a high-density liquid hydrogen carrier, can be used in DMFC.[147] DMFC is a safe, convenient, and greatly simplified system of high efficiency. When methanol is reacted with oxygen or air over a suitable metal catalyst in DMFC, it forms CO_2 and H_2O and produces electricity. The high efficiency of the fuel cell will allow its use in electric cars. Compared with efficiencies of internal combustion engines (less than 20%), DMFC efficiency is close to 40% with possible further improvements (theoretical efficiency at ambient conditions is 97%).

Isomerization of straight chain to branched alkanes also increases the octane number, as do alkylates produced by alkene–isoalkane *alkylation* (such as that of isobutane and propylene, isobutylene). These large-scale processes are by now an integral part of the petroleum industry. Refining and processing of transportation fuels became probably the largest scale industrial operation.

A much pursued alternative to the internal combustion engine in transportation vehicles is electric propulsion. *Electric vehicles*, thus far have been used for only specific and limited applications, although they are clean, noiseless, and safe. The main difficulty is that existing batteries are relatively inefficient in providing suitable range at reasonable weights. Pending a major breakthrough in battery technology, this will greatly hinder the wider use of electric vehicles. As mentioned, CO_2-based methanol can be directly used in fuel cells (DMFC). It must also be kept in mind when considering clean battery based electricity-powered vehicles that we are only transferring the potential environmental pollution from individual vehicles to the electric power plants where electricity is generated by combustion of fossil fuels (if not nuclear). In large power plants, CO_2 capture and recycling to methanol (CCR) can alleviate this problem significantly.

1.9.3 Chemical Products, Plastics, and Pharmaceuticals

About 8.5% of petroleum is used as raw material for the production chemicals and plastics. It was coal tar–based aromatics and calcium carbide–based acetylene that led to the establishment of the chemical and plastic industries. World War II, however, brought about rapid development of the petrochemical industry with ethylene becoming the key starting material. A large variety of the chemical and plastics products are now produced. A multitude of synthetic hydrocarbons and their derivatives, fertilizers for agriculture, pharmaceuticals, dyes, cosmetics, synthetic fibers, polymers, and countless other products that are essential for everyday life are manufactured worldwide.

The reader will find discussion and references to the practical applications, as well as the underlying chemistry of the diverse and significant use of hydrocarbons in the following chapters.

References

1 (a) All textbooks of organic chemistry contain discussion of hydrocarbons and their classes. (b) *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 1999–2016. (c) H.-J. Arpe, *Industrial Organic Chemistry*, 5th ed., Wiley-VCH, Weinheim, 2010.

2 BP Statistical Review of World Energy, 65th ed. June, 2016; Available at https://www.bp.com/content/dam/bp/pdf/energy-economics/statistical-review-2016/bp-statistical-review-of-world-energy-2016-full-report.pdf.

3 U.S. Census Bureau, *Statistical Abstracts of the United States 2012.* Section 19, Energy and Utilities.

4 G.A. Olah, A. Goeppert, G.K.S. Prakash, *Beyond Oil and Gas: The Methanol Economy*, 2nd ed., Wiley-VCH, Weinheim, 2009.

5 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 2, p. 43.

6 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 5, p. 163.

7 (a) M. Siskin (Exxon) is thanked for communicating in the mid-1980s a review of his on coal chemistry. (b) W.H. Wiser, in *Magnetic Resonance: Introduction, Advanced Topics and Applications to Fossil Energy*, L. Petrakis, J.P. Frassards, eds. D. Reidel, Dordrecht, 1984, p. 325.

8 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 3, p. 85.

9 (a) S.J. Chemett, C.R. Maechling, R.N. Zare, P.P. Swan, R.M. Walker, *Science*, **262**, 721 (1993). (b) S.G. Loue, D.E. Brownlee, *Science*, **262**, 550 (1993). (c) E.J. Zeman, *Phys. Today*, **47**(3), 17 (1994).

10 P. Lucier, *Invent. Technol.*, 1991, p. 56.

11 (a) O.P. Strausz is thanked for communicating a review of his on tar-sand chemistry. (b) O.P. Strausz, T.W. Mojelsky, J.D. Payzant, G.A. Olah, G.K.S. Prakash, U.S. Patent 5,290,428 (1994).

12 K.E. Woodcock, M. Gottlieb, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2004, Vol. 12, p. 365.

13 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 24, p. 127.

14 F. Asinger, *Paraffins, Chemistry and Technology*, Pergamon Press, Oxford, 1968.

15 U.S. Energy Information Administration, “Review of Emerging Resources: U.S. Shale Gas and Shale Oil Plays,” 2011.

16 G.A. Olah, G.K.S. Prakash, Patent Appl. WO2015077153 A1, 2014.

17 A. Demirbas, *Methane Gas Hydrate*, Springer, London, 2010, Chapter 4.

18 G.A. Olah, A. Goeppert, G.K.S. Prakash, *J. Org. Chem.*, **74**, 487 (2009).

19 (a) M.T. Luu, D. Milani, A. Bahadori, A. Abbas, *J. CO_2 Util.*, **12**, 62 (2015). (b) M. Pérez-Fortes, J.C. Schöneberger, A. Boulamanti, E. Tzimas, *Appl. Energy*, **161**, 718 (2016).

20 *Handbook of Climate Change Mitigation and Adaptation*, 2nd ed., W.-Y. Chen, T. Suzuki, M. Lackner, eds., Springer, New York, 2016. (a) D. Sengupta, p. 1723. (b) S. Mahalaxmi, C. Williford, p. 1777. (c) D. Sengupta, R.W. Pike, p. 1855.

21 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 7, p. 241.

22 (a) M. Patel, A. Kumar, *Renewable Sustainable Energy Rev.*, **58**, 1293 (2016). (b) *Handbook of Biofuels Production: Processes and Technologies*, 2nd ed., R. Luque, C.S.K. Lin, K. Wilson, J. Clark, eds., Elsevier, Amsterdam, 2016.

23 A. Corma, O. de la Torre, M. Renz, *Energy Environ. Sci.*, **5**, 6328 (2012).

24 H. Olcay, A.V. Subrahmanyam, R. Xing, J. Lajoie, J.A. Dumesic, G.W. Huber, *Energy Environ. Sci.*, **6**, 205 (2013).

25 S.W. Banks, A.V. Bridgwater, in *Handbook of Biofuels Production: Processes and Technologies*, 2nd ed., R. Luque, C.S.K. Lin, K. Wilson, J. Clark, eds., Elsevier, Amsterdam, 2016, Chapter 14, p. 391.

26 (a) T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, *Environ. Progr. Sustainable Energy*, **31**, 191 (2012). (b) T.L. Marker, L.G. Felix, M.B. Linck, M.J. Roberts, P. Ortiz-Toral, J. Wangerow, *Environ. Progr. Sustainable Energy*, **33**, 762 (2014). (c) B. Balagurumurthy, T. Bhaskar, *Biomass Conv. Bioref.*, **4**, 67 (2014).

27 A. Deneyer, T. Renders, J. Van Aelst, S. Van den Bosch, D. Gabriëls, B.F. Sels, *Curr. Opin. Chem. Biol.*, **29**, 40 (2015).

28 (a) M. Al-Sabawi, J. Chen, S. Ng, *Energy Fuels*, **26**, 5355 (2012). (b) M. Al-Sabawi, J. Chen, *Energy Fuels*, **26**, 5373 (2012).

29 A. Reller, C. Padeste, P. Hug, *Nature*, **329**, 527 (1987).

30 (a) C. Padeste, A. Reller, H.R. Oswald, *Mater. Res. Bull.*, **25**, 1299 (1990). (b) A. Tsuneto, A. Kudo, N. Saito, T. Sakata, *Chem. Lett.*, **21**, 831 (1992). (c) N. Yoshida, T. Hattori, E. Komai, T. Wada, *Catal. Lett.*, **58**, 119 (1999).

31 D. Jagadeesan, M. Eswaramoorthy, C.N.R. Rao, *Chem. Sus. Chem.*, **2**, 878 (2009).

32 (a) H. Tulhoff, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2012. (b) S.T. Oyama, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2015.

33 (a) K. Holzrichter, in A. Knott, B. Mertschenk, J. Salzinger, *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 1999–2014. (b) W. Cameron, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2010.

34 (a) P. Pässler, W. Hefner, K. Buckl, H. Meinass, A. Meiswinkel, H.-J. Wernicke, G. Ebersberg, R. Müller, J. Bässler, H. Behringer, D. Mayer, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 1999–2014. (b) R.E. Gannon, R.M. Manyik, C.M. Dietz, H.B. Sargent, R.O. Thribolet, R.P. Schaffer, in *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, 2003, Vol. 1, p. 177.

35 (a) T. Gold, *Gas Res. Inst. Digest*, **4**(3) (1981). (b) *Chem. Week*, **131**(24), 19 (1982); *Chem. Eng. News*, **69**(43), 48 (1991).

36 (a) N.A. Kudryavtsev, *Oil Econ.*, **9**, 17 (1951). (b) V.G. Kutcherov, V.A. Krayushkin, *Rev. Geophys.*, **48**, RG1001 (2010).

37 R.G. Glasby, *Resour. Geol.*, **56**, 83 (2006).

38 (a) G. Etiope, B.S. Lollar, *Rev. Geophys.*, **51**, 276 (2013). (b) R. Kietäväinen, L. Purkamo, *Front. Microbiol.*, **6**, art. 725 (2015).

39 (a) T. Owen, *Nature*, **438**, 756 (2005). (b) M.G. Tomasko, B. Archinal, T. Becker, and 36 colleagues, *Nature*, **438**, 765 (2005). (c) H.B. Niemann, S.K. Atreya, S.J. Bauer, G.R. Carignan, J.E. Demick, R.L. Frost, D. Gautier, J.A. Haberman, D.N. Harpold, D.M. Hunten, G. Israel, J.I. Lunine, W.T. Kasprzak, T.C. Owen, M. Paulkovich, F. Raulin, E. Raaen, S.H. Way, *Nature*, **438**, 779 (2005).

40 J.H. Waite, Jr., W.S. Lewis, W.T. Kasprzak, V.G. Anicich, B.P. Block, T.E. Cravens, G.G. Fletcher, W.-H. Ip, J.G. Luhmann, R.L. McNutt, H.B. Niemann, J.K. Parejko, J.E. Richards, R.L. Thorpe, E.M. Walter, R.V. Yelle, *Space Sci. Rev.*, **114**, 113 (2004).

41 F. Capaccioni, A. Coradini, G. Filacchione, S. Erard, G. Arnold, and 80 colleagues, *Science*, **347**, aaa0628 (2015).

42 G.A. Olah, T. Mathew, G.K.S. Prakash, G. Rasul, *J. Am. Chem. Soc.*, **138**, 1717 (2016).

43 G.A. Olah, T. Mathew, G.K.S. Prakash, *J. Am. Chem. Soc.*, **138**, 6905 (2016); *J. Am. Chem. Soc.*,**139**, 566 (2017).

44 J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, Amsterdam, 2011, Chapter 8, p. 281.

45 P.C. Vollhardt, N.E. Shore, *Organic Chemistry*, 2nd ed., Freeman, New York, 1994.

46 (a) M.A. Fahim, T.A. Alsahhaf, A. Elkilani, *Fundamentals of Petroleum Refining*, Elsevier, Amsterdam, 2010. (b) *Handbook of Petroleum Processing*, S.A. Treese, P.R. Pujadó, D.S.J. Jones, eds., 2nd ed., Springer International, Cham, 2015.

47 (a) A.P. Bolton, in *Zeolite Chemistry and Catalysis*, ACS Monograph 171, J.A. Rabo, ed., American Chemical Society, Washington, DC, 1976, Chapter 13. (b) C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York, 1991, Chapter 9.

48 (a) *Fluid Catalytic Cracking*, ACS Symp. Ser. Vol. 375, M.L. Occelli, ed., American Chemical Society, Washington, DC, 1988. (b) *Fluid Catalytic Cracking II*, ACS Symp. Ser. Vol. 452, M.L. Occelli, ed., American Chemical Society, Washington, DC, 1991. (c) *Fluid Catalytic Cracking III, Methods and Processes*, ACS Symp. Ser. Vol. 571, M.L. Occelli, P. O'Connor, eds., American Chemical Society, Washington, DC, 1994. (d) *Fluid Catalytic Cracking: Science and Technology*, Studies in Surface Science and Catalysis, Vol. 76, J.S. Magee, M.M. Mitchell, Jr., eds., Elsevier, Amsterdam, 1993. (e) *Fluid Cracking Catalysts*, M.L. Occelli, P. O'Connor, eds., Marcell Dekker, New York, 1998.

49 (a) *Handbook of Petroleum Refining Processes*, 3rd ed., R.A. Meyers, ed., McGraw-Hill, New York, 2004. (b) M.A. Fahim, T.A. Alsahhaf, A.S. Elkilani, *Fundamentals of Petroleum Refining*, Elsevier, Amsterdam, 2010. (c) J.G. Speight, *Handbook of Industrial Hydrocarbon Processes*, Elsevier, 2011. (d) J.G. Speight, *The Refinery of the Future*, Elsevier, Amsterdam, 2011. (e) J.G. Speight, *Chemistry and Technology of Petroleum*, 5th ed., CRC Press, Taylor and Francis, Boca Raton, FL, 2014.

50 D.M. Little, *Catalytic Reforming*, Penn Well, Tulsa, 1985.

51 (a) *Catalytic Naphtha Reforming*, G.J. Antos, A.M. Aitani, J.M. Parera, eds., Marcel Dekker, New York, 1995. (b) M.P. Lapinski, S. Metro, P.R. Pujadó, M. Moser, in *Handbook of Petroleum Processing*, 2nd ed., S.A. Treese, P.R. Pujadó, D.S.J. Jones, eds., Springer International, Cham, 2015, p. 229.

52 *Toluene, the Xylenes and Their Industrial Derivatives*, E.G. Hancock, ed., Elsevier, Amsterdam, 1982.

53 H. Pines, N.E. Hoffman, in *Friedel-Crafts and Related Reactions*, Vol. 2, G.A. Olah, ed., Wiley-Interscience, New York, 1964, Chapter 28.

54 G.A. Olah, G.K.S. Prakash, Á. Molnár, J. Sommer, *Superacid Chemistry*, 2nd ed., John Wiley & Sons, Inc., Hoboken, NJ, 2009.

55 N.Y. Chen, W.E. Garwood, F.G. Dwyer, *Shape Selective Catalysis in Industrial Applications*, Marcel Dekker, New York, 1996.

56 (a) *Industrial and Laboratory Alkylations*, ACS Symp. Ser. Vol. 55, L.F. Albright, A.R. Goldsby, eds., American Chemical Society, Washington, DC, 1977. (b) D. Sullivan, S. Metro, P.R. Pujadó, in *Handbook of Petroleum Processing*, 2nd ed., S.A. Treese, ed., Springer International, Cham, 2015, p. 479.

57 (a) *Friedel-Crafts and Related Reactions*, Vol. 2, G.A. Olah, ed., Wiley-Interscience, New York, 1964. (b) R.M. Roberts, A.A. Khalaf, *Friedel-Crafts Alkylation Chemistry*, Marcel Dekker, New York, 1984.

58 R.L. Banks, *Top. Curr. Chem.*, **25**, 39 (1972).

59 (a) J.K. Ivin, *Olefin Metathesis*, Academic Press, London, 1983. (b) K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.

60 (a) V. Dragutan, A.T. Balaban, M. Dimonie, *Olefin Metathesis and Ring-Opening Polymerization of Cyclo-Olefins*, Editura Academiei, Bucuresti, and Wiley, Chichester, 1985. (b) V. Dragutan, R. Streck, *Catalytic Polymerization of Cyclolefins: Ionic, Ziegler–Natta and Ring-Opening Metathesis Polymerization*, Elsevier, Amsterdam, 2000.

61 (a) R.H. Grubbs, A.G. Wenzel, A.K. Chatterjee, in *Comprehensive Organometallic Chemistry III*, R.H. Crabtree, D.M.P. Mingos, eds., Elsevier, Amsterdam, 2007, Chapter 11.06, p. 179. (b) *Olefin Metathesis: Theory and Practice*, K. Grela, ed., Wiley, Hoboken, NJ, 2014. (c) *Handbook of Metathesis*, R.H. Grubbs, A.G. Wencel, D.J. O'Leary, E. Khosravi, eds., 2nd ed., three-volume set. Wiley-VCH, Weinheim, 2015.

62 D.C. Pepper, in *Friedel-Crafts and Related Reactions*, Vol. 2, G.A. Olah, ed., Wiley-Interscience, New York, 1964, Chapter 30.

63 J. Skupinska, *Chem. Rev.*, **91**, 613 (1991).

64 J. Boor, Jr., *Ziegler–Natta Catalysis and Polymerization*, Academic Press, New York, 1979.

65 J.P. Kennedy, E. Maréchal, *Carbocationic Polymerization*, Wiley-Interscience, New York, 1982.

66 M. Morton, *Anionic Polymerization: Principles and Practice*, Academic Press, New York, 1983.

67 *Handbook of Polymer Science and Technology*, N.P. Cheremisinoff, ed., Marcel Dekker, New York, 1989.

68 *Comprehensive Polymer Science*, G. Allen, J.C. Bevington, eds., Pergamon Press, Oxford, 1989.

69 *Handbook of Polymer Synthesis*, H.R. Kricheldorf, ed., Marcel Dekker, New York, 1992.

70 M. Szwarc, M. Van Beylen, *Ionic Polymerization and Living Polymers*, Chapman & Hall, New York, 1993.

71 (a) *Polymer Science: A Comprehensive Reference*, K. Matyjaszewski, M. Möller, eds., Elsevier, Amsterdam, 2012. (b) *Ullmann's Polymers and Plastics: Products and Processes*, Wiley-VCH, Weinheim, 2016.

72 *Comprehensive Organic Synthesis II*, P. Knochel, G.A. Molander, eds., Vol. 4: *Addition to and Substitution at C–C π-bonds*, S. Ma, J. Zhang, eds., Elsevier, Amsterdam, 2014.

73 (a) *New Syntheses with Carbon Monoxide*, J. Falbe, ed., Springer, Berlin, 1980. (b) M. Yamasita, K. Nozaki in *Comprehensive Organometallic Chemistry III*, R.H. Crabtree, D.M.P. Mingos, eds., Elsevier, Amsterdam, 2007, Chapter 11.13, p. 435.

74 *Friedel-Crafts and Related Reactions*, Vol. 3, G.A. Olah, ed., Wiley-Interscience, New York, 1964.

75 (a) S.C. Eyley, in *Comprehensive Organic Synthesis*, B.M. Trost, I. Fleming, eds., Pergamon Press, 1991, Vol. 2: *Additions to C–X π-Bonds*, Part 2, C.H. Heathcock, ed., Chapter 3.1, p. 707. (b) H. Heaney, in *Comprehensive Organic Synthesis*, B.M. Trost, I. Fleming, eds., Pergamon Press, 1991, Vol. 2: *Additions to C–X π-Bonds*, Part 2, C.H. Heatchock, ed., Chapter 3.2, p. 733.

76 R.O.C. Norman, R. Taylor, *Electrophilic Substitution in Benzenoid Compounds*, Elsevier, Amsterdam, 1965.

77 H. Cerfontain, *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*, Interscience, New York, 1968.

78 E.S. Huyser, *Free-Radical Chain Reactions*, Wiley-Interscience, New York, 1970, Chapter 5.

79 M.L. Poutsma, in *Free Radicals*, Vol. 2, J.K. Kochi, ed., Wiley-Interscience, New York, 1973, Chapter 15.

80 G.A. Olah, R. Malhotra, S.C. Narang, *Nitration: Methods and Mechanisms*, VCH, New York, 1989.

81 (a) D.J. Hucknall, *Selective Oxidation of Hydrocarbons*, Academic Press, London, 1974. (b) R.A. Sheldon, J.K. Kochi, *Metal-Catalyzed Oxidations of Organic Compounds*, Academic Press, New York, 1981. (c) *Organic Syntheses by Oxidation with Metal Compounds*, W.J. Mijs, C.R.H.I. de Jonge, eds., Plenum Press, New York, 1986.

82 *Modern Oxidation Methods*, J.-E. Bäckvall, ed., Wiley-VCH, Weinheim, 2010.

83 P.S. Bailey, *Ozonation in Organic Chemistry*, Academic Press, New York, 1978, 1982.

84 (a) *Singlet Oxygen*, H.H. Wasserman, R.W. Murray, eds., Academic Press, New York, 1979. (b) *Singlet* O_2, A.A. Frimer, ed., CRC Press, Boca Raton, FL, 1985.

85 A. Bielanski, J. Haber, *Oxygen in Catalysis*, Marcel Dekker, New York, 1991.

86 *New Developments in Selective Oxidation II, Studies in Surface Science and Catalysis*, Vol. 82, V.C. Corberán, S.V. Bellón, eds., Elsevier, Amsterdam, 1994.

87 (a) *Heterogeneous Hydrocarbon Oxidation*, ACS Symp. Ser. Vol. 638, B.K. Warren, S.T. Oyama, eds., American Chemical Society, Washington, DC, 1996. (b) G. Centi, F. Cavani, F. Trifirò, *Selective Oxidation by Heterogeneous Catalysis*, Kluwer–Plenum, New York, 2001.

88 *Comprehensive Organic Synthesis II*, P. Knochel, G.A. Molander, eds., Elsevier, Amsterdam, 2014. Vol. 7: *Oxidation*, P. Knochel, ed.

89 P.N. Rylander, *Catalytic Hydrogenation over Platinum Metals*, Academic Press, New York, 1967; *Catalytic Hydrogenation in Organic Syntheses*, Academic Press, New York, 1979.

90 A.P.G. Kieboom, F. van Rantwijk, *Hydrogenation and Hydrogenolysis in Synthetic Organic Chemistry*, Delft University Press, Delft, 1977.

91 M. Bartók, J. Czombos, K. Felföldi, L. Gera, Gy. Göndös, Á. Molnár, F. Notheisz, I. Pálinkó, G. Wittmann, Á.G. Zsigmond, *Stereochemistry of Heterogeneous Metal Catalysis*, John Wiley & Sons, Ltd., Chichester, 1985.

92 B.R. James, *Homogeneous Hydrogenation*, John Wiley & Sons, Inc., New York, 1973.

93 F.J. McQuillin, *Homogeneous Hydrogenation in Organic Chemistry*, D. Reidel, Dordrecht, 1976.

94 D.N. Kursanov, Z.N. Parnes, M.I. Kalinkin, N.M. Loim, *Ionic Hydrogenation and Related Reactions*, Harwood, Chur, 1985.

95 *Comprehensive Organic Synthesis II*, P. Knochel, G.A. Molander, eds., Elsevier, Amsterdam, 2014. Vol. 8: *Reduction*, J. Clayden, ed.

96 (a) R.L. Augustine, *Heterogeneous Catalysis for the Synthetic Chemists*, Marcel Dekker, New York, 1996, Chapter 15. (b) F. Notheisz, *Heterogeneous Catalysis in Organic Chemistry*, Academic Press, San Diego, 1999, Chapter 2.

97 F. Bergius, Nobel Lecture, May 21, 1932, in *Nobel Lectures in Chemistry 1922-1941*, Elsevier, Amsterdam, 1966, p. 244.

98 F. Fischer, H. Tropsch, Ger. Patent 484,337 (1929); *Chem. Zbl. I*, 434 (1930), and discussion in Chapter 3.

99 C.D. Frohning, in *New Syntheses with Carbon Monoxide*, J. Falbe, ed., Springer, Berlin, 1980, Chapter 4.

100 M.E. Dry, in *Applied Industrial Catalysis*, Vol. 2, B.E. Leach, ed., Academic Press, 1983, Chapter 5.

101 101(a) R.B. Anderson, *The Fischer–Tropsch Synthesis*, Academic Press, Orlando, 1984. (b) *Advances in Fischer–Tropsch Synthesis, Catalysts, and Catalysis*, B.H. Davis, M.L. Occelli, eds., CRC Press, Boca Raton, 2010.

102 C.N. Satterfield, *Heterogeneous Catalysis in Industrial Practice*, McGraw-Hill, New York, 1991, Chapter 10.

103 (a) M.C. Alvarez-Galvan, N. Mota, M. Ojeda, S. Rojas, R.M. Navarro, J.L.G. Fierro, *Catal Today*, **171**, 15 (2011). (b) J. Baltrusaitis, I. Jansen, J.D.S. Christus, *Catal. Sci. Technol.*, **4**, 2397 (2014). (c) W. Taifan, J. Baltrusaitis, *Appl. Catal. B–Environ.*, **198**, 525 (2016).

104 (a) E.V. Kondratenko, M. Baerns, in *Handbook of Heterogeneous Catalysis*, G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, eds., Wiley-VCH, Weinheim, 2008, Chapter 13.17, p. 3010. (b) B.L. Farrell, V.O. Igenegbai, S. Linic, *ACS Catal.*, **6**, 4340 (2016).

105 U. Zavyalova, M. Holena, R. Schlögl, M. Baerns, *ChemCatChem*, **3**, 1935 (2011).

106 J.J. Spivey, G. Hutchings, *Chem. Soc. Rev.*, **43**, 792 (2014).

107 C.D. Chang, *Hydrocarbons from Methanol*, Marcel Dekker, New York, 1983.

108 (a) U. Olsbye, M. Bjørgen, S. Svelle, K.P. Lillerud, S. Kolboe, *Catal. Today*, **106**, 108 (2005). (b) M. Bjørgen, F. Joensen, K.-P. Lillerud, U. Olsbye, S. Svelle, *Catal. Today*, **142**, 90 (2009). (c) J.L. White, *Catal. Sci. Technol.*, **1**, 1630 (2011). (d) U. Olsbye, S. Svelle, M. Bjørgen, P. Beato, T.V.W. Janssens, F. Joensen, S. Bordiga, K.P. Lillerud, *Angew. Chem., Int. Ed.*, **51**, 5810 (2012).

109 G.A. Olah, H. Doggweiler, J.D. Felberg, S. Frohlich, M.J. Grdina, R. Karpeles, T. Keumi, S. Inaba, W.M. Ip, K. Lammertsma, G. Salem, D.C. Tabor, *J. Am. Chem. Soc.*, **106**, 2143 (1984).

110 G.A. Olah, *Acc. Chem. Res.*, **20**, 422 (1987).

111 *Methanation of Synthesis Gas*, Advances in Chemistry Series 146, L. Seglin, ed., American Chemical Society, Washington, DC, 1975.

112 *Chem. Eng. News*, **72**(13), 29 (1994); *Chem. Week*, **154**(11), 14 (1994).

113 A.M. Appel, J.E. Bercaw, A.B. Bocarsly, H. Dobbek, D.L. DuBois, M. Dupuis, J.G. Ferry, E. Fujita, R. Hille, P.J.A. Kenis, C.A. Kerfeld, R.H. Morris, C.H.F. Peden, A.R. Portis, S.W. Ragsdale, T.B. Rauchfuss, J.N.H. Reek, L.C. Seefeldt, R.K. Thauer, G.L. Waldrop, *Chem. Rev.*, **113**, 6621 (2013).

114 R. Masel, Z. Liu, D. Zhao, Q. Chen, D. Lutz, L. Nereng, in *Commercializing Biobased Products: Opportunities, Challenges, Benefits, and Risks*, S.W. Snyder, ed., RSC Green Chemistry Series, Vol. 43, The Royal Society of Chemistry, Cambridge, 2016, Chapter 10, p. 215.

115 (a) G.A. Olah, A. Goeppert, M. Czaun, G.K.S. Prakash, *J. Am. Chem. Soc.*, **135**, 648 (2013). (b) G.A. Olah, G.K.S. Prakash, A. Goeppert, M. Czaun, T. Matthew, *J. Am. Chem. Soc.*, **135**, 10030 (2013). (c) G.A. Olah, A. Goeppert, M. Czaun, T. Matthew, R.B. May, G.K.S. Prakash, *J. Am. Chem. Soc.*, **137**, 8720 (2015).

116 (a) J.-P. Jones, G.K.S. Prakash, G.A. Olah, *Israel J. Chem.*, **54**, 1451 (2014). (b) J. Qiao, Y. Liu, F. Hong, J. Zhang, *Chem. Soc. Rev.*, **43**, 631 (2014).

117 T.-Y. Chang, R.-M. Liang, P.-W. Wu, J.-Y. Chen, Y.-C. Hsieh, *Mater. Lett.*, **63**, 1001 (2009).

118 J.A. Keith, E.A. Carter, *J. Am. Chem. Soc.*, **134**, 7580 (2012).

119 *Methane Conversion*, Studies in Surface Science and Catalysis, Vol. 36, D.M. Bibby, C.D. Chang, R.F. Howe, S. Yurchak, eds., Elsevier, Amsterdam, 1988.

120 *Natural Gas Conversion*, Studies in Surface Science and Catalysis, Vol. 61, A. Holmen, K.-J. Jens, S. Kolboe, eds., Elsevier, Amsterdam, 1991.

121 *Methane Conversion by Oxidative Processes: Fundamental and Engineering Aspects*, E.E. Wolf, ed., Springer Science, New York, 1992.

122 (a) G.A. Olah, J.A. Olah, *J. Am. Chem. Soc.*, **93**, 1256 (1971). (b) D.T. Roberts, Jr., E.L. Calihan, *J. Macromol. Sci., Chem.*, **7**, 1629, 1641 (1973). (c) M. Siskin, *J. Am. Chem. Soc.*, **98**, 5413 (1976). (d) M. Siskin, R.H. Schlosberg, W.P. Kocsis, *ACS Symp. Ser.*, **55**, 186 (1977). (e) J. Sommer, M. Muller, K. Laali, *New. J. Chem.*, **6**, 3 (1982). (f) G.A. Olah, J.D. Felberg, K. Lammertsma, *J. Am. Chem. Soc.*, **105**, 6529 (1983).

123 G.A. Olah, U.S. Patents 4,443 192 (1984); 4,513,164 (1984); 4,465,893 (1984); 4,467,130 (1984); 4,513,164 (1985).

124 (a) A.E. Shilov, *Activation of Saturated Hydrocarbons by Transition Metal Complexes*, D. Reidel, Dordrecht, 1984, Chapter 5. (b) *Metal Complexes in Biomimetic Chemical Reactions*, CRC Press, Boca Raton, 1997. (c) *Activation and Functionalization of Alkanes*, C.L. Hill, ed., Wiley-Interscience, New York, 1989. (d) *Selective Hydrocarbon Activation*, J.A. Davies, P.L. Watson, A. Greenberg, J.F. Liebman, eds., VCH, New York, 1990. (e) A.E. Shilov, G.B. Shul'pin, *Activation and Catalytic Reactions of Saturated Hydrocarbons in the Presence of Metal Complexes*, Kluwer, Dordrecht, 2000.

125 (a) S. Srinivasan, *Fuel Cells: From Fundamentals to Applications*, Springer, 2006. (b) V.S. Bagotsky, *Fuel Cells: Problems and Solutions*, 2nd ed., John Wiley & Sons, 2012. (c) *Handbook of Fuel Cells: Fundamentals, Technology and Applications*, John Wiley & Sons, 1999–2014.

126 G.A. Olah et al., U.S. Patent 5,559,638 (1997).

127 M.E. Boot-Handford, J.C. Abanades, E.J. Anthony, M.J. Blunt, S. Brandani, N. Mac Dowell, J.R. Fernández, M.-C. Ferrari, R. Gross, J.P. Hallett, R.S. Haszeldine, P. Heptonstall, A. Lyngfelt, Z. Makuch, E. Mangano, R.T.J. Porter, M. Pourkashanian, G.T. Rochelle, N. Shah, J.G. Yao, P.S. Fennell, *Energy Environ. Sci.*, **7**, 130 (2014) and references cited therein.

128 A. Goeppert, M. Czaun, J.-P. Jones, G.K.S. Prakash, G.A. Olah, *Chem. Soc. Rev.*, **43**, 7995 (2014).

129 (a) A. Goeppert, M. Czaun, G.K.S. Prakash, G.A. Olah, *Energy Environ. Sci.*, **5**, 7833 (2012). (b) Y.-N. Li, L.-N. He, Z.-F. Diao, Z.-Z. Yang, *Adv. Inorg. Chem.*, **66**, 289 (2014).

130 (a) C.-H. Yu, C.-H. Huang, C.-S. Tan, *Aerosol Air Qual. Res.*, **12**, 745 (2012). (b) P. Styring, H. de Coninck, H. Reith, K. Armstrong, *Carbon Capture and Utilisation in the Green Economy*, The Centre for Low Carbon Futures 2011 and CO2Chem Publishing, 2012. (c) N.V. von der Assen, A.M.L. Lafuente, M. Peters, A. Bardow, in *Carbon Dioxide Utilisation: Closing the Carbon Cycle*, P. Styring, E.A. Quadrelli, K. Armstrong, eds., Elsevier, Amsterdam, 2015, Chapter 4, p. 45. (d) P. Markewitz, R. Bongartz, in *Carbon Capture, Storage and Use*, W. Kuckshinrichs, J.-F. Hake, eds., Springer, Switzerland, 2015, Chapter 2, p. 13.

131 (a) N. von der Assen, J. Jung, A. Bardow, *Energy Environ. Sci.*, **6**, 2721 (2013). (b) R.M. Cuéllar-Franca, A. Azapagic, *J. CO_2 Util.*, **9**, 82 (2015). (c) T.E. Müller, W. Leitner, P. Markewitz, W. Kuckshinrichs, in *Carbon Capture, Storage and Use*, W. Kuckshinrichs, J.-F. Hake, eds., Springer, Switzerland, 2015, Chapter 4, p. 67. (d) T. Bruhn, H. Naims, B. Olfe-Kräutlein, *Environ. Sci. Policy*, **60**, 38 (2016).

132 J.W. Cornforth, *Aust. J. Chem.*, **46**, 157 (1993).

133 M.B. Smith, *March' Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*, 7th ed., John Wiley & Sons, Inc., Hoboken, NJ, 2013, and references cited therein.

134 (a) *Friedel–Crafts and Related Reactions*, Vol. 1–4, G.A. Olah, ed., Wiley-Interscience, New York, 1963–1965. (b) G.A. Olah, *Friedel–Crafts Chemistry*, Wiley-Interscience, New York, 1973.

135 G.A. Olah, G.K.S. Prakash, K. Wade, Á. Molnár, R.E. Williams, *Hypercarbon Chemistry*, 2nd ed., John Wiley & Sons, Inc., Hoboken, 2011, and references cited therein.

136 H. Pines, W.M. Stalick, *Base-Catalyzed Reactions of Hydrocarbons and Related Compounds*, Academic Press, New York, 1977.

137 L. Eberson, *Electron Transfer Reactions in Organic Chemistry*, Springer, New York, 1987.

138 (a) D. Astruc, *Organometallic Chemistry and Catalysis*, Springer, Berlin, 2007. (b) Pérez, ed., *Alkane C–H Activation by Single-Site Metal Catalysis*, Springer, Dordrecht, 2012. (c) P.H. Dixneuf, H. Doucet, eds., *C–H Bond Activation and Catalytic Functionalization*, Springer, in *Top. Organomet. Chem.*, Vols 55 and 56, 2016.

139 R.H. Crabtree, (a) *Chem. Rev.*, **85**, 245 (1985). (b) *J. Organomet. Chem.*, **689**, 4083 (2004). (c) *The Organometallic Chemistry of the Transition Metals*, 4th ed., John Wiley & Sons, Inc., Hoboken, NJ, 2005.

140 (a) J.A. Labinger, J.E. Bercaw, *Nature*, **413**, 507 (2002). (b) M.E. Thompson, S.M. Buxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, *J. Am. Chem. Soc.*, **109**, 203 (1987).

141 (a) R.N. Perutz, S.S.- Etienne, *Angew. Chem., Int. Ed.*, **46**, 2578 (2007). (b) Z. Lin, *Coord. Chem. Rev.*, **251**, 2280 (2007). (c) R. Waterman, *Organometallics*, **23**, 7249 (2013).

142 (a) P.L. Watson, *J. Am. Chem. Soc.* **105**, 6491 (1983). (b) P.L. Watson, G.W. Parshall, *Acc. Chem. Res.*, **18**, 51 (1985).

143 (a) M.E. Thompson, J.E. Bercaw, *Pure Appl. Chem.*, **56**, 1 (1984). (b) M.E. Thompson, S.M. Baxter, A.R. Bulls, B.J. Burger, M.C. Nolan, B.D. Santarsiero, W.P. Schaefer, J.E. Bercaw, *J. Am. Chem. Soc.*, **109**, 203 (1987).

144 E.F. Sousa-Aguiar, L.G. Appel, in *Catalysis*, RSC Catalysis Series, Vol. 23, J.J. Spivey, K.M. Dooley, eds., The Royal Society of Chemistry, Cambridge, 2011, Chapter 8, p. 284.

145 B. Allen, *Green Chem.*, **1**, G142 (1999).

146 J.H. Vautrain, *Oil Gas J.*, **97**(3), 18 (1999).

147 (a) S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. LaConti, J. Kosek, G.K.S. Prakash, G.A. Olah, *J. Power Sour.*, **47**, 377 (1994). (b) K. McGrath, G.K.S. Prakash, G.A. Olah, *J. Ind. Eng. Chem.*, **10**, 1063 (2004).