# Metal Oxides in Heterogeneous Oxidation Catalysis: State of the Art and Challenges for a More Sustainable World

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# Metal Oxides in Heterogeneous Oxidation Catalysis: State of the Art and Challenges for a More Sustainable World

Jacques C. Védrine*[a]

This Review presents current knowledge, recent results, and challenges for the future in heterogeneous oxidation catalysis in liquid and gaseous phases on solid metal oxide catalysts. Metal oxides that are used as catalysts and their main structures and properties are summarized, as well as their catalytic properties in selective and total oxidation reactions, which were studied intensively, experimentally and theoretically, by Professor Jerzy Haber during his scientific life. Some emphasis is placed on the classical and unusual catalyst activation proce-
dures for improving catalytic properties for better efficiency. For a more sustainable world, several examples are given of the oxidation of biomass derivatives to synthesize valuable chemicals and of other applications of metal oxides, such as depollution, photocatalysis, hydrogen production and fuel-cell components. The importance of metal oxide catalysis in environmental and green chemistry and sustainability is discussed, and challenges for the future are considered.

## 1. Introduction

Catalysis plays a major role in chemical, physical, and biological sciences. Since the 1950s, it has become one of the most important fields in industrial chemistry, as some 85–90% of chemical processes include at least one catalytic step (Figure 1), and, more recently, in environmental and green chemistry for a more sustainable society.[1, 2]
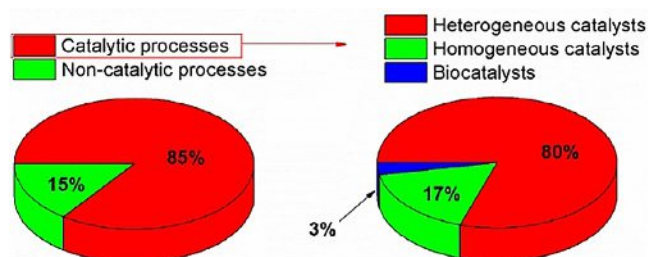


**Figure 1.** Catalytic processes in chemical industry and heterogeneous catalysis compared to other catalytic processes. Reproduced from Ref. [3].

Developing active, selective and energy-efficient heterogeneous catalytic processes has become a key factor in a sustainable future and is quite promising for the eventual transition to carbon-neutral operations.[4, 5] The design and implementation of robust and selective heterogeneous catalytic processes are expected to have a positive impact on the environment. It has long been recognized, since Berzelius in 1836,[6] that the main role of a catalyst is to decrease the activation energy of a chemical reaction and, in a multi-product reaction, to favor the most important one, that is, to favor selectivity, which is now a major concern to avoid the formation of unwanted byproducts, even at the expense of the reaction conversion, that is,

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catalyst activity. Catalysis helps to decrease atmospheric pollution through the design of environmentally friendly technologies for more efficient and more selective reactions, for pollutant abatement and wastewater treatment and is considered to be a pillar of green chemistry in the preservation of our environment.

Among all catalysts and all catalytic reactions performed industrially, metal oxide catalysts have become essential in most refining and petrochemical processes, in synthesizing specialty chemicals and, more recently, in improving environmental issues, in particular for depollution by maximizing reaction selectivity to avoid waste byproducts. This holds particularly for the pharmaceutical and fine-chemicals fields. Metal oxide catalysts became prominent in the mid-1950s, when they were found to effectively catalyze a wide variety of oxidation, hydrotreating and acid–base reactions, particularly in petroleum chemistry. In this Review, major types of metal oxide catalysts and processes that use these catalysts are reviewed, but the major focus is on oxidation reactions in gas/solid and liquid/solid phases with solid metal-oxide-type catalysts, whether bulk or supported, in coherence with Jerzy Haber's own scientific interests.[7, 8] In other words, metals and multimetal catalysts, supported or bulk carbons (graphene, carbides), sulfides and so forth, are excluded or just mentioned, although they constitute a large part of the field of heterogeneous catalysis, in particular for petroleum refining and treatment, petrochemicals and specialty chemicals syntheses. By extension of Jerzy Haber's contribution to the science of metal oxides, this Review considers also some aspects of semiconductors, fuel cells, new energy carriers such as hydrogen, and biomass conversion to give new raw materials for a more sustainable society. This Review deals with selective oxidation reactions that are involved in many industrial processes, such as those leading to olefins from alkanes or aldehydes, carboxylic acids and nitriles from olefins or alkanes in petrochemical industries, and deals also with total oxidation, used mainly in suppressing atmospheric pollution, as well as pollutant degradation in gas and liquid phases and for wastewater treatment.

In catalysis, the activity of metal oxides is enhanced on decreasing their particle size to the nanoscale, which results in improved catalytic activity per unit weight. The objective of early studies was mainly to study the size effect, but it has recently shifted and broadened to the effect of the oxide particle morphology related to the method used to prepare the catalysts. Recent research in catalysis science of metal oxides has

permitted the synthesis of catalysts with high selectivity by means of new preparation and activation procedures.[9–11] It is well accepted nowadays that the performance of a solid catalyst depends on the size of its solid particles, their shape, which may favor certain facets and is important for structure-sensitive reactions,[12,13] their crystallinity, their chemical composition (bulk or surface), and their preparation and activation procedures. New strategies for the preparation of metal oxide catalysts have resulted in the development of catalysts exhibiting active single sites that lead to 100% selectivity, at least theoretically. Nanocrystals, with sizes of a few nanometers, show the highest catalytic efficiencies, as the number of surface sites is high. However, the use of a support, such as silica, alumina, silica–alumina, carbons, zeolites, mesoporous silicas as MCM-41, SBA-15, or metal–organic frameworks (MOFs), is also an important factor, as it may favor high dispersion of metal oxide particles and synergistic activation of substrates, increase electron conductivity (an important parameter in redox reactions), thermal conductivity (an important factor for exo/endothermal reactions in industrial reactors), and so on. The activity, selectivity, resistance to deactivation and ability for regeneration are the properties that characterize the usefulness of catalysts, and they have been improved in the last sixty years by advanced

Jacques Védrine was awarded his Ph.D. degree at the University Claude Bernard, Lyon-1 (1968). He worked at Institut de recherches sur la catalyse (IRC), now Institut de recherches sur la catalyse et environnement de Lyon (IRCELyon), in Lyon-Villeurbanne, France up to 1998 and was deputy director for the last ten years. He then moved to the chemistry department at Liverpool University (1998–2003) as full professor and deputy director of the Leverhulme Centre for Innovative Catalysis (LCIC) and then to Paris part time at the Ministry of Higher Education as chargé de mission at MSTP and part time at Ecole Nationale Supérieure de Chimie for three years before joining his present laboratory, Laboratoire de Réactivité de Surface at Sorbonne University. He was elected president of Division de Catalyse de la Société Française de Chimie (1994–1997), a member of the French national committee of scientific research (1996–2001), and a member of the EUROCAT group in the 90s sponsored by the Conseil de l'Europe. He was elected president of the European Federation of Catalysis Societies (EFCATS, 1997–1999) and of the acid–base group. He has served as visiting professor at Tsinghua University, Beijing in 2010 and at Xiamen University in 2011. He was an editor for *Applied Catalysis A: General* (1981–2014) and has authored more than 400 publications in international journals, seven books on catalysis, and presented at 250 conferences, including more than 30 plenary lectures and 50 invited or keynote lectures. His scientific interests cover heterogeneous catalysis, combinatorial catalysis, and physical techniques of catalyst characterization. He has edited several books on physical techniques used for characterizing heterogeneous catalysts.

research and by improved chemical engineering aspects of reactors in industrial catalytic processes that use metal oxides.

Energy consumption is increasing continuously with time and because the classical sources of energy (oil, natural gas, coal, shale oil) are inexorably decreasing, it is urgent not only to decrease energy consumption in our everyday life and also in chemical processes, particularly in developing new catalytic processes with low energy consumption, but also to find new energy sources. Fossil fuels account for 85% of total energy supplies (Figure 2) and it is expected that they will still supply more than three-quarters of energy demand by 2035.[14] Global annual energy demand of over 12 billion tons of oil equivalent (Btoe) results in the emission of 39.5 Gt of $CO_2$, and the annual $CO_2$ emission should increase to 75 Gt of $CO_2$ when future energy demand doubles by 2050.
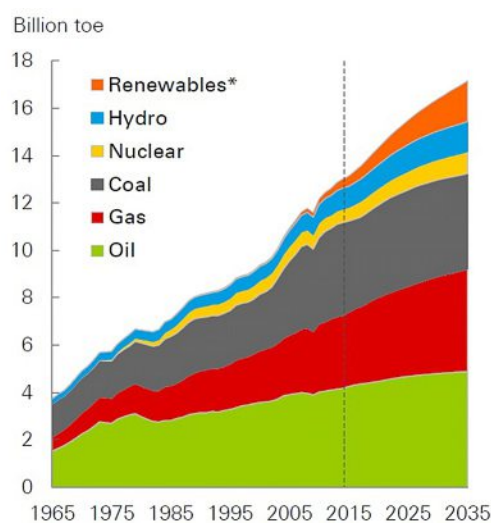


**Figure 2.** Primary energy consumption by fuel (toe = tonnes of oil equivalent). * Renewables includes wind, solar, geothermal, biomass, and biofuels. Reproduced from Ref. [14].

## 2. Main Metal Oxide Catalysts and Heterogeneous Oxidation Catalysis

### 2.1. General features of the field

As mentioned above, metal oxide catalysts are involved in the majority of acid–base and selective- and total-oxidation industrial catalytic processes.[15–17] These catalysts include simple oxides such as silica, alumina, silica–alumina, hydrotalcites, layered clays, zeolites, titania, zirconia, ZnO and CuO, porous and mesoporous metal oxides such as MOFs, complex oxides such as polyoxometalates (POMs) of Keggin or Dawson type, phosphates (e.g., $(VO)_2P_2O_7$, $FePO_4$, silica phosphoric acid), multicomponent mixed oxides (e.g., molybdates, antimonates, tungstates, MoVTe(Sb)NbO), perovskites, hexaaluminates, and so forth. Some of them have specific arrangements of $MO_6$ (M = Mo, V, Te, Nb, etc.) octahedra (Figure 3).[18]

These metal oxides have specific properties such as acidity and/or basicity (Lewis and/or Brønsted) and redox behavior (if transition metal ions are present), which lead to particular cata-
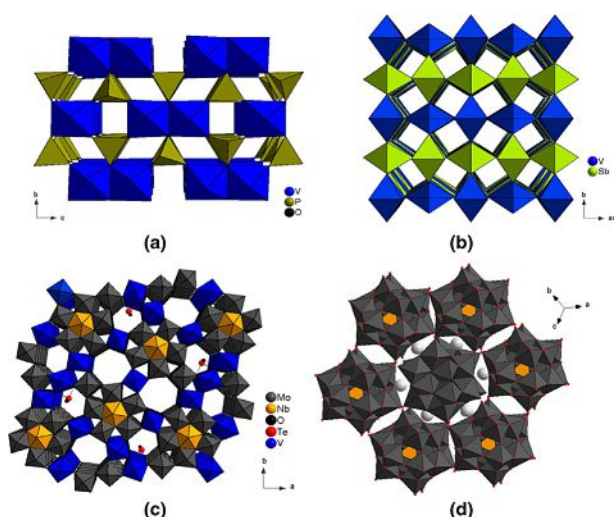
**Figure 3.** Structures (composed of $MO_6$ octahedra) of the most studied catalysts in alkane partial oxidation: a) Vanadyl pyrophosphate (VPO), b) VSbO rutile phase, c) M1 phase MoVTe(Sb)NbO, and d) Keggin molybdophosphoric acid. Adapted from ref. [18b] with permission from Elsevier.

lytic properties. They are also the basis for mono- or multimetal catalysts, for hydrodesulfurization (HDS) reactions ($CoMoO_4$-, $NiMoO_4$-, or $NiWO_4$-based). Their main catalytic domains cover oxidation (selective or total), acid and base reactions, hydrogenation, hydrotreating, photocatalysis, and depollution ($deNO_x$, $deSO_x$, wastewater treatment and biomass conversion). Metal oxides may also be used simply as supports of active phases, for example, silica, alumina, silica-alumina, mesoporous oxides, hierarchical porous oxides, or MOFs, which may influence catalytic properties owing to synergistic interactions, electron conductivity and/or thermal conductivity effects, which stem from metal oxide–support interactions.

Solid acid and base metal oxide catalysts are mainly used in refining and petrochemical processes. Many of them are replacing homogeneous catalysts to decrease the E-factor, defined by Sheldon[19] as weight of waste/weight of product. At the origin of green chemistry in the early 1990s, the E-factor was conceived for evaluating the environmental impact of chemical processes. It was calculated that, for refining and

bulk chemicals, E-factors are approximately 0.1 and 1–5, respectively, and for fine chemicals and pharmaceuticals they are 5–50 and 25–100, respectively. Although the annual production scales of fine chemicals and pharmaceuticals are much smaller ($10^2$–$10^4$ and $10$–$10^3$ t, respectively) than those of refining and bulk chemicals, the amounts of waste produced are comparable. Hence great efforts are required to improve E-factors in all industrial processes and this has led to intensive research both in academia and in industry. The number of processes that use heterogeneous acid and base catalysts rather than homogeneous acid and base catalysts for fine-chemical synthesis is limited at present, but increasing with time. This represents a great challenge for the future. Some industrial applications of metal oxides are summarized in Table 1.

Metal oxides[5, 20] are a class of inorganic materials that have applications as sensors, catalysts, and in fuel cells. Metal oxide surfaces are terminated by $O^{2-}$ anions, the size of which is generally larger than that of the $M^{n+}$ cations, and this results in lowering the coordination of surface $M^{n+}$ cations with respect to the bulk and their accessibility to reactant molecules. Moreover, metal oxides contain different types of defects and sites [anionic and cationic vacancies (□), kinks, steps, terraces], which play a determining role in the catalytic phenomenon, for instance, by resulting in structure sensitivity of metal oxides to catalytic oxidation reactions.[12, 13] This surface unsaturation is usually compensated by a reaction with water, leading to the formation of surface hydroxyl groups according to $□ + O^{2-} + H_2O \rightarrow 2\,OH^-$, and thus to specific acid–base and redox properties.

Single or complex metal oxides based on first-row transition metals show a wide variety of nonstoichiometric features, as in the case of $A_xBO_3$ perovskites exhibiting cation deficiency in A or B sites. These nonstoichiometries and vacancies greatly influence the catalytic properties owing to the presence of defects or changes in redox and electrical properties of the solids. For instance, $WO_3$ is an insulator, whereas $A_xWO_3$ is a semiconductor at small $x$ values and metallic at high $x$ values. Oxygen-deficient perovskites, which have attracted much attention in the past 30 years, exhibit high oxygen storage capacity, like ceria-doped oxides, and interesting redox properties, which are useful for total oxidation reactions or for $deNO_x$

**Table 1.** Some important heterogeneous metal oxide catalysts used industrially and prepared classically by precipitation or co-precipitation.

| Catalysts | Important applications |
| --- | --- |
| $SiO_2$–$Al_2O_3$, acid zeolites | acid-catalyzed reactions, for example, FCC, isomerization |
| $Fe_2O_3$, $CoO_x$ | Fischer–Tropsch reaction, ethyl benzene dehydrogenation to styrene |
| $TiO_2$ | major component of $deNO_x$ catalysts and photocatalysts |
| $ZrO_2$–$SO_4^{2-}$ | isomerization |
| Cu–$ZnO$/$Al_2O_3$ | methanol synthesis from $H_2$/CO mixtures |
| $(VO)_2P_2O_7$ | selective oxidation of butane to maleic anhydride, of pentane to phthalic anhydride + maleic anhydride |
| $FePO_4$ and its hydrates | oxidation of methacrolein to methacrylic acid |
| Cu–Cr oxides | hydrogenation, combustion reactions |
| $AlPO_4$ | acid-catalyzed reactions, polymerization |
| Sn–Sb oxides | selective oxidation, as propene to acrolein or isobutene to methacrolein |
| Bi molybdates | propene selective oxidation/ammoxidation to acrolein/acrylonitrile |
| V–Mo oxide | selective oxidation of acrolein to acrylic acid |
| MoVTeNbO | direct propane (amm)oxidation to acrylic acid (acrylonitrile) |

and deSO$_x$ reactions. For instance, in fully oxidized CaMnO$_{3-\delta}$ and CaFeO$_{3-\delta}$ perovskites, Mn and Fe are in the $+4$ oxidation state, $\delta=0$ and the material can accommodate up to 17% oxygen vacancies without losing its structure. The Sr$_{1-x}$La$_x$Co$_{1-y}$Fe$_y$O$_{3-\delta}$ series, with brownmillerite-type oxygen defects, exhibits high electronic/oxygen-ion mobilities. Such types of materials have been studied particularly for depollution applications.[21] Details of these solid metal oxide materials, of the creation of defects and vacancies and their influences on electrical, thermal and ion mobilities can be found in reviews.[20,22] Their subsequent influences on catalytic properties, particularly for depollution reactions, can be found in Ref. [21].

Methods for the preparation of solid catalysts[9–11] can involve various different procedures, particularly co-precipitation at a given pH (mainly used in industry), sol–gel processes, "chimie douce" (soft chemistry), and hydrothermal synthesis, for example, of zeolitic and microporous materials, and also recently of hierarchical microporosity for multiple applications.[23] Such materials are often precursors of active catalysts and must be activated by thermal treatment to eliminate inorganic anions (e.g., sulfate, nitrate, chloride), organic templates or surfactants under given conditions (e.g., reducing or oxidizing or under catalytic conditions), atmospheres, pressures, time on stream, and so on. However, unconventional activation methods that are nonthermal have also been developed with no external source of heating. They are based on ultrasound (US) or microwave (MW) irradiation, ball milling (mechanical grinding) and electrochemical and photo-activated processes. In such cases, the catalysts can be activated 1) by the technology itself through the action of light, pressure, electric field, waves and so forth or 2) by heat generated in situ (MW). These activation processes are summarized in Figure 4. Eco-friendly physical ac-
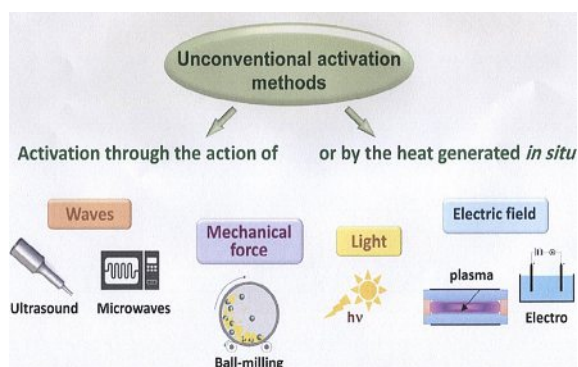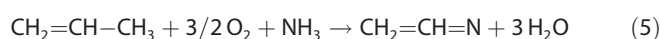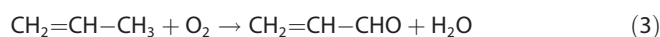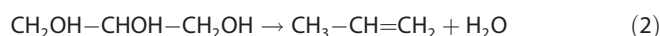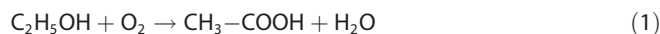


**Figure 4.** Nonthermal technologies for catalyst activation that do not require any external usual source of heating.

tivation methods[24,25] such as sonochemistry, MW, mechanochemistry, electrochemistry and photochemistry offer challenging opportunities for the development of clean, selective and energy-efficient activation strategies, both for the production of high value added compounds and for pollutant abatement. Several examples are given in Sections 2.2 and 3.

## 2.2. Recent developments in academia and industry and challenges in heterogeneous catalytic oxidation reactions

Industrial processes involve mainly selective (partial) and total oxidation reactions. They use mainly redox metal oxides, although noble metals are also used for total oxidation. Two different types of catalytic C—H bond activation are involved in partial oxidation, that is, activation by transition metal ions that exchange redox equivalents with the feed molecule (the well-known Mars–van Krevelen mechanism[26]) and activation of the oxide by direct exchange of redox equivalents between a hydrocarbon molecule and a surface oxygen species.[27] In the former case, support effects depend on their reducibility, for example, when comparing the behaviors of V$_2$O$_5$/CeO$_2$ and V$_2$O$_5$/SiO$_2$. The rate-determining step is the first H abstraction by an M—O bond according to: $O=M(d^n)+H-CH_2R \rightarrow HO-M(d^{n+1})+{}^{\bullet}CH_2R$. The latter case corresponds to oxidative CH$_4$ coupling on Li-doped MgO. However, recent theoretical studies[28a] have shown that the C—H activation is not due to homolytic splitting involving atom transfer to [$^{\bullet}$O-Li$^+$]$_{MgO}$ sites, as was suggested by Lunsford,[28b] but rather to CH$_4$ heterolytically chemisorbed on morphological facets according to: [Mg$^{2+}$ O$^2$]$_{MgO}$ + H—CH$_3$ + O$_2 \rightarrow$ [(MgCH$_3$)$^+$HO$^-$]$_{MgO}$ + O$_2 \rightarrow$ (O$_2$$^{\bullet-}$)[Mg$^{2+}$ HO$^-$]$_{MgO}$ + $^{\bullet}$CH$_3$, in which surface O$_2$ accepts an electron to form a superoxo surface species.

Selective oxidation of many organic compounds is one of the major fields for heterogeneous catalysis and its industrial applications.[29] For instance, selective oxidation of alcohols to carbonyl compounds (e.g., aldehydes, ketones, carboxylic acids, esters) is an important reaction for organic synthesis and a key domain for industry, particularly for pharmaceutical products, cosmetics, agrochemicals and lubricants,[30] as well as in the oxidation of long-chain alkanols, compounds having low reactivity, hydrophobicity and high boiling and melting points.[31] Conventional processes use stoichiometric oxidants, with a rather negative environmental impact. Implementation of green chemistry principles for these chemicals requires new catalysts, for example, gold and silver metallic nanoparticles, new processes using air or oxygen as oxidants, and reaction temperatures and pressures as low as possible. V- and Nb-containing tungsten bronzes (e.g., W–V–O and W–Nb–O on KIT-6 as inert support) have been suggested[32] for the aerobic transformation of ethanol into acetic acid and glycerol into acrolein/acrylic acid/acrylonitrile according to Equations (1)–(5):

$$C_2H_5OH + O_2 \rightarrow CH_3-COOH + H_2O \tag{1}$$

$$CH_2OH-CHOH-CH_2OH \rightarrow CH_3-CH=CH_2 + H_2O \tag{2}$$

$$CH_2=CH-CH_3 + O_2 \rightarrow CH_2=CH-CHO + H_2O \tag{3}$$

$$CH_2=CH-CHO + O_2 \rightarrow CH_2=CH-COOH + H_2O \tag{4}$$

$$CH_2=CH-CH_3 + 3/2\,O_2 + NH_3 \rightarrow CH_2=CH=N + 3\,H_2O \tag{5}$$

Gas- and liquid-phase oxidation of 2-methyl-1,3-propanediol (C$_4$H$_{10}$O$_2$) to methacrylic acid (C$_4$H$_6$O$_2$) according to C$_4$H$_{10}$O$_2$ + 2 O$_2 \rightarrow$ C$_4$H$_6$O$_2$ + 2 H$_2$O was shown[33] to occur over heteropoly-

acid catalysts, for example, of the Cs Keggin type with inserted V atoms and Cu promoter, such as $Cs_x(NH_4)_{3-x}PMo_{12}O_{40}(VO)Cu_{0.5}$, which replace acetone cyanohydrin [$(CH_3)_2C(OH)CN$] in the ACH process, which is known to provide large quantities of unwanted ammonium bisulfate byproduct due to facile decomposition to acetone and hydrogen cyanide, which is particularly toxic. This is an important improvement, as methyl methacrylate can be polymerized to poly(methyl methacrylate), which is known as Plexiglass or Altuglass and is used for coatings and paints.

Light olefins ($C_2$–$C_4$) are important chemicals, particularly for their polymerization to polyethylene and polypropylene, the strongly increasing demand for which has led to intensive research into new processes and technologies. The main industrial process is the direct dehydrogenation (DH) of light alkanes such as ethane, propane and isobutane to their corresponding olefins, which is an endothermic and thermodynamically limited reaction. It is still used commercially in well-established industrial processes such as Catofin (Lummus), Olefex (UOP), Linde-BASF, Snamprogetti-Yarsintez and Star (Philipps petroleum) with chromia–alumina in a fixed bed, supported Pt in a moving bed, chromia–alumina in a fixed bed, chromia–alumina in a fluid bed and supported Pt in a moving bed, respectively. However, endothermicity is a strong limitation, and high coke formation, due to thermal cracking, necessitates frequent catalyst regeneration, Moreover, olefin yield is thermodynamically limited. These drawbacks make the process unattractive and have opened an opportunity for processes involving transformation and oxidative dehydrogenation (ODH) of biomass derivatives. For more sustainable products, many efforts have been devoted to conversion of biomass compounds to olefins or oxygenates[34–36] through processes such as fermentation, gasification, cracking, oxidation and deoxygenation of biomass derivatives. However, none of these processes has yet attained sufficient productivity to be commercialized and to replace the DH processes. This is a highly promising and challenging domain for future research into the discovery and development of new catalysts and novel processes.

The selective oxidation of light alkanes to produce light olefins ($C_2$–$C_4$) by ODH and carboxylic acids or aldehydes is therefore an important and quite challenging alternative to processes that are well established and still in use, such as direct DH of alkanes to olefins and selective oxidation of olefins to carboxylic acids or aldehydes, such as bismuth molybdate-based catalysts for propene to acrolein and V–Mo–O catalysts for acrolein to acrylic acid (SOHIO process in the 1960s[37]). Selective oxidation of light alkanes has therefore been widely studied in the past 40 years, but only a few new industrial processes have been developed, such as propane to acrylonitrile over MoVTeNbO catalyst. These catalysts were developed by Union Carbide for ODH of ethane to ethylene in the 1970s,[38] for which $Mo_{0.61}V_{0.31}Nb_{0.08}$ was found to be optimum, but not commercialized at that time. Ammoxidation of propane to acrylonitrile was further developed by Japanese companies following the work of Ushikubo et al.[39] and the discovery of $Mo_5O_{14}$-type based catalysts. The basic structure of $Mo_5O_{14}$ is shown in Figure 5. Certain amounts of other cations, such as V, Ta, Te, Sb
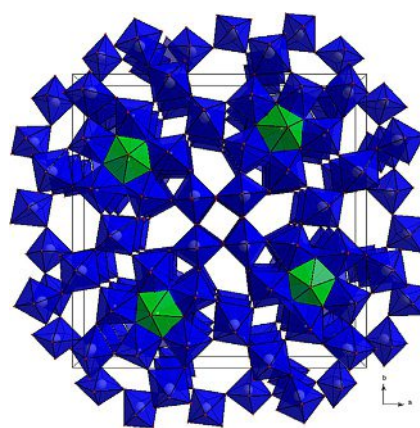


**Figure 5.** Crystal structure of $Mo_5O_{14}$ crystal composed of $MoO_6$ octahedra with insertion of a foreign element (Te, Nb) in green.

and Nb, can be incorporated in the structure, as determined by XRD analysis (lattice-parameter changes).[40]

Such a material, published in 1978 by Union Carbide researchers,[37] was later found, after insertion of cations such as V, Nb, Sb and Te,[41] to also catalyze direct oxidation of propane to acrylic acid[42] and ammoxidation of propane to acrylonitrile,[43] and this led to a new industrial process for acrylonitrile production. Two main components of such material were found to be catalytically active for the reaction, namely, the phases designated M1 and M2 (Figure 6), which were found to act synergistically in propane (amm)oxidation.

Later, Lemonidou and co-workers[46] proposed NiO materials as active catalysts for such reactions, mixed Ni–Nb–O catalysts, particularly $Ni_{0.85}Nb_{0.15}$[47] and catalysts with other added promotors.[48] However, deactivation was still too high and the process has not yet been developed. The influence of the particle size and the presence of Ni and O vacancies on the catalytic process was also mentioned.[49] Vanadium-based oxides have attracted great attention both in homogeneous and in heterogeneous catalyses[50] and are present in many catalyst formulations, such as $(VO)_2P_2O_7$ for direct oxidation of butane to maleic anhydride and alkyl aromatic ammoxidation of toluene, xylenes and picolines (alkyl pyridines) to produce valuable aromatic nitriles, including nicotinonitrile, which is a precursor for nicotinic acid, a B-type vitamin.

Catalysis for clean air, which includes automotive exhaust catalysis, desulfurization, wastewater treatment[51] and removal of volatile compounds (VOCs), is important application of heterogeneous catalysis (Table 2). In the case of VOCs, such as formaldehyde, which is released from households and responsible for many health risks, noble metals such as Pt or Pd on different supports are applied industrially. Moreover, carbon-supported catalysts have been proposed[52] for elimination of benzene–toluene–xylenes (BTX), in which the roles of hydrophobicity and mesoporosity were shown to be important for catalytic performance. However, metal oxide catalysts were also suggested to replace expensive noble metals, for instance, cobalt-based mixed oxides such as Co–Mn oxides for total oxidation of binary mixtures of toluene and 2-propanol.[53] Gas phase/solid catalyst total oxidation for depollution treatment
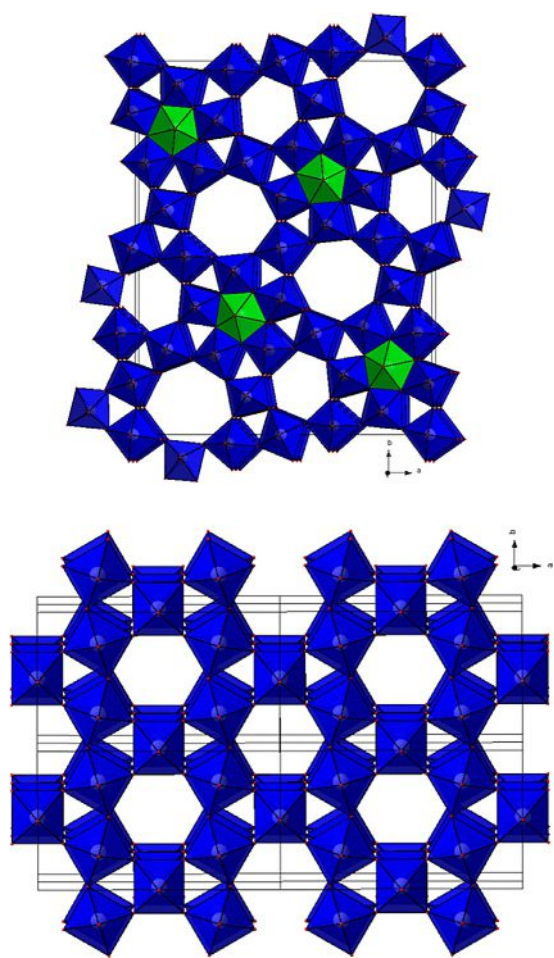
**Figure 6.** Structures of the phases M1 (top) and M2 (bottom) along the *c*-axis MO$_6$ octahedra. Adapted from Refs. [44, 45] with permission from Elsevier.

**Table 2.** Catalytic removal of the major toxic chemicals.

| Toxic chemicals | Origin of pollutants | Removal process |
|---|---|---|
| hydrocarbons (VOCs) | solvents, car exhaust, petrochemistry, household | oxidation |
| CO | car exhaust | oxidation |
| SO$_2$ | oil refineries, power plants, heating | reduction to sulfur |
| NO$_x$ | car exhaust, power plants | reduction to N$_2$, trapping, oxidation NO$_2$→HNO$_3$, photocatalysis TiO$_2$ coatings |
| wastewater | chemical plants | photocatalysis (TiO$_2$, ZnO) |
| soil | chemical plants | photocatalysis (TiO$_2$), oxidation (Fe$^0$, peroxides) |

has been applied to atmospheric pollutants such as industrial VOCs and/or highly diluted VOCs. Hybrid treatments combining catalytic oxidation with other technologies (e.g., light, ozonation, nonthermal plasma) have also been developed. Among the metal-oxide-based catalysts used for VOC elimination, perovskite oxide materials have unique physicochemical proper-

ties such as good chemical/thermal stability, high ionic conductivity and excellent electrocatalytic performance in redox reactions.
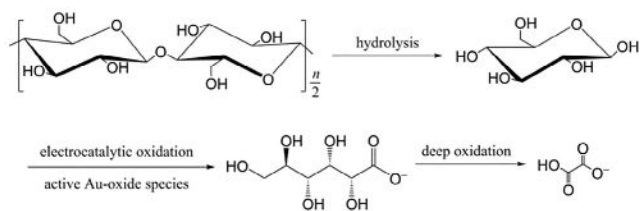
Among calcium phosphates, calcium hydroxyapatite (Ca$_{10}$(PO$_4$)$_6$(OH)$_2$, designated HAP) has been found to be a versatile material that is able to play an important role in different fields of the applied science, from medical engineering to pollution remediation. In environmental applications, HAP has gained attention as a solid adsorbent because of its unique characteristics of chemical stability, low cost, high availability and high water insolubility.[54] HAP can permanently immobilize polluting hazardous metal cations (e.g., Cu, Pb, Cr) from the aqueous phase and be quite efficient compared to most known adsorbents. HAP has even found a role in catalysis because of its easy functionalization.[55] Different metal species of catalytic interest (e.g., Cu, Co, Mn)[56] can be deposited on an HAP surface with uniform dispersion of the metal centres, thanks to its peculiar surface properties. With a view to more sustainable activity for both environmental and industrial interest, HAP materials could be used as sorbents for polluting metal species, for example, for demetallation of wastewaters by using metal-loaded HAPs as catalysts. Various reactions of environmental interest could also take advantage of metal ions dispersed on amphoteric surfaces, such as deNO$_x$, deVOC, NH$_3$ oxidation and NO oxidation. Cu–ZnO/HAP catalysts are effective catalysts for water–gas shift reactions, useful for fuel-cell applications.[57]

## 3. Sustainability Challenges for Oxidation of Renewable Resources

Since the 1990s, the utilization of resources other than fossil resources has become of prime importance for overcoming environmental issues and for the elaboration of a more sustainable world. One such resource is biomass, in particular sugars, for example, from sugar cane, and lignocellulosic biomass from wood (lignin, hemicellulose and cellulose fractions), which has been studied extensively in the last two or three decades towards the production of high added value products. Biodiesel synthesis by esterification of bio derivatives and utilization of glycerol, its major byproduct, are also important topics, already widely studied worldwide and discussed in Section 2.2. Interestingly, biodiesel could be produced from waste shells of eggs, oysters and clams with basic catalysts such as CaO.[58] An interesting review by Crestini and co-workers[59] deals with the oxidative functionalization and upgrading of lignin based on organometallic catalysts (MTO, salen, POMs), biomimetic catalysts (porphyrins) and enzymatic catalysts (laccase, peroxidase). P, S+Zn and Ti modified H-MFI was found[60] to be useful in the utilization of renewable lignocellulose biomass. Such catalysts have anticoking ability, which avoids hindrance of refined bio-oil production. In a recent study[61] super adsorbent polymers (SAPs) in disposable baby diapers waste (DBDW) were calcined at 500 °C and used as catalyst for synthesizing glycerol carbonate by the transesterification of glycerol with dimethyl carbonate with 95.6% conversion, a GC yield of 93.6% and high reusability.

It is well recognized that heterogeneous catalysis is a pillar of the chemical industries and a central domain for the ecological transition to carbon-neutral reactions and the production of useful chemicals. Great efforts have been made to use biomass derivatives to produce new chemicals with zero carbon consumption, although the chemical industry still depends mainly on fossil carbon resources. Biomass coming from wood contains mainly cellulose, hemicellulose and lignin. The tendency to use renewable feedstocks to reduce or eliminate waste byproducts and wastes, mainly wastewaters, and to increase catalyst efficiency, energy storage and sustainability, has been growing for chemicals production.[62,63] In recent years, strong development of innovative photo- and electrocatalysts has been realized, based on nontoxic and noncritical earth-abundant raw materials. For instance, catalysts have been discovered for ammonia synthesis at room temperature and atmospheric pressure, directly from water, involving $N_2$ and water splitting reactions, and for the synthesis of acetic acid directly from $CO_2$. The effect of halogens on BiOX (X = Cl, Br, I)/$Bi_2WO_6$ heterojunctions for visible-light-driven photocatalytic selective oxidation of benzyl alcohol has been studied,[64] and BiOBr was found to be optimum for enhancing the photocatalytic properties of $Bi_2WO_6$, which was interpreted as due to a good match between the energy-band structures of the two partners resulting in highly efficient separation of photogenerated charges.

Development of chemical engineering for nano-structured nanoanodes and advanced photoelectro-catalytic (PEC) solar cells has been important in recent years. Solar utilities and solar fuel feedstocks ($CO_2$, $H_2O$, and solar energy) are captured on site or transported to the refinery.[65] The solar utility provides energy in the form of heat, electricity or photons used to convert $CO_2$ and $H_2O$ to fuels, either by direct $CO_2$ reduction or solar activation of $CO_2/H_2O$ to $CO/H_2$ and subsequent catalytic conversion to fuels (e.g., by methanol synthesis or by the Fischer–Tropsch reaction). Scheme 1 shows electrocatalytic oxidation of a biomass derivative (cellulose) to exemplify this concept, and Figure 7 gives an example of the effect of electrical and magnetic fields on the oxidation of woody biomass[66] to vanillin and vanillic acid with CuO and $H_2O_2$ in comparison with the conventional thermal process. Advanced oxidation processes (AOPs) aim to oxidize organic compounds near room temperature and atmospheric pressure and are based on in situ generation of highly reactive oxidants, such as OH· radi-
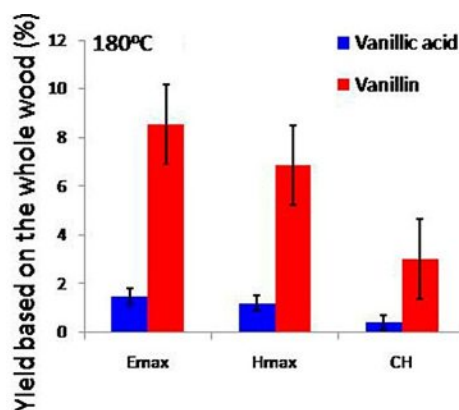


**Figure 7.** Comparison of the yields of vanillin and vanillic acid by microwave electric (Emax) and magnetic (Hmax) effects and conventional heating (CH) in a cavity perturbation heating system. Adapted from [66] with permission from the American Chemical Society.
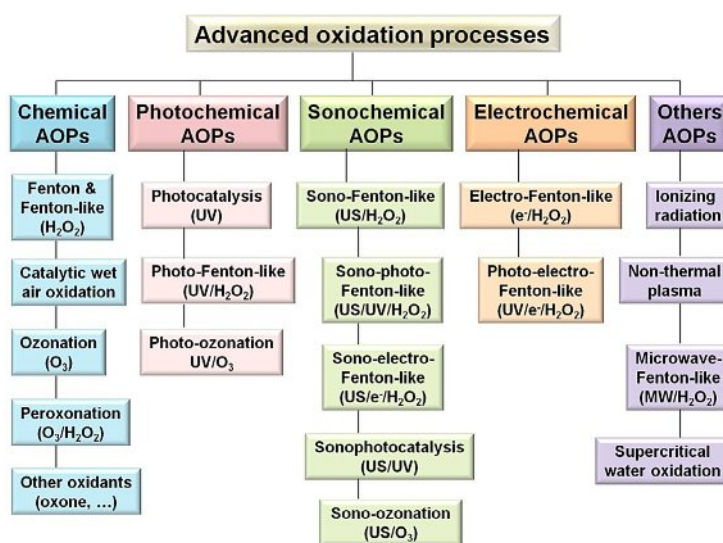


**Figure 8.** Classification of advanced oxidation processes (AOPs). The nature of the catalysts used in these AOPs has not been mentioned for the sake of clarity.

cals in the Fenton process or pollutant elimination by using conventional methods, such as as $O_3$, $H_2O$, or UV. Moreover, less usual techniques have been developed, such as ionizing radiation, sonochemical, photochemical, and electrochemical processes, nonthermal plasma, or supercritical conditions (Figure 8).

Heterogeneous photocatalysis[67] represents a promising technology to overcome challenges in the fields of energy, green chemistry and environmental care for sustainable development. Indeed, cheap and abundant solar energy is expected in the future to substitute thermal energy in activating redox processes such as hydrogen production by water splitting, $CO_2$ reduction to methane, organic synthesis and pollutant degradation. Conversion and selectivity of photocatalysts depend on electronic features, morphology and crystallinity of semiconductors such as $TiO_2$. Surface properties such as defectivity, extent of hydroxylation, polarity (thus, its affinity to target reactants), decoration with elements such as noble metals, and



**Scheme 1.** Electrocatalytic oxidation of cellulose to gluconate.

electron- and energy-transfer abilities, also play important roles. Porous titanium oxide materials are attractive for energy-related applications such as photocatalysis. However, many materials suffer from low stability and poor crystallinity. A robust MOF comprising a $Ti_{12}O_{15}$ oxo cluster and a tetracarboxylate ligand was synthesized.[68] It undergoes an unusual irreversible thermally induced phase transformation, resulting in a highly crystalline porous solid that exhibits photoconductive behavior. Introduction of a conductive polymer into its pores leads to a significant increase in charge-separation lifetime under irradiation. Additionally, the inorganic unit of this Ti-MOF can be easily modified by doping with other metal elements. The combined advantages of this compound make it a promising functional scaffold for practical applications.

In the last few decades, many achievements have been made in the domains of new catalysts and new biomaterials for depollution and treatment of exhaust gases and transformation of a wide variety of wastes into products of lower toxicity. In the effective utilization of natural resources, only a few new industrial processes have been developed.[69] The production of value-added organic acids by selective oxidation of biomass resources appears to be of great importance. Transition metal simple oxides, such as CuO, have been studied for the selective conversion of glucose to lactic acid and acetic acid under hydrothermal conditions.[70] Lactic acid has been produced by conversion of a variety of cellulosic biomass derivatives over mixed-metal oxides of the perovskite type.[71] Moreover, acid–base catalysts have turned out to be key players in the conversion of glucose, xylose, and cellulose into lactic acid in water under subcritical conditions. The treatment of toxic nitrogen-containing compounds stemming from the chemical and pharmaceutical industries is one of the major applications of catalytic wet air oxidation (CWAO) processes. Many studies have been performed on the oxidation of aniline, which is often chosen as model dye-industry pollutant. Particular attention has been paid to selectivity toward organic byproducts (especially azo, nitroso and nitro compounds, phenolic compounds and carboxylic acids) and inorganic forms of nitrogen ($NH_4^+$, $NO_2^-$, $NO_3^-$). Ammonia is one of the most refractory byproducts, which unfortunately is formed during catalytic oxidation of nitrogen-containing organic pollutants and is itself a pollutant. More information on CWAO processes for the treatment of refractory organic pollutants and industrial wastewaters can be found in recent reviews.[72,73]

Metal oxide catalysts may also be used for thermochemical storage of solar energy[74] in concentrated solar energy plants (CSP) to store heat, which can be used in the absence of sunlight to generate electricity, hydrogen or produce solar fuels. This process operates by the formation of oxygen vacancies at high temperatures ($>700\,°C$ or even $1300\,°C$) to give reduced metal oxides, such as zinc, cobalt and cerium oxides as well as perovskites, for solar decomposition of water and $CO_2$. Reduced metal catalysts release heat and catalyze the formation of $H_2$ by water splitting and CO to give syngas with an $H_2$/CO ratio adjustable by means of the initial $H_2O$/$CO_2$ ratio. Oxygen vacancies are considered to be the active sites of the oxides, and the $H_2$/CO mixture can be transformed into chemicals and fuels by many catalytic processes (e.g., Fischer–Tropsch, methanation, methanol/dimethyl ether).

## 4. Conclusions and Challenges for a Sustainable Future[75,76]

It is nowadays clear that the world is still highly dependent on fossil fuels (coal, petroleum, shale oil and natural gas), which have a large and negative influence on the environment[77] and human health, while world reserves are diminishing inexorably. This situation cannot last very long, and substantial advances are urgently needed. A great challenge for cleaner energy sources may be based on simple elements that are present in large amounts worldwide: biomass, sunlight, $CO_2$ and water. Hence, the major challenges for catalysis can be divided into three areas: electrocatalytic water splitting for the production of hydrogen as energy carrier, $CO_2$ conversion to valuable products and biomass conversion to various high-value chemicals.[76] At present, most of the innovative systems for $CO_2$ conversion are based on copper and zinc as the main active components. Higher activity and selectivity come from the high dispersion and surface activity of Cu/ZnO. Moreover, two modified systems, namely, CuNi/ZnO and Cu/Zn-SBA-15, have been proposed. The first modification aimed at increasing the hydrogenation function of the catalyst by addition of Ni to the metallic Cu clusters, by promoting the reaction pathway proceeding via formate as the main intermediate. The other modification was protonation due the presence of stronger acid sites in the support.

$CO_2$ emissions are still increasing despite more strict regulations worldwide. This has resulted from increased energy demand and lack of technology for large-scale $CO_2$ utilization or storage. There are several ways of utilizing $CO_2$, including the synthesis of organic compounds by $CO_2$ hydrogenation, for example, formic acid, methane, dimethyl ether, methanol ($CH_3OH$) and other hydrocarbon products such as ethylene and propylene.[78] These products can be easily utilized directly as fuels or fuel components by using existing technology. However, $CO_2$ is inert and thermodynamically very stable ($\Delta H_f^\circ = -394\,kJ\,mol^{-1}$), and its conversion requires high energy consumption and highly active catalysts. Another important future aspect of heterogeneous catalysis is the use of renewables, mainly based on biomass derivatives.[79] This constitutes a major challenge for the future (see Section 2.2).

Hydrogen has emerged as a new and promising energy source with high specific capacity and provides a potential foundation for a clean, flexible and secure future. Its combustion produces more energy per weight ($39.5\,kWh\,kg^{-1}$) than the combustion of any other fuel, for example, 2.4 and 2.8 times more than for methane and gasoline combustion, respectively. As hydrogen is accessible in the form of water, which is present on the earth in huge quantities, this makes it highly attractive. When hydrogen is used as fuel, either by combustion or electrochemically in a fuel cell, the only byproduct is water. Hydrogen has low energy density of $2.8\,kWh\,L^{-1}$, that is, 3.5 times lower than that of gasoline. However, storing it as liquid in high-pressure tanks is not at all practical. One

possibility is to use it in low-temperature fuel cells, which have been widely studied in the recent past. PEC water splitting under solar irradiation has been studied worldwide. Pt is known as one of the best metals for electrodes, but it is very sensitive to CO (poisoning), which has led to the development of the PROX process to oxidize CO in the presence of hydrogen, in particular for hydrogen arising from the Fischer–Tropsch process $[(2n+1)H_2+nCO\rightarrow C_nH_{2n+2}+nH_2O]$ after the water–gas shift reaction of methane: $CH_4+H_2O\rightleftharpoons CO+H_2$. The natural-gas WGS reaction can be used to deliver hydrogen but also large amounts of CO, and hence a CO-PROX catalyst must be used. A quite active catalyst is Cu/ZnO, which is highly stable at $250\,°C$ ($12\,wt\%$, Cu/Zn$=3$ for optimum catalytic efficiency) and resistant to sintering. Rapid production of high-purity hydrogen could be achieved by microwave-promoted catalytic dehydrogenation of alkanes with abundant and cheap metals, such as Fe and Ni nanoparticles on silicon carbide.[80]

Hydrogen can also be used in low-temperature fuel cells. Since hydrogen in its molecular form is not present in nature, it must be produced and can be regarded as a convenient energy carrier. Hydrogen production today in fact leads to $CO_2$ emissions ($13.7$ kg of $CO_2$ per kilogram of $H_2$). At present, approximately $96\%$ of hydrogen is derived from fossil fuels, for example, by methane steam reforming, and only $4\%$ is produced by electrolysis, and this is expected to increase in the near future. Hydrogen is used in fertilizers, hydrocracking of heavy petroleum and the manufacture of methanol and hydrochloric acid. Production and uses of hydrogen are shown schematically in Figure 9.
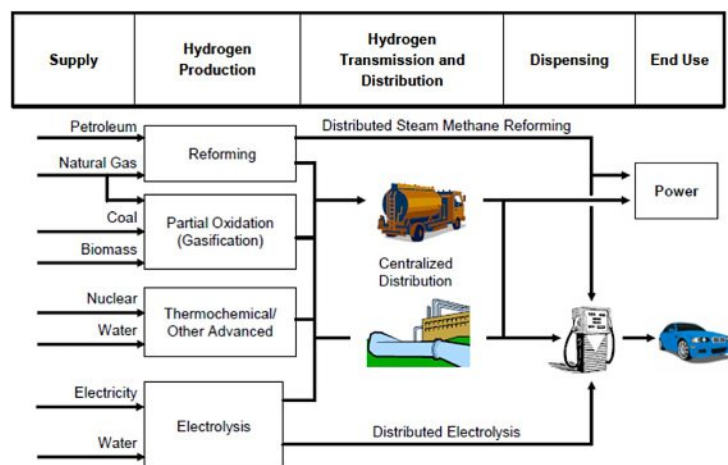


**Figure 9.** Main sources, means of production, and uses of hydrogen.

The oxygen evolution and reduction reactions (OER and ORR, respectively) are two extremely important reactions for energy applications. Currently, the OER hinders the efficient operation of electrolyzer devices that convert water to molecular $H_2$. This $H_2$ can subsequently be used in a $H_2/O_2$ fuel cell for the renewable generation of electricity with only $H_2O$ as by-product. However, this fuel-cell process is not economically feasible due to the slow kinetics of the ORR at the cathode. Moreover, research has been carried out worldwide in the

search for cheap and efficient catalysts to replace the expensive platinum-based catalysts currently used. Layered transition metal oxides, based on the oxides of cheap transition metals such as Mn, Co, Ni and Fe have been reported as catalysts for the OER and ORR. Layered structures have an advantage over nonlayered materials owing to their higher surface area. The fabrication process and post-synthetic treatments, for example, anion exchange or exfoliation, of these materials can alter their catalytic activity. Various synthetic methods and modifications to tailor the performance of layered transition metal and hydroxide-based catalysts for the ORR and OER have been reviewed recently.[81]

Interestingly, the location of activity in catalysis has been moving with time. In the 18th and 19th centuries, major discoveries and industrial developments were made in Europe. In the 20th century, both Europe and the USA made major contributions to discoveries and new industrial processes, as well as Japan and Korea in the second half of the century. In the 21st century, China, Korea, Japan and other Asian countries are expected to become quite strong and active in the field of catalysis.

The development of surface, bulk and in situ characterization techniques, molecular modelling, advances in chemical engineering of reactors[82] and advanced synthesis methods[9–11, 83] have transformed the preparation of solid catalysts and the characterization of their physical and chemical (catalytic) properties.[84] Such a trend should continue in the future with new generations of scientists, engineers and researchers. Not only catalyst preparation procedures, with recent developments such as soft chemistry versus co-precipitation and impregnation at controlled pH values, but also catalyst activation processes other than classical thermal ones are important. Although major industrial processes have been discovered and developed by the second half of the 20th century, progress is still needed, and the major challenges for the future are to reach $100\%$ selectivity and to use less energy. In this respect, unconventional activation methods based on US[85] and MW irradiation, ball milling, plasma, light, electrochemical and photo-activated processes, are viewed as green chemistry approaches to increase reaction rates and shorten reaction times while enhancing yields and selectivities.[24, 25, 86, 87]

Recent innovations in the field of catalytic air, water, wastewater and soil treatment have been proposed, and innovations in the use of heterogeneous catalysis for obtaining sustainable energy and chemicals as well.[27] Catalysis for sustainable energy conversion, such as PEC water splitting for the production of hydrogen, syngas ($CO+CO_2+H_2$) conversion for the synthesis of high-energy fuels from $CO_2$ on Cu/ZnO/Al$_2$O$_3$ catalysts, esterification and transesterification for clean synthesis of biodiesel[88] and $CO_2$ methanation for solar energy storage[89] are important examples that are still in their infancy and developing rapidly. In short, three important and fast-developing domains are PEC production of hydrogen, conversion of carbon dioxide into val-

uable products, and conversion of biomass into valuable products.[90]

Legislative requirements to make new compounds in an environmentally friendly and sustainable way have led to the development of catalysts with increasing selectivity and efficiency. Selectivity remains the most important aspect of catalysis to avoid any waste byproducts, most of which are environmentally unacceptable. Heterogeneous catalysis, which does not require any organic solvent, in contrast to homogeneous catalysis, appears to be a key technology for a sustainable future. The challenge for the 21st century is to design industrial processes with 100% selectivity for a desired product in uni- or multipath reactions, in a unique reactor, that can be designated green chemistry.

## Conflict of interest

*The author declares no conflict of interest.*

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