The past, present and future of heterogeneous catalysis

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ABSTRACT

This review highlights key catalytic discoveries and the main industrial catalytic processes over the last 300 years that involved commodities, fine chemicals, petrochemicals, petroleum transformation for fuels and energy supply, emission control, and so forth. In the past, discoveries have often followed events such as wars or embargoes, whereas the current driving forces of studies, researches and then discoveries aim at a better understanding of catalytic processes, at reducing the costs of raw materials and processes, at developing new catalytic materials and at addressing environmental issues. This review focuses on the history of many catalytic industrial processes, environmental issues, catalytic materials, especially their expected catalytic properties, on catalyst characterisation by physical methods and development of in situ conditions, i.e., characterisation under actual working conditions with reactants and products analyzed on-line. Emphasis is also placed on high selectivity in catalytic reactions and the major challenges for the future, such as environmental issues, energy supply, pollution control for vehicles and industrial plants, air/VOCs/water purification, hydrogen sources and carbon dioxide storage/up grading, transformation of biomasses as a promising source of raw materials, and catalytic water splitting perspectives.

This review is a survey of heterogeneous catalysis and is not comprehensive but leads to the conclusion that, although many catalysts and catalytic processes have already been discovered and developed over the past century, many opportunities nevertheless exist for new developments, new processes and new catalytic materials. It follows that substantial challenges exist for the younger generation of researchers and engineers, as emphasized at the end of the manuscript.

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1. Introduction

Catalysis is an important field in chemistry, with some 90% of chemical processes involving catalysts in at least one of their steps [1]. At present, because of environmental issues, catalysis appears to be even more important than before and to constitute one of the major sources of improvements in our society [2,3]. A survey of U.S. industries revealed that the annual revenue from chemical and fuel production topped all other industrial sectors. The survey also showed that more than 60% of the 63 major products and 90% of the 34 process innovations from 1930 to 1980 have involved catalysis, which illustrates the critical role of this field in the fuel and chemical industries.

This review is intended to present some historical background of catalysis and the major challenges that this field has faced in the last half century and that it still must face in the future. This review is focused only on heterogeneous catalysis.

Our aim in this manuscript is to highlight the major catalysis-related discoveries and processes that have been developed over the past three centuries. The history of catalysis and its contribution to chemical industries has already been widely described in the literature, e.g. [4–6]. We intended to review some historically significant steps in the development of catalysis and catalytic processes. Without discussing ancient beer or wine fermentation, it is interesting to recall some old processes, as summarized in Table 1 [7–13].

Some of these processes have been developed in response to driving forces designated as “pullers” like the expected Chilean embargo on salt peter as a nitrate source, which motivated Haber and Bosch to develop a process for the fixation of atmospheric nitrogen in ammonia synthesis (1909). Similarly, the need for a more energetic gasoline inspired racing driver and French chemical engineer Eugène Houdry to develop the oil (hydrocarbon) acid cracking process (1930), and catalytic reforming and alkylation (1940), which have allowed the Allied forces to access a powerful fuel for air planes during World War II.

More recently, driving forces (pullers) have changed and now correspond more to a market-driven strategy, in which simpler
Table 1
Historical aspects in heterogeneous catalysis [7–13].

<table>
<thead>
<tr>
<th>Catalytic process</th>
<th>Catalyst</th>
<th>Main author</th>
<th>Year</th>
</tr>
</thead>
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<tr>
<td>Sulfuric acid</td>
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</tr>
<tr>
<td>Combustion</td>
<td>Pt</td>
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<tr>
<td>Decomposition NH₃</td>
<td>Fe &gt; Cu &gt; Ag &gt; Au &gt; Pt</td>
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<tr>
<td>Oxidation</td>
<td>Pt</td>
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<td>Oxidation SO₂ to SO₃ (contact process)</td>
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<td>Definition of catalysis</td>
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<td>Oxidation of NH₃ to nitric acid</td>
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<td>Esterification of acid</td>
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<td>1879</td>
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<tr>
<td>Hydrolysis of esters</td>
<td>Acid</td>
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<td>1879</td>
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<tr>
<td>Sulfuric acid</td>
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<td>Friedel-Crafts reactions</td>
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<td>Industrial process of NH₃ synthesis under pressure</td>
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<td>Haber</td>
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<tr>
<td>CO + H₂ → CH₃OH</td>
<td>ZnO-chromia</td>
<td>BASF</td>
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<tr>
<td>CO + H₂ → hydrocarbons</td>
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<td>Fischer &amp; Tropsch</td>
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<td>Contact catalysis theory</td>
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<td>1925</td>
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<td>Hydrogenation vegetable oils</td>
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<td>Raney</td>
<td>1926</td>
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<tr>
<td>Catalytic cracking of petroleum</td>
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<tr>
<td>Synthesis gas</td>
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<td>Bergus &amp; Bosch</td>
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<tr>
<td>Allylation reaction for gasoline fuel</td>
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<td>1940</td>
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<tr>
<td>Synthetic zeolites</td>
<td></td>
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<tr>
<td>Exhaust gas treatment</td>
<td></td>
<td>General Motors &amp; Ford</td>
<td>1976</td>
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</table>

and less-capital-incentive processes and the use of cheaper feed stocks are preferred. Since the end of the twentieth century, societal concerns have also become an important modern motivation, with intensive research being devoted to convert by-products to useful products and to treat all kinds of wastes for the preservation and protection of the environment. More stringent legislation has been established which has led to research on new catalytic materials and more efficient processes. More specifically, with respect to environmental issues, hydrodesulfurization started in the 1960s as an important method for the removal of sulfur from fuels. Hydrodesulfurization has resulted in a considerable reduction in global emissions of sulfur oxides, while creating increased demand for the selective methane reaction (SMR) for H₂ production; auto emission control catalysts developed in 1974 (oxidation), 1978 (three-way), and in the 1990s (Pd three-way); the selective catalytic reduction of NOₓ by NH₃ or N₂H₄ (SCR) for power plants in 1980 using V, W, and Ti oxides extruded into monolith forms [14]; ozone emission control catalysts developed by Engelhard (now BASF); the replacement of CFCs by HFCs for the reduction of topospheric ozone concentration (ozone holes), the catalytic destruction of volatile organic compounds from the consumer products industry; the production of foods and chemicals; the development of diesel oxidation exhaust catalysts in 1990 using cerium salt as additive; a variety of solutions that use metal oxides for catalytic decomposition of N₂O (which resulted in an 81% reduction of all N₂O emissions from the world adipic acid plants); the development of Pt–Rh-alkali NOₓ storage catalysts; the development of the Toyota Motor in 1994; the development of diesel particulate elimination catalysts in 2003; the development of urea SCR for NOₓ emissions control in vehicles in 2004; the development of NOₓ removal in FCC regenerator units in 2007, and so forth.

New studies have also appeared in the past two or three decades under driving forces considered as “pushers” for the development of a molecular-level understanding of catalyst function, surface sensitive spectroscopies, in situ/operando characterisation techniques, scientific computing, quantum chemistry, molecular modelling, thermodynamics and kinetics, reaction and reactor modelling, high-throughput catalyst screening and testing, and so forth. Significant improvements have been made in all of these domains, and further developments should continue in the future.

2. The catalysts

Since ancient times, the development and use of materials have been one of the basic objectives of our world. Eras, the Stone Age, the Bronze Age, and the Iron Age, have been named after the fundamental material used by mankind to construct their tools. Materials science is the modern activity that provides the raw material for this endless need, demanded by the progress in all fields of industry and technology, for new materials for the development of society.

The International Union of Pure and Applied Chemistry (IUPAC) has defined a catalyst as “a substance that increases the rate of a reaction without modifying the overall standard Gibbs energy change in the reaction” [15]. The chemical process of increasing the reaction rate is called catalysis, and the catalyst is both a reactant and a product of the reaction, i.e., the catalyst is restored after each catalytic act. Furthermore, the catalyst does not influence the thermodynamical equilibrium composition after the cessation of the reaction.

More efficient catalytic processes require improvements in the catalytic activity and selectivity. Both aspects can be improved by the tailored design of catalytic materials with the desired structures and the desired dispersion of active sites. Materials such as zeolites, AlPO, SAPO, mesoporous materials, PILC, MOFs, etc. offer such possibilities in this regard, with controlled large and accessible surface areas of the catalysts but without standalone
fine particles. Moreover, one of the most important applications of these novel porous solid catalysts is the replacement of environmentally hazardous, corrosive, difficult-to-separate-and-dispose-of homogeneous catalysts (viz. mineral and Lewis acids, organic and inorganic bases and toxic metallic compounds) employed in the liquid-phase synthesis of bulk and fine chemicals (vide infra) [16]. There are many families of solids catalysts like metals, oxides, sulfides, carbons, etc. as bulk materials or supported on a more or less catalytically active support like silica, alumina, zirconia, titania, ceria, carbons, etc. These materials may possess specific chemical properties, such as acid-base or redox or dehydrogenating or hydrogenating or oxidizing, and physical properties like porosity, high surface area, attrition resistance, thermal and/or electrical conductivity, etc. The largest family corresponds to oxides whatever zeolites, clays, mesoporous materials, mixed oxides as catalysts or as supports. Among them porous materials present some fascinating properties, which are described below.

2.1. Zeolites

In the petrochemistry and organic synthesis fields, zeolites have played a major role in the twentieth century. Zeolites are inorganic crystalline aluminosilicates which structures consist of a three-dimensional arrangement of TQ₄ tetrahedra (where T is usually Si⁴⁺ and Al³⁺ tetrahedrally coordinated atoms) assembled together through the sharing of oxygen atoms to form subunits, which repeat to form an infinite lattice [17], consisting of three-dimensional, fourfold interconnected TQ₄ tetrahedra linked via T–O–T bridges. The T–O–T angles are ideally 140–150° and rarely over 180°. The existence of Al in a tetrahedrally coordinated Si structure leaves a negative framework charge, which requires the existence of compensating cations, located in the porous system.

Consequently, an interesting feature of zeolites is the versatility of their structures that arises from a large number of modification procedures which also tailor their catalytic properties. The catalytic activity is associated with the presence of active centres in the framework. Such centres may be acid, their strength and number (Bronsted, Lewis) being adjusted in a controlled manner either during synthesis by isomorphous replacement of the central Si atom in tetrahedral sites in the zeolite lattice, by for example trivalent elements like Al, B, Fe, Cr, Sb, As, or Ga, and tetravalent elements like Ge, Ti, Zr, or Hf; and/or post-synthesis including the steam procedure, chemical vapor deposition, ion exchange of interstitial cations, reduction of exchanged metal ions at a lower valence state.

A distinction has been made between small-, medium- and large-pore zeolites. In the case of small-pore zeolites, such as zeolite A, eight SiO₄ tetrahedra form a ten member ring (10MR) with a diameter of 0.41 nm and in the case of large-pore zeolites, such as Y-zeolite (Fig. 1), a cavity with a diameter of 0.74 nm is formed by twelve SiO₄ tetrahedra. The medium-pore zeolites, such as pentasil zeolites, contain a ten member ring with an ellipsoidal tubular diameter of 0.55 × 0.56 nm. The system of channels and cavities in these molecular sieves produces solids with very high surface areas and pore volumes, which are capable of adsorbing large amounts of hydrocarbons.

Zeolites can be used as sorbents and as catalysts in some catalytic processes. The major breakthrough in zeolite catalysts arose from the fluid catalytic cracking (FCC) process for oil transformation to fuels and chemicals. The addition of zeolites (FAU and MFI) to acid clays and silica–alumina cracking catalysts in the mid-1960s resulted in a drastic increase in conversion and gasoline yields as well as in lower quantities of coke and dry gas [18]. The new catalysts gave gasolines with lower octane numbers, primarily because of their lower olefinicity [19–21]. The first octane-enhancing FCC catalysts were introduced by catalyst manufacturers in USA in the mid-1970s. Octane FCC catalysts consist of two major components, and the zeolites can be used to boost gasoline octane. Chester et al. [22] have reported that, in addition to MFI (ZSM-5), different members of the MFI family of zeolites (MEL, ZSM-12, ZSM-23, ZSM-35, ZSM-38) have octane-boosting abilities. Zeolites beta (BEA) [23] and offretite (OFF) [24] have been reported to produce higher gasoline octane numbers than conventional Y (FAU) zeolites and can be used as octane-boosting additives.

Major milestones in this domain are summarized below:

- R. Milton (Union Carbide in 1950s), D. Breck, R. Barrer and E. Flanigen developed commercially viable routes to various zeolites and MeAPOs.
- J. Rabo, working at Union Carbide, applied the use of zeolites to petroleum refining (isomerization, 1959), whereas C. Plank and E. Rosinski of Mobil Oil applied zeolites to catalytic cracking (1962) of heavy oil fractions.
- P. Weisz and V. Friellette of Mobil Oil developed the concept (1960) of shape-selective catalysts, and W. Haag applied shape selectivity to the production of aromatics.
- G. Kerr of Mobil Oil discovered high silica zeolites in 1967 (ZSM-5, subsequently designated as MFI) and the first large scale commercial cracking trial was run in 1983.
- W. R. Grace discovered the steaming of Y zeolite to produce ultrastable Y (USY) zeolite in 1969.
- Mobil Oil developed the siliceous mesoporous-type materials designated as MCM, HMS, and so forth in the late 1990s.
- UOP/HYDRO (1995) developed SAPO-34, a silicoaluminophosphate molecular sieve applied for methanol to olefins (MTO process).

Another fascinating property of zeolites arises from their molecular size porous network, which allows certain reactants to enter and products to easily leave the pores or cavities, or to remain trapped, or to leave the pores with difficulty if they are too bulky. This concept, of shape selectivity, pioneered by Mobil scientists [25], has been developed to explain reactions that do not obey the classical laws of thermodynamics and that are strongly influenced by the size of the pores or cavities relative to the size of the reactant or product molecules. Matching the size and configuration of reacting molecules, intermediates and products with the geometry and tortuosity of the zeolite channel/cavity system provides the basis for controlled shape selectivity. Diffusion and shape-selectivity catalysis in zeolites have been reviewed in several publications [26–28]. However, the shape selectivity in zeolites can manifest itself through: reactant selectivity, product selectivity, transition-state selectivity, molecular traffic control, etc.

Fig. 1. Framework of Faujasite (FAU) zeolite (Y or X-Type Si/Al = 2.5 or 1).
The reactant selectivity, results in the exclusion of molecules too large to diffuse into the zeolite pores; a simple example is the dehydration of alcohols. Over the narrow-pore zeolite (CaA), n-butanol is dehydrated, and isobutanol is not. Conversely, as expected, isobutanol is more readily dehydrated than n-butanol over NaX (which has wider pores). The former result is readily explained because both forms can enter NaX, but the bulkier isobutanol is excluded from CaA – product selectivity. In addition to size exclusion, entrance to zeolite crystals may hinder when the unfavorable orientation of a reactant is caused by electrostatic effects. In this case, the alignment of a zeolitic electrostatic field (perpendicular to the plane of the window) and a molecule dipole may restrict entry by electrostatic repulsion, which allows only small molecules formed during the reaction to diffuse out of the zeolite pores. For example, in the alkylation of toluene by methanol over H-MFI, yields of p-xylene are enhanced because the diffusivity of p-xylene is much greater than that of o- and m-xylene (vide infra). Even if the primary product of alkylation is not rich in p-xylene, its more rapid exit from the zeolite allows further isomerization of o- and m-xylene and results in increased yields of the p-isomer. Restricted transition-state selectivity occurs when certain reactions are prevented because the corresponding transition state would require more space than is available in the pores. Molecular traffic control [29] occurs in zeolites with two types of channel systems. The relationship between the length of the molecules and the size of the zeolite cage as well as variations in molecular oscillations [30] also affect zeolite shape selectivity. In addition to geometric factors, shape selectivity can be due to electrostatic effects [31] which result from the interaction between the electric field at the pore mouth and the dipole moment of the reactant molecule. Such an interaction can favour or inhibit the diffusion of the reactant molecule into the zeolite.

The shape selectivity of zeolites can be modified by ion exchange, dealumination, changes in the framework Si/Al ratio, or by any modification that affects the pore size or geometry [32–45]. The shape selectivity of a zeolite is often characterized by its “constraint index,” which is the ratio of the cracking rate constants for n-hexane and 3-methylpentane [46]. Large-pore zeolites have constraint indices less than 1; medium-pore zeolites have constraint indices between 1 and 12; small-pore zeolites have constraint indices higher than 12.

The shape selectivity phenomenon is illustrated in Fig. 2 for the synthesis of 4,4′-di-isopropyl-biphenyl and 2,
6-di-isopropyl-naphthalene compounds that are intermediates for polyesters or liquid crystals, by alkylation of naphthalene by propylene on dealluminated mordenite. The narrow size of the mordenite (10-membered ring) zeolite favours the formation of the less-bulky para isomer of the di-isopropyl naphthalene, followed by the ortho isomer relative to the meta isomer, as is expected from the thermodynamic equilibrium of approximately 25:25:50, respectively.

Another aspect of zeolite properties is the confinement effect, as developed by E. Derouane [47–49], which simply considers van der Waals forces, i.e., neglecting Pauli repulsive forces, as illustrated in Fig. 3.

Derouane et al. have proposed the following equation of the van der Waals energy (W) of a spherical molecule of van der Waals radius (d) confined in a spherical micropore of a radius (a):

\[ W(s) = -\frac{C}{4d^2} \cdot \left(1 - \frac{s}{2}\right)^{-3} \]

where \( C = \hbar \omega \alpha / 2 \), with \( \alpha = e^2 / \text{m} \text{r}^2 \) is the polarizability of an atom seen as a punctual dipolar moment, fluctuating at a frequency \( \omega \), and \( s \) is the surface curvature. This latter parameter, \( s = d/\alpha \), can vary between 0 and 1, depending on the relative sizes of the confined molecule and the micropore. The van der Waals force is

\[ F = \frac{3C}{4d^2} \left[1 - \left(1 - \frac{s}{2}\right)^{3/2}\right]. \]

The extreme cases correspond to a flat surface (\( s = 0 \)) and to a molecule with the same size as the pore (\( s = 1 \)); this latter case has been referred to by Derouane et al. as a “floating molecule” which should diffuse very rapidly because its motion is not hindered by its interaction with the wall, as compensated by the van der Waals force. It also follows from the van der Waals equation that \( W_{s=1} = 8W_{s=0} \), which means that, according to this model, the adsorption energy due to the van der Waals confinement factor within the zeolite pore can be up to 8 times greater than that corresponding to a flat surface. The type of variation of \( W \) versus \( s \) can be found in Fig. 4.

As a consequence, molecules within the pores may interact more or less strongly with their environment depending on their size relative to that of the pores, e.g., 90 kJ mol\(^{-1}\) for \( p \)-xylene in SAPO-11. They can also contract themselves to enter the pores, whereas the zeolitic lattice may also slightly contract upon adsorption, as shown by XRD [50].

At present, more than 300 different types of zeolite frameworks are known, with only a few (BEA, FAU, MFI, MOR, SAPO-34) having important industrial catalytic applications; however, many more have applications for the manufacture of fine chemicals. Some studies are described below to exemplify some of their properties.

The synthesis of adipic acid is an interesting example. The classical process (annual production of 0.7 Mt, off-gas concentration of 25–40%) uses nitric acid as an oxidizing agent with the formation of \( N_2O \), which has to be re-oxidized further to nitric acid and which is an important greenhouse gas. A catalytic process was subsequently developed for \( N_2O \) decomposition. However, a process that uses an Fe-MFI catalyst, which is able to oxidize benzene directly to phenol [51–58] has been discovered at the Boreskov Institute of Catalysis in Novosibirsk, RU. A process was developed with Monsanto Co in a spin-off company called Soluita, but does not appear to be commercialized, according to our knowledge. This process is much more environmentally friendly because \( N_2O \) is used instead of oxygen to oxidize benzene to phenol. The scheme for this process is presented in Fig. 5.

Another interesting example is Friedel–Crafts reactions on acidic zeolites. The first mention of acylation related to the later \( Al_2Cl_6 \) method of Friedel and Crafts appeared in 1873 in a preliminary communication by Grucaevic and Merz [59], as reported by Olah in a historical review about Friedel–Crafts chemistry [60,61] on the metal-catalyzed acylation of aromatic compounds. The Friedel–Crafts acylation reaction consists primarily of the production of an aromatic ketone by reaction of an aromatic substrate with an acyl component in the presence of a catalyst. Many papers and books have been published and numerous patents have been granted on this topic, as summarized in a recent review [62]. Interests in electrophilic acylation studies and in the optimization of preparative processes were spurred by the considerable practical value of the aromatic ketone products, which constitute important intermediates in the pharmaceutical, fragrance, flavour, dye and agrochemical industries. The electrophilic acylations are catalyzed by Lewis acids (such as ZnCl\(_2\), AlCl\(_3\), FeCl\(_3\), SnCl\(_4\), and TiCl\(_4\)) or protic acids (such as HF or H\(_2\)SO\(_4\)). However, the use of metal halides causes problems associated with the hydrolysis of the complex, which results in the loss of catalyst and the generation of large volumes of corrosive waste streams. Great efforts have thus been made to achieve the goal of making the Lewis acid using heterogeneous solid catalysts, in particular acid zeolites. A detailed description of Friedel–Crafts reactions for arenes (e.g., benzene, toluene, xylene), aromatic ethers (e.g., anisole) with acetic anhydride or other acylating agents on zeolites and on clays, metal oxides, and so forth is given in Ref. [60]. The roles of shape selectivity and deactivation by the products and hydrophobicity versus hydrophilicity for zeolites have been emphasized. For example, acylation of anisole or toluene with acetic anhydride was performed on BEA zeolite at 90 °C, to replace the classical AlCl\(_3\) catalyst which led to many salts in the effluents, corrosion problems, low selectivity and a short lifetime.

Fig. 4. Variations of van der Waals energy \( W \) and the force between a spherical molecule (radius \( d \)) and a spherical micropore (radius \( a \)) vs. curvature (\( s = d/a \) [47–49]).

Fig. 5. Adipic acid processes using the old process (left) and the new process (right).
of the catalyst, as already discussed. At variance, the use of H-BEA zeolite resulted in 6 times fewer steps, 10 times less solid and 100 times less aqueous discharge, primarily because the hydrophilicity versus the hydrophobicity of the zeolite, for more or less polar reactants, which allowed the reactant molecules to enter more or less easily within the pores while the solvent molecules were prevented from entering. The relative adsorption rates of reactant molecules within the pores regulate the stoichiometry of the reaction inside the pores, i.e., depending on the relative adsorption rates of the reactants, and one has thus to choose a stoichiometry in the liquid medium surrounding the zeolite particles that is different from that expected from the reaction. For example, a 20:1 stoichiometry might be chosen for a 1:1 reaction for toluene (non polar reactant) acylation by acetic anhydride (polar reactant). This holds true particularly for gas phase reactions with solid zeolites, but also for liquid phase reactions on solid zeolites, which is an important aspect of fine chemical reactions in zeolites, as schematized in Fig. 6.

Another interesting example relates to the production of para-xylene (p-xylene). Xylenes, especially the para isomers, are compounds in high demand in the organic chemical industry for the production of polyethylene terephthalate (PET) fibres, plastics, resins, films, and so forth as p-xylene is a chemical intermediate in these processes. The main source of xylenes is the C₈ cut produced by catalytic reforming and steam cracking [65–68]. However, a convenient way to increase p-xylene production is to transform less-valuable C₇ and C₉ methylanilamides by catalytic alkylation of toluene with methanol followed by disproportionation and transalkylation with trimethylbenzene. Catalysts for these reactions range from common Brønsted acids (H₂SO₄, H₃PO₄, HF) to Lewis acids (metal halides) and further to solid acids (Al₂O₃, SiO₂-Al₂O₃, zeolites). It must be noted, that as a consequence of environmental concerns, the zeolite-based catalysts currently play a significant role in the production of alkyl aromatics. Studies reported in the literature describe a wide variety of zeolitic catalysts that are active in the alkylation of toluene with methanol [36,38,39,69–78], toluene disproportionation [79–84], transalkylation of toluene–trimethylbenzene [85–89], and xylene isomerization [90–92]. In general, the catalytic properties (especially the selectivity) and the surface deactivation of zeolites during these reactions strongly depend on the nature, number and strength of the acid centres in the catalyst. For example, the catalysts with strongly acidic sites have been reported to be less selective and easily deactivated by coke [93]. Modification of the acidity and structure of zeolites (with large and medium pores) can be considered a way to reduce by-reactions and improve the selectivity to p-xylene. High activity and predominant shape selectivity was observed on ZSM-5 [94–97], and the reaction is effective above 450 °C. The high p-selectivity of modified ZSM5 has been attributed to the restricted diffusion inside the channels, i.e., the p-xylene, which rapidly diffuses out of the narrow channels, is preferentially produced. Large-pore zeolites with 12-member channel systems, particularly mordenite [98,99], have also emerged as shape-selective catalysts. Although the size of pores is important for the para selectivity, this phenomenon was observed on large-pore zeolites when the acidity was modified by isomorphous substitution or ionic exchange with rare-earth metals. The formation of p-xylene was also investigated on the zeolite MCM-22 [100–102], discovered by Mobil, which has a unique crystal structure [103]. It is composed of two channel systems, both of which are accessed through a 10-membered ring (10-MR) window. One system consists of two-dimensional, sinusoidal channels with 10-MR opening, whereas the other contains large supercages that consist of 10-MR and 12-MR openings with an inner free space of 0.71 × 0.71 × 1.82 nm. These channel systems are independent of each other, and molecules cannot pass from one to the other within the same crystallographic unit cell. The catalytic properties, such as the shape selectivity of MCM-22, have been shown to be intermediate between 10-MR and 12-MR zeolites in various reactions. The results for MCM-22 highlight the influence of cages and windows on the shape selectivity. In such cases, the experimentally observed shape selectivity was attributed to variations in the Si/Al ratio and the nature of the extra framework cations. Toluene disproportionation over dealuminated MCM-22 was found to occur mainly in the supercages of MCM-22 but not in the 10-MR channels of MCM-22 at the investigated temperatures. The fraction of p-xylene was higher than its equilibrium value and increased further by the
dealumination. p-Xylene formed within the supercages as a primary product would be isomerized to o- and m-xylene by the acid sites not only on the external surface but also within the 10-MR channels. The improvement in the para selectivity by dealumination resulted from the suppression of isomerization activity; the dealumination treatment probably eliminated framework Al atoms predominantly on the external surface and inside the 10-MR channels compared with those inside the supercages [102].

Many other fine-chemical reactions have been developed by Corma, Garcia and their teams [2] at ITQ, Universidad de Valencia, Spain. These reactions pertain largely to the field of applications of zeolites in catalysis, which has previously been limited to petrochemical reactions.

2.2. AlPO₄-n SAPO₄-n, Me-AlPO₄-n, Me-APSO₄-n

In the early 1980s, the discovery of a new family of molecular sieves was reported by researchers at Union Carbide. Wilson et al. [104,105] described the microporous aluminophosphates prepared hydrothermally from alumina, phosphoric acid and an amine or quaternary ammonium salt as organic templates. The product composition for these materials is xAl₂O₃·1.0±0.2 P₂O₅·yH₂O, where R is an organic template located in the intracrystalline pore system. The crystallized materials consist of alternating AlO₂ and PO₂ tetrahedra joined together into electrovalently neutral, three-dimensional frameworks whose structure depends upon the preparation conditions. These frameworks contain no Al—O—Al or P—O—P bonds. The AlPO₄-5 structure consists of 4- and 6-membered rings joined together to form the unidimensional cylindrical channels of 12-membered rings with a free diameter of approximately 0.8 nm [106,107,50,108,109]. The porosity of the structures described by Union Carbide researchers varies from very small pores (0.3 nm) to relatively large pores (0.8 nm). Because AlPO₄ frameworks are neutral, they have no ion-exchange capacity. They exhibit good thermal and hydrothermal stability and have weakly acidic catalytic properties. The absence of strong acidity limits the application of these materials in cracking catalysis. By isomorphous substitution of a series of elements into the AlPO₄ framework, a new generation of crystalline molecular sieves was prepared [110]. The elements include framework cationic species that range from monovalent to pentavalent, such as Li, Be, B, Mg, Si, Ga, Ge, As, Ti, Mn, Fe, Co, and Zn. The addition of silicon to the aluminum and phosphorous framework elements results in silicoaluminophosphate (SAPO) molecular sieves [111]. The SAPO structures are mildly hydrophilic and have low-to-moderate acidity, depending upon the silicon concentration and

![Fig. 8. Self-assembly of polymetallic cluster nodes (left; top: m4-oxo \{M₄O₆(CO₂)₆\}; bottom: \{M₂(-CO₂)₄ \} paddlewheel) and organic linkers (right) yielding metal–organic frameworks (center). [125,126].](image)

![Fig. 9. MOFs structures: Left: MIL-53, metal terephthalate (with Al, Cr, Fe ou V), which captures hydrogen into the framework formed of tunnels. Centre and right: MIL-100, whose octahedra, constituted by chromates (CrO₆), organise in tetrahedra and form cavities of diameter 2–3 nm as observed by electron microscopy from [127].](image)
the structure type. According to Martens [112], even the highly siliceous SAPOs have a lower catalytic activity as compared with zeolites, such as USY. SAPO-37 is very active cracking catalyst [113]. Several patents describe the use of SAPO-5, SAPO-11, SAPO-37 and SAPO-40 in octane FCC catalysts [114]. The isomorphic substitution of metal ions into AlPO4 frameworks results in metal aluminophosphates (MeAPO), whereas the isomorphic substitution of metal ions into SAPOs results in metal silicoaluminophosphate frameworks (MeAPSOs). Their properties are similar to those of the parent molecular sieves. The thermal and hydrothermal stability of MeAPO is somewhat lower than that of AlPO4 and SAPO molecular sieves. MeAPSOs exhibit weak to strong acidity, depending on the metal type and the framework structure.

2.3. Pillared interlayer clays (PILCs)

Pillared interlayer clays (PILCs) have been studied since the late 1970s as microporous materials with larger pore size (0.4–2.0 nm, but less uniform) and more tunable compositions than those of zeolites [115–117]. PILCs were identified as good candidates for heterogeneous catalysis because their pore size distribution is quite broad and is still largely in the microporous range [2]. The parent clay materials are composed of charge-balancing cations sandwiched between negatively charged aluminosilicate sheets. PILCs are prepared by swelling the clay sheets, ion exchanging the cations with [AlO2Al2(OH)24(H2O)]4+ aluminum polyoxocations, and calcining the material to create aluminum oxide pillars within the clay sheets. The result is a highly porous structure with a large intracrystalline surface area suitable for molecular sieving, adsorption and catalysis [118]. PILC-like materials, termed PCHs (porous clay heterostructures) have been prepared using surfactant templating within the clay sheets [119]. The PCHs have controllable, uniform pore sizes of 1.4–2.2 nm and retain the sheet-like characteristics of the original clay material.

2.4. Layered double hydroxides (LDHs)

Layered double hydroxides (LDHs), also known as hydrotalcite-like compounds, are ionic lamellar compounds that consist of positively charged hydroxide sheets with their interlayers filled with anions and water molecules. Their structure is linked to that of the natural mineral brucite, Mg(OH)2 [120,121]. The most common group of LDHs can be represented by the general formula [M2+1xM3+[OH]2x] [A n−x[(H2O)x]], where M2+ and M3+ are di- and tri-valent metal cations that occupy octahedral positions within the host layers of hydroxide sheets, and An− is an interlayer anion that compensates for the charge on the layers. Positive charge on the host layers arises from isomorphous replacement of a fraction of the divalent cations with trivalent cations. The combination of Mg and Al has been studied most frequently, with a variety of Mg:Al ratios and interlayer anions.

2.5. Metal organic frameworks (MOFs)

The metal–organic frameworks, designated MOFs, are new materials that were discovered approximately 40 years ago by polymer scientists. The rapid proliferation of papers in the literature started only approximately 20 years ago [122,123]. Their synthesis corresponds to the reaction of organic and inorganic groups, such as arsenates, silicates, sulfates, phosphates, phosphonates, etc. This reaction builds up three-dimensional frameworks formed of inorganic and organic moieties linked by strong bonds. The organic part is variable in nature, length and amount of space occupied because it includes more- or less-branched carboxylic acids, amino complexes, etc. The history of MOFs is schematized in Figs. 7 and 8.

Fig. 10. MOF MIL-101 metal terphthalate with cages of 3.2 nm [128].

Fig. 11. Schematic behavior observed upon adsorption, desorption of guest molecules (a) induced pores (b) breathing pore; (c) pores exchanging guest with deformation, (d) annealing pores [129].
molecules can access the large pores, which should be important for catalytic purposes, if the MOF structure has been functionalised or has active sites and presents accessible framework atoms or metal cationic sites (Table 2).

Garcia et al. have described [131] the use of metal–organic frameworks (MOFs) as heterogeneous catalysts for oxidation reaction using hydroperoxides or molecular oxygen. The authors have limited themselves to the oxidation of cycloalkanes, oxidation of benzylic positions, oxidation of cycloalkanes and aerobic oxidation of alcohols, but many more oxidation reactions may be imagined and studied. The use of MOFs as catalysts for enantioselective oxidations has also been considered with the peculiarity of the required oxidants and the advantages of having homochiral MOFs.

Main applications of MOFs concern: adsorption, gas storage (H₂, CO₂, etc.), gas separation, acid (Lewis; Brønsted), basic, redox and enantioselective (chirality) catalyses, biomass transformation, biomimetism, enzymes, drug delivery, magnetism, non linear optic, lasers, sensors, luminescence, etc. In catalysis, the thermal stability and leaching have been a big problem for many years and restrained researches, but now some new systems have been claimed to be stable up to 500 °C. The MOFs may not replace zeolites in petrorefining but well for fine chemistry under more gentle reaction conditions. Already many papers have appeared for some reactions such as oxidation, Lewis-type reaction of cyanosilkylation of acetaldheyde [137], etc.

It is clear that catalytic studies with MOFs are in their infancy. It is certainly possible to go into more sophisticated materials with organic ligands between the metals could be formed by transition metal complexes with one or two metals at controlled distance. Such types of materials will allow synthesis of heterogeneous catalysts based not only on transition metal complexes but also by the combination of mono- or multimetallic sites. Such design may lead to materials having a catalytic behaviour similar to that observed with enzymes.

The possibility to synthesise MOFs with a large variety of transition metals could be largely exploited for Lewis acid-type catalysis, provided that the metal is accessible (free valency available) and able to accept electrons from the reactant. In addition, the organic component of the MOF should support acid, base, or acid-base pairs and should allow one to perform successive reactions. There may be interest in the chemical industry in exploiting MOFs as heterogeneous catalysts. Examples include epoxide ring aperture with alcohols by zinc carboxylates, fine chemical reactions as Fries rearrangements, acylations, alkylation oxidation using cobalt salts in acetic acid, etc. MOFs offer also some promises as enantioselective catalysts, a topic that has not been possible to develop using zeolites. Asymmetric syntheses are routinely practiced in the synthesis of drugs, and these reactions are almost completely performed using expensive homogeneous catalysts. By using chiral ligands, a vast number of new MOFs could be available and tested in this field. Considering the simplicity of the synthesis of MOFs and their affordability, it will be important to know if MOFs can outperform in large-scale or asymmetric reactions to replace expensive homogeneous processes.

Finally, there is a need for theoretical studies in this new field, assisting the design of MOFs and providing insight into the interaction of the substrates and MOFs. Clarifying the reaction mechanism, the geometry of the transition states, and the controlling step in the reaction mechanisms may help to develop MOFs in which each of the components plays the expected role, as catalytic sites of natural enzymes.

### 2.6 Hierarchical zeolites

Hierarchical and mesoporous zeolites and mesoporous oxides (alumina, titania, etc.) have received increasing attention because of their improved performance in catalyzed reactions with respect to conventional (purely microporous) zeolites or common metal oxides [59,138,139]. The principle involves the creation of mesoporosity within the zeolite or within any metal oxide particles. Combined micro- and mesoporous materials have been claimed to

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**Table 2**

Comparison of MOFs with zeolites for some properties relevant to catalysis [131].

<table>
<thead>
<tr>
<th>Properties</th>
<th>Zeolites</th>
<th>MOFs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewis acidity</td>
<td>High</td>
<td>Low to medium</td>
</tr>
<tr>
<td>Brønsted acidity</td>
<td>Bridging Si(OH)Al hydroxyl groups</td>
<td>Introduced by post synthesis</td>
</tr>
<tr>
<td>Pore volume</td>
<td>~200–500 m² g⁻¹</td>
<td>Up to 5000 m² g⁻¹</td>
</tr>
<tr>
<td>Thermal stability</td>
<td>&gt;450 °C</td>
<td>Over 1 cm³ g⁻¹</td>
</tr>
<tr>
<td>Chemical stability</td>
<td>High</td>
<td>300 °C</td>
</tr>
<tr>
<td>Diffusion</td>
<td>High</td>
<td>Limited, depends on solvents</td>
</tr>
<tr>
<td>Basicity</td>
<td>Arises from framework oxgens</td>
<td>High but strongly influenced by linkers</td>
</tr>
<tr>
<td>Metal site density</td>
<td>Low</td>
<td>Introduced post synthesis or through linkers</td>
</tr>
<tr>
<td>Framework defects</td>
<td>Important role in many reactions</td>
<td>Expected to play a minor role</td>
</tr>
<tr>
<td>Active site environment</td>
<td>Mostly hydrophobic</td>
<td>Considerably hydrophobic</td>
</tr>
<tr>
<td>Poisoning of active sites</td>
<td>Reactivation by thermal treatment</td>
<td>Thermal treatment not valid</td>
</tr>
<tr>
<td>Chirality</td>
<td>Not possible or difficult</td>
<td>Homochiral solid from chiral linkers or post synthesis modifications</td>
</tr>
</tbody>
</table>

Fig. 12. Comparison of sizes of cavities and organic molecules diameters [132].
have advantages compared with the exclusively micro- or mesoporous materials. The reactant molecules are thus expected to diffuse more easily [140] within these pores to reach the active zeolite sites. These materials provide better hydrothermal stability [141], better multifunctionality to process a large variety of feedstocks, more controlled leaching rates for a constant and gradual release of active components, and are more capable of encapsulating wastes in the micropores [142–144]. Different porous materials that combine micro- and meso-pores, such as SBA-15, plugged hexagonal templated silica (PHTS), mesoporous aluminum silicates (MAS), mesoporous titanium silicates (MTS), UL-ZSM-5, and zeolites, have been developed within the last few years. Of these materials, the latter four are mesoporous materials built up from zeolite precursors. Such porosity in the mesoporous materials with zeolite character can be created after synthesis by chemical treatments, including hydrothermal, acidic, basic, desilication/dealumination [2] or recrystallization treatments [145,146], or templating [147–149] or carbon-based [150–153] approaches. Desilication in alkaline media has become a widely applied preparation method to tailor these modified zeolites because of the method’s optimal combination of efficiency and simplicity. Alkaline treatment is also a key step in strategic combinations with other post-synthesis modifications.

2.7. Carbon materials

Carbon nanotubes (CNTs) constitute another class of porous materials. They have been widely studied since their discovery in 1991 [154]. CNTs have highly unique electronic, mechanical, catalytic, adsorption, and transport properties, which make them interesting for a variety of applications. Carbon multiwall nanotubes (MWNTs) and single-wall nanotubes (SWNTs) should be distinguished. They are easily fabricated and may be employed either as catalyst supports, by entrapping active moieties within the pores, or to improve photoconversion and electrical energy storage (vide infra) [136,155–160]. Other forms of nanographic carbon may also prove to be promising in the development of renewable energy devices. For example, graphene, which consists of a single sheet of graphite, is considered a promising form of carbon for device engineering applications and catalysis [161–165]. A significant volume of literature devoted to graphene and other forms of carbon, including graphic nanofibers, has suggested that CNTs are not the only promising nanostructures for either photoconversion or electrical energy storage applications. The highly unique physical properties of carbon nanotubes have been demonstrated for a variety of photovoltaic devices as well as for improved Li-ion batteries and electrochemical capacitors.

2.8. Mesoporous materials

Many mesoporous silica-type materials have been synthesized in the years after the pioneering works by Mobil researchers on the M41S family (MCM-41, MCM-48, MCM-50) [166–168]. MCM-n mesoporous materials are synthesized using surfactants as structure-directing agents and can be characterized by well-defined pores of tunable sizes in the range between 2 nm and 10 nm and by specific surface areas between 600 m² g⁻¹ and 1300 m² g⁻¹. The most representative M41S materials are MCM-41 and MCM-48. MCM-41 consists of regular pseudo-one-dimensional pores in a honeycomb arrangement, whereas MCM-48 exhibits cubic symmetry that consists of two interwoven but unconnected three-dimensional pore systems of cylindrical pores. MCM-48 is more difficult to synthesize and high-quality materials can typically be obtained in the pore-size range between 2 and 5 nm [169]. MCM-50 comprises a lamellar phase. Independently, a family of mesoporous silica materials with properties similar to those of MCM-41 was discovered [170,171]; an important member of this family is FSM-16 [171]. At the microscopic scale, these materials are essentially amorphous. Whereas the pore diameter range of MCM-41 materials is restricted to 10 nm, ordered mesoporous silica with pore diameters up to approximately 30 nm (SBA-15) can be obtained using an amphiphilic block copolymer as a template [172,173]. SBA-15 (similar to MCM-41) consists of a hexagonal packing of cylindrical channels; however, depending on the details of the synthesis procedure, this material can possess irregular intrawall micropores that connect adjacent channels [174,175]. Moreover, a great variety of mesoporous materials have been synthesized, such as SBA-1, SBA-2, SBA-12, SBA-16, HMS [176], MSU [177], KSW-2 [178–180], TUD-1 [181], periodic mesoporous organosilicas (PMOs) [182–184], nanoporous carbon with ordered mesostructures [CMK-1, CMK-3] [185,186]. Pure-silica mesoporous materials are known to exhibit low catalytic activity because of the absence of active sites, which typically require heteroatoms. Therefore, one of the emerging trends in the area of mesoporous materials synthesis is the incorporation of heteroatoms that serve as catalytically active sites. Considerable research interest currently exists in the preparation and use of heteroatoms that contain mesoporous silicas as heterogeneous catalysts. Several elegant procedures have been reported for the incorporation of heteroatoms that also permit the design of the catalysts with active sites located on highly accessible internal surfaces of the pore channels. These procedures include impregnation [187–190], grafting by liquid–solid reaction [191–196], grafting by gas–solid reaction [197], grafting by solid–solid reaction [198,199], isomorphous substitution [200–210], molecular designed dispersion approach [211–213] and
template ion exchange method [214, 215]. The objective was to synthesize porous materials able to accommodate bulky molecules and thus treat heavier petroleum feedstocks. For example, the introduction of AI into such silica frameworks led to medium-strength acidity compared with the acidity of normal zeolites because of larger Si–O–Al bond angles. The applications of such materials in petrochemistry were subsequently limited. At present, research is focused on the introduction of catalytically active functions within the mesopores (i.e., functionalization of the walls) or of nanoparticles of metals or oxides. Interesting results were obtained; however, to our knowledge, no study has yet produced a breakthrough in catalytic processes. H-Al-MCM41 materials have been used as catalysts for the conversion of a large variety of substrates in reactions as diverse as hydrocarbon cracking, hydrocracking and hydroisomerization, olefin polymerization, oligomerization and isomerization, Friedel–Crafts aromatic and phenol alkylation and acylation, acetylation, Beckmann rearrangements, glycosidation, aldo condensations, and Prins condensations. Several reviews on the subject have been published [2, 216, 217].

Interesting results for the metal-mesoporous materials were reported with respect to the Fischer–Tropsch reaction [218, 219], hydrodesulfurization [220–222], the conversion of methycloptene [199, 201], the acylation of phenol [223], the naphthalene hydrogenation [224], the hydrogenation of arenes [225], cyclohexane hydrogenation [226], NO reduction with CO [227], the acylation of aromatic compounds [228], the benzylation of benzene [229], the metathesis of oct–1–ene [230], and the photocatalytic decomposition of NO [231], the oxidation reactions [232, 233] and so forth.

2.9. Versatile heterogeneous catalytic systems

Combining confinement and synergy effects has appeared recently as a promising way to synthesize efficient and versatile heterogeneous catalytic systems. For instance, many studies have been performed in the past half century to immobilize homogeneous catalysts on solid supports to synthesize heterogeneous catalysts [234], known to result in easy separation of the catalyst from the reactants and products. Originally, the active centres were designed to be away from a support surface in order to minimize the support destructive influence on the catalytic sites and to maintain the homogeneous metal complexes environment of ligands with a long spacer and thus catalytic properties [235]. Later on, it was observed that a support can even have some beneficial effects on the anchored homogeneous catalysts [236] such as confinement [237] and synergy effects [238–240]. Heterogeneous bifunctional and even trifunctional catalysts could then be prepared and studied because a synergy between multifunctional groups could be developed within confined spaces. An important further objective was to try to synthesize heterogeneous catalysts with enantioselectivity enhanced after chiral catalysts are introduced into confined spaces. For example, Raja and Thomas [241] have shown that, compared with the racemic products obtained in homogeneous catalysis, improved enantioselectivity (ee% 53–94%) in asymmetric hydrogenation reactions was obtained after chiral Rh complexes were introduced into the channels of mesoporous silica. He et al. [242] have also shown that after a bifunctional catalyst, 9-thiouracylepi-quinine, was incorporated in the channels of mesoporous silica SBA-15, the heterogeneous catalyst exhibited improved selectivity and enantioselectivity (92.5% selectivity and 99.2% ee versus 83.8% selectivity and 93.2% ee) in asymmetric Friedel–Crafts reaction between indoles and imines.

Layered compounds, with two-dimensional flexible interlayer regions, are also promising supports for the immobilization of homogeneous catalysts. For instance, the immobilization of copper complexes in laponite clay was found [243] to increase the ee from virtually zero to values ca. 40% in the reaction of methyl phenylidiazooacetate with tetrahydrofuran.

The idea is to graft, anchor or tether catalytic active entities to mesoporous silica. These species may be identical or different which may lead to bifunctional, trifunctional entities within the pores. Their proximity may result in synergistic effect for some reactant within a confined space and opens an important field of discovery of new catalysts, by taking advantage of continuum range of distance between anchored functional groups and intrinsic active sites on the support surface. Synergistic effects within anchored bifunctional catalysts, between two anchored functional groups, and between the anchored groups and hydroxyl groups on solid surface have been used to synthesize multifunctional catalysts. Let’s also remind that synergistic effects are widely utilized in nature such as for enzymes which with limited functional groups can catalyze many reactions smoothly with high activity and selectivity at near room temperature. [244]

3. Energy resources

Currently, petroleum and natural gas represent more than 60% of the primary energy supplied to 7 billions inhabitants on earth. Coal also remains an important source of energy, primarily in Asia. Whether used for energy production, transport, heating or as a source of chemical raw materials, the consumption of oil, natural gas and coal is expected to rise in the near future, while the development of alternative sources is expected to rise rapidly after a slow development in the past 20 years. The significant increase in energy demand over the past twenty years has primarily been satisfied by increasing the production of fossil sources. Because of this situation, several governments are approving new laws aiming to reduce CO2 emissions by promoting the utilization of renewable energy sources and biofuels. The total world consumption in 2005 was of 13 TW (~87 Gbarrels of oil), of which 81% came from fossil resources, as shown in Fig. 13.

Ten percent of the world energy use is derived from biomass, and 7% is derived from nuclear power. Nuclear power is desirable as long as the isotope uranium–235 (235U) is employed. However, a less than twenty-year supply of U235, which may be recovered at a reasonable cost, is available. When the supply of 235U will be exhausted, it will then be necessary to employ breeder reactors. Unfortunately, the by-product of this reaction is the very hazardous element, plutonium–239, 239Pu (238Pu → 239Pu). Moreover since the disaster following the tsunami in Japan in 2011 and the collapse of the nuclear plant in Fukushima, the construction of nuclear plants have been hardly questioned in many countries, although nuclear power is non CO2 producer and non fossil resource consumer.

3.1. The case of oil

It is difficult to evaluate the exact oil reserves because it corresponds to rough estimations called current reserves, which are contingent resources (conventional and extra-heavy+ bitumen) concentrated in a limited number of countries (Saudi Arabia, with 20%, Iran, Iraq, and Venezuela; these four countries possess 50% of the world reserves), with 75% in concentrated in 11 countries. The current reserves correspond to approximately 1000 Gbarrels therefore, approximately 35 years of production at actual consumption level, but less than the oil already extracted) and one may add 200 Gbarrels for conventional resources and 200–300 Gbarrels more for extra-heavy oil and bitumen. Oil is extracted either by simple pumping (20% of world production), by the injection of water (2/3 of oil produced), or by the injection of water + chemicals or gas (air, CO2 or gas produced (15%)). Efforts to discover new resources are clearly important, and the substitution of oil by
3.3. Biomass as a source of raw materials and future energy

Biomass, i.e., all products from plants (crops, algae, wood, agricultural wastes, etc.), has emerged as an important future source of energy and raw chemicals to replace, at least in part, coal, oil and natural gas. The origin of biomass from CO₂ and water under solar photons and chlorophyll to produce sugar blocks at the origin of cellulose, hemicellulose, lignin, and so forth is well known. Lignin constitutes one of the three major components of lignocellulosic biomass; the other two components consist of cellulose and hemicellulose. Lignin is a three-dimensional amorphous polymer that consists of methoxylated phenylpropane structures. In plant cell walls, lignin fills the spaces between cellulose and hemicellullose and acts as a glue that holds the lignocellulose matrix together. Cross-linking with the carbohydrate polymers then confers strength and rigidity to the system [245,247].

In 2005, more than 3% of the total energy consumption in the United States was supplied by biomass, and it recently surpassed hydroelectric energy as the largest domestic source of renewable energy. Similarly, the European Union receives approximately 66% of its renewable energy from biomass, which surpassed the total combined contribution from hydropower, wind power, geothermal energy, and solar power. In addition to energy, the production of chemicals from biomass is also essential because it is the only renewable source of liquid transportation fuel.

Over the last 30 years, three generations of biomass products have emerged [248,249], which are distinguished by their nature. Whereas oil was the principal source of energy in the twentieth century, the 21st century is expected to bring new sources of energy, particularly renewable energies such as bioenergies [248].

Three strategies for biomass valorization can be followed [249]. In the first strategy, biomass is gasified to syngas or degraded by pyrolysis to a mixture of small molecules, which can be used to produce chemicals using technologies developed for petroleum feedstocks. In the second strategy, extensive removal of the functional groups present on the lignin monomers yields simple aromatic compounds, such as phenol, benzene, toluene and xylene. These platform chemicals are then reacted in a second step using existing catalytic technology developed for petroleum refineries to produce bulk and fine chemicals. In the third strategy, biomass is converted directly to valuable chemicals in a one-pot process, which requires highly selective catalysts that eliminate functionalities and linkages. This strategy is best suited for the production of fine chemicals with a high degree of functionality, such as vanillin, that already resemble the lignin structure; however, more complicated target molecules may also be produced with additional improvements in catalytic technology. Indeed, this approach could yield a plethora of complex aromatics that are not otherwise readily available via conventional petrochemical routes. Because none of these strategies is expected to yield a single product in high yield, product separation is an important component of each process. In each case, after the catalytic processing of the lignin stream, the chemicals or fuels produced must be purified, which obviously must be taken into account in evaluations of the environmental impact of the whole process. Components from the cellulose and hemicelluloses streams are integrated within the lignin framework, but the process arrows are not fully depicted for clarity [245] – Fig. 15.

The transformation of cellulose, which is the main constituent of the most abundant renewable lignocellulosic feedstock and is non-edible, into chemicals and fuels has attracted significant attention in recent years. Compared with other conversion routes, such as high-temperature gasification and pyrolysis and enzymatic fermentation, a low-temperature and selective catalytic route for the transformation of cellulose in, e.g., a water medium, into a platform molecule, which may be easily transformed into valued

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3.2. Perspectives with natural gas (NG)

Natural gas constitutes the largest reserves of fossil resources. Eleven countries possess 75% of world gas resources, with 45% for Russia, 28% for Iran, and 25% for Qatar. The current reserves are estimated to reach 175–200 Tera m<sup>3</sup> (T = tera = 10<sup>12</sup>); however, large resources exist in the form of methane hydrates, which are located primarily in Polar Regions or in deep-water acreage. Natural gas can be used as an energy source (in power plants or as a heating source, for instance), but it can also be transformed into many basic materials for chemicals. Nevertheless, currently, only its conversion to syngas via steam reforming, partial oxidation or autothermal oxidation appears to be industrially viable [246]. All direct transformations to, for instance, methanol, dimethyl ether, formaldehyde, aromatics, or olefins are still not economically viable. This lack of viability constitutes a real challenge for the future, although many approaches have been attempted over the past 50 years, starting with the dimerization reaction in the 1970s, without commercialization success. The main possible reactions are summarized below:

<table>
<thead>
<tr>
<th>Reaction Type</th>
<th>Reaction Equation</th>
<th>ΔH&lt;sub&gt;298K&lt;/sub&gt; (kJ mol&lt;sup&gt;-1&lt;/sup&gt;)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam reforming</td>
<td>CH₄ + H₂O → CO + H₂</td>
<td>-206</td>
</tr>
<tr>
<td></td>
<td>CH₄ + nH₂O → nCO + (n + m/2) H₂</td>
<td>-1175 (for nC₃H₆)</td>
</tr>
<tr>
<td></td>
<td>CO + H₂O → CO₂ + H₂ (WGS)</td>
<td>+41</td>
</tr>
<tr>
<td>CO₂ (dry) reforming</td>
<td>CH₄ + CO₂ → 2CO + 2H₂</td>
<td>-247</td>
</tr>
<tr>
<td>Autothermal reforming (ATR)</td>
<td>CH₄ + 1/2O₂ → CO + 2H₂</td>
<td>+520</td>
</tr>
<tr>
<td></td>
<td>CH₄ + H₂O → CO + 3H₂</td>
<td>-206</td>
</tr>
<tr>
<td></td>
<td>CO + H₂O → CO₂ + H₂</td>
<td>+41</td>
</tr>
<tr>
<td>Catalytic partial oxidation (CPO)</td>
<td>CH₄ + 1/2O₂ → CO + 2H₂</td>
<td>+38</td>
</tr>
<tr>
<td>Total oxidation</td>
<td>CH₄ + 2O₂ → CO₂ + 2H₂</td>
<td>+802</td>
</tr>
<tr>
<td>Boudouard reaction</td>
<td>2CO → C + CO₂</td>
<td>+172</td>
</tr>
</tbody>
</table>

The main chemical products from natural gas are summarized in Table 3.

---

Fig. 14. Some perspectives of oil demand in a near future from WEO 2006. Note that billions tonnes should read giga tonnes.
It can be concluded that biomass is currently the leading renewable energy source in the world. Moreover, the introduction of biomass into energy systems presents certain advantages, such as a reduction in greenhouse gas emissions, because its synthesis uses CO₂ and water. However, its mobilization still presents many challenges relative to the competition between uses and the management of local natural resources (e.g., water, soil, biodiversity, farmer land and forest private properties). Therefore, the technologies involved should be structured so that this resource is developed to be truly sustainable. Two technologies exist for the production of diesel replacement fuels: vegetable-oil methyl esters (VOME) and hydrotreated vegetable oils (HVO). The latter oils, blended with kerosene, have begun to be used as aviation fuel.

Crop yields depend on the nature of the biosource, as detailed in Table 4. Wood is an important source for lignin. The production and transformation of wood into biofuel is presented in Table 5. Algae as oil seed appears to be particularly efficient (yield of 70 t ha⁻¹ and fuel efficiency of 14 toe ha⁻¹), whereas sugar cane and sugar beets have high yields (ca. 70 t ha⁻¹) but lower fuel efficiency (ca. 3 toe ha⁻¹). For comparison, the majority of the other biomass resources have yields of 10–20 t ha⁻¹ and efficiencies of 2–4 toe ha⁻¹. The cultivation of microalgae to produce oil biomass, cellulose or hydrogen is free of many terrestrial constraints. Such microalgae are cultured in photobioreactors and need only be in proximity to water, light, heat and CO₂. Microalgae constitute the prevailing trend in current research.

In the future, solar, geothermal, wind and presumably nuclear power plants will presumably be used for electricity; biomass, natural gas, coal and oil will be used for syngas and chemicals, hydrogen will be used for GTL and hydroprocessing, and

---

**Table 3**

Main chemical products from natural gas.

<table>
<thead>
<tr>
<th>Products</th>
<th>Production (Mtons/y)</th>
<th>Energy consumption (GJ/t)</th>
<th>CO₂ (t/t)</th>
<th>Main technology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>120</td>
<td>29</td>
<td>1.6</td>
<td>Syngas/synthesis</td>
</tr>
<tr>
<td>Ethylene</td>
<td>100</td>
<td>15</td>
<td>0.65</td>
<td>Steam cracking</td>
</tr>
<tr>
<td>Propylene</td>
<td>55</td>
<td>–</td>
<td>0.28</td>
<td>Syngas/synthesis</td>
</tr>
<tr>
<td>Methanol</td>
<td>30</td>
<td>28</td>
<td>9.0</td>
<td>Steam reforming</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>20</td>
<td>12.6</td>
<td>1</td>
<td>Syngas/synthesis</td>
</tr>
<tr>
<td>Synfuel</td>
<td>15</td>
<td>67</td>
<td>–</td>
<td>Syngas/synthesis</td>
</tr>
</tbody>
</table>

Source: IFP Energies Nouvelles.

---

It can be concluded that biomass is currently the leading renewable energy source in the world. Moreover, the introduction of biomass into energy systems presents certain advantages, such as a reduction in greenhouse gas emissions, because its synthesis uses CO₂ and water. However, its mobilization still presents many challenges relative to the competition between uses and the management of local natural resources (e.g., water, soil, biodiversity, farmer land and forest private properties). Therefore, the technologies involved should be structured so that this resource is developed to be truly sustainable. Two technologies exist for the production of diesel replacement fuels: vegetable-oil methyl esters (VOME) and hydrotreated vegetable oils (HVO). The latter oils, blended with kerosene, have begun to be used as aviation fuel.

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---

**Fig. 15.** Lignocellulosic biorefinery scheme with particular emphasis on the lignin stream [245].
refineries will be used to produce heat, electricity, transports, and bulk chemicals (CO₂ sequestration).

4. Hydrogen as a future energy source

The future supply of energy is dependent on hydrogen as a clean energy carrier. Hydrogen can be produced from fossil fuels, water electrolysis and splitting or biomass. However, the current debates concerning hydrogen economy are intimately linked to the clean production of hydrogen from fossil fuels (e.g., natural gas, coal, propane, methane, gasoline, light diesel), from dry biomass and biomass-derived liquid fuels (e.g., methanol and biodiesel), and from water. Because of the low cost and wide availability of coal, gasification to syngas and then to hydrogen through the water–gas shift (WGS) reaction is a promising route to cheap hydrogen. The success of such a hydrogen production route will only be possible if carbon dioxide is sequestered safely and economically. The key to the cost effective conversion of coal to hydrogen and carbon capture is the development of nanomaterials, such as catalysts for the WGS reaction and inorganic membranes for hydrogen/CO₂ separation. In the future, hydrogen will be the dominant fuel and will be converted to electricity in fuel cells, leaving only water as a product.

4.1. Water–gas shift reaction (WGS)

Since the early 1940s, the WGS reaction has represented an important step in the industrial production of hydrogen [257]. Interest in the study of WGS catalysts has recently been renewed because of the importance of such catalysts in PEM fuel cell applications [258,259]. The WGS reaction is an old industrial process in which water in the form of steam is mixed with carbon monoxide to obtain hydrogen and carbon dioxide. The WGS reaction is reversible and exothermic. Because of its moderate exothermicity, the WGS reaction is thermodynamically unfavorable at elevated temperatures, as illustrated by the continuous decline and eventual sign change in the Gibbs free energy as a function of temperature and the corresponding decreasing equilibrium constant as the temperature is increased. Low temperatures thermodynamically favour higher CO conversion. For maximum efficiency and economy of operation, many plants operate both a high-temperature stage (350–400 °C) and a low-temperature stage (180–240 °C). The commercial catalyst is composed of copper, zinc oxide, and alumina. The copper and zinc oxide forms are stable under WGS reaction conditions. Copper, the active species, remains active at temperatures as low as 200 °C. The zinc oxide provides some protection of the copper from sulfur poisoning by reacting with adsorbed sulfur compounds while also acting as a support for the copper. Because of the relatively low melting point of copper, the commercial low-temperature stage catalyst is more sensitive to deactivation caused by sintering. Different catalysts are employed in the WGS reaction, including Fe [260,261], Ni [262,263], Cu [264,265], Ru [266,267], Au [268,269], Pt [270].

The essential role of the industrial WGS reaction is to increase the production of hydrogen for refinery hydroprocesses, bulk storage and redistribution. This role includes the need for gases of appropriate H₂/CO ratios in the production of organic bulk chemicals such as ammonia, methanol, and alternative hydrocarbon fuels through Fischer–Tropsch synthesis. These gas mixtures, when applied in industry, are usually referred to as synthesis gas, or syngas, and are produced in low-scale facilities by the high-temperature reaction of carbonaceous materials in the presence of water or oxygen and supported-nickel catalysts.

4.2. Hydrogen production by steam reforming of ethanol

Ethanol is an excellent candidate for the production of hydrogen. The aim of the procedure for the steam reforming of ethanol is to generate a large amount of hydrogen and carbon dioxide by breaking the ethanol molecule in the presence of steam over an appropriate catalyst [271–275]. However, numerous reaction pathways occur in the ethanol steam-reforming process that depends on the nature of the catalysts used. These pathways include the dehydration of ethanol to ethylene and water followed by ethylene polymerization to form coke [276], the decomposition or cracking to methane followed by steam-reforming [277], dehydrogenation to acetaldehyde [274] followed by decarboxylation or steam-reforming of C₂H₄O, decomposition into acetone, CH₃COCH₃, followed by steam reforming [278], and steam reforming of ethanol to syngas [274]. These processes are accompanied by the water–gas shift reaction, coking reaction, and other reactions. Tremendous progress is needed to obtain a highly selective catalyst to develop a process for hydrogen generation by ethanol steam- ing, which is a sustainable solution for the problem of hydrogen production.

4.3. Water splitting as a hydrogen source [279]

Pure hydrogen may be the final destination in the evolution of fuel usage from coal to petroleum to natural gas, which has

---

**Table 4**

<table>
<thead>
<tr>
<th>Crops mobilised for energy proposes versus total production in 2007.</th>
<th>Total harvest (Mt)</th>
<th>% for bioenergies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corn</td>
<td>606</td>
<td>0.3</td>
</tr>
<tr>
<td>Rape sunflower</td>
<td>120</td>
<td>1</td>
</tr>
<tr>
<td>Soybean</td>
<td>77</td>
<td>17</td>
</tr>
<tr>
<td>Palm oil</td>
<td>221</td>
<td>51</td>
</tr>
<tr>
<td>Sugar beet</td>
<td>144</td>
<td>2</td>
</tr>
<tr>
<td>Sugar cane</td>
<td>193</td>
<td>0.2</td>
</tr>
<tr>
<td>Wheat</td>
<td>165</td>
<td>0.3</td>
</tr>
<tr>
<td>Wheat</td>
<td>427</td>
<td>4</td>
</tr>
<tr>
<td>Wheat</td>
<td>1591</td>
<td>15</td>
</tr>
<tr>
<td>Wheat</td>
<td>606</td>
<td>0.3</td>
</tr>
</tbody>
</table>

From FAOSTA, FAPRI.

---

**Table 5**

<table>
<thead>
<tr>
<th>Commercial uses of wood (in Mm³) and breakdown of conventional energy uses in 2007.</th>
<th>Wood harvest</th>
<th>Sawn wood</th>
<th>Wood for paper</th>
<th>Wood for board</th>
<th>Wood for fuel</th>
<th>Fuel wood %</th>
</tr>
</thead>
<tbody>
<tr>
<td>World</td>
<td>3,591</td>
<td>1,007</td>
<td>354</td>
<td>266</td>
<td>1,886</td>
<td>53</td>
</tr>
<tr>
<td>Europe</td>
<td>729</td>
<td>330</td>
<td>102</td>
<td>84</td>
<td>153</td>
<td>21</td>
</tr>
<tr>
<td>North America</td>
<td>640</td>
<td>386</td>
<td>149</td>
<td>56</td>
<td>54</td>
<td>8</td>
</tr>
<tr>
<td>South America</td>
<td>366</td>
<td>82</td>
<td>36</td>
<td>15</td>
<td>184</td>
<td>53</td>
</tr>
<tr>
<td>Asia</td>
<td>1,027</td>
<td>150</td>
<td>55</td>
<td>105</td>
<td>787</td>
<td>77</td>
</tr>
<tr>
<td>Africa</td>
<td>672</td>
<td>25</td>
<td>6</td>
<td>3</td>
<td>603</td>
<td>90</td>
</tr>
</tbody>
</table>

Source: IFP Energies Nouvelles, D. Lorne, Panorama 2010 Source: FAOSTAT.
followed a trail of increasing hydrogen content. A major bottleneck for the hydrogen vehicle is the issue of hydrogen storage. Hydrogen has the highest energy per unit mass, but occupies a large volume. Even in liquid form, the energy density of hydrogen is only 8.4 MJ/L, compared with 31.6 MJ/L for gasoline. MLL-53 is a potentially useful material for hydrogen storage, as are graphene [280] and bimetallic Pd-based alloys.

Because of its high energy capacity and environmental friendliness, hydrogen has been identified as a potential energy carrier in many low-greenhouse-gas (GHG) energy scenarios. In a proposed hydrogen energy system, hydrogen-containing compounds, such as fossil fuels (mainly methane), biomass, or even water, are potential sources of hydrogen. When hydrogen is derived from hydrocarbons such as fossil fuels or biomass, the capture and sequestration of CO2 are required in a low-GHG scenario. Although hydrogen produced from water does not present the challenge of unwanted emissions at the point of conversion, it does require that energy be supplied from an external resource. If this energy can be obtained from a renewable energy source, such as solar energy, hydrogen can then be considered a green energy alternative, and it is becoming increasingly relevant in our world. However, the technology to produce hydrogen in a cost-effective, low-GHG manner has not yet been developed. Since the discovery of hydrogen evolution through the photoelectrochemical splitting of water on n-type TiO2 electrodes, the technology of semiconductor-based photocatalytic water splitting to produce hydrogen using solar energy has been considered one of the most important approaches to solving the world energy crisis. Consequently, the development of the necessary semiconductor photocatalysts has been the subject of considerable research. Over the past 40 years, many photocatalysts have reportedly exhibited high photocatalytic activities for splitting water into a stoichiometric mixture of H2 and O2 (2:1 by molar ratio) in the UV-light region. These photocatalysts include La-doped NaTaO3, Sr2M2O6 (M= Nb, Ta), La2Ti2O7, K2La2Ti3O10, NiO/NaTaO3, and β-Ge2N4, among others, photocatalyst, which shows the highest activity, with a quantum yield of 56% at 270 nm. However, these oxide photocatalysts are only active under UV irradiation. With respect to the solar spectrum, only a small fraction (ca. 4%) of the incoming solar energy lies in the ultraviolet region, whereas the visible light in the solar spectrum is far more abundant (ca. 46%). It is essential, therefore, as an alternative to UV-active photocatalysts, to develop visible-light-driven photocatalysts that are stable and highly efficient for the practical, large-scale production of hydrogen using solar energy. In recent years, continuous breakthroughs have been made in the development of novel visible-light-driven photocatalysts, which has led to the enhancement of photocatalytic activity for water splitting and has inspired great enthusiasm. A large number of semiconductor materials have been developed as photocatalysts for the splitting of water to hydrogen under visible-light irradiation. Significant process has been achieved [281] with respect to semiconductor-based photocatalytic hydrogen generation through water in the hydrogen energy system.

Photocatalytic systems for water splitting are classified as one of two main kinds: sacrificial-reagent-containing water-splitting systems and overall water-splitting systems. Thus far, the sacrificial-reagent-containing water-splitting systems constructed from the Pt/CdS, Pt-Pd/CdS, and Zn/Cr layered double-hydroxide photocatalysts have demonstrated the best performance for hydrogen production and oxygen production, with highest quantum yields of ca. 60%, 93%, and 60%, respectively, at 420 nm. However, the efficiency of overall water-splitting systems based on visible-light-driven photocatalysts is still quite low, with a maximum quantum efficiency of ca. 5.9% over Rh2−3Cr2O7/GaN−ZnO in the range of 420–440 nm. This result is still far from the quantum efficiency (ca. 30% at 600 nm) designated as the initial starting point for practical applications or the critical conversion efficiency of light energy to hydrogen from photocatalytic water decomposition (15%). Therefore, more efficient visible-light-driven photocatalysts need to be developed to allow the construction of the necessary high-efficiency and cost-effective water-splitting systems. To develop more efficient visible-light-driven photocatalysts, the band gaps need to be narrowed to harvest visible light in longer-wavelength regions of the spectrum and to enhance the photogenerated charge separation during photocatalysis. Band-gap engineering for the modification of the band structure of semiconductor photocatalysts using ion doping, semiconductor sensitization, or solid solutions all present significant opportunities to render such materials active in the visible-light region. Computational predictions based on first-principles calculations could provide an efficient way to identify candidates.

The loading of co-catalysts on the surface of the host photocatalysts has been shown to be rather effective in inhibiting charge recombination. Alternative, more economical co-catalysts, such as the non-noble metals and other derived metal-based compounds, also need to be tested as possible substitutes for the most frequently used noble metals, such as Pt, which is very efficient but expensive. In addition, new insights are needed into the water-splitting mechanism, particularly regarding the identification of any thermodynamic and kinetic bottlenecks. Such determinations would facilitate the design of the most effective photocatalytic water-splitting systems.

Presently, the available efficiency for overall water-splitting systems for the simultaneous production of hydrogen and oxygen under visible-light irradiation is still low because of the fast charge recombination and backward reactions. To achieve enhanced and sustainable hydrogen production, the continuous addition of electron donors is required to make up half of the water-splitting reaction to reduce H2O to H2. These sacrificial electron donors can irreversibly consume photogenerated holes and thus prohibit undesirable charge recombination. Taking into account the decreasing cost of solar-to-H2 energy conversion, polluting byproducts from industries and the low-cost renewable biomass from animals or plants are preferential sacrificial electron donors in water-splitting systems. At little or no cost, they could be exploited to simultaneously accomplish the task of hydrogen production and that of waste treatment and biomass reforming. Nevertheless, such an admirable goal for the practical application of water-splitting systems is especially interesting considering worldwide energy and environmental concerns, but is still in its infancy.

The current lack of industrial applications of the semiconductor-based photocatalytic hydrogen generation is largely due to two reasons: the low photocatalytic efficiency and the lack of extensive studies for a successful scale-up of the laboratory setup to an industrially relevant scale.

In addition to TiO2, heterogeneous photocatalysts such as ZrO2, NaTaO3, BaTaO6, SrTa2O6, K2NbO4, and K2Ta2O7 can decompose water to evolve O2 and H2 without loading any co-catalysts under UV irradiation [282]. The activities of the majority of these photocatalysts are augmented by the loading of a co-catalyst, such as NiOx, as a proton-reduction site. In this regard, high-donor-doped layered perovskites loaded with NiO have demonstrated photocatalytic ability for water splitting under UV irradiation. These layered structures with a basic composition A2+mB2O5+m−2, where m=4 or 5, A=Ca or Sr, and B=Nb or Ti, showed elevated quantum yields and a stoichiometric evolution of H2 and O2. However, SrTiO3, KTaO3, Ta2O5, Rb2NbO4, K2La2Ti3O10, Rb2La2Ti3O10, Cs2La2Ti3O10, Cs2La2Ti3O10, Na2Ti6O13, and BaTi4O9 can also evolve O2 and H2 with the aid of co-catalysts, such as Pt, Rh, and RuO2 [282].
5. Challenges for refineries

In refineries, we expect the synthesis of clean fuels components (syngas to liquids, reformulated gasoline with solid acid alkylation to obtain branched C<sub>8</sub> alkanes of high octane number values), the reduction of S to less than 10 ppm after 2010 by the development of new catalysts and new reactor technologies and by bio-desulfitzation, the reduction of aromatics (hydrogenation, gasification, cracking), and the reduction of heavy metals from crude oil by bio-demetalization will predominate. High-octane non-aromatic blend stock that is sulfur and olefin free will be needed to meet the new specifications. The future production of hydrogen without the formation of CO<sub>2</sub> should come from photocatalytic splitting of water (vide infra) and the conversion of methane and light alkanes (C<sub>1</sub>–C<sub>3</sub>) to higher/aromatic hydrocarbons and hydrogen.

5.1. Fischer–Tropsch synthesis (FT)

In 1922, Franz Fischer and Hans Tropsch converted a CO/H<sub>2</sub> mixture to a mixture of hydrocarbons (HCs) and oxygenated compounds using an iron-based catalyst. The cobalt catalysts for this process were discovered a few years later. Although these processes are old technology, they are still relevant. Fischer–Tropsch (FT) synthesis is a heterogeneous catalytic process for the production of clean hydrocarbon fuels or chemicals from synthesis gas, which can be derived from a variety of non-petroleum carbon resources, such as natural gas, coal, biomass, oil sands, or oil shales [283]. During World War II, FT technology was used in Germany to produce synthetic fuel (16 kbarrels per day) on Co catalysts [284] and later, in South Africa (SASOL), in synergy with coal gasification to produce synthetic fuel because of an embargo. Later, SASOL switched to natural gas (NG) for the production of syngas for FT. The FT synthesis has received renewed interest in recent years because of the global demand for a decreased dependence on petroleum for the production of fuels and chemicals. The product distributions with conventional FT catalysts usually follow the Anderson–Schulz–Flory (ASF) distribution and are typically unselective with respect to the formation of hydrocarbons from methane to waxes. Selectivity control is one of the formidable challenges in this area.

The most common catalysts used in FT synthesis are still based on iron or cobalt compounds that work at high pressures (1–6 MPa) and at temperatures between 200 and 300 °C. Under these conditions, the fuel is of high quality because of the low aromaticity and the absence of sulfur. The iron-based catalysts produce gasoline, hydrocarbons, and linear alpha-olefins, as well as a generally unwanted mixture of oxygenates, such as alcohols, aldehydes, and ketones, and excessive amounts of carbon dioxide. With cobalt catalysts, high yields of long-chain linear paraffins, which can be efficiently transformed into valuable products (middle distillates) by hydrosprocessing, are possible. Moreover, the syngas step should be adapted to the type of catalysts to be used to optimize the CO/H<sub>2</sub> ratio in reference to the optimal ratio for the FT catalyst/reactor. To promote FT over methanation, the FT reactor typically operates at a low temperature (200–240 °C), a mild pressure (2–3 MPa), and in the presence of a catalyst (Co- or Fe-based). However, various catalysts have been tested in the FT reaction [285–287]. To optimize the overall liquid production, it is necessary to produce high molecular weight linear waxes for further hydrosprocessing steps. To explain the mechanism of the FT reaction, some authors have derived the Langmuir–Hinshelwood or Eley–Rideal types of rate expressions for the reactant consumption, where, in the majority of cases, the rate-determining step was supposed to be the formation of the building block or monomer, methylene.

Recent developments in core–shell-structured catalysts that contain conventional FT catalysts, such as Co/Al<sub>2</sub>O<sub>3</sub> as the core and zeolite (H-ZSM-5) membrane as the shell, have increased the selectivity to C<sub>5</sub>–C<sub>11</sub> isoparaffins because of the hydrocracking and isomerization ability of zeolite [288]. The use of mesoporous zeolite (meso-ZSM-5) as the support for Ru nanoparticles significant enhanced the selectivity to C<sub>5</sub>–C<sub>11</sub> hydrocarbons to greater than 80%, which was significantly higher than expected from the selectivity based on the ASF distribution (4–5%) [289]. The use of CNTs can also increase the selectivity to a particular fraction of hydrocarbons. For example, Ru/CNT gave a C<sub>10</sub>–C<sub>20</sub> selectivity of ~60% [290]. The confinement of iron oxide particles inside the CNTs or carbon spheres could increase the selectivity to C<sub>5</sub>+ because of the facile transformation of iron precursors to iron carbides, which are believed to be responsible for C–C coupling [291,292].

5.2. Hydrodesulfitzation (HDS) and fluid catalytic cracking (FCC)

Gasoline has the highest concentration of sulfur compounds in the FCC (fluid catalytic cracking) stage of the refinery process. Environmental regulations are becoming increasingly stringent with regard to the sulfur content in fuels. At the same time, olefins present in the FCC naphtha make a major contribution to the octane number in gasoline [293–295]. In this context, desulfitzation must be performed to hamper olefin saturation in FCC gasoline [296]. Hydrodesulfitzation (HDS) of petroleum feedstock is one of the most important processes in petroleum refining for the production of clean, high quality fuels [296–299]. Sulfur compounds in petroleum fractions include sulfides, disulfides, polysulfides, mercaptans, thiophene, benzothiophene and dibenzothiophene, but thiophene, benzo thiophene and dibenzothiophene are used in HDS studies as model molecules. For example, hydrodesulfitzation of thiophene is one of the most important reactions that occur in the second-stage hydrogenation of pyrolysis gasoline in olefin plants [300,301]. A two-stage hydrogenation process is usually used in industry to eliminate these impurities: (1) hydrogenation for selective hydrogenation of diolefins and (2) thiophene hydrodesulfurization. Therefore, there is a strong incentive to develop catalytic systems for the FCC/HDS processes. Sulfided Co–Mo or Ni–Mo(W)-based catalysts have been extensively used in industry for HDS reactions [302,303] and have attracted attention as catalytically active sites where Co decorates the edge sites of highly dispersed MoS<sub>2</sub> crystallites [304–308]. However, the precise structures of the active sites and the HDS reaction mechanism still remain ambiguous. The active sites of the catalysts are considered to be extensively promoted by their selective preparation. The use of a chelating agent in the preparation of HDS catalysts [309–312] has been found to be highly effective in increasing the amount of Co(Ni)MoS by increasing the coverage of Co(Ni) on the edges of MoS<sub>2</sub> particles. The preparation of HDS catalysts using citric acid as a chelating agent significantly improves their catalytic activity [313–316].

The literature contains reports of various attempts to develop selective catalysts for this purpose including oxides [317–322], zeolites [323–326] and mesoporous materials [327–329], clays [330–332] and noble metal catalysts [300,324,333–349]. Excellent studies were conducted on the mild oxidation of thiophenes and thioethers using “green” oxidizing agents [350] on mesoporous materials [351,352].

6. CO<sub>2</sub> emissions as a prospective source for fuels and chemicals [353–358]

CO<sub>2</sub> is a major contributor to the so-called greenhouse effect, which supposedly leads to warming of the earth and thus to
Changes in the climate. The energy sector, which is the largest source of CO₂ emissions, is responsible for approximately 25% of global CO₂ emissions. Great efforts have been conducted in the past to use carbon dioxide as a chemical raw material with a very low or even negative cost rather than as a waste, e.g., CO₂ reductions under photolrradiation, or under electrolytic conditions, or production of synthetic gas by reforming natural gas. However, many of these reactions produce rather simple molecules such as carbon monoxide and formic acid. CO₂ has the advantages of being non-toxic, abundant, and economical, attractive as an environmentally friendly chemical reagent, especially useful as a phosgene substitute. The largest obstacle for establishing industrial processes based on CO₂ as a raw material is its low energy level. In other words, a large energy input is required to transform CO₂. There are several methodologies to transform CO₂ into useful chemicals, such as the use of high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics; the choice of oxidized low-energy synthetic targets such as organic carbonates or the supply of physical energy such as light or electricity. Selecting appropriate reactions can lead to a negative Gibbs free energy of the reaction [353–358].

Possibilities for the chemical recycling of carbon dioxide to fuels have been studied largely as a complementary technology to carbon sequestration (CSS) and storage. CSS requires the minimization of hydrogen consumption to produce fuels [29,258], which can be easily stored and transported, and to use renewable energy sources. From this perspective, the preferable option is to produce alcohols (preferably C2H₅OH) by use of solar energy to produce the protons and electrons necessary for CO₂ reduction. The chemical transformation of CO₂ includes a reverse water–gas shift reaction and hydrogenation to produce hydrocarbons, alcohols, dimethyl ether and formic acid, a reaction with hydrocarbons to syngas (such as dry reforming of methane), and photo- and electro-catalytic and thermochemical conversions [257,258,359–361]. CO₂ can be used as a building block in organic syntheses to obtain valuable chemicals and materials has been discussed in many reports and review articles. The main applications of CO₂ as chemical raw materials [353] are syntheses of polycarbonates and polyurethanes. Organic carbonates are roughly categorized into cyclic and linear carbonates, which both compounds have three oxygen in each molecule, and are suitable from a thermodynamic point of view as synthetic targets starting from CO₂. Four industrially important organic carbonates are ethylene carbonate (EC), propylene carbonate (PC), dimethyl carbonate (DMC), and diphenyl carbonate (DPC). EC, DMC and DPC are useful intermediates for manufacturing polycarbonates through a non-phosgene process [353]. In addition, EC, PC and DMC are employed as electrolytes in lithium ion batteries and are widely used as aprotic polar solvents. Furthermore, the excellent properties of DMC as a fuel additive have attracted much attention. DMC can be synthesised from methanol and CO₂, over homogeneous catalysts or heterogeneous such as solid acid catalysts of zirconia modified by Ce and acid additives such as phosphoric acid, or as a support for heteropolyacids, or via cyclic carbonates (CO₂ with epoxides), the cycloaddition of oxiranes and oxetanes and CO₂ over e.g. CeO₂-ZrO₂ or homogeneous metal complexes catalysts, or copolymerisation of CO₂ and oxiranes on metal complexes, the synthesis of urea (CO₂+NH₃) and urethane derivatives, e.g. CO₂ + secondary or primary amines giving carbamic acid which reacts with organic halides or alcohols giving carbamates (urethanes) or are dehydrated to isocyanate without using phosgene, the synthesis of carboxylic acids, e.g. acrylic acid, the synthesis of esters and lactones by combining CO₂ with unsaturated compounds such as vinyl ethers, the hydrogenation and hydroformylation of alkenes by CO₂ and H₂, and so forth [353].

Currently, the utilization of CO₂ as a chemical feedstock is limited to a few processes, such as the synthesis of urea (for nitrogen fertilizers and plastics), salicylic acid (a pharmaceutical ingredient) and polycarbonates (for plastics). It is worth noting that the actual use of CO₂ corresponds to a small percentage of the potential CO₂ that is suitable to be converted into chemicals; thus, a chemical transformation of CO₂ may significantly contribute to a reduction of its emissions, in particular for the fuel pool, the worldwide consumption of which is two orders of magnitude greater than that of chemicals. Note that CO₂ transformation requires energy, which may produce CO₂. Thus, the importance of the transformation of CO₂ into useful chemicals should be closely related to the importance of utilizing a renewable feedstock [353].

Different options exist in heterogeneous catalysis for the conversion of CO₂. The hydrogenation of CO₂ to form oxygenates and/or hydrocarbons are the most intensively investigated area of CO₂ conversion. Methanol synthesis from CO₂ and H₂ has been investigated at the pilot-plant stage with promising results. An alternative possibility is the production of DME, which is a potential diesel substitute. Ethanol formation, either directly or via methanol homologation, and the conversion of CO₂ to formic acid are also potentially interesting routes. Methanol, ethanol, and formic acid may also be used as feedstocks in fuel cells, which provide a route to store energy from CO₂ and then produce electricity.

The hydrogenation of carbon dioxide to hydrocarbons consumes much more hydrogen (per unit of product) than the formation of oxygenates. Therefore, this route is, in principle, only valuable when hydrogen is made primarily from renewable or non-fossil resources; however, other thermodynamic aspects must also be considered. The dry reforming of methane with CO₂ is a known technology that is available on a nearly industrial scale, although the positive impact on CO₂ emissions is questionable [362–364]. Specifically, it is important to ensure that CO₂ emissions due to energy consumption are not greater than the amount of CO₂ consumed in the reaction. An improvement in the positive direction is tri-reforming, which operates autotermically and does not require a pure CO₂ feed stream; however, large-scale demonstration units are necessary [365,366].

The conversion of CO₂ at room temperature and atmospheric pressure using solar light represents a highly challenging approach to close the CO₂ cycle and develop approaches that mimic photosynthesis. An interesting solution could be a photoelectrochemical (PEC) reactor that operates in the gas phase and uses nanoconfined electrodes that differ from those used in conventional PEC systems, as described [247].

7. Activation and upgrading of light alkanes

Alkanes are currently two to three times cheaper than the corresponding olefins and are thus quite valuable for upgrading. Olefins are mainly used for polymerization processes. There are several possibilities to upgrade to higher alkanes (C₂–C₆). An isomerization reaction on an acid catalyst can yield branched alkanes of higher octane number. An acid catalyzed alkylation reaction on isobutane with butene can yield trimethyl pentanes of high octane number or other isomers, such as dimethyl hexanes, of much lower octane number [367–369]. The main industrial catalysts are HF and H₂SO₄ in solution [370], although significant efforts have been made in the past 30 years to find a solid substitute without yielding any reliable/promising process. No industrial processes could emerge as deactivation due to fouling by butene polymerization residues was too important and selectivity to TMP versus dimethyl hexanes (DMH) of low octane number was too low (50–60). Another approach is to proceed by dehydrogenation, e.g., on Pt-Sn/Al₂O₃, or by oxydehydrogenation of alkanes on V-based mixed oxides. The former reaction is endothermic and highly sensitive to deactivation by coke deposits [371–373]. The latter is exothermic with
low deactivation by coke fouling, but it may lead to total oxidation and CO₂ formation and, thus, to a lower selectivity to alkenes. A third way is oxidizing/ammonoxidizing the alkanes to the corresponding oxygenates or oxynitriles such as aceto or acrylo-nitriles, aldehydes, ketones or acids. Two processes have been developed industrially, oxidation of butane to maleic anhydride on a vanadyl pyrophosphate based VPO catalyst or ammonoxidation of propane to acrylonitrile on MoVTeNb mixed oxide catalysts. Maleic anhydride is a raw monomer for resin and for THF an industrial solvent produced by Reppe process of maleic anhydride reduction pd pd catalysis as well as a monomer for segmented polyurethanes (LYCRA®) and copolyester elastomers (Hytre®, Vynandel®). Vanadium-based catalysts [374] and in particular, vanadium phosphates (VPOs) are very well known as the only catalysts for industrial process of n-butane oxidation to maleic anhydride [375–378], which is a precursor of polyester resins [379]. In general, VPO catalysts are inexpensive and attractive in selective oxidation processes since they are environmentally friendly [380]. The reaction follows Mars van Krevlen mechanism where the adsorbed organic molecule is oxidized by lattice oxygen from the catalyst, which is subsequently restored by oxygen reaction feed. Acrylonitrile was produced in ammonoxidation reaction of propylene using Fe–Bi–Mo–O and Fe–Sb–O systems as catalysts but this process would be replaced in a near future by ammonoxidation of propane due to the lower cost and abundance of propane. Acrylonitrile is the main raw material for production of synthetic fibers, plastics, elastomers and polymers as styrene–acrylonitrile and acrylonitrile–butadiene–styrene. By polymerization of acrylonitrile with butadiene synthetic rubber is produced. This process includes multifunctional monolyses and ammoniates as catalysts. However, propane conversion is about ten times lower than that of propylene in the same conditions since the activation energy of C–H bond is higher. The more performing catalyst developed recently by Japanese industrialists [381,382] is a mixed MoVNBSe oxide active for the (amm)oxidation of propane to acrylonitrile acryl acid [381–384]. A process, designated AlkyClean using a solid acid catalyst (HY-zeolite based) and claimed to be competitive with other two processes, was proposed [355] by Akzo Nobel, ABB Lummus Global and Fortum with a demonstration unit constructed at Fortum facilities in Porvoo, Finland. The reaction is carried out in liquid phase at 50–90 °C with isobutane to olefin ratio (i/o) of 8 to 10 against 4–10 °C and i/o = 8–10 for H₂SO₄ and 32–38 °C and i/o = 12–15/1 for HF respectively. Regeneration was realized at 250 °C under hydrogen. For this research part see special issue of Appl Catal A, Ed. G.S. Patience, J.M. López-Nieto [385].

8. Waste air, water and VOCs treatments

Wet air oxidation (WAO) is a liquid-phase reaction between organic material in water and oxygen. The WAO process is used around the world to treat industrial wastewaters and sludges at moderate temperatures (180–315 °C) and at pressures from 2 to 15 MPa. Under these conditions, complex organic compounds are primarily oxidized to carbon dioxide and water, along with simpler forms that are biodegradable. Unlike other thermal processes, WAO produces no NOₓ, SO₂, HCl, dioxins, furans or fly ash. However, the efficiency of aqueous-phase oxidation can be significantly improved by the use of catalysts, either heterogeneous or homogeneous. Moreover, key points to be solved are the stability of the heterogeneous catalysts and the recycling of the homogeneous catalysts. Commercial catalytic WAO (CWAO) processes started as early as the mid-1950s in the USA. Several Japanese companies developed CWAO technologies that relied on heterogeneous catalysts based on precious metals deposited on titania or titania–zirconia. Compared with conventional WAO, CWAO offers lower energy requirements and significantly higher oxidation efficiencies. Further developments of this technology should include highly durable and low-cost catalysts. CWAO provides an environmentally attractive option to manage the growing problems of the treatment of organic sludge and toxic wastewater [386,387].

The treatment of toxic nitrogen-containing compounds, which are mainly produced in the chemical and pharmaceutical industries, is one of the major applications of the wet air oxidation (WAO) process. Many studies have dealt with the oxidation of aniline, which is often chosen as a model molecule of a dye–industry pollutant. Particular attention has been paid to selectivity toward organic by-products (especially azo, nitroso and nitro compounds, phenolic compounds and carboxylic acids) and inorganic forms of nitrogen (NH₄⁺, N₃⁻, NO₂⁻, NO₃⁻). Usually, similar catalysts can be used for the CWAO of oxygen-containing (phenol, carboxylic acids) and nitrogen-containing organic compounds. Ammonia is one of the most refractory by-products formed during catalytic WAO of nitrogen-containing organic pollutants and is itself a pollutant. Very high selectivities to dinitrogen have been obtained on certain noble-metal catalysts. As a rule, catalysts that are active and selective for ammonia oxidation are different (nature of active phase, support, etc.) from the solids proven to be the best catalysts for the CWAO reactions of organic compounds. Multifunctional catalysts are therefore required for the treatment of nitrogenous organic compounds.

Volatile organic compounds (VOCs) are significant atmospheric pollutants due to their high toxicity and malodorous nature. VOC emissions arise from mobile sources and industrial applications. In this context, the degradation of VOCs has become a major area of research in environmental protection during recent decades [388,389]. Common VOCs such as halogenated hydrocarbons, ketones, alcohols and aromatic compounds have been widely used in many industries and are often found in the emissions flow [390,391].

Traditional methods of removing VOCs from the polluted air stream include adsorption onto activated carbon or zeolite and thermal combustion. These methods have inherent limitations. The adsorption process includes recovery treatments that require the regeneration of the adsorbent and also requires durability, whereas the high temperature of VOC degradation makes thermal degradation not economically feasible.

Many advanced technologies have been developed for the rapid and economical removal of VOCs from indoor air. Among these, catalytic oxidation is the most innovative and promising approach. This oxidation process is promising for air purification because the pollutants can be oxidized to H₂O and CO₂. The catalysts play the most important role by converting polluting compounds into relatively harmless compounds at low operating temperatures. A series of catalysts were evaluated for VOC decomposition [388,389,392–402]. The most active catalysts are the noble metal catalysts dispersed on high surface area supports. The dispersion increases both the available metal surface area and the thermal stability. Many researchers have suggested that the performance of noble metal supported catalysts for the oxidation of VOCs is highly dependent on the oxidation state of the metal. Some authors have suggested that the oxide species are more active than the metallic species for catalytic oxidation, while others argue the opposite. In the case of catalysts with the same oxidation state, the particle sizes may play a more important role in the catalytic activity [403]. Several studies have shown a correlation between the catalytic activity and the oxidation state of the catalyst, the nature of the support, the metal-support interaction, and the morphology of the catalyst particles [389,403–417]. However, the use of noble metals leads to a high cost purification system and the natural reserve of noble metals is limited. Therefore, the substitution of noble metals with ubiquitous elements is required for environmental and economic reasons. Metal oxides have been reported as relatively
high activity catalysts for the complete oxidation of VOC [392,393]. Research efforts in this field are oriented towards the development of new catalytic materials with low manufacturing costs that show high activities at moderate temperatures.

9. Photocatalysis

In the 1930s, the term photocatalysis was introduced as a new branch of catalysis. Photocatalysis is defined as a change in the rate of a chemical reaction under the action of light in the presence of photocatalysts that absorb light quanta and are involved in the chemical transformations of the reaction participants [418,419]. The photocatalyst is defined as a solid that functions by photoinduced electron transfer at molecule–semiconductor interfaces [282,420–423].

Among photocatalytic applications, photocatalytic oxidation and the reduction of organic compounds in water have become important and have received considerable attention during the last few years [282,424–427]. These applications involve the oxidation or reduction of an organic compound to an intermediate that contains oxygen or to carbon dioxide, water, and a mineral acid if a heteroatom such as nitrogen or chlorine is present. The mechanism of the photocatalytic decomposition of organic compounds is supposed to follow these steps: under UV-light illumination, the absorption of photons creates an electron–hole pair if the photon energy is greater than that of the band gap; thereafter, the pairs migrate to the surface and are trapped by OH surface groups and other surface sites, thereby forming hydroxyl (OH⁻), hydroxylperoxide (H₂O₂) and superoxide (O₂⁻) radicals; these free radicals finally cause the oxidation of the organic compounds [425–428]. This process can be used in various areas such as the elimination of odor from drinking water, the degradation of oil spills in surface-water systems, and the degradation of harmful organic contaminants, such as herbicides, pesticides, and refractive dyes.

One of the most widely studied metal oxides is semiconducting TiO₂ [423]. Three common TiO₂ polymorphs exist in nature, which, in the order of abundance, are rutile, anatase, and brookite. An additional synthetic phase, called TiO₂(B), and some high-pressure polymorphs are also known [428]. The rutile and anatase polymorphs are primarily used in photocatalysis. Both the rutile and anatase crystal structures comprise distorted octahedra. In rutile, a slight distortion from orthorhombic geometry occurs, where the unit cell is stretched beyond a cubic shape. In anatase, the distortion of the cubic lattice is more significant, and thus, the resulting symmetry is less orthorhombic [429]. Titania, in anatase form, exhibits a strong photocatalytic effect, which generates electron–hole pairs. As a result, the material can harvest photons in the near-UV region (∼410 nm) to provide its surface strong oxidizing power to decompose organic molecules. Photocatalysis is a rapidly growing field of study that has attracted intense attention of chemical and materials researchers in recent years.

Even though TiO₂ exhibits excellent photocatalytic activities in the decomposition of VOCs and other organic compounds, the study new photocatalysts with different structures that exhibit higher activity is desirable. In this regard, the novel photocatalysts made of highly donor-doped (110) layered perovskites, which have recently been developed and were found to be much more efficient than bulk-type TiO₂. This higher activity results from the highly donor-doped electronic structure, which leads to a narrower depletion region and a more facile separation of the charge carriers.

Selective photocatalysis can be achieved using proper molecular sieves, such as the titanosilicate ETS-10, which provides an alternative approach. The photocatalytic activity of ETS–10 is due to the presence of photoexcitable Ti–O–Ti chains and the three-dimensional interconnected pore system of large 12-membered ring channels in its structure, which endow the material with excellent diffusion properties [430]. This regular channel system has a direct effect in determining the shape selectivity of the degradation process [431]. Another approach is the introduction of some transition metals, such as Cr, V, Fe, Cu, Mn, Co, Ni, Mo, or La, into the synthesis mixture of the MCM-41 and MMO [432]. The authors then demonstrated that the presence of the transition-metal salts in the gel during the hydrothermal synthesis process hinders the action of the template, which results in MCM-41 pores that are not well formed. These materials were then loaded with TiO₂ via the sol–gel method, and the activity of the TiO₂/TM–MCM–41 catalysts toward the degradation of 4-chlorophenol was tested in the presence of UV and/or visible light. The results showed that, although some metals were deleterious, others improved the performance of the photocatalysts and even enabled them to utilize visible light. A wide range of other semiconductors and materials have been tested for photocatalytic activity. In general, they have been found to be less active than titanium dioxide; significant work has been conducted with V₂O₅, Fe₂O₃, ZnO, ZnS, Cds, Pt/CdS, ZnTe, ZrTiO₄, MoS₂, SnO₂, Sb₂O₅, Sn/SbO₂, CeO₂, WO₃, and Nb₂O₅.

10. Solar photon conversion [433]

The efficient and cost-effective direct conversion of solar photons into solar electricity and solar fuels is one of the most important scientific and technological challenges of this century. At least 20 TW of carbon-free energy (1.5 times the total amount of all forms of energy consumed today globally), in the form of electricity and liquid and gaseous fuels, are estimated to be required by 2050 to avoid the most serious consequences of global climate change and to ensure an adequate global energy supply that will avoid economic chaos. However, for solar energy to contribute a major fraction of future carbon-free energy supplies, it must be priced competitively with, or perhaps even be less costly than, energy from fossil fuels, nuclear power and other renewable energy resources. The challenge of delivering very low-cost solar fuels and electricity will require breakthrough advances in both fundamental and applied sciences. These required advances include new concepts for low-cost photovoltaic (PV) energy based on chemistry, solar water splitting, redox catalysis for water oxidation and reduction, photoelectrochemical energy conversion, and photoinduced electron transfer. Note that the total energy capacity at the end of 2009 was approximately 7 GW-years (0.2% of global electricity usage). Thus, there is potential for the PV industry to grow substantially in the future (by a factor of 100–300) for it to provide a significant fraction of the total global electricity needs (currently approximately 3.5 TW).

Presently, solar-derived fuels are produced from biomass (labeled as biofuels) and are generated through biological photosynthesis. The global production of liquid biofuels in 2009 was approximately 1.6 million barrels/day, equivalent to a yearly output of approximately 2.5 EJ (about 1.3% of global liquid fuel utilization). The direct conversion of solar photons to fuels produces high-energy chemical products that are labeled as solar fuels; these fuels can be produced through nonbiological approaches, which are generally referred to as artificial photosynthesis. The feedstocks for artificial photosynthesis are H₂O and CO₂, which react either as coupled oxidation–reduction reactions, as in biological photosynthesis, or by first splitting H₂O into H₂ and O₂ and then reacting H₂ with CO₂ (or CO produced from CO₂) in a second step to produce fuels through the known chemical routes previously described such as syngas, water–gas shift reaction, or alcohol synthesis. The solar generated H₂ can itself be used as a gaseous fuel, such as in fuel cells. However, currently, no solar-fuels industry exists. Significant
research and developments are required to create a solar–fuels industry, which constitutes one of the key challenges for the future.

11. Green chemistry – selectivity in catalysis

A new area of research emerged in the 1990s based on the 12 principles of green chemistry [434,435] including the atom economy, the use of reusable catalysts and the minimization of waste [436]. The principle of green chemistry is that rather than using every possible chemical process, only those that are environmentally benign should be used [437]. Within green chemistry, there is an increasing interest in developing novel materials that can be applied as heterogeneous catalysts for chemical processes, replacing effective but hazardous chemicals, such as H$_2$SO$_4$, HF and AlCl$_3$. Processes using these novel compounds, such as zeolites, have very high E-factors, a quantitative parameter that can be used to assess the environmental acceptability of a process [438]. It corresponds to the ratio of kilograms of waste divided by kilograms of product. For example, the zeolites used in the petrochemical industry have an E-factor of 0.1 (high greenness) and have been widely implemented in very large scale industrial processes because they can easily be separated from the products and reused. Because of their lack of toxicity, they constitute a prime example of green chemistry.

Moreover, a challenge for the XXIst century is the control of technological processes in the chemical, petrochemical, and pharmaceutical industries to develop atom– economical, environmental friendly processes without by-products [3,439–441]. The chemical and petrochemical industries have always attempted to improve process efficiency and reduce waste using heterogeneous catalysts [293,442–447]. High selectivity is the most important aspect of a catalyst. The noble metal catalysts show high activity and selectivity, but suffer from several drawbacks, including sensitivity to metal site poisoning, the limited abundance, and the environmental impact of these metals. As a result, the tendency now is to replace the noble metal catalysts [199,201,447–449]. In light of the ubiquitous restrictions imposed by environmental and economical legislation, use of nanostructured porous molecular sieves, which can be very selective for the desired products at low temperature and are recyclable, is one alternative to the use of traditional noble metal catalysts. We have summarized in Fig. 16 the main factors that influence selectivity in catalysis and that must be taken into account in all processes.

12. Major challenges for the future

12.1. Scientific challenges

These challenges cover the design, preparation, evaluation, and optimization of new catalytic materials, the probing/understanding of catalyst behavior (activity and selectivity) at the molecular level, the enhancement of technology transfer between academia and industry (bridge the gap), the development of multifunctional reactors, combinatorial catalysis, high-throughput catalyst testing, the characterisation of catalysts using highly improved physical and chemical techniques, particularly used under working conditions and simultaneously with several other techniques together [451]. Heterogenisation of homogeneous catalysts (vide supra Section 2.9), the coupling of chemical and engineering kinetics, and so forth.

12.2. Environmental challenges

These challenges consist of minimizing and/or managing by-products by converting them to useful products, replacing multistep processes by direct schemes to avoid exposure to dangerous intermediates, reducing effluents (gases, solvents, salts), and using sustainable sources of raw materials and energy supplies. The development of biomass for raw chemical materials and energy sources should become a key point for the future. The development of biorefineries is in its infancy; however, with reference to the past the in petroleum industry, one may imagine that great improvements will be developed with continuous research in this field.

12.3. Economical challenges

Economical challenges naturally correspond to the use of cheaper, readily available raw materials, increased productivity, decreased lag-time between discovery to commercialization, the discovery novel catalytic reactions, the development of processes that are more selective and intensive, the accelerated discovery of new catalysts–based on non noble metals [199,201], and the evaluation and scale-up of processes.

12.4. Energy challenges

Energy challenges correspond to reduce energy consumption, e.g. by favouring of hydrogen production as a source of energy and as an important chemical material, to develop efficient water-splitting technologies, and to enhance uses [452] of biomass and other renewable sources, such as solar, wind, hydroelectric, and nuclear energies. All these technologies must be developed as alternative sources to fossil energies. One is still very far from replacing fossil energies, and great effort is required on a short time scale. The future will rely on solar energy and the implementation of efficient methods for electrical energy storage [450,453]. However, significant scientific advancement is still required for the practical and safe deployment of both of these technologies. In 2005, 7% of the world energy use was derived from nuclear power (Fig. 13), 10% was derived from biomass, 2% was derived from hydroelectric sources, and a mere 1% of the energy consumed was obtained from alternate renewable resources. Closer examination of the tiny 1% fraction shows that both solar energy in the form of photovoltaics and wind power are drastically underemployed (Fig. 13). These technologies, of course, represent two renewable resources of an infinite supply.

12.4.1. Challenges in automotive catalysis

Since the introduction of exhaust gas converters in cars in 1976 by Ford, many advances have been realized in reformulated gasoline or diesel, in particular emission/trapping control and in
Table 6

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<tr>
<th>Challenge</th>
<th>Drivers</th>
<th>Problem</th>
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<tr>
<td>Lean burn gasoline engine</td>
<td>Efficiency higher by ca. 25%</td>
<td>NO\textsubscript{x} trapping; SO\textsubscript{x} tolerant traps</td>
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<tr>
<td>Dry particulate emissions from diesel engines</td>
<td>DOC reduces SO\textsubscript{2}, HC, and CO\textsubscript{x}; no current catalyst/system to treat dry soot</td>
<td>Catalyst to lower lightoff T of soot; addition of Cu and Ce-organometallics to fuel</td>
</tr>
<tr>
<td>Diesel engine lean NO\textsubscript{x}</td>
<td>Direct decomposition or reduction of NO\textsubscript{x} in O\textsubscript{2}-rich atmosphere</td>
<td>Larger operating window for PM or BM-catalysts, NH\textsubscript{3} or urea SCR</td>
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13. Conclusions

As we have described in this review, our dependence on fossil fuels (coal, petroleum, and natural gas) is largely due to their chemical energy being the most convenient and useful form of transportable energy. However, the extensive use of fossil fuels has dramatically influenced the environment and peoples’ health, while world reserves are diminishing inexorably, although new fields are still being discovered and although methane hydrates may provide a substitute for some time. This situation cannot last for long, and substantial advances are urgently needed.

We have also shown that the solution to the challenge of clean energy can arise from simple components: sunlight and water \[455\]. Sunlight and water are infinite resources and can provide the required diversity of energy supplies. To store energy from sunlight, water can be split to generate hydrogen, a clean and portable energy carrier that can then be used to supply electricity when needed. High-performance, light-weight batteries can be used to power electric vehicles. However, such technological advances require systems that are capable of producing electricity, breaking H\textsubscript{2}O bonds with the separation of H\textsubscript{2} and O\textsubscript{2}, and storing the energy either in batteries or as molecular hydrogen. Currently, such systems pose formidable challenges in terms of the required materials, efficiency, cost, and design of practical devices.

The locus of activity in catalysis continues to move. In the eighteenth and nineteenth centuries, major discoveries and developments were performed in Europe. In the twentieth century, both Europe and the USA were the major contributors, although Japan and Korea also provided important efforts and discoveries in the second half of the century. For the twenty-first century, China, Korea, Japan, and other Asian countries are expected to lead in the field of catalysis.

At the end of the last century, major large chemical industrial companies have more or less abandoned large catalysis research centres within their laboratories. They now rely on catalyst producers, institutes and/or academic researchers to discover new catalysts or develop new technologies.

The development of surface, bulk and in situ characterisation techniques \[451\], molecular modelling, and advanced synthesis methods have transformed the preparation of solid catalysts and the characterisation of their physical and chemical (catalytic) properties from an art into a science. Such a trend should and will continue in the future with the new generations of scientists, engineers and researchers.

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