# Heterogeneous catalytic partial oxidation of lower alkanes (C 1 –C 6 ) on mixed metal oxides

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## A B S T R A C T

This review paper aims at analysing the state of the art for partial oxidation and oxidative dehydrogenation (ODH) reactions of lower alkanes $C_1$–$C_6$ into olefins and oxygenated products (aldehydes, anhydrides, carboxylic acids) on metal oxide catalysts with cations of variable oxidation state, such as Mo and V in particular. Key parameters to be met by the catalysts, such as their redox properties, their structural aspects, active sites composed of ensembles of atoms isolated one from the others, mechanisms of reactions, are discussed. Main features of the different reactions of $C_1$–$C_6$ alkanes and catalysts are analysed and their generalisation for determining more active and more selective catalysts is attempted. Prospective views for the future of the domain are proposed.

## 1. Introduction

Considerable efforts have been carried out to the oxidative transformation of alkanes using different classes of catalytic materials or catalytic-system designs [1–5]. These efforts have been driven by the possibility of developing new environmentally friendly and low cost processes to synthesise olefins and partially oxidised organic compounds. Furthermore, with increase in the world production of medium-to-long chain alkanes, there is a need to convert them into useful products. Selective oxidation of alkanes is difficult, since they are quite inactive compounds, which necessitate to using high temperatures and/or pressures and, hence, lead to dominantly radical reactions. Moreover, the product molecules are more reactive than alkanes, and may easily be sur-oxidised into $CO_2$. The gas-phase selective oxidative transformation of light alkanes to alkenes (e.g., $C_{2n}H_{2n+2} \rightarrow C_2H_{2n}$) with $n = 2$–6 or oxygenates (aldehydes, acids) with $n = 1$–6 is an important challenge as it aims at reducing the number of process steps, at decreasing both the energy required and $CO_2$ emissions, and at improving the atom economy.

Up to now, transformation of light alkanes ($C_2$–$C_6$) to olefins by direct dehydrogenation constitutes the major industrial processes available, unless strong drawbacks (endothermicy and strong deactivation by coking). Subsequently, both oxidative dehydrogenation (ODH) and O-insertion of $C_1$–$C_6$ alkanes constitute important reactions to deal with, in particular any method for a better selective oxidative transformation of methane ($C_1$) and best catalytic systems constitute also an important challenge.

The importance of olefins in further applications to chemicals is summarised in Fig. 1.

In Table 1, important processes industrially developed or under development are listed.

In Fig. 2 are reported the numbers of patents vs. open literature scientific publications for $C_2$–$C_4$ alkanes. It is clear that at present simple dehydrogenation is more developed in the industry than ODH at variance with academic researches.

## 2. General features of selective catalytic oxidation reactions

### 2.1. The most important catalysts, which have been used or studied

They are listed below, some of their structures being shown in Fig. 3 and their catalytic properties reminded below in the following different sections. Such solid materials are composed, most of the time, of arrangements of $MO_6$ octahedra (M = Mo,V,Nb,Te,Sb,) creating some empty holes filled by additional cations.

- Basic solids such as VMgO (e.g., for propane to propene).
- Bulk vanadates or molybdates.
- $V_2O_5$ deposited on oxidic supports ($SiO_2$, $TiO_2$, $ZrO_2$, $Al_2O_3$, HDT, MCM-41 or SBA-15).
- Heteropoly oxo metallates (POMs) Mo based (Keggin-type structure mainly).
- VPO-type catalysts (e.g., butane to maleic anhydride or pentane to maleic anhydride).

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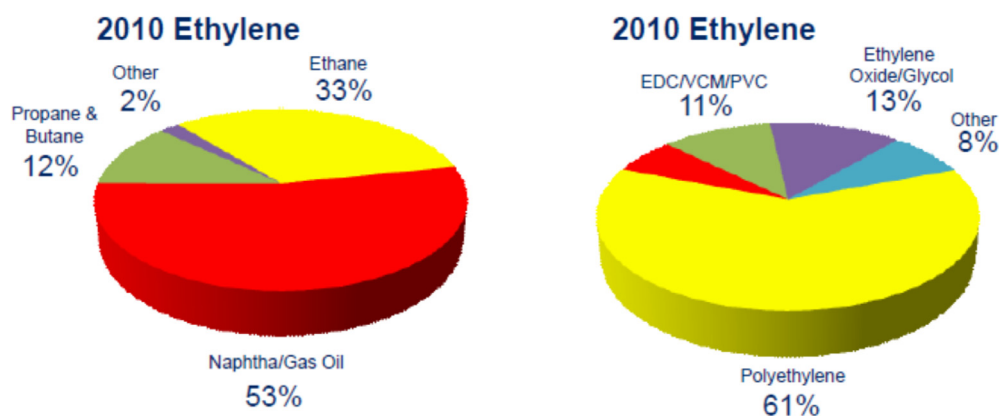  *E-mail address:* jacques.vedrine@upmc.fr

**Fig. 1.** Schematic importance of olefins worldwide applications (Personal communication by J.M. Lopez Nieto, Valencia).

- Mixed oxides MoNbTe(Sb)V-O for propane to acrylic acid/acrylonitrile.
- NiMoTeP-O, NiNb-O, for ethane to ethylene....

In the case of metal oxides deposited on an oxide support, it is well accepted that the synthesis procedure obeys some specific laws related to pH of the solution vs. the zero charge point (ZPC) of the support surface. In other words, in the case of impregnating a given salt on an oxide surface, when the pH value of the solution is less than ZPC, the surface is positively charged and anionic species can be adsorbed. At variance if pH > ZPC, the surface is negatively charged and cationic species are adsorbed. This is the case, for instance, of Pt cationic complex ($Pt(NH_3)_4^{n+}$) vs. anionic complex ($PtCl_4^-$) adsorbed on alumina (amphoteric) vs. zeolite (acidic) surfaces, to adsorb Pt either on alumina or on zeolite, as H-FAU.

### 2.2. Main aspects of selective oxidation on metal oxides catalysts

An important aspect to consider in oxidation reaction is the number of electrons necessary for the reaction to occur, for
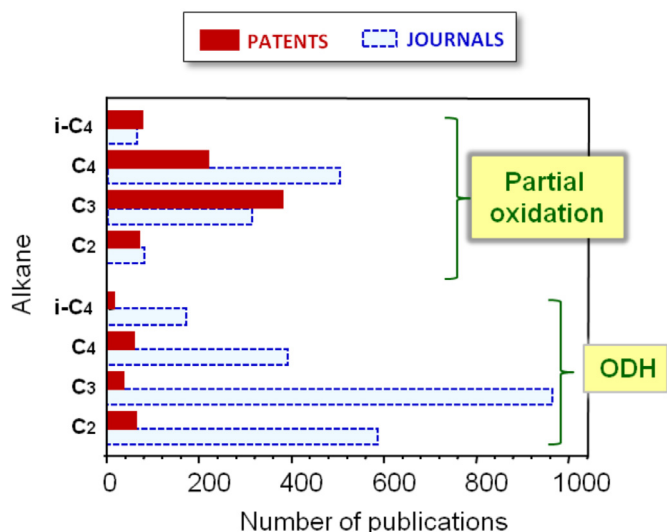
**Fig. 2.** Number of publications in the last two decades (1989–2009) dealing with short chain alkanes ODH and partial oxidation products including acetic acid, acrylic acid, methacrolein, methacrylic acid, maleic anhydride (From [6] Fig. 24.1).

**Table 1.** Industrial processes, processes under study or development for the oxidative transformation of light paraffins ($C_1$–$C_6$).

| Raw material | Product | Stage of development |
|---|---|---|
| Methane | Methanol | Pilot plant |
| Methane | Syngas | Pilot plant |
| Methane | Ethylene | Pilot plant |
| Ethane | 1,2-Dichloroethane,vinyl chloride | Pilot plant |
| Ethane | Acetaldehyde | Research |
| Ethane | Acetic acid | Research |
| Ethane | Ethylene | Research |
| Propane | Acrolein, acrylic acid | Research |
| Propane | Propyl alcohol | Research |
| Propane | Acrylonitrile | Industrial |
| Propane | Propylene | Research |
| n-Butane | Acetic acid | Industrial |
| n-Butane | Maleic anhydride | Industrial |
| n-Butane | Butadiene | Industrial, abandoned |
| Isobutane | Methacrylic acid | Pilot plant |
| Isobutane | Isobutene | Research |
| Isobutane | t-Butyl alcohol | Research |
| n-Pentane | Phthalic anhydride | Research |
| Cyclohexane | Cyclohexanone | Industrial |
| Cyclohexane | Cyclohexanone | Research |

instance $CH_3-CH_2-CH_3 + O^{2-} \rightarrow CH_3-CH=CH_2 + H_2O + 2e^-$ while the dissociation of molecular oxygen into $2O^{2-}$ requires $4e^-$. Table 2 assembles such electron numbers involved in oxidative transformation of lower alkanes.

The three main features of metal oxides, which are essential for their application in catalysis, are (i) the coordination environment of surface atoms, (ii) the redox and, subsequently, acid–base properties, number of electrons involved and (iii) the oxidation states of the surface cations. For selective oxidation reaction the main reaction mechanism is the Mars and van Krevelen one [7], schematised below, and which involves cations of variable oxidation state such as Ce, Co, Cr, Cu, Fe, Mo, Ni, V, W.

$$2[CatO] + R\text{-}CH_3 \rightarrow 2[Cat] + R\text{-}CHO + H_2O$$

$$2[Cat] + O_2 \text{ (gas)} \rightarrow 2[CatO]$$
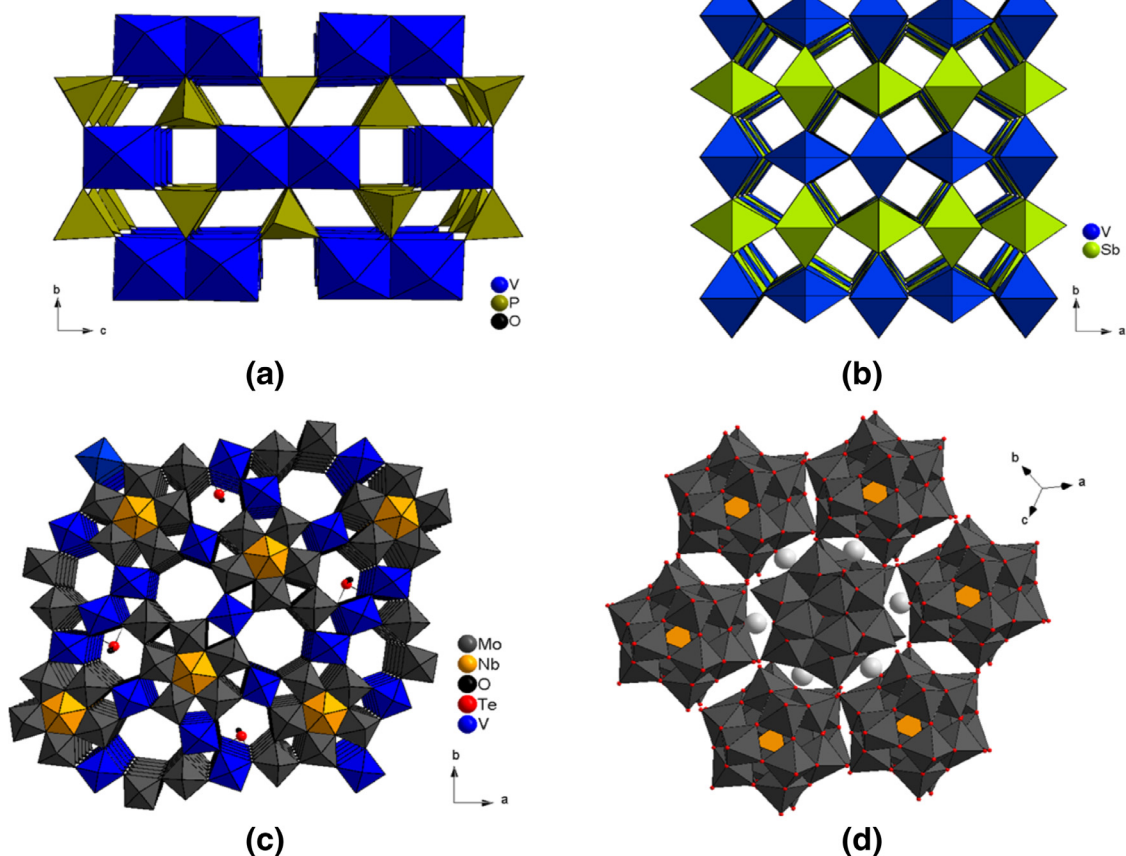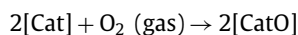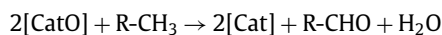

**(a)**


**(b)**


**(c)**


**(d)**

**Fig. 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 molybdophophoric acid.

**Table 2.** Main catalytic heterogeneous oxidation reactions industrialised (I), at pilot stage (P) or not industrialised yet (NI) or under research (R).

| Reaction | Reactants | Products | Number e- | Catalysts | Y (mol%) | Status |
|---|---|---|---|---|---|---|
| Oxidative coupling | $CH_4$ | Ethane | 2 | $Li_2O/MgO$ | 25 | NI |
| – | – | +ethylene | 4 | – | – | – |
| ODH | Ethane | Ethylene | 2 | Pt/oxides | 60 | NI |
| – | Propane | Propene | 2 | Pt/oxides | 40 | NI |
| – | n-butane | Butenes | 2 | Metal molybdates | 38 | NI |
| – | – | Butadiene | 4 | – | – | – |
| Oxychloration | Ethane,$Cl_2$ | Vinyl chloride | 4 | AgMnCo-O | 15 | NI |
| Hydroxylation | $CH_4$ | $CO+H_2$ | 2 | Pt,Ni | 90 | R |
| – | – | HCHO | 4 | MoSnP-O | 16 | R |
| Partial oxidation | Ethane | $CH_3COOH$ | 6 | MoVNb-O | 10 | P |
| – | Propane | Acrylic acid | 6 | MoV(Nb,Te,Sb)-O | 8 | NI |
| – | n-butane | Maleic anhydride | 14 | $(VO)_2P_2O_7$ | 70 | I |
| – | i-butane | Methacrylic acid | 8 | Heteropolyacids | 11 | R |
| Ammoxidation | Propane+$NH_3$ | Acrylonitrile | 8 | VSb-O,MoV-O, MoVTeNb-O | 30 | I |

where [CatO] represents the oxidised catalyst surface and [Cat] its reduced state, $r_{red}$ the rate of catalyst reduction by reactant and $r_{ox}$ rate of its re-oxidation by co-fed oxygen, R–$CH_3$ and R-C–O the reactant and the product. The kinetic equation involves the relative concentration of reduced ($\theta$) and oxidised ($1-\theta$) sites of the catalyst surface. At steady state, $r_{red} = r_{ox}$ or $k_{red}\, p_{HC}\, (1-\theta) = k_{ox}\, p_{O2}\, \theta$ with $p_{HC}$, $p_{O2}$ partial pressure of HC and $O_2$ and $k_{red}$, $k_{ox}$ rate constants of reduction of catalyst (1st step) and $r_{ox}$ rate of oxidation by $O_2$ (2nd step). The relative rate value of $r_{red}$ and $r_{ox}$ is important for the selectivity in the product and involves lattice oxygen anions, which may be incorporated in the reactant and the corresponding vacancy created is then replenished by gaseous oxygen in the re-oxidation step. If $k_{red}\, p_{HC} \gg k_{ox}\, p_{O2}$, re-oxidation of the surface is the rate determining step; if $k_{red}\, p_{HC} \ll k_{ox}\, p_{O2}$, reduction of the surface is the rate determining step. Thus, reoxidability and reducibility of the catalyst will leave to different kinetic expressions.

According to this mechanism the substrate is oxidised by the catalysts and not directly by the gaseous oxygen and the role of oxygen is to regenerate or maintain the oxidised state of the catalyst. Lattice oxygen is introduced into the substrate or into $H_2O$ for ODH reaction. This involves two active sites: an active cationic site and a site active for oxygen reduction. The process starts with the abstraction a proton, accompanied by a two electron transfer which reduces the transition metal cations. This step is followed by a nucleophilic addition of an oxide ion from the catalyst to the oxidised hydrocarbon with formation of oxygen vacancies, which are filled by oxygen with re-oxidation of the metal cation, in a kind of reversible breathing motion. This is schematised in Fig. 4.

In majority of cases, selective oxidation reactions involve Mars and van Krevelen or redox mechanism or minorly other mechanisms as reminded below in Table 2.

- The reaction proceeds at a single site (atoms or clusters/ensembles of atoms) [9].
- Principle of site isolation, and phases cooperation introduced by Grasselli et al. [10].
- The reaction proceeds as a sequence of consecutive steps, the first one being usually an H atom abstraction, which is the rate determining step (rds).
- Other steps, such as product desorption, O insertion, other H atom abstraction, are usually faster and do not influence the rds.
- An acidic surface favours desorption of acidic product whereas a basic surface favours desorption of basic products such as olefins.
- In a landmark contribution to catalytic theory, Haber [8] has suggested that a catalysed chemical reaction is not catalysed over the entire solid surface of the catalyst but only at certain “active sites” or centres. He has also suggested that chemisorption may be an activated process and may occur slowly. Moreover, he conceived the idea that chemically active sites might be composed of an atom or an ensemble of atoms and could be sparse on the surface of a catalyst and, hence, could be inhibited/poisoned with relatively few molecules. Since that time, many descriptions of active sites have been proposed, in particular for metal oxides used in selective oxidation reactions, as revisited recently [11].

As a general rule the concept of “7 pillars”, as proposed by Grasselli [12], has to be satisfied:

(1) Nature of lattice oxygen anions: nucleophilic (selective) rather than electrophilic (total oxidation).
(2) Redox properties of the metal oxide (removal of lattice oxygen and its rapid reinsertion).
(3) Host structure (permits redox mechanism to take place without structure collapse). An example is given in Fig. 5.
(4) Phase cooperation in multicomponent catalyst or supported catalyst (epitaxial growth and synergetic effects).
(5) Multifunctionality (e.g., $\alpha$-H abstraction and O-/NH- insertion).
(6) Active site isolation (to avoid a too high lattice O surface mobility and thus over-oxidation).
(7) M–O bond strength (to be not too weak (total oxidation) nor too strong (inactivity) (Sabatier principle).

Catalytic partial oxidation reactions are more efficient on mixed metal oxides based mainly on V and Mo cations attached to other redox cations such as Sb, Nb, Te, Ta, as $MO_6$ octahedra assembled as shown above in Fig. 3 and which are composed of several phases acting in synergy one with respect to the other(s) and leading to very complex chemical compositions as we will give examples in Section 3.3 below, for instance in the case of the mixture of M1 and M2 phases in MoVTeNb-O catalyst used for propane amm/oxidation to acrylonitrile/acrylic acid.

As the selectivity depends on the nature of surface oxygen species ($O^{2-}$) associated to cation(s) $Me^{n+}$, to their bond energy Me-O (of the lattice or with adsorbed O), and to their distribution on the surface, it is reasonable to conclude that oxidation reactions are demanding, i.e., are structure sensitive. They are more demanding when the number of electrons involved in the reaction is high. For instance, if many catalysts are able to transform propane to propylene (reaction with $2e^-$) only three are able to (Cu–O, Bi–Mo–O, Sn–Sb–O) are able to transform propylene to acrolein ($4e^-$ reaction) and only one ($(VO)_2P_2O_7$) for butane to maleic anhydride (a $14e^-$ reaction) or (VTi–O) for o-xylene oxidation to phthalic anhydride (a $12e^-$) reaction.
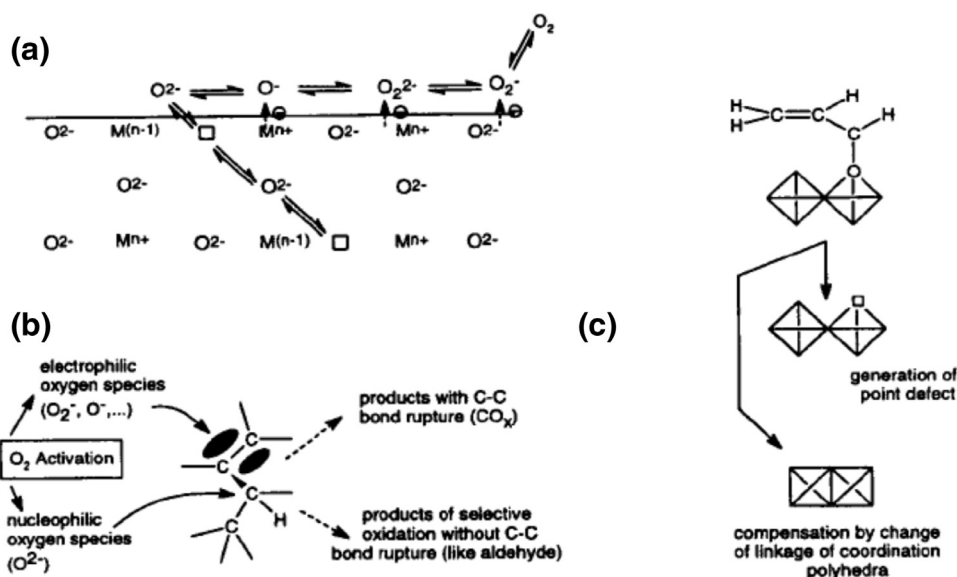
**Fig. 4.** Schematic representation of the mechanism of O insertion in a hydrocarbon molecule and its consequence in O vacancy reversible creation in a metal oxide (right part) $P_2O_7^{4-} + O^{2-} \leftrightarrow 2\ PO_4^{3}$. From J. Haber [8].
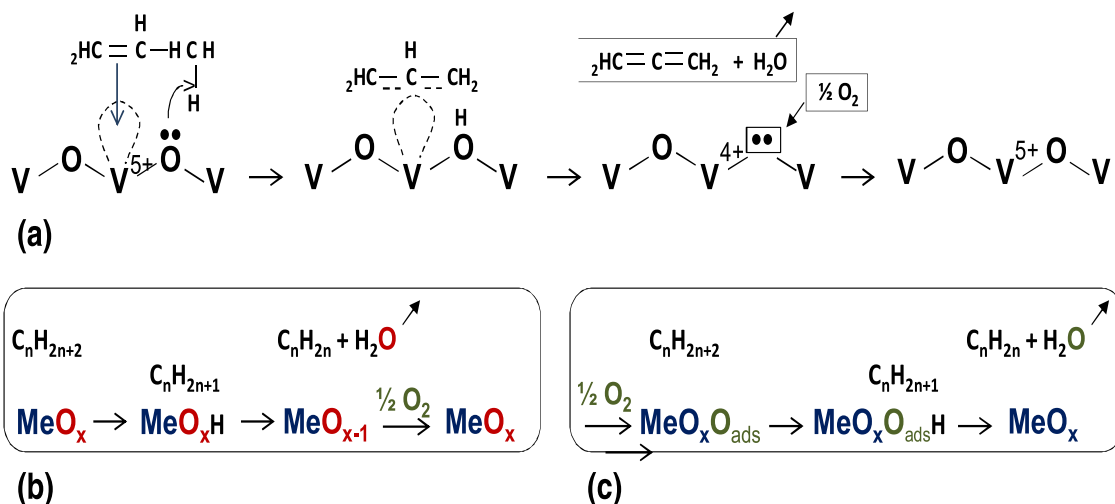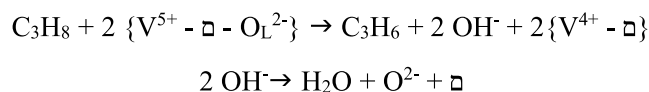
$$C_3H_8 + 2\ \{V^{5+} - \square - O_L^{2-}\} \rightarrow C_3H_6 + 2\ OH^- + 2\{V^{4+} - \square\}$$

$$2\ OH^- \rightarrow H_2O + O^{2-} + \square$$



**Fig. 5.** Over-simplified reaction schemes (a) propene adsorption O−V−O site and formation of an allene, (b) reaction of an alkane according to a redox mechanism, and (c) reaction of an alkane with oxygen.

Partial oxidation catalysts contain usually one transition metal ion from first column of the periodical table (Ti, V, Cr, Mo). As this cation is very small, highly charged and very polarising it can form oxo cations, such as oxo vanadium ($VO^{3+}$), vanadyl ($VO^{2+}$), molybdenyl. In first approximation, one can estimate that during reduction of $V^{5+}$ to $V^{4+}$ (or $Mo^{6+}$ to $Mo^{5+}$) and reversely in oxidation, the transfer of one $e^-$ is easy, resulting in good catalytic properties. As a matter of fact, a redox catalyst is more active when the principle of small changes in structure and oxidation state is satisfied. By contrast, the situation is less favourable for other redox couples such as $Fe^{3+}/Fe^{2+}$ et $Cu^{2+}/Cu^+$, for which either the size of the ions, (e.g., 0.017 nm difference for $Cu^{2+}/Cu^+$ with Cu at the same coordination of six), or coordination, are very different.

Vanadium is a typical example of structure sensitivity. Ionic radius $r_i$ of $V^{5+}$ ($r_i = 0.054$ nm) is very small compared to that of oxygen anion $O^{2-}$ ($r_i = 0.140$ nm). In an octahedral environment of six $O^{2-}$, vanadium get closer to $O^{2-}$ forming a short bond to be more stable. The V...O bond in trans position being longer, its bond energy is weaker and O can be easily been withdrawn. Then V coordination becomes 5. For the same reason, crystal cuts easily perpendicularly equatorial plane. Considering octahedral environments [$VO_6$] in $V_2O_5$ and in $V_2O_4$ the bonds O... $V^{4+}$ are respectively shorter (0.158–0.164 nm) (0.278–0.270 nm) than their homologs with $V^{5+}$, and the average height of the octahedron changes very little. The same holds true for $Mo^{6+}/Mo^{5+}$ couple in the same coordination [$MoO_6$] ($r_i = 0.059$ nm et 0.061 nm pour
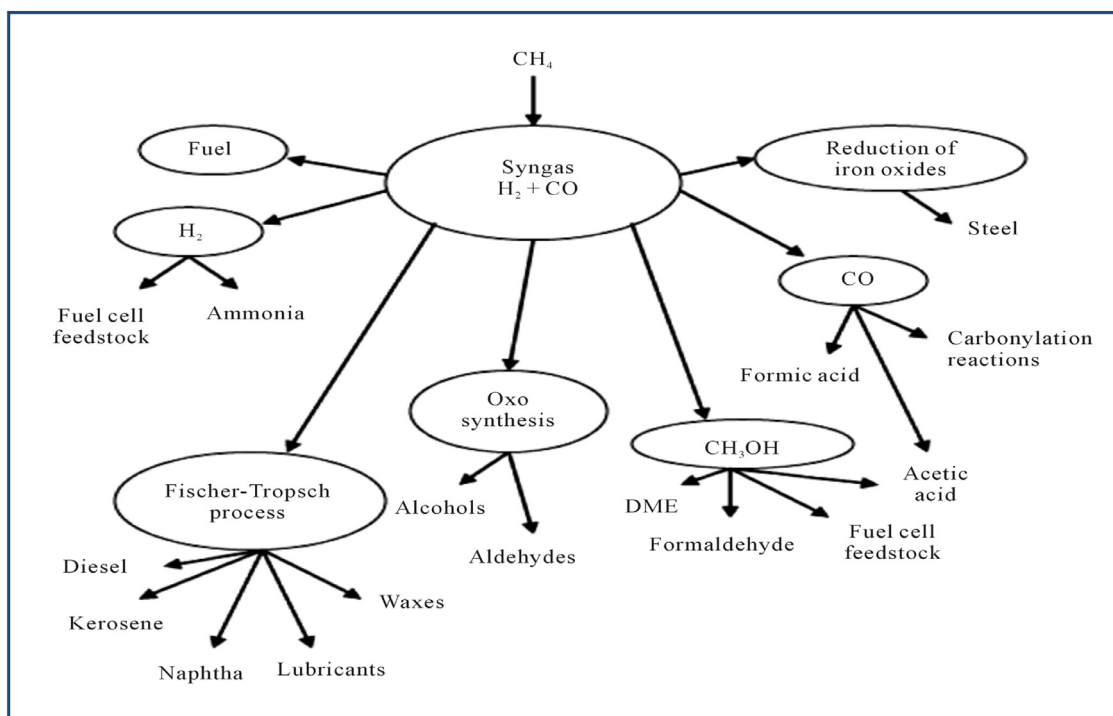
**Fig. 6.** Schemes of methane up-grading to valuable chemicals.

**Table 3.** Main reaction mechanisms in heterogeneous catalysis.

| Mechanism | Kinetic equation |
|---|---|
| Power law model | $r = k_0\, P_A^m\, P_B^n\, \left(-\frac{E_A}{RT}\right)$ |
| Eley–Rideal model (ER) | $r = \frac{k\, K p_A\, p_B}{1+\, K\, p_A}$ |
| Langmuir–Hinshelwood model (LH) | $r = \frac{k\, K_A\, K_B}{(1+\, K_A p_A + K_B p_B + K_C p_C)^2}$ |
| Mars van Krevelen model (MvK) | $r = \frac{k_{ox} k_{red}\, p O_2^n\, p_p}{k_{ox}\, p O_2^n + k_{red}\, p_p}$ |

$Mo^{6+}$ et $Mo^{5+}$, respectively). $V^{5+}$ and $Mo^{6+}$ ions can easily accept coordination VI, V et IV, but coordination IV is less frequent for $V^{4+}$ and $Mo^{5+}$.

### 2.3. Main reaction mechanisms involved in heterogeneous catalytic reactions

The main reaction mechanisms involved in oxidative transformation of alkanes are schematised in Table 3.

A reaction mechanism involving cations such as V or Mo at different oxidation states and lattice oxygen ($O^{2-}$) extraction and re-insertion is proposed below following the scheme detailed above in Fig. 4, whereas the number of cationic sites involved in a reaction is shown in Fig. 5 below:

$$C_3H_8 + 2\ \{V^{5+} - \square - O_L{}^{2-}\} \rightarrow C_3H_6 + 2\ OH^- + 2\{V^{4+} - \square\}$$

$$2\ OH^- \rightarrow H_2O + O^{2-} + \square$$
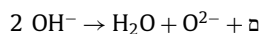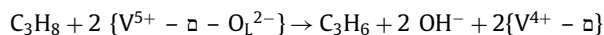
## 3. Cases studies

### 3.1. Natural gas

Depending on its origin, natural gas contains mainly methane but also and in different amounts $C_2$–$C_4$ alkanes, which necessitate some up grading or uses. The following equations and Fig. 5 describe some processes in use at present or in perspective, such as: $CH_4 + air \rightarrow CH_3OH$, HCHO
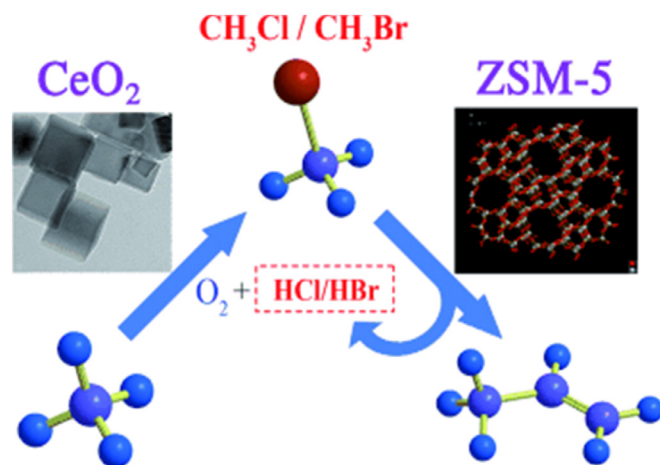


**Fig. 7.** Transformation of methane to propylene: a two-step reaction route catalyzed by modified $CeO_2$ nanocrystals and F-MFI zeolite from Ref. [17].

or $CO + H_2$ or $C_2H_6 / C_2H_4$ (methane oxidative coupling); $CH_4 + air + SO_3 \rightarrow CH_3OSO_3H \rightarrow CH_3OH$ (see below and Fig. 6); $CH_4 + HCl \rightarrow CH_3Cl + H_2$ or $C_2H_6 + air \rightarrow C_2H_4$ (oxidative dehydrogenation (ODH) or $CH_3COOH$), $C_3H_8 + air \rightarrow C_3H_6$(ODH) or $CH_2 = CH–COOH$ (acrylic acid); $C_3H_8 + NH_3 + air \rightarrow CH_2–CH–CN$ (acrylonitrile).

### 3.2. Case of methane

Ideally many transformations of methane into valuable chemicals could be possible as schematised in Figs. 6 and 7 and in the bullet list below, but at present only methane partial oxidation to $CO + H_2$ mixture (syngas) and its further transformation is industrially viable.

- Methane oxidation to syngas: $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ ($\Delta H°_{298} = -36$ kJ/mol) followed by $CO + H_2$ transformation

to methanol/dimethyl ether by known processes (e.g., Cu/ZnO catalyst) and further MTO or MTG, processes or hydrocarbon mixtures in Fisher–Tropsch processes, etc.

- Methane to ethane/ethene by oxidative coupling: studied for many decades since pioneered works on Li/MgO system by Ito et al. [13] and on Ln-type oxides (Ln = Ne, Sm, Gd) without any process developed up to now [14].
- Methane oxidation to oxygenate compounds: methanol, formaldehyde still in research domain although some successes have been gained.
- Non oxidative methane aromatization (to benzene, naphthalene, etc.) at high temperature > 700 °C upon Mo/MFI catalyst [15].
- Two-step conversion of methane to methanol via methyl bisulfate using oleum as an oxidant [16].
- Methane to propylene in a two-step route via methane oxy chlorination/bromination to $CH_3Cl$ or $CH_3Br$ on $CeO_2$ and H-MFI catalyst [17] (See Fig. 6).
- Methane to formaldehyde on $VO_x/SiO_2$ prepared according to a new method [18].
- NiO small clusters/$ZrO_2$–$CeO_2$ acting as Lewis acid sites for methane to methanol [19].
- Silica-supported tantalum hydride, $(\equiv SiO)_2Ta$–H for the direct non-oxidative coupling transformation of methane into ethane and hydrogen at 250 °C, with a high selectivity (>98%) [20].
- Iron phosphate ($FePO_4$) to give methanol by oxidation of methane with $O_2$ when co-fed with $H_2$ [21], and also to oxidise ethane to ethylene when using $O_2$ as an oxidant [22] and oxygenated products by $O_2$ in the presence of $H_2$ and $N_2O$ [23].

Many other examples of methane activation can be found in the literature but none had a chance to be commercialised in a near future. One can cite an example of methane and ethylene selective oxidation in water [24], for which it has been shown that stable $\mu$-nitrido di-iron phthalocyanine activates $H_2O_2$ to form a high-valent di-iron oxo species. This species is a very powerful oxidant which oxidises methane in pure water at 25–60 °C to methanol, formaldehyde and formic acid [24]. The catalytic activity can significantly be increased in the presence of a diluted acid solution. Thus, a high turnover number of 209 was attained in 0.075 M $H_2SO_4$. Oxidation of ethylene resulted in the formation of formic acid as a major product and formaldehyde with high turnover numbers. The practical and green features of this approach as well as the relevance to biological oxidation (binuclear structure of bio-inspired complex) are of great importance both from practical and fundamental points of view.

### 3.3. Case of lower alkanes $C_2$–$C_6$ oxidatively transformed into olefins (ODH) [25] or oxygenates with O-insertion

This topic has already been largely studied in the literature and many review articles [6,26] and books [27] can be found on the subject with vanadium ion being a key element in the solid catalyst.

More recently a new family of catalysts based on NiO was published [28] for ethane selective oxidation. Such catalysts present high catalytic activity for ethane conversion and ethylene selectivity. The preparation procedure of the catalysts (sol–gel or precipitation methods) has been observed to govern its catalytic properties, whatever activity and selectivity [29,30]. When Nb was deposited on NiO, the catalytic activity for ethane conversion and ethylene selectivity were improved. This phenomenon was assigned to electron transfer enhancement played by Nb, leading to easier activation of the C–H bond of ethane.

Another aspect of ethane partial oxidation is not only the formation of ethylene but also that of acetic acid. The main pro-
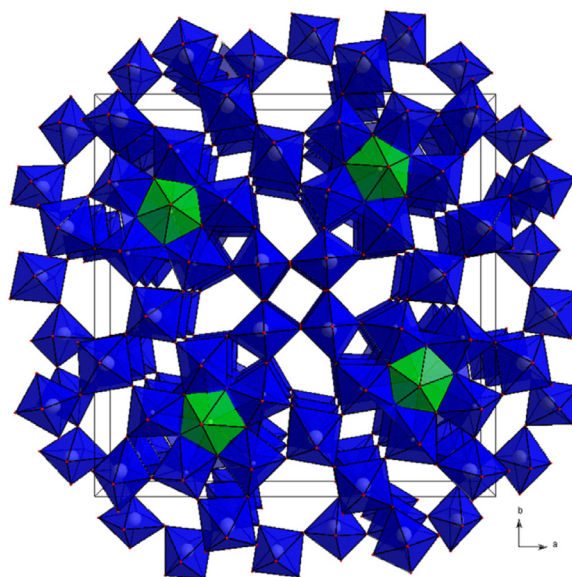


**Fig. 8.** Crystal structure of $Mo_5O_{14}$ crystal composed of $MoO_6$ octahedra.

cesses for synthesis of acetic acid include methanol carbonylation on Rh or Ir-based catalysts (originally by Monsanto, now also by Celanes, BP-Cativa, etc), liquid phase oxidation of acetaldehyde, n-butane and naphta and more recently ethylene oxidation in gas phase (Showa Denko), butenes liquid phase oxidation (Wacker) and gas phase ethane oxidation. The later reaction $C_2H_6 + (3/2)$ $O_2 \rightarrow CH_3COOH + H_2O$ is only viable, if ethane is easily available on the industrial platform and cheap. Different classes of catalysts have been proposed but the most performant ones are a mixed $(VNbMo)_5O_{14}$ based oxide described by Thorsteinson et al. [31] with a D-spacing close to 0.40 nm. The best composition was claimed to be $Mo_{0.73}V_{0.18}Nb_{0.09}O_x$ with 10% ethane conversion at 286 °C and almost total selectivity to ethylene. At 200 °C catalysts based on $(MoVNb)_5O_{14}$ microdomains in $MoO_3$, were found to give 45% selectivity both in acetic acid and ethylene, at 25% ethane conversion. It was suggested that ethane first adsorbs on $Mo^{6+}$ or $V^{5+}$ to form an ethoxide species which transforms to ethylene by $\beta$-elimination, but also possibly oxidises and then acetaldehyde by $\alpha$-elimination, transformed to surface acetate and then to acetic acid by its hydrolysis. MoVNb-O catalyst family thus appears as the most promising possibility at present for ethane to ethylene and acetic acid, the problem being that both products are formed and limiting acetic acid formation, if desired, is difficult. However, when adding Pd the selectivity to acetic acid may reach 80% [32,33], whereas adding water in the feed increases acetic acid formation [34]. The same effect holds true for propane oxidative dehydrogenation by Pt-$H_3PMo_{12}O_{40}$ [35] with $O_2$ and $H_2$, for propane ammoxidation to acrylonitrile. High transformation to acetic acid were claimed by Saudi Basic on MoVNbP-O; MoVLaPd-O; MoVNbPd-O under pressure 1–2 MPa. The technology developed by Saudi Basic is now commercial [36], as the catalyst presents multifunctionality, ethylene as well as acetic acid are rather stable compounds and do not transform to $CO_2$ in the catalytic conditions chosen, unconverted ethane and ethylene being recycled.

The basic structure of $Mo_5O_{14}$ material is shown in Fig. 8. It is known that some amounts of other cations such as V, Ta, Te, Sb or Nb can be incorporated in the structure as determined by XRD analysis (see Fig. 9).

At this stage, it is important to note that such a structure initiated in 1978 has been found later on after inserting cations such as V, Nb, Sb and Te [38] to also catalyse propane direct oxidation to acrylic acid and ammoxidation to acrylonitrile and to lead to a
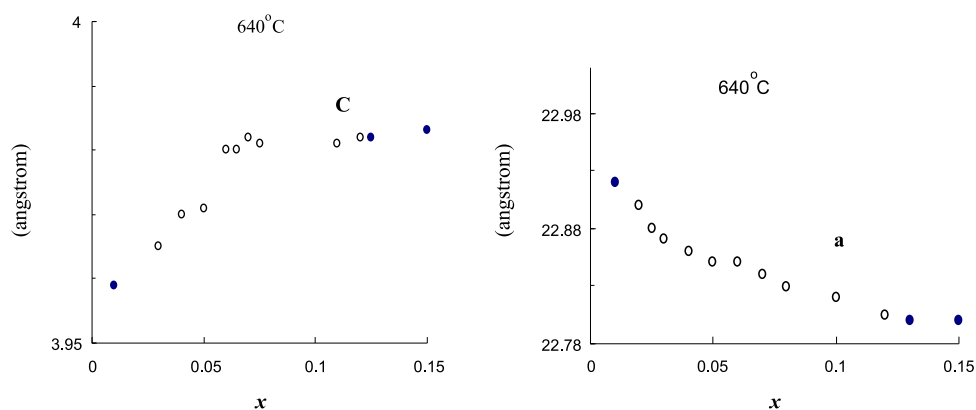
**Fig. 9.** Lattice parameters vs. $x$ in $(Mo_{1-x}V_x O)_{2.8}$ upon insertion of V (left) and Nb (right) in $Mo_5O_{14}$ from Ekström et al. [37].
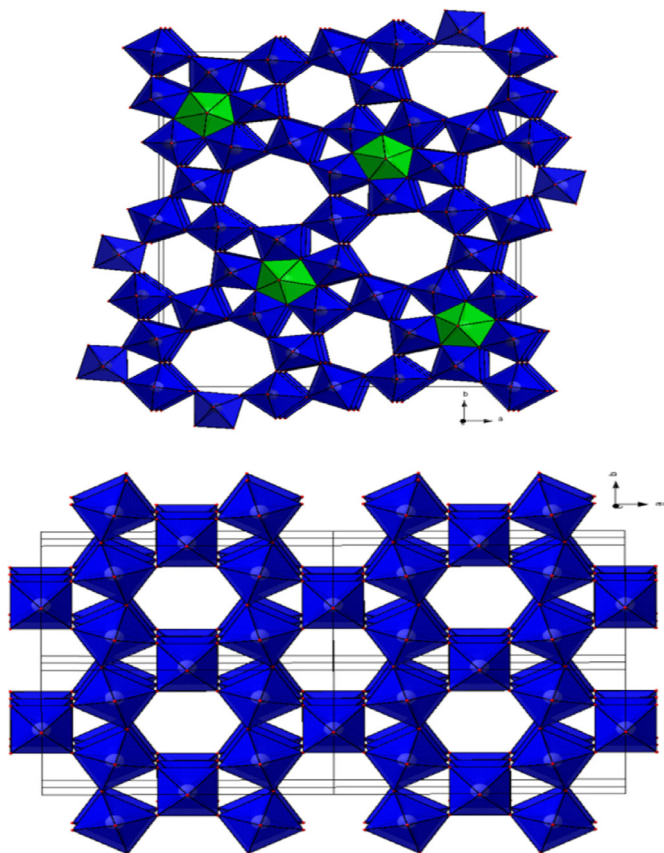


**Fig. 10.** Representation of the structure of the phases M1 (top) M2 (bottom) along the $c$-axis $MO_6$ octahedra, from Ref. [39].

new industrial process for acrylonitrile. Two main components of such material have been identified to be determining the phases designated M1 and M2 (shown in Fig. 10), who were found to act synergetically in propane oxidation reaction.

The propane to acrylic acid reaction proceeds via the following reaction steps on MoVTeNb-O, whereas the active sites were suggested to be either 4 monomeric or two dimeric units of redox storage to deal with one $O_2$ molecule (see Fig. 11 right).

- $4V^{+4}\text{-OH} + 4OH^- \rightarrow 4V^{+5} = O + 4e^- + 4H_2O$.
- $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$.
- $4\ V^{+4}\text{-OH} + O_2 \rightarrow 4V^{+5} = O + 2H_2O$.
- $O = V\text{-O-V} = O + C_3H_6 \rightarrow O = V\text{-O-V-}OC_3H_5 + H^+ + e^-$.
- $O = V\text{-O-V} = OC_3H_5 + H^+ + e^- \rightarrow HO\text{-V-O-V-}OC_3H_5$.

- $HO\text{-V-O-V-}OC_3H_5 + 3OH^- \rightarrow HO\text{-V-O-V-}OC_3H_4O + 2H_2O + 3e^-$.

A large number of catalysts, in majority V based, have been investigated for propane ODH but propene yield varies in the 8–20% range. The upper yield was attained with VMgO, $Mg_2V_2O_7$ or $MgV_xSb_yO_z$, or with orthovanadate on hydrotalcite [42], while $V_2O_5$ supported on $Al_2O_3$, $Bi_2O_3$, $La_2O_3$, $Nb_2O_5$, $SiO_2$, $Sm_2O_3$ or $TiO_2$ gives inferior performances. Co and Ni molybdates were also investigated with different dopants such as Fe, Mg, Ni or P and gave yield near 15% with high productivity and no production of undesirable oxidised products. The major problem is that in addition to alkane activation such metal oxide catalysts may possess also O- or NH-insertion properties and thus may give undesired oxygenates or nitriles in addition to the olefin. The use of Pt based catalyst and of short contact times may be a solution to get mainly the olefin, which is known to be a reaction intermediate. At variance, one may add a catalyst known to transform the olefin to unsaturated carboxylic acids or nitriles for complete transformation of alkanes to carboxylic acids or nitriles, but both operating temperature and chemical compatibility of both catalysts need to be optimised.

Another aspect in ODH reaction is the nature and surface density of surface oxygen species. For instance, in the case of propane ODH both propylene and ethylene can be formed depending on the reaction mechanism by dehydrogenation or cracking. Comparing non reducible (rare earth/alkaline earth oxides) and reducible (V based oxides) catalysts, it was shown [43] that the ratio propylene over ethylene depends on the strength and mainly the density of oxidising active sites (DOS), high DOS favouring propylene. The oxidising sites are those active for H-atom abstraction, usually $V^{5+} = O$ and or bridged $V^{5+} - O - M$ (M = metal cation in the next cationic position, i.e., V or another metal atom from the structure or support).

In the case of n- and i-butane ODH reaction to butene and isobutene on catalysts of the same type as for ethane or propane such as VMgO or metal molybdates or $\gamma$-$Al_2O_3$ supported vanadium pentoxide. MgO supported vanadium was reported as a very selective catalyst in propane and n-butane ODH, and to exhibit a good selectivity to ethylene for ethane ODH but a poor selectivity in the ODH of n-butane. The acid–base character of the support was suggested to lead to this different behaviour. On MgO, a support with basic properties, the interaction between vanadium species and the support leads to the formation of vanadate compounds. In the case of more acid supports, such as $SiO_2$ or $Al_2O_3$ a weak interaction is expected leading to less dispersed vanadium species on the surface favouring the formation of $V_2O_5$ crystallites.

However, the most important process concerns butane (pentane) partial oxidation on $(VO)_2P_2O_7$ catalyst designated as VPO and which has substituted the old benzene oxidation process in

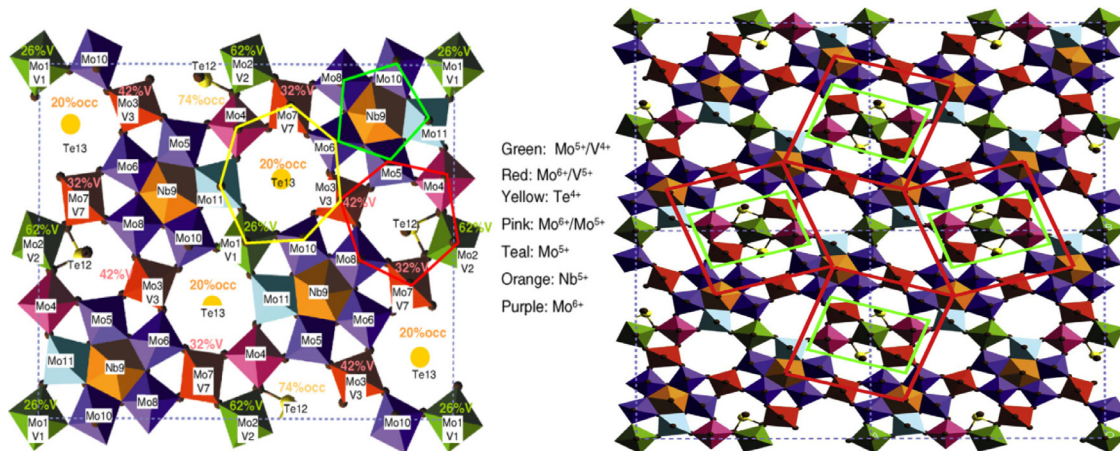**Fig. 11.** Bulk ab planes of M1 phase (right). Refined orthogonal structure had the space group Pba2, formula unit $Mo_{7.8}V_{1.2}NbTe_{0.937}O_{28.9}$, and lattice parameters, $a = 2.1134$ nm, $b = 2.6658$ nm, and $c = 0.40146$ nm with $z = 4$, from Ref. [40]. Active site in $Mo_{7.8}V_{1.2}NbTe_{0.94}O_{28.9}$ (M1): $2 \times 2$ unit cell structure model of M1 in [001] projection showing four isolated catalytically active centres (left). The active sites are isolated from each other by four Nb-bipyramids that are surrounded by five $MO_n$-octahedral. From Fig. 10 in Ref. [41].
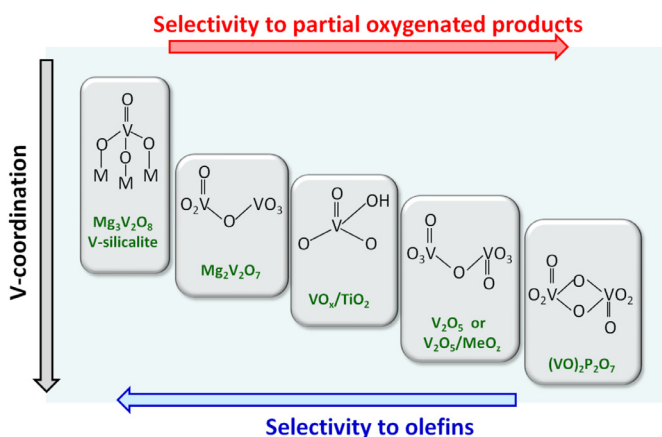


**Fig. 12.** Importance of the V-structure in V-catalysts for H-abstraction and O-insertion. From Fig. 24.3 in Ref. [6].

**Table 4.** Summary of the best results in the literature for partial oxidation of $C_2$–$C_3$ alkanes from Ref. [6] p.772 and references herein.

| | T ( °C) | Conversion (%) | Selectivity (%) | Yield (%) |
|---|---|---|---|---|
| *Ethane → ethylene* | | | | |
| MoVTeNbO | 400 | 85 | 88 | 75 |
| NiNbO | 400 | 51 | 90 | 47 |
| VCoAPO-18 | 600 | 57 | 60 | 34 |
| *Ethane → acetonitrile* | | | | |
| NbSbO/Al$_2$O$_3$ | 540 | 40 | 50 | 20 |
| Co-BEA | 476 | 47 | 57 | 26 |
| *Ethane → acetic acid* | | | | |
| MoVSbNbReCaO | 277 | 14 | 78 | 11 |
| MoVNbPdO$x$ | 300 | 5 | 82 | 4.1 |
| *Propane → propylene* | | | | |
| VMgO | 540 | 62 | 38 | 24 |
| V-silicalite | 550 | 30 | 70 | 21 |
| *Propane → acrylonitrile* | | | | |
| MoVTeNbO | 420 | 86 | 72 | 62 |
| VSbWO$x$/SiO$_2$-Al$_2$O$_3$ | 500 | 67 | 60 | 40 |
| *Propane → acrylic acid* | | | | |
| MoVTeNbO | 432 | 69 | 67 | 46 |
| MoVTeNbO A relevant | 380 | 80 | 61 | 49 |

the 1980s. Active sites have been described as ensembles of four dimers of octahedral $VO_6$ entities isolated by $P_2O_7$ groups [44]. In such a reaction, maleic anhydride is relatively stable to further oxidation which permits high yields. This is also why in a moving bed technology, developed in Asturias, Spain by Du Pont Co, the catalyst encapsulated by porous silica to limit attrition of catalyst grains, maleic anhydride was further transformed to less stable tetrahydrofurane (THF) by reduction on Pd based catalyst.

For a more general point of view the role of vanadium atom oxygen arrangement in catalytic properties is schematised in Fig. 12.

The process of propane ammoxidation is an eight-electron oxidation reaction and requires a catalyst or combination of catalysts which are even more complex than those for the ammoxidation of olefins (e.g., propylene): $CH_3CH_2CH_3 + NH_3 + 2O_2(air) \rightarrow CH_2 = CHCN + 4H_2O$.

There has been great studies to develop an ammoxidation process based on propane rather than propylene, as the price and availability of propane are more favourable than for propylene. The task is difficult from a commercial standpoint, since the well-established and well-functioning propylene based process is constantly being further improved, and the catalysts therefore constantly made better, more efficient and environmentally friendlier. It is simply a moving target, difficult to hit, yet not out of reach

and will be achieved in due time. Many catalysts have been tested for the ammoxidation of propane to acrylonitrile, and the most effective of them fall, as do propylene ammoxidation catalysts, into two main classes: they are either antimonates or molybdates. Among the antimonates, the most studied belong to the family VSb*xMy*, where M can be many different elements, with the most frequently used dopants being W, Te, Nb, Sn, Bi, Al, and Ti. Virtually all of these antimonates possess the rutile or trirutile structure. Some of the highest acrylonitrile yielding catalysts are summarised in Table 4.

The molybdate family is represented by VMo*xMyOz*, where M is most often Bi or Te. Some catalysts are of the scheelite structure, others are multiphase and of more complex structure. Among these molybdates, the highest acrylonitrile yields are claimed for a catalyst composition having the empirical formula $V_{0.3}Te_{0.23}Nb_{0.12}MoO_x$ supported on $SiO_2$.

### 3.4. Active sites in metal oxides for partial oxidation of light alkanes

From the analysis of many publications dealing with subject and the main features of the solid catalysts one may make further suggestions. It is clear that ensembles of atoms constitute the
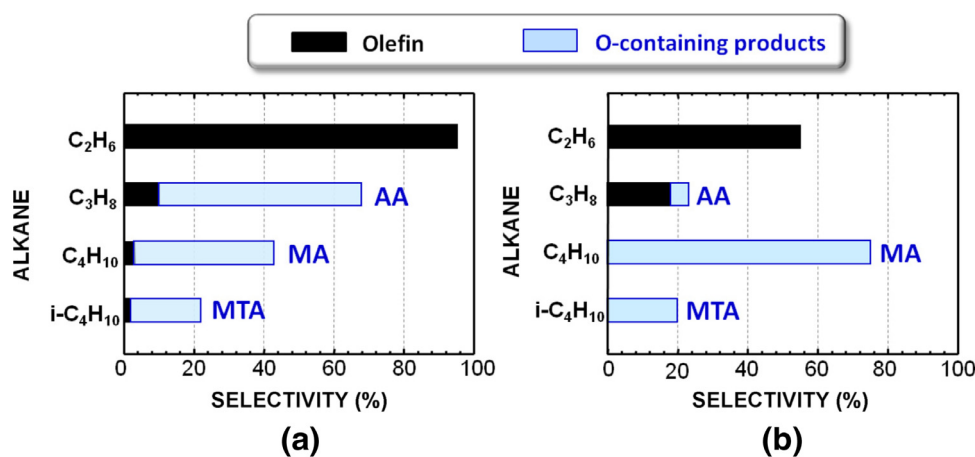
**Fig. 13.** Selectivity to the main partial oxidation products achieved during the partial oxidation of $C_2$–$C_4$ alkanes over MoVTeNbO (a) and VPO (b) catalysts. AA = Acrylic acid; MA = maleic anhydride; MTA = methacrolein. From Fig. 24.5 in Ref. [6].
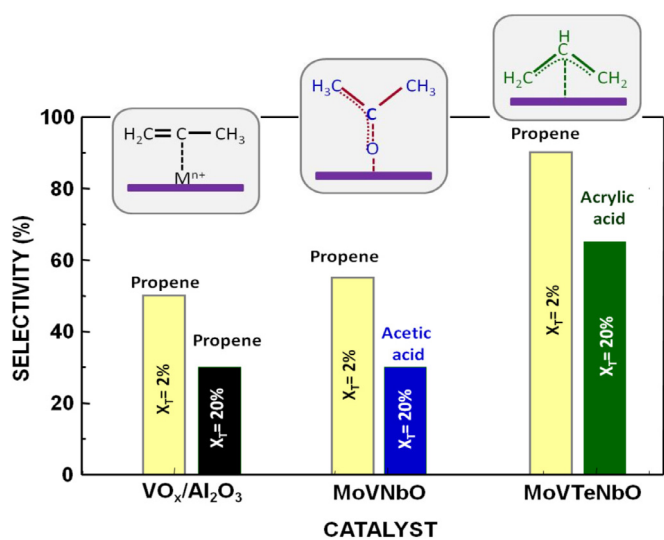


**Fig. 14.** Selectivity to the main partial oxidation product achieved at low conversion (XT = 2%) and high conversion (XT = 20%) during propane oxidation at 400 °C on $VO_x$/$Al_2O_3$; Mo–V–Nb mixed oxides calcined in air at 450 °C (amorphous); Mo–V–Te–Nb mixed oxides heat-treated at 600 °C in $N_2$ presenting M1 phase (MoVTeNbO). The main adsorbed species observed during the adsorption of propylene on each catalyst is shown. From Fig. 24.4 in Ref. [6].

active site but the size and arrangement of such atoms in the ensemble looks important. If one considers the data in Figs. 12–14, it appears that many metal oxides can catalyse many reactions but the activities and selectivities depend on the organic reactant molecule, in particular on its size vs. active site size and the number of electrons involved in the redox process.

## 4. Conclusions

Catalytic selective oxidation is a scientific area in which recent advancements have led to remarkable steps forward towards a more sustainable chemical industry. This may require rethinking the chemical productions through an innovative vision. However, the key-issue still remains selectivity. In catalytic oxidation, the recent developments clearly show that better selectivity, better sustainability and improved economics often go hand in hand. One may summarise the general aspects in heterogeneous selective oxidation reactions.

(1) Flexibility of the oxide surface under catalytic (redox) conditions (living surface) avoiding any structure collapse during the redox process [45].
(2) Collective properties: electron transfer (electrical conductivity), changes in adsorption properties.
(3) Influence of the co-adsorbate on the bond between the adsorbate and the surface.
(4) Role of catalyst surface adlayer composition on activity and selectivity as very often met [46].
(5) Oxygen species involved in the reaction: lattice oxygen anions, weakly adsorbed oxygen species.
(6) Mechanism and anisotropy of oxygen migration.
(7) Importance of surface species which do not play a direct role in the reaction mechanism, e.g., $H_2O$, carbon deposit (fouling), as spectators.

For the future, more efficient integration of oxidation reactions with up- or down-stream processes, and more efficient oxidation technologies should be developed. The main rules and advices for the development of more sustainable oxidation processes can be summarised in some bullet points:

(1) Make reactions where the amount of co-product is minimal – first, use reactants with maximum atomic incorporation into final products.
(2) Search for solvents, when needed, that are non-toxic, and can be easily separated and re-utilised.
(3) Search for methods to immobilise catalysts (anchoring, grafting,…) over supports that can be filtered.
(4) Consider that the reaction may be a part of a more complex process. Integration has to be thought from the beginning of the research activity.
(5) From a scale-economy approach to a modular design based on parallel small units (intensification, microreactors technology).
(6) Search for reaction conditions at which the selectivity is the highest (analysis of the reaction scheme), rather than productivity or yield.

All these aspects show that large efforts in researches, process development, reactors design [47], new catalysts, new activation procedure, are necessary to improve selective oxidation reaction, looking mainly on providing a better selectivity.

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