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**Review paper.** Special issue of the Chinese Journal of Catalysis for the 70th anniversary of DICP.

## **Importance, features and uses of metal oxide catalysts in heterogeneous catalysis**

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**Abstract.** This short review paper aims at assembling the present state of the art of the multiuses of metal oxides in heterogeneous catalysis, concerning liquid and gaseous phases of the reactant mixtures on solid catalysts. It includes the description of the main types of metal oxide catalysts, of their various preparation procedures and of the main reactions catalysed by them (acid-base type, selective and total oxidations, bi-functional catalysis, photocatalysis, biomass treatments, environmental catalysis and some of the numerous industrial applications). Challenges and prospectives are also discussed.

**Key Words.** Heterogeneous catalysis, metal oxide catalysts, preparation procedures, acid-base reactions, selective & total oxidation reactions, photocatalysis, environmental catalysis, industrial processes.

### **Introduction.**

Catalysis plays a major role in chemical, physical and biological sciences. It has become, during the years, one of the most important field in chemistry, as some 85-90% of industrial processes include at least one catalytic step and, more recently, in environmental chemistry. The main role of a catalyst is to decrease the activation energy of a chemical reaction and, in a multiproduct reaction, to favour the most important one, i.e. to favour *selectivity* which is now a major concern to avoid at most the formation of unwanted by-products, even at the expense of the reaction activity.

Catalysis is important in the refinement of petroleum, in the manufacturing of synthetic fibres and plastics, in the production of many specialty chemicals, in the processing of foods, in the production of drugs and pharmaceutical compounds, etc. It helps in the decrease of atmospheric pollution, in the design of environmentally friendly catalytic technologies, and of new processes to generate energy, and it is considered as a pillar of green chemistry in the

preservation of our environment. From the viewpoint of an academic scientist, catalysis is viewed as a cross-disciplinary field, including organometallic chemistry, physical chemistry, chemical engineering, surface science, solid-state chemistry, and theoretical/computational chemistry.

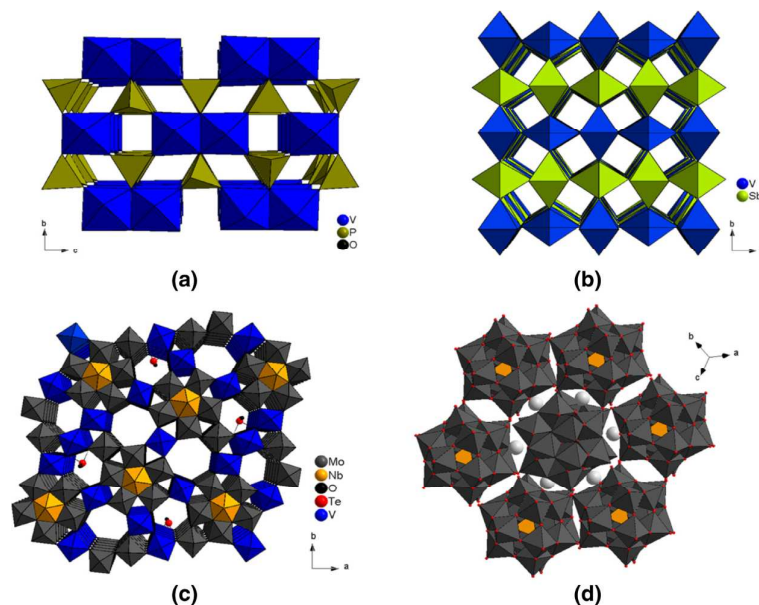
Among all catalysts and catalytic reactions, metal oxide catalysts and catalytic reactions are essential in most refining and petrochemical processes, in synthesizing specialty chemicals and more recently in improving environmental issues (depollution, high selectivity in reactions to avoid un-useful by-products). Metal oxide catalysts became prominent in the mid-1950s, when they were found to effectively catalyse a wide variety of oxidation and acid-base reactions. In this review paper, major types of metal oxide catalysts and processes, that use these catalysts, are reviewed. I have decided to focus its content on heterogeneous catalysis (mainly gas/solid and liquid/solid), in heterogeneous media, using metal oxide-type catalysts, whatever bulk or supported catalysts. In other words, catalysis by metals, by multi-metallic catalysts, supported or bulk catalysts, or by carbons (graphene, carbides), sulfides, etc., are excluded, although they constitute a large part of the catalysis field, in particular for petroleum and petrochemicals.

Advanced researches in catalysis with metal oxides have permitted the development of catalysts with high selectivity and with new preparation procedures. The performance of a solid catalyst relies on its grain size, shape, composition and preparation. New strategies for the preparation of metal oxide catalysts have resulted in the development of catalysts with single sites, that lead to 100% selectivity. The advent of nanoscience has promoted bottom-up over top-down strategies. Nanocrystals, with sizes of only a few nanometres, present the best catalytic efficiencies. However, the use of a support (silica, alumina, silica-alumina, carbons, etc.) could be important for the synergistic activation of substrates, electron conductivity enhancement in redox reactions, thermal conductivity enhancement for exo/endothral reactions, etc. The activity, selectivity, resistance to deactivation, and ability for regeneration are the properties, that characterise the usefulness of catalysts, and have been improved in the last fifty years by advanced researches and by improved industrial processes in catalysis with metal oxides.

### **1. Main metal oxide catalysts [1,2,3,4]**

Metal oxide catalysts are involved in majority of industrial catalytic processes. They include *simple oxides*, such as silica, alumina, clays, zeolites, titania, zirconia, ZnO, porous and mesoporous metal oxides, or *complex oxides* such as polyoxometalates (POMs) of Keggin

or Dawson type, phosphates (e.g.,  $(VO)_2P_2O_7$ ,  $FePO_4$ , silica phosphoric acid (SPA)), multicomponent mixed oxides (molybdates, antimonates, tungstates,  $MoVTe(Sb)Nb-O$ , etc.), perovskites, hexaaluminates, etc. Some of them correspond to specific arrangements of  $MO_6$  ( $M = Mo, V, Te, Nb$ , etc.) octahedra as schematised in figure 1.



**Figure 1.** 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.

These metal oxides present specific properties such as acidity (Lewis or/and Brønsted-types), basicity, redox features (when transition metal ions are present), which lead to specific catalytic properties. They are also the basis for metallic (mono- or pluri-metallic) catalysts, for hydrodesulfuration (HDS) catalysts ( $CoMoO_4$  -,  $NiMoO_4$  -,  $NiWO_4$  - based), for  $deNO_x$ ,  $deSO_x$  reactions, as perovskites or ceria based doped oxides. The main catalytic domains cover oxidation (selective or total), acid and base catalyses, photocatalysis, depollution and biomass conversion. Metal oxides are sometimes used simply as supports of active phases, such as silica, alumina, silica-alumina, mesoporous oxides, MOFs, etc., which may influence catalytic properties due to synergistic, electron conductivity or/and thermal conductivity effects, which stem from metal oxide - support interactions.

Metal oxides [1] constitute a class of inorganic materials, which exhibit peculiar and various properties and applications as sensors, catalysts, fuel cells, etc. Metal oxide surfaces terminate by oxygen  $O^{2-}$  anions, which size is larger than that of  $M^{n+}$  cations. It follows that the symmetry, coordination and accessibility to reactant molecules of  $M^{n+}$  cations are lost at

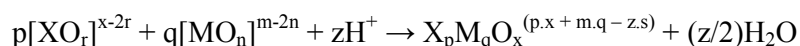
the surface. Moreover, the surface of an oxide may contain different types of defects and environments (kinks, steps, terraces), which may play a role in the catalytic phenomenon, for instance resulting in structure sensitivity of metal oxides to catalytic reactions [<sup>5,6</sup>]. This surface unsaturation is usually compensated by a reaction with water vapour, leading to the formation of surface hydroxyls according to :  $O^{2-} + H_2O \rightarrow 2OH^-$ . These OH groups are conjugated acids of lattice oxygen ions  $O^{2-}$ , which are strong bases and conjugated bases of water molecules.

Single or complex metal oxides based on the first transition series present a wide variety of non-stoichiometric phenomena, which originate from the unfilled 3d electron shell. For instance, Fe sites can be vacant in FeO of rocksalt framework ( $Fe_{1-x}O$  with  $0.05 < x < 0.18$ ). In  $ABO_3$  perovskite oxides, non-stoichiometry arises from a cation deficiency in A or B sites ( $A_xWO_3$ , A being an alkali ion) or oxygen anions excess. Cation A has a great influence on electrical properties. For instance,  $WO_3$  is an insulator, while  $A_xWO_3$  is a semiconductor at low x values and metallic at high x values. Oxygen-deficient perovskites have attracted much attention because of their oxygen storage ability and their redox properties, quite useful for total oxidation reactions. In fully oxidised  $CaMnO_{3-\delta}$  and  $CaFeO_{3-\delta}$  perovskites, Mn and Fe are at +4 oxidation state and  $\delta = 0$ , the material can accommodate up to 17% oxygen vacancies without losing its structure. The  $Sr_{1-x}La_xCo_{1-y}Fe_yO_{3-\delta}$  series, with brownmillerite-type oxygen defects, exhibits high electronic/oxygen ion mobilities. In some perovskites a small oxygen excess can be accommodated by the formation of cation vacancies at A- or B-sites, leaving the oxygen sub-lattice intact. Electronic defects may be created upon reduction and oxidation of metal cations at different oxygen partial pressures ( $pO_2$ ). At low  $pO_2$ , the material loses oxygen, which generates electrons, enhancing the n-type conductivity, according to :  $O_O \leftrightarrow (1/2) O_2 + V_O^{\bullet\bullet} + 2e^-$ . At high  $pO_2$ , oxygen is incorporated into an oxygen vacancy and takes two electrons from the valence band, leading to holes contributing to the p-type conduction, according to  $(1/2) O_2 + V_O^{\bullet\bullet} \leftrightarrow O_O + 2h^\bullet$ . A consequence of the trapping of electronic defects is that the solid becomes insulating at low temperatures. Defect associations between oxygen vacancies and acceptor dopants are observed in Y-ZrO<sub>2</sub>, where  $V_O^{\bullet\bullet}$  are trapped by  $YZr^\bullet$  defects leading to a drastic decrease in oxide ion conductivity.

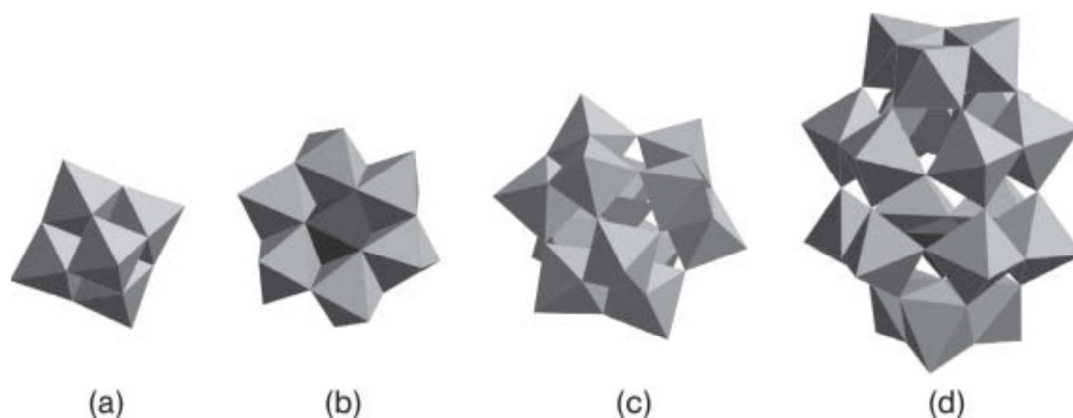
Protonic defects, associated with acceptor dopants, limit protonic conduction in metal oxides. As all metal oxides contain impurities, the defect mechanism of “pure” oxides is similar to that of doped oxides. For instance, strontium titanate,  $SrTiO_3$ , has a similar defect chemistry to acceptor-doped  $SrTiO_3$ , because the impurities are ions at lower oxidation states such as  $Fe^{3+}$ ,  $Al^{3+}$ ,  $Mg^{2+}$ ,  $Na^+$ , etc., and their concentrations, typically ca.  $10^2$ – $10^3$  ppm, are

sufficient to dominate the defect chemistry, especially at high pO<sub>2</sub>. All these aspects should be taken into account when considering the reaction mechanisms and kinetics on metal oxide catalysts, for instance in selective or total oxidation reactions on mixed metal oxides, where electrons and oxygen anions mobilities and lattice oxygen diffusion or storage capacity are important, for instance in a redox or in total catalytic oxidation reactions.

Polyoxometallates (POMs) constitute a large class of nanosized transition metal-oxygen clusters intermediate between molecules and oxides [7]. They are formed of anions of metal-oxygen octahedra as basic structural units, linked together to constitute a stable and compact skeleton of polymeric oxoanions, as shown in the equation :



with M = metal (designated as addenda atom) of valency m, X = heteroatom of valency x, and s = the oxygen balance. The most common M atoms are Mo and W and less frequently Ta, V, Nb as d<sup>0</sup> element. There are more than 20 structures incorporating 4 to 40 metal atoms and 1 to 9 heteroatoms. One distinguishes the structures of "Linqvist" [M<sub>6</sub>O<sub>19</sub>]<sup>n-</sup> (Oh symmetry of 6 MoO<sub>6</sub> edge-shared octahedra); "Keggin" α-[(XO<sub>4</sub>)M<sub>12</sub>O<sub>36</sub>]<sup>n-</sup> (Td symmetry of 4 M<sub>3</sub>O<sub>13</sub> groups of 3 MO<sub>6</sub> octahedra); "Dawson" α-[(XO<sub>4</sub>)<sub>2</sub>M<sub>12</sub>O<sub>54</sub>]<sup>n-</sup> (D<sub>h</sub> symmetry of 2 Keggin fragments α-XM<sub>9</sub>O<sub>34</sub>); "Anderson" [H<sub>x</sub>(XO<sub>6</sub>)O<sub>18</sub>]<sup>n-</sup> (D<sub>3h</sub> symmetry planar arrangement of 7 edge-shared MO<sub>6</sub> octahedra); (XO<sub>12</sub>)M<sub>12</sub>O<sub>30</sub> structure (I<sub>h</sub> symmetry with an XO<sub>12</sub> icosahedron surrounded by 6 equivalent M<sub>2</sub>O<sub>9</sub> groups of face shared MO<sub>6</sub> octahedra, linked by corner sharing tetravalent cations). The most common POMs used in catalysis are Keggin-type either as acid-base catalyst such as heteropolyacids (HPA) or as redox (for partial oxidation reactions) catalysts. Their properties are controlled, among a large range, by varying the chemical composition, e.g. changing the M element as in H<sub>3+x</sub>PV<sub>x</sub>M<sup>VI</sup><sub>12-x</sub>O<sub>40</sub>, the support, the extent of hydration and thermal treatment. For acid samples the following order of acidity range has been established [8] : H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> > H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> ~ H<sub>4</sub>GeW<sub>12</sub>O<sub>40</sub> > H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> > H<sub>4</sub>SiMo<sub>12</sub>O<sub>40</sub> ~ H<sub>4</sub>GeMo<sub>12</sub>O<sub>40</sub>. Several industrial processes have been developed, in particular in Japan, such as hydration of propylene to isopropanol in 1972, oxidation of methacrolein to methacrylic acid in 1982, direct oxidation of ethylene to acetic acid in 1997 and production of ethyl acetate in 2001, among other new processes. Giant heteropolyoxometalates compounds have also been synthesised [9], such as the Bielefeld "wheel" [Mo<sup>VI</sup><sub>126</sub>Mo<sup>V</sup><sub>28</sub>O<sub>462</sub>H<sub>14</sub>(H<sub>2</sub>O)<sub>70</sub>]<sup>14-</sup> or a Keplerate capsule superfullerene type [Mo<sup>V</sup><sub>172</sub>Mo<sup>V</sup><sub>60</sub>O<sub>372</sub>(CH<sub>3</sub>COO)<sub>30</sub>(H<sub>2</sub>O)<sub>72</sub>]<sup>42-</sup> [10] but with no industrial application yet, to my knowledge. Representations of the main heteropolyoxometalate structures are shown in figure 2 and some catalytic reactions are reported in table 1.



**Figure 2.** Types of polyoxometalates formed by different arrangements of  $\text{MO}_6$  octahedra. (a) Lindqvist, (b) Anderson, (c) Keggin, (d) Dawson.

**Table 1.** Some heterogeneous acid and selective oxidation reactions catalysed by heteropolyacids (HPAs)

Catalyst	Reaction	Specific features
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \rightarrow \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$	T = 150 °C, selectivity 91% at 90% conversion
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	Alkylation of aromatics	T = 30 - 100 °C
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	Alkylation of isobutane by butene	T = 20-40 °C
$\text{Pd}_{1.5}\text{PW}_{12}\text{O}_{40}$	Isomerisation of alkanes	T = 210 °C
$\text{H}_3\text{PW}_{12}\text{O}_{40}$	$\text{CH}_3\text{OH}(\text{CH}_3\text{OCH}_3) \rightarrow \text{C}_1\text{-C}_6$ hydrocarbons	T = 300 °C
$\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$	Isobutene + methanol $\rightarrow$ methyl isobutyl ether	T = 290 °C, selectivity ( $\text{C}_2\text{-C}_4$ alkenes) 74%
$\text{H}_6\text{P}_2\text{W}_{18}\text{O}_{62}$	Benzene + $\text{HNO}_3 \rightarrow$ nitrobenzene	T = 50 °C
-----		
$\text{CsH}_3\text{PMo}_{11}\text{V}_1\text{O}_{40}$	Methacrolein to methacrylic acid	T = 280 °C, 80-85 % selectivity
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$	Isobutane to methacrylic acid	T = 350 °C, 45% selectivity
$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	Isobutyric acid to methacrylic acid	T = 300 °C, 72% select., 52% conv.
$\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$	Pentane to phthalic + maleic anhydrides	T = 310 °C, 55% selectivity in MA

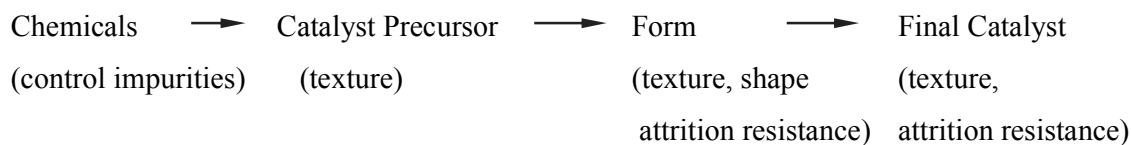
## 2. Metal oxide catalyst preparations [11,12].

This section addresses the broad topic of metal oxide syntheses of bulk and supported metal oxide catalysts. It corresponds to three main areas: 1) synthesis of simple metal oxides, 2) synthesis of mixed oxides and 3) preparation of supported metal oxides. A typical industrial operation for manufacturing catalysts comprises:

- Precipitation at a given pH or other synthesis process (e.g. sol-gel, solid-solid, flame hydrolysis, vapour deposition),
- Hydrothermal transformation,
- Decantation, filtration, centrifugation, washing,
- Crushing and grinding,

- Forming and/or shaping operations,
- Calcination, activation, reduction.

Catalyst syntheses are schematically represented by:



For *simple oxides*, it is important to control the nature of the solid catalyst, its morphology, textural properties (surface area, porosity), thermal, chemical and mechanical stabilities. Beside thermal methods, which do not permit a fine control of these parameters, three main preparation routes based on the reactions between water or an organic solvent and inorganic precursors are usually employed, namely aqueous-phase precipitation, sol-gel (hydrolytic and non-hydrolytic) process, solvothermal syntheses in presence of organic molecules and templating procedures resulting into materials with controlled morphology and textural properties, in particular organized microporous, mesoporous, macroporous and hierarchically-organized oxides. The complexation, solvent-free activated reactive synthesis, allows one to overcome the limited surface area reached after crystallization at high temperature. Organization of the porosity by hard or colloidal templating is a recent approach to maximise the specific surface area leading to mesoporous and hierarchical porosity materials.

The preparation of *mixed oxide* catalysts involves co-precipitation of two or more mixed salts in solution at a given pH, followed by the classical heat treatments. One can also proceed by solid-solid interaction between both salts at high temperature.

Industrially one usually employs either *bulk catalysts* composed of active components but with some inert binder added (e.g. silica, alumina, silica-alumina) to aid the forming and/or shaping operation and to avoid important attrition, mainly in moving/fluidized bed reactors. This is the case, for instance, for silica-alumina for cat-cracking, copper and chromium oxide for the water gas shift (WGS) reaction, iron molybdate for the oxidation of methanol to formaldehyde, vanadyl pyrophosphate for butane oxidation to maleic anhydride, etc. A description of some structural component of some catalysts are shown in figure 2. However, in some cases, bulk catalysts are used as prepared, without the need for addition of the binder. Typically, this involves catalysts prepared by high temperature fusion, e.g. the iron-based ammonia synthesis catalyst. A schematic representation of the influence of preparation parameters is given in figure 3.

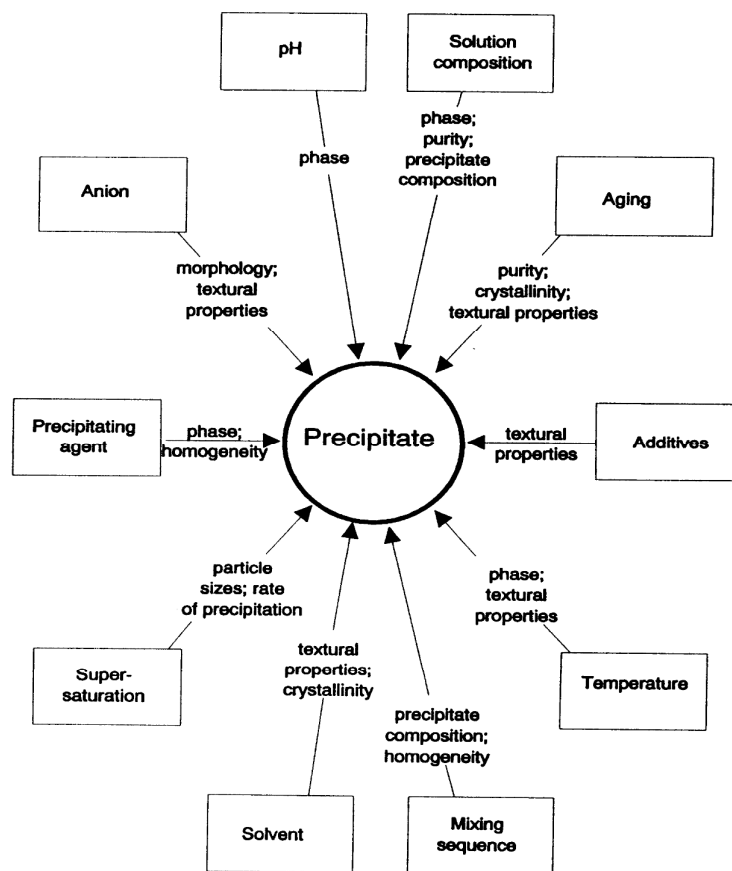


**Table 2.** Some industrial catalysts prepared by precipitation, coprecipitation techniques

Catalysts	Important applications
SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Acid catalysed reaction, e.g. FCC, isomerisation
Fe <sub>2</sub> O <sub>3</sub>	Fisher Tropsch reaction, ethyl benzene oxidehydrogenation to styrene
TiO <sub>2</sub> , CeO <sub>2</sub>	Major component of deNO <sub>x</sub> catalysts
ZrO <sub>2</sub> -SO <sub>4</sub> <sup>2-</sup>	Strong acid reactions
Cu-ZnO/Al <sub>2</sub> O <sub>3</sub>	Methanol synthesis from CO+H <sub>2</sub>
(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>	Selective oxidation of butane to maleic anhydride
	Oxidation of pentane to phthalic anhydride + maleic anhydride
Cu-Cr oxides	Hydrogenations, combustion reactions
Sn-Sb oxides	Selective oxidations, e.g. 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
MoVTenb oxide	Selective direct ammo/oxidation of propane to acrylonitrile/acrylic acid

**Table 3.** Some industrial catalysts prepared by sol-gel or hydrothermal (templated) techniques

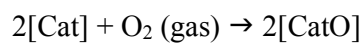
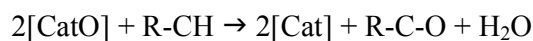
Catalysts	Important applications
V <sub>2</sub> O <sub>5</sub> , V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> , V <sub>2</sub> O <sub>5</sub> -WO <sub>3</sub> /TiO <sub>2</sub>	Selective catalytic reduction of NO <sub>x</sub>
Nb <sub>2</sub> O <sub>5</sub> /SiO <sub>2</sub>	Isomerisation of n-butene
Cr <sub>2</sub> O <sub>3</sub>	Fluorination of C <sub>2</sub> Cl <sub>3</sub> F <sub>3</sub> with HF
Pt-Sn/Al <sub>2</sub> O <sub>3</sub>	n-heptane dehydrocyclisation, propane dehydrogenation
transition metal /Al <sub>2</sub> O <sub>3</sub>	Polymerisation/co-polymerisation of alkenes
Ni-Mo/TiO <sub>2</sub> -ZrO <sub>2</sub>	Hydrodesulfurisation of gas-oil
PbO-ZrO <sub>2</sub> , PbO-Al <sub>2</sub> O <sub>3</sub>	Nitroxidation of alkenes
Li <sup>+</sup> /MgO promoted by Cl <sup>-</sup>	Oxidative dehydrogenation of ethane
Pt/TiO <sub>2</sub>	Oxidation of CO
Pd/SiO <sub>2</sub>	Hydrogenation of phenylacetylene
Zeolites	Acid reactions e.g. FCC, alkanes & alkenes isomerization, methanol to gasoline (MTG) or to olefins (MTO)
AlPO <sub>4</sub> , SAPO-34	Acid-catalysed reactions, polymerisation, methanol to olefins (MTO)



**Figure 3** Parameters affecting the properties of the final precipitation

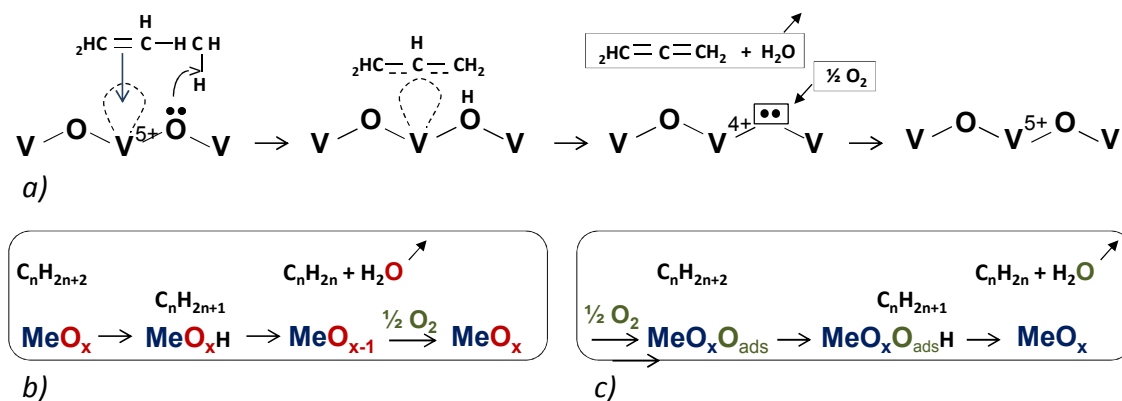
### 3. Main domains of catalytic reactions using metal oxides [2]

The main domains of heterogeneous catalysis by metal oxides cover acid, base, acid-base (bifunctional), selective oxidation reactions, total oxidation reactions and combustion, photocatalysis and biomass conversion. The first three domains have been described in detail in many reviews or books (see ref.1 to 3) and will not be discussed here. The main catalysts have been described above and include silica, alumina, silica-alumina, acid or base zeolites, polyoxometalates (POMs), hydrotalcites, hexaaluminates, perovskites, etc. The selective oxidation domain is very important and has been described in many papers and books [13]. It deals with transition metal ion oxides exhibiting redox properties, such as V, Mo, Cr, Te, Sb, Bi, Fe, etc. and usually proceeding via the famous *Mars and van Krevelen* mechanism [14]. In this mechanism, shown below and illustrated in figure 4, the lattice oxygen anions  $O^{2-}$  are incorporated into the hydrocarbon and give aldehydes or carboxylic acids or  $H_2O$  leading to a reduction of the catalyst. The corresponding vacancy created is then replenished by gaseous oxygen in the re-oxidation step.



Scheme of the Mars and van Krevelen mechanism,

where, [CatO] represents the oxidised catalyst surface and [Cat] its reduced state,  $r_{\text{red}}$  the rate of catalyst reduction by a reactant and  $r_{\text{ox}}$  the rate of its re-oxidation by co-fed oxygen, R-CH and R-C-O the reactant and the product. The relative rate of  $r_{\text{red}}$  and  $r_{\text{ox}}$  determines the selectivity in the product and involves lattice oxygen anions, which may be incorporated into the reactant, and If  $k_{\text{red}} p_{\text{HC}} \gg k_{\text{ox}} p_{\text{O}_2}$ , re-oxidation of the surface is the rate-determining step; if  $k_{\text{red}} p_{\text{HC}} \ll k_{\text{ox}} p_{\text{O}_2}$ , reduction of the surface is the rate-determining step. Thus reoxidisability and reducibility of the catalyst will lead to different kinetic expressions. Note that for partial oxidation reactions on transition metal oxides vanadium element has appeared as a key element, acting as schematised in figure 4.



**Figure 4.** Simplified schemes of: a) propene adsorption O–V–O and formation of a  $\pi$ -allyl complex intermediate; b) case of an alkane; c) effect of adsorbed oxygen.

(VO)<sub>2</sub>P<sub>2</sub>O<sub>7</sub> for butane to maleic anhydride, multicomponent Bi molybdate + Co(Fe) MoO<sub>4</sub> for propene to acrolein, MoVTenb(Sb)-O for propane direct ammoxidation to acrylonitrile or oxidation to acrylic acid, MoV-O for acrolein oxidation to acrylic acid, are among the most important catalysts used industrially [15], as described in § 6 below and assembled in Tables 2,3,4.

In the case of catalytic partial oxidation reactions mixed metal oxides based catalysts are mainly on V and Mo cations attached to other redox cations such as Sb, Nb, Te, and Ta. V<sub>2</sub>O<sub>5</sub> and MoO<sub>6</sub> octahedra are assembled as shown in Figure 1 and are often composed of several phases acting synergetically between them and giving complex chemical compositions. For instance, this is the case of the mixture of M1 and M2 phases in the MoVTenb-O catalyst used for propane amm/oxidation to acrylonitrile/acrylic acid.

In these partial oxidation reactions, the selectivity to the desired compounds (olefins, aldehydes, carboxylic acids, nitriles...) depends on the nature of surface oxygen anions ( $O^{2-}$ ) being nucleophilic (selective) or nucleophilic (non selective) associated to the cation(s)  $Me^{n+}$ , on Me-O bond energy and their distribution on the surface. This may come from the fact that oxidation reactions are demanding, i.e., are structure-sensitive [4], when the number of electrons involved in the reaction is high. For instance, many catalysts are able to transform propane to propylene (reaction with  $2e^-$ ), whereas only three (Cu-O, Bi-Mo-O, Sn-Sb-O) are able to transform propylene to acrolein ( $4e^-$  reaction) and only one ( $(VO)_2P_2O_7$ ) to oxidise butane to maleic anhydride (a  $14e^-$  reaction) or (VTi-O) for o-xylene oxidation to phthalic anhydride (a  $12e^-$  reaction).

#### 4. Biomass transformation reactions [16,17,18].

From the view point of chemicals and energy resources, utilization of the resources other than fossil resources is important in overcoming the environmental issues and for building a sustainable society. One of the possibilities for chemicals is biomass, in particular cellulosic biomass. Solid acids and bases should play important roles in conversion. Actually, the conversions of biomass and biomass-derived products have been studied extensively in recent years. Among them, biodiesel synthesis and utilization of glycerol are important topics [19,20], though only one process has been industrialized for biodiesel production on ZnO-Al<sub>2</sub>O<sub>3</sub> catalysts. Note that the solid acids and bases applicable to biomass conversions should be water-tolerant catalysts [21,22].

Currently, acrolein is produced primarily by the gas-phase oxidation of propylene on multicomponent catalysts (e.g. BiFeCoMoO<sub>4</sub>). However, as the use of propylene derivatives, particularly polymers, has recently been sharply increased, and since this trend is likely to continue in the foreseeable future, the availability and cost of propylene is going to increase. One approach to substitute propylene relies on the use of new raw materials. For instance, catalysts and processes have been developed for the direct conversion of glycerol to acrolein [23]. However, in such processes/catalyst two major difficulties were observed, namely rapid deactivation, and selectivity limited to less than 80%. There is thus a need to develop novel routes for the production of acrolein. One approach could be the conversion of allyl alcohol, which is produced in an initial step either by biomass fermentation, or through the dehydration of 1,3-propanediol, or the dehydration/oxidation of glycerol [24,25]. The MTO (methanol to olefin, mainly C<sub>2</sub><sup>-</sup> & C<sub>3</sub><sup>-</sup>) has been successfully developed recently in China, using SAPO-34 catalyst. [26]. The world first

commercial unit of MTO process was constructed and started to operate by Shenhua group in 2010, which was an important progress for coal to chemicals.

A series of  $\text{Mo}_3\text{VO}_x/\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{Al}_2\text{O}_3$  catalysts, as bifunctional catalysts, have been prepared and applied for the one-step oxydehydration of glycerol to acrylic acid [27]. It was found that acetic acid was produced in parallel with acrylic acid at similar yield when adjusting  $\text{Mo}_3\text{VO}_x$  content in the catalysts. Increasing calcination temperature from 350 to 650 °C led to structural evolution of supported active species and subsequent activity change. Crystallinity of  $\text{Mo}_3\text{VO}_x$  increased with calcination temperature and a large amount of  $(\text{V},\text{Mo})\text{O}_x$  hetero-polyoxo mixed oxides were formed above 550 °C. The Keggin structure of  $\text{H}_4\text{SiW}_{12}\text{O}_{40}$  began to dissociate around 450 °C causing the formation of various  $\text{WO}_x$  species. Above 450 °C, the yield of acrylic acid dropped while that of acrolein reached its maximum value with increase of the catalyst calcination temperature. In contrast, the yield of acetic acid exhibited a minor change. Based on the catalytic and characterization data, possible active centres and reaction pathways have been proposed, while for the improvement of the bi-functional catalyst for the one-step conversion of glycerol, it was proposed that both the acidic and redox properties of catalysts should be finely tuned. The  $(\text{V}_{0.07}\text{Mo}_{0.93})_5\text{O}_{14}$  entities were suggested to be the active species for acrolein oxidation, while isolation of dehydration and oxidation active centres was also suggested to improve acrylic acid yield.

## 5. Photocatalysis [28,29,30,31,32]

Photocatalysis is a relatively young science, which is already of great interest for green and environmental chemistries, as it operates at room temperature and does not need thermal energy, the catalyst being activated by the photons. The technique is able to excite electrons  $e^-$  from the conduction band or to generate electron holes  $h^+$  in the valence band. The catalysts, simple oxide as  $\text{TiO}_2$  or doped oxides, sulfides, etc, are polyphasic: solid catalyst, liquid or gaseous reactants and electromagnetic (photons from solar light or UV-rays). The first example was discovered accidentally from a thermogravimetric study of oxygen chemisorption on evacuated  $\text{TiO}_2$ , which was observed to lead to different weight increases and colour changes under oxygen, depending on the solar or unsolar day in the laboratory at Claude Bernard University (Lyon-1) in France. The same results were obtained by irradiating the sample with UV light. The pioneers (S. Teichner et al.) took advantage of this labile oxygen  $\text{O}^*$  species to study at room temperature selective oxidation of alkanes  $\text{C}_n\text{H}_{2n+2}$  (with  $n \geq 2$ ) to the corresponding aldehydes and extended further to

the oxidation of cycloalkanes, alkenes, substituted aromatics, amines, etc. Electrical photoconductivity experiments have shown that oxygen is photoadsorbed as ionic  $O_2^-$  and  $O^-$  species [33],  $O^-$  being the precursor of the activated  $O^*$  species according to  $O^-_{ads} + h^+ \rightarrow O^*_{ads}$ . In presence of water (gas or liquid) adsorbed  $H_2O$  molecules dissociate to  $OH^-_{ads}$  and  $H^+_{ads}$  and  $OH^-_{ads} + h^+ \rightarrow OH^\circ_{ads}$ , radical, which is very nucleophilic and thus non selective in oxidation reactions. This aspect has led to the use of photocatalysis for pollution abatement of organic compounds such as pesticides, in particular organophosphorous compounds as phenitrothion [(CH<sub>3</sub>)<sub>2</sub>-P(=S)-O-C<sub>6</sub>H<sub>3</sub>(NO<sub>2</sub>)-CH<sub>3</sub>] or dyes.

Among all the semiconductor materials under investigation, metal oxides represent the most important candidates due to their unique physiochemical properties. Producing hydrogen fuel via photocatalytic water splitting on semiconductor materials has attracted intense interest in the past decades due to its potential to address important energy and environmental problems. As the main sector for implementing photocatalytic reactions, semiconductor materials have been the focus of the research efforts.

Since the report of using TiO<sub>2</sub> for photoelectrochemical water splitting, metal oxide-based semiconductors have received great attention in the field of solar energy conversion. In particular, significant advances have been achieved on using metal oxide semiconductors for photocatalytic water splitting reactions. The objective is the development of novel metal oxide-based photocatalysts with appreciable solar light absorption and electronic properties. The tuning of the electronic structures of existing photocatalysts to obtain enhanced light absorption and more efficient charge separation and transportation has been intensively studied. However, there is still a huge gap between the actual solar-to-hydrogen (STH) efficiency achieved and the theoretical maximal value. Currently, the highest STH efficiency achieved on metal oxide photocatalysts is only *ca.* 1%, which is far away from what is required for any practical application. Therefore, there is still a long way to go before the large-scale application of photocatalytic water splitting for solar energy conversion. In the future, efforts should be devoted to the development metal oxide with wide solar light absorption and appropriate band edge positions for water splitting. Recently, MIL-101 (Fe) particles have been coated with an amorphous shell of titania and were observed [34] to lead to hydrogen production from water using visible light, while neither component alone was able to do it.

## 6. Industrial applications of metal oxides [35]

Industrial applications of metal oxide catalysts cover mainly the synthesis of petrochemicals (chemical intermediates such as acrylonitrile, maleic anhydride, acrolein, acrylic acid and substituted aromatic compounds) [36] in which V element appears as key partner and for fuels manufacture. Many processes have been developed as summarised in table 4.

Table 4. Some industrial processes using metal oxide catalysts or supports

Reaction	Catalyst
Steam reforming of hydrocarbons to CO + H <sub>2</sub>	Ni/Al <sub>2</sub> O <sub>3</sub>
Water gas shift (CO + H <sub>2</sub> O → CO <sub>2</sub> + H <sub>2</sub> )	Fe oxide or mixed oxides Zn, Cu, Cr
Methane dry reforming (CO <sub>2</sub> + CH <sub>4</sub> → 2CO + 2H <sub>2</sub> )	Ni/Al <sub>2</sub> O <sub>3</sub>
Methanol synthesis from CO + CO <sub>2</sub> + H <sub>2</sub>	Cu-Zn-O/Al <sub>2</sub> O <sub>3</sub>
Methanol steam reforming (CO <sub>2</sub> + 3H <sub>2</sub> )	Cu-Zn-O/Al <sub>2</sub> O <sub>3</sub>
Methanol to hydrocarbons (MTG process)	H-MFI zeolite, SAPO-34
Methanol to light olefins (MTO process)	Fe <sub>2</sub> (MoO <sub>4</sub> ) <sub>3</sub>
Methanol oxidation to formaldehyde	V <sub>2</sub> O <sub>5</sub> /diatomaceous earth
SO <sub>2</sub> → SO <sub>3</sub> for H <sub>2</sub> SO <sub>4</sub>	Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub> or /α-Al <sub>2</sub> O <sub>3</sub>
H <sub>2</sub> S oxidation to SO <sub>2</sub> and H <sub>2</sub> SO <sub>4</sub>	V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> (anatase)
O-xylene + O <sub>2</sub> → phthalic anhydride	Re-O, Ru-O & W-O
Metathesis	Ga-MFI zeolite
C <sub>3</sub> -C <sub>4</sub> alkane dehydrocyclisation to aromatics	V <sub>2</sub> O <sub>5</sub> + (WO <sub>3</sub> or MoO <sub>3</sub> ) /TiO <sub>2</sub>
Selective catalytic reduction of NO <sub>x</sub>	Cu/chabazite zeolite
SCR of NO <sub>x</sub> at high T	Bismuth molybdate
Propene ammoxidation to acrylonitrile	MoVTeNb-O (M1 phase)
Propane ammoxidation to acrylonitrile	Bismuth molybdate
Propene oxidation to acrolein	Mo-V-O
Acrolein oxidation to acrylic acid	Zirconia
Aromatic carboxylic acids hydrogenation to aldehydes	CoMo-O, NiMo-O, Ni-W-O/γ-Al <sub>2</sub> O <sub>3</sub>
Hydrosulfurization of oil distillates	Supported Co and Fe catalysts
Synthesis gas (CO + H <sub>2</sub> ) to hydrocarbons (Fuel range)	Supported W-O and sulfated ZrO <sub>2</sub>
Parafins (C <sub>5</sub> -C <sub>12</sub> ) isomerization	Titanosilicate (TS1)
Olefin epoxidation	Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> or Pt/Al <sub>2</sub> O <sub>3</sub>
Alkanes (C <sub>2</sub> -C <sub>5</sub> ) dehydrogenation to olefins	V based catalysts
Alkanes oxidative dehydrogenation to olefins	(VO) <sub>2</sub> P <sub>2</sub> O <sub>7</sub>
Butane to maleic anhydride	Doped rare earth oxides
Methane oxidative coupling to ethylene	ZnO, Cr <sub>2</sub> O <sub>3</sub> , CuO
Ethylene + HCl + O <sub>2</sub> to dichloroethane	Pt-Rh-Pd alloys on oxides
Exhaust gases elimination	

Currently, most of the acrylic acid produced world-wide is made using the same process, namely the two-stages oxidation of propylene. In this process, propylene is oxidised to acrolein in a first reactor on scheelite Bi molybdate-based catalyst (defect structure of scheelite (Bi<sub>2/3</sub>□<sub>1/3</sub>Mo<sub>3</sub>O<sub>12</sub>, where □ represents a cation vacancy in the ideal ABO<sub>4</sub> structure), containing Co and Fe molybdates [37] and acrolein is further oxidised to acrylic acid in a second reactor without intermediate separation. The second stage catalysts are MoVWCu-O mixed oxides as key formulation. These catalysts are mostly X-ray amorphous and contain V in a reduced state.

It was observed that an oxide catalyst consisting of molybdenum, vanadium and niobium was able to yield high conversion of ethane and high selectivity to both ethylene and acetic acid products [38]. The best catalyst was found to be  $\text{Mo}_{0.61}\text{V}_{0.31}\text{Nb}_{0.08}$ . Further, two defect oxide structures of molybdenum and vanadium were identified as the likely catalysts for the selective oxidation of ethane. These two phases are uniquely described by the stoichiometry  $\text{Mo}_4\text{V}_6\text{O}_{25}$  and  $\text{Mo}_6\text{V}_9\text{O}_{40}$  with the inclusion of niobium to stabilise the structure and promote microcrystallinity. Propane direct oxidation to acrylic acid has been studied [39] on mixed oxides, such as  $\text{MoVTe(Sb)Nb-O}$  of structure derived from the above one  $\text{MoVNb-O}$  for ethane to ethylene, as well as the dehydration of lactic acid and 3-hydroxypropionic but have not been commercialised yet. Recently, a crucial discovery [40] was the calcination of the mixed oxide, which was previously done in air at around 350°C, in a non-oxygen containing (i.e. inert) atmosphere (nitrogen gas) at around 620°C. This resulted in acrylonitrile yields of up to 59% (92% propane conversion; 64% acrylonitrile selectivity), which made the system competitive with the previous processes starting from propene. The active phase was identified as the so-called M1 phase [41]. Acrylonitrile hydrolysis, as well as the Reppe chemistry to get acrylic acid, have been used in the past, but are no longer economically attractive. At variance, direct ammoxidation of propane to acrylonitrile on the same  $\text{MoVTe(Sb)Nb-O}$  catalysts have been successively industrialised. Among the disclosed compositions is  $\text{Mo}_1\text{V}_{0.4}\text{Te}_{0.2}\text{Nb}_{0.1}\text{O}_x$  with reported per pass yield of acrylonitrile of ca 14% (23% propane conversion; 61.5% acrylonitrile selectivity). Yields were improved to up to 25% (58% propane conversion; 44% acrylonitrile selectivity) with the addition of various elements as promoters.

Recently glycerol dehydration to acrolein has received much attention to generate a route to renewable acrylic acid. A shift to new reactor technologies, such as microstructured reactor or thermoplate reactors, able to better handle the reaction heat triggered the need for more active catalysts. However currently incremental improvements of the catalyst and process are to be expected, since all the installed capacities are using the same type of technology: multitubular fixed bed reactors operating slightly above the upper flammability limit, over  $\text{MoVWCu}$ -mixed oxide catalysts.

The nitrile functionality serves as a useful reactive centre for transformation into a wide spectrum of commercially valuable chemical products, via polymerization, hydrogenation, hydration and condensation, the production of aromatic nitriles using mixed metal oxide catalysts. Commercial application of alkyl aromatic ammoxidation is based on three categories of feedstocks - toluene, xylenes, and picolines (alkyl pyridines). Catalysts for alkyl aromatic ammoxidation are vanadium oxide based. The ammoxidation reaction produces the corresponding aromatic nitrile.



The nitrile products are intermediates for industrially important chemicals including amines, isocyanates for polyurethanes, phthalocyanine dyes and vitamin B compounds (niacin).

An interesting case is the up grading of methane to ethane by oxidative coupling (OCM), which has led to huge researches, worldwide, since the pioneered early 70s works by Lunsford at Texas A&M on Li/MgO based catalysts. Unfortunately, none industrial processes were developed using such types of catalysts and technology. Recently the company Siluria [42] has developed a process to convert methane to ethylene by OCM. The catalyst is prepared with rare earth oxides either unsupported or supported on MgO, CaO or AlPO<sub>4</sub> and containing at least two dopants (a metal element, a semi metal element and a non-metal element). A demonstration plant has been set in La Porte, Texas and a commercial plant is scheduled for 2019.

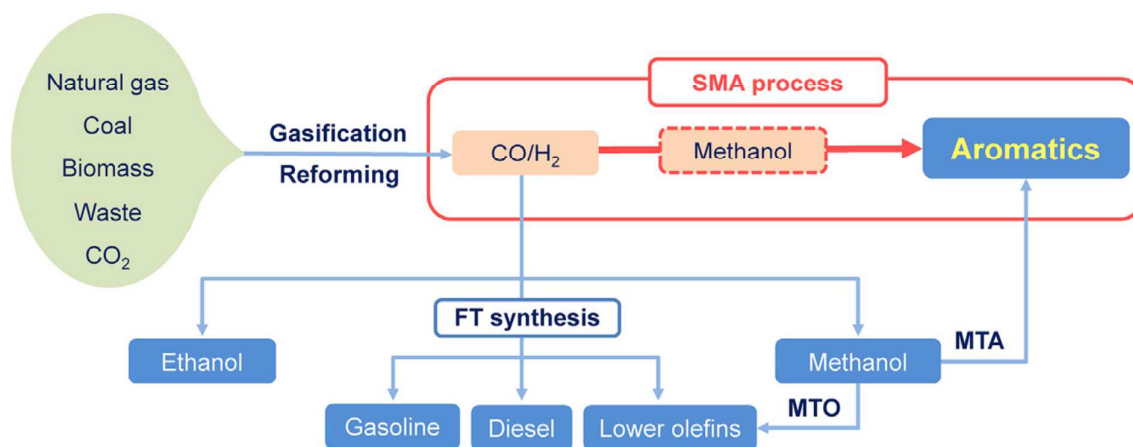
## **7. Challenges and concluding remarks [43].**

Metal oxide catalysis is a still growing field reflecting the wide range of catalytic reactions involved. It appears that, although great improvements and new developments have been discovered in the second part of the 20<sup>th</sup> century, it remains plenty of room for young researchers from academia and industry to discover and develop new metal oxide catalysts and new or improved processes. It can be expected that the first part of the 21<sup>st</sup> century will see development of new catalysts and development of commercial processes related to environmental issues and legislation constraints.

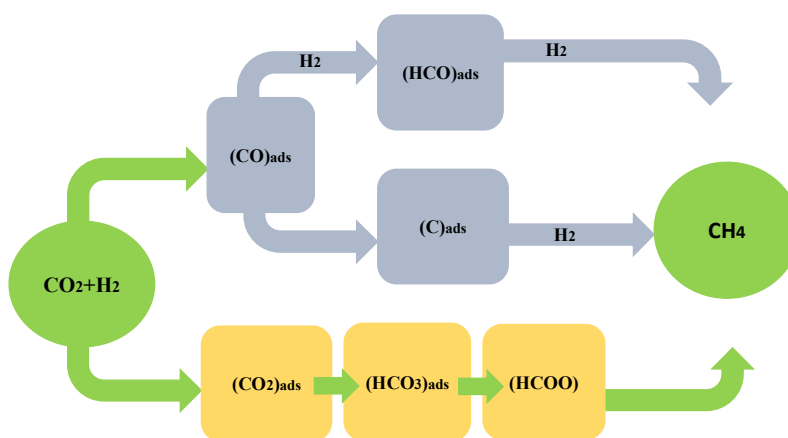
The challenge of catalysis in the 21st century is to achieve 100% selectivity of the desired product molecule in uni- or multi-path reaction (designated as “green chemistry”) and develop renewable energy based processes. In catalysts syntheses nanoscience, synthetic methods have been developed to produce monodisperse metal oxide nanoparticles (NPs) in the 0.8-10 nm range with controlled shape, oxidation states, and composition; these NPs can be used as selective catalysts since chemical selectivity appears to be dependent on all of these experimental parameters. New spectroscopic and microscopic techniques have been developed that analyse and characterize catalysts under reaction conditions and reveal the dynamic change of molecular structure of catalysts and adsorbed molecules as the reactions proceed with changes in reaction intermediates, catalyst composition at the surface, and oxidation states. Photo water splitting, methane and carbon dioxide conversion, are important research directions in renewable energy conversion.

Let us end this paper by analysis the current trends in applied heterogeneous catalysis [44]. Since the 1990s major themes of researches and developments have emerged. For instance, auto exhaust catalysts for CO, NO<sub>x</sub> and hydrocarbons eliminations from cars and trucks, catalysts for

electrochemistry (utilising solar energy with cheap and stable materials, like reduction of water to  $H_2$ , of  $CO_2$  to methanol) and photochemistry (like photo water splitting or solar driven clean-up of environmentally harmful by-products using  $TiO_2$  as photocatalyst), quest for enantioselective catalyst by asymmetric site on heterogeneous catalysts, immobilised transition metal complexes to heterogeneous homogeneous catalysts, immobilised enzymes and cells, catalytic antibodies, catalytic oxidation of widely abundant methane to syngas  $CO + H_2$  and further methanol and onward to hydrocarbon mixtures (MTO and MTG processes), alkane up-grading, in particular by selective partial oxidation, e.g. propane oxidation/ammoxidation to acrylic acid/ acrylonitrile, etc. Some perspectives are summarized in figures 5 & 6.



**Figure. 5** Typical reaction processes related to syngas chemistry (from ref. 98). The red-line route demonstrates SMA process for the direct synthesis of aromatics via reaction coupling. FT= Fischer Tropsch, MTO = methanol to olefins, MTA = methanol to aromatics, SMA = syngas to methanol to aromatics.



**Figure 6.** An example of a difficult challenge for the use of carbon dioxide

In short, sustainability, efficiency, oil refinery, energy, transport, hydrogen synthesis and stocking,  $CO_2$  and  $CH_4$  up-grading and catalytic transformations, (e.g. dry reforming), alkanes up-

grading to olefins, aldehydes or carboxylic acids, gaseous NO<sub>x</sub> emissions, greenhouse gases emissions, new catalysts (e.g. MOFs [45]), new processes, biocatalysis are, at present, the main drivers in catalysis related R&D.

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### **Graphical abstract:**

