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Advances and future trends in selective oxidation and ammoxidation catalysis

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Abstract

A review of the current status and future trends in oxidation catalysis is presented. The topics entail the (amm)oxidation of propylene to acrylonitrile using complex multicomponent mixed metal molybdates and antimonates as catalysts, the ammoxidation of propane to acrylonitrile using V-Sb-oxides or V-Te-Nb-Mo-oxides, the oxydehydrogenation of light paraffins using Ni-Co-molybdates or Mg-V-Sb-oxides, dehydrogenation of propane combined with selective hydrogen oxidation using Group VIII elements, oxidation of propane to acrylic acid using complex molybdates, and the (amm)oxidation of xylenes to terepthalic acid or terepthalonitrile using Fe-Mo-modified ZSM-5 catalysts.

The respective reaction mechanism of the prevailing selective catalytic oxidations are discussed, as are the specific functionalities of the various elements contained in the mixed metal catalysts. Some new approaches to the rational design and synthesis of improved catalysts are offered.

Keywords: Selective oxidation; Ammoxidation catalysis; Oxydehydrogenation; Molybdates; Antimonates; Phosphates; Olefins; Paraffins; Aromatics

1. Introduction

Selective catalytic oxidation and ammoxidation processes of hydrocarbons comprise approximately one quarter of the value produced by all catalytic processes world wide. They contribute hence significantly to the gross national product of industrial countries and afford future opportunities for developing countries.

These processes are not only important from a commercial standpoint and their contribution to the well-being of modern mankind, but they also present the opportunity for significant fundamental research. Such research aims at the molecular level understanding of catalytic behavior, forming a basis for rational design of catalyst improvement of existing processes and the discovery of totally new catalysts and processes.

This paper limits itself to the chemistry of selective oxidation and ammoxidation processes of large volume chemicals and intermediates, addressing their current status and presenting the author's views of future opportunities. Although only the catalysis of large volume chemicals is addressed, the principles advanced are also applicable to the catalysis of fine chemicals production.

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2. Discussion

2.1. Ammoxidation of olefins

The ammoxidation of propylene to acrylonitrile commands the foremost commercial position among all ammoxidation processes [1,2]:

$$CH_2{=}CHCH_3 + NH_3 + 3/2O_2 \text{ (air)} \xrightarrow{\text{catalyst}} CH_2{=}CHCN + 3H_2O$$

More than 10 billion pounds of acrylonitrile are produced worldwide by this SOHIO (now BP America) invented process. Acrylonitrile is a versatile petrochemical intermediate used extensively in the production of acrylic fibers, resins, rubbers and specialty products.

As is well documented in [1,2], ammoxidation is a six-electron redox process (Fig. 1) requiring catalysts able to activate propylene through the abstraction of an α-hydrogen, followed by NH-insertion, subsequent rearrangements of the chemisorbed activated surface species with additional hydrogen abstraction, and culminating in the desorption of the so formed acrylonitrile from the catalyst surface. The catalyst which is reduced in this propylene ammoxidation process is continuously regenerated in situ by gaseous oxygen present in the air of the feed gas mixture. This occurs by facile lattice oxygen transport from a surface reoxidation site, where dioxygen is built into the catalyst, to the reduced active center as shown in Fig. 1. In this manner the catalytic cycle of ammoxidation is completed: one molecule of propylene and ammonia, and one and one half dioxygens are consumed with the production of one molecule of acrylonitrile and three molecules of water, and the catalysts' active center is reconstituted to its original fully oxidized form.

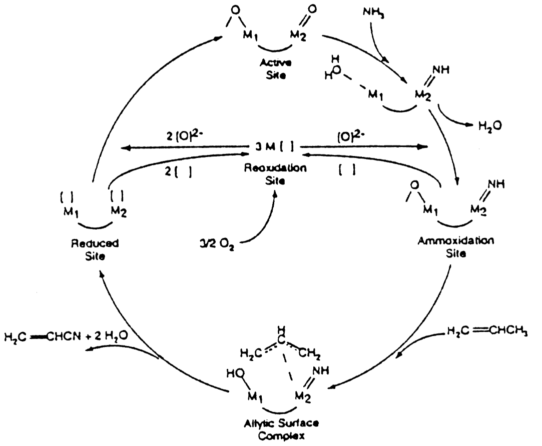

Fig. 1. Generalized mechanistic cycle for alkane ammoxidation [2].

The most commonly used catalysts for this reaction are either those based on mixed metal molybdates or mixed metal antimonates. These systems continue to dominate the field.

2.1.1. Multicomponent complex mixed metal molybdates

Over the past 20 years several generations of multicomponent molybdates have been developed, and the compositions are becoming ever more sophisticated and complex, giving ever better yields of the desired acrylonitrile product. The last three catalyst generations, summarized according to their empirical formulae, are presented in Table 1.

These compositions have been fine tuned for maximum acrylonitrile yield production in fluid bed reactors, the reactors of choice in commerce, and each element contained within these compositions has its designated function and performs accordingly.

For example, it is by now well known that the primarily function of bismuth [1,2] in these compositions is its ability to activate the surface adsorbed propylene through the abstraction of an α-hydrogen. The function of molybdenum is to chemisorb propylene and activate the ammonia molecule by generating chemisorbed NH-species which are capable of inserting into the chemisorbed allylic intermediate, creating the acrylonitrile precursors. The function of iron is to serve as an efficient redox couple ($Fe^{3+/2+}$), capable of efficient lattice oxygen transfer to the Bi–O–Mo active site in its 3+ oxidation state. In its 2+ state it is capable of efficient dioxygen chemisorption, its reductive transformation to lattice oxygen (O^{2-}) and hence its incorporation into the lattice.

Since it is very difficult to maintain a sufficient number of Fe^{2+} surface sites in an overall oxidizing gaseous atmosphere, it is necessary to stabilize the Fe^{2+} state structurally. To this end divalent elements such as Ni, Co, Mg and Mn form stable isostructural molybdates with Fe^{2+} molybdates, and by virtue of

Table 1

	Acrylonitrile in-tank yield (mole % based on feed propylene)	Reference
$K_a(Ni,Co)_9Fe_3BiPMo_{12}O_x$–$SiO_2$	~75	[3,4]
$(K,Cs)_a(Ni,Co,Mn)_{9.5}(Fe,Cr)_{2.5}BiMo_{12}O_x$–$SiO_2$	~78–80	[5]
$(K,Cs)_a(Ni,Mg,Mn)_{7.5}(Fe,Cr)_{2.3}Bi_{0.5}Mo_{12}O_x$–$SiO_2$	>80	[6]

solid solutions stabilize the Fe^{2+} state. Thus Ni, Co, Mg and Mn have the function of providing the host structure for Fe^{2+} in these multifunctional, multiphase catalysts.

In a similar manner, Fe^{3+} is stabilized through its limited solubility in the α-bismuth molybdate phase, the latter phase providing the host structure for Fe^{3+}. The $Cr^{3+/2+}$ is a redox couple of its own, generally, effective at a temperature higher than that of the iron couple. But it also acts as a structural diluent to iron and booster of the Fe^{3+} state in the Bi-molybdate matrix.

The role of the alkali is to annihilate the most acidic cracking sites of the compositions, to serve as a spacer and contact enhancer of the two functionally distinct but epitaxially matched catalyst phases. The two phases are composed of the Fe^{3+} containing catalytically active α-bismuth molybdate phase and the Fe^{2+} containing (Ni, Co, Mg, Mn) molybdate phase. These two phases must cooperate with each other, and therefore, they must be in utmost proximity of each other; they would be ineffective if remotely separated from each other. For this reason it is of interest that the most effective multiphase oxidation catalysts have at least one face which is for all practical purposes epitaxially essentially matched (principle of phase cooperation [7]).

A schematic representation of such a phase cooperation between two functionally distinct phases of typical multicomponent multiphase catalysts enumerated above is shown in Fig. 2.

The necessity of having two functionally distinct phases to attain high acrylonitrile yield efficiency is illustrated in Fig. 3 [8]. It is obvious that the Fe^{3+} containing Bi-molybdate active phase, as well as the Fe^{2+} containing M^{2+}-molybdate regeneration phase, must be present at the same time to attain high acrylonitrile product yields.

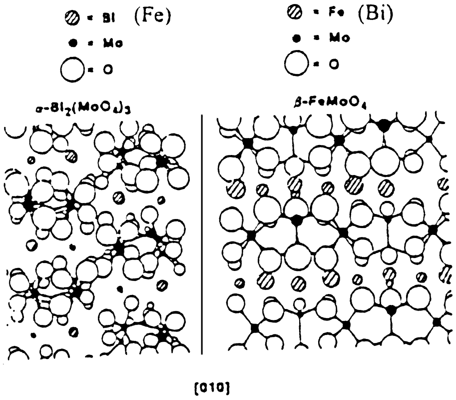

Fig. 2. Epitaxial match at the (0 1 0) face of $Bi_2Mo_3O_{12}$ and β-$FeMoO_4$ [7].

Future trends. While a great deal has already been achieved in the propylene ammoxidation catalysis, there is still ample room for further improvement. Since the process is not thermodynamically limited, there is another 20% acrylonitrile to be conquered. Approaches that might be fruitful towards this end would include attempts to discover catalysts capable of activating ammonia at lower temperatures; thus allowing for lower temperature process operation and hence anticipated higher acrylonitrile yields and less byproducts caused by cracking reactions and waste forming CO_x processes. Another approach might be aimed at discovering single phases which might be capable of accommodating the two above described distinct catalytic functions within a single phase, by propriciously placing these functionalities in an ordered and optimally designed spatial arrangement. There is also ample latitude left in optimizing the texture of these complex ammoxidation catalysts. Surely there are other approaches to be pursued to achieve higher desired product yields and environmentally more optimal product mixes.

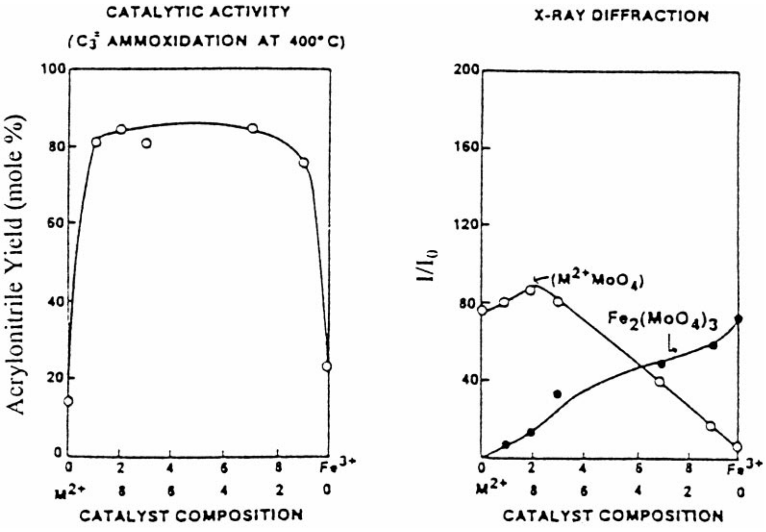

Fig. 3. Relationship between catalytic activity and phase composition of $K_a^{1+}M_b^{2+}M_{10-b}^{3+}Bi_xMo_yO_z/SiO_2$ [8].

2.1.2. *Multicomponent complex mixed metal antimonates*

The pinnacle of commercial antimonate catalysis was reached some years ago with the introduction of the $USb_3O_{10}\cdot 0.8Sb_2O_4\text{–}SiO_2$ [9–11] catalyst which used ^{235}U depleted uranium. However, its commercial dominance was rather short, not because of its product yield structure or catalyst life problems, but rather because of presumed environmental concerns owing to minimal residual radiation from the depleted uranium contained in the catalyst.

The successor catalyst became an Fe–antimonate system. This latter Fe–Sb oxide based catalyst has undergone extensive study and compositional changes over the years, with concomitant improvements in acrylonitrile yield. Without these changes the complexity of the composition has also increased greatly.

Catalysts currently used on commercial scale can be described by the following empirical formula:

$$Na_{0-3}(Cu,Mg,Zn,Ni)_{0-4}(V,W)_{0.05-1}Mo_{0.1-2.5}Te_{0.2-5}\,Fe_{10}Sb_{13-20}O_x\text{–}SiO_2$$

(cf. [12,13]). They typically yield ~75% in-tank acrylonitrile.

As is the case with the complex molybdates described above, the individual functions of the various elements contained in the complex antimonates are also well understood, but will not be described here, because of space constraints.

Although the in-tank acrylonitrile yields of the above antimonate catalyst compositions are respectable, they do not measure up to the productivities of the best molybdate catalysts discussed. In addition, the antimonate based catalysts are much more fragile than the molybdate based systems under commercial operation. Therefore, it is imperative to operate the antimonate systems under rigidly controlled operating conditions, in order to prevent possible plant upsets and irreversible reduction which leads to the destruction of the antimonate catalysts. In contrast, the later generation molybdate based catalysts are almost indestructible and can easily withstand inadvertent plant upsets, including severe reductions. It is for these reasons that the complex mixed metal molybdates are currently the industrially preferred catalysts for the ammoxidation of propylene to acrylonitrile.

Future trends. The greatest advance in antimonate catalysts would be to improve their redox stability and irreversible structural changes caused by severe reduction. This problem has been partially addressed by incorporating efficient redox components such as Fe–molybdates and Fe–tungstates to the compositions. All advanced Fe–antimonates contain some molybdenum, and mostly also some tungsten. It is difficult to match these phases, and special preparational and calcination techniques are required to achieve these goals. Another desirable aim would be to replace the tellurium by another element having similar selectivity imparting properties in antimonates since tellurium is easily reducible and thus rather volatile and poisonous. Attempts to replace the Te with Bi have not fully achieved the desired goal. The search is still on. In fluid bed reactors, a raised sparger (i.e., propylene and ammonia feed inlets) and lowered air inlet, constituting an auto-regenerative zone [14], are useful engineering expedients towards improved catalyst stability and life.

2.2. *Ammoxidation of paraffins*

Among paraffin ammoxidations, the ammoxidation of propane is furthest advanced, although not as yet fully commercialized. BP America (formerly SOHIO) has announced on several occasions that it is commercializing the process [15,16]; however thus far this has not been realized, although the process is allegedly in pilot plant stage at BP.

The process is an eight-electron oxidation and requires a catalyst or combination of catalysts which are even more complex than those for the ammoxidation of olefins (e.g., propylene):

$$CH_3CH_2CH_3 + NH_3 + 2O_2 \text{ (air)} \xrightarrow{\text{catalyst}} CH_2{=}CHCN + 4H_2O$$

There is ample incentive to develop an ammoxidation process based on propane rather than propylene, since the price and availability of propane are substantially more favorable than those of 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_xM_y, where M can be many different elements, with the most frequently used dopants being W, Te, Nb, Sn, Bi, Al, and Ti [17–19]. Virtually all of these antimonates possess the rutile or trirutile structure. Some of the highest acrylonitrile yielding catalysts are summarized in Table 2.

Table 2

	Conversion	Selectivity	Yield
$VSb_5W_{0.5}Te_{0.5}Sn_{0.5}O_x$–$SiO_2$/$Al_2O_3$ [13,17,18]	68.8	56.7	39
$VSb_5Bi_2Fe_2O_x$–Al_2O_3 [20]	39	84	32
VSb_5Sn_5 [21]	14	60	8

The molybdate family is represented by $VMo_xM_yO_z$, where M is most often Bi or Te [22,23]. Some catalysts are of the scheelite structure [24], 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 [25]. A calcination step in nitrogen at 620°C appears to be crucial for these compositions to attain the proper catalytic solid state structure and herewith the desired acrylonitrile yield. A maximum yield of 55.1% acrylonitrile at 86.7% conversion and 63.5% selectivity has been reported [25]. It is unclear at this time what the desired structure of this composition might be, it has variously been claimed to be a "K-phase" [26] and then again an "M-phase" [27]. The *d*-spacing of the main X-ray diffraction lines are stated to be located at: 4.02 (1 0 0), 3.16 (20–150), 2.48 (5–60), 2.00 (2–40), 1.82 (2–40). Quite a latitude of intensities are recorded and herewith possible differences in catalytic performance. The underlying structure is not all that different from that of Thorsteinson's $V_{0.51}Nb_{0.13}MoO_x$, doped by Te [28]. Unfortunately, thus for it has been rather difficult to independently reproduce the Mitsubishi claimed performance, primarly because of the difficulties connected with the preparation of the catalyst.

The V–antimonate based catalysts have been thoroughly studied structurally, kinetically and mechanistically by several research groups. They are multiphase, containing $VSbO_4$ with rutile structure and α-Sb_2O_4 as a spectator phase, a ready source of excess antimony during the redox process. Working catalysts contain also supra-surface antimony sites

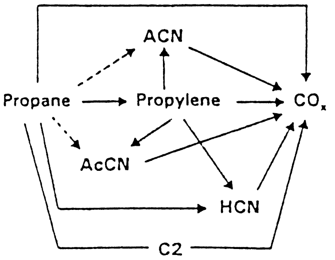

Fig. 4. Kinetic reaction network for propane ammoxidation on V–Sb–Al oxide based catalysts [30]. Legend: ACN acrylonitrile; AcCN acetonitrile.

[29] on top of the $VSbO_4$ phase as a result of antimony migration from the spectator phase during catalytic reaction.

Extensive kinetic studies (Fig. 4) [30] show unequivocally that propylene is a desorbed primary product and the main precursor of acrylonitrile from propane. These and other supporting data suggest that propane is activated by a V–O$^\bullet$ moiety [31,32] of the catalyst by abstracting the first hydrogen from the methylene group of the molecule in the rate limiting reaction of the overall process. The desorbed propylene reacts further on adjacent Sb^{3+}–O–Sb^{5+} surface sites, whereby the Sb^{3+}–O site is responsible for the rate limiting abstraction of an α-hydrogen from the propylene molecule and an Sb^{5+}=NH site for the nitrogen insertion into the chemisorbed allylic surface complex, which after rearrangement and additional hydrogen loss desorbs as product acrylonitrile [33]. The reoxidation of the catalyst occurs by lattice oxygen (O^{2-}) migration from the reoxidation site to the active site with anion vacancy migration in the opposite direction. The reoxidation sites contain V^{4+} moieties capable of dioxygen dissociation and its incorporation as lattice oxygen into the catalyst structure. This process keeps the lattice oxygen concentration at a steady state during the redox process of propane ammoxidation.

The V–Sb oxide based paraffin ammoxidation catalysts are multiphase in nature, containing a paraffin activating phase ($VSbO_4$) and an olefin ammoxidation phase (e.g., Sb^{3+}–O–Sb^{5+} overlayers on top of $VSbO_4$; or an excess Sb containing solid solution of a $VSbO_x$; or $FeSb_aO_x$; $SnSb_aO_x$; $TeSb_aO_x$; etc.). The matching of these phases still needs to be improved to improve ammoxidation yields.

The V–molybdate based catalysts are also multiphase in nature. Here too a V–O$^\bullet$ moiety of a VMo_xO_y phase is responsible for the propane activation and propylene is the primary first formed product. The propylene reacts further on an olefin ammoxidation co-phase such as $TeMo_xO_y$ or $BiMo_xO_y$ to form acrylonitrile, as is customary of such phases [33,34]. Here too, it is of great importance to bring these two functionally diverse phases into concert. Further matching is still needed to improve yields.

Future trends. The approach thus far has been rather empirical in the search for propane ammoxidation catalysts. The catalysts reported in the patent literature contain elements with paraffin activating properties (e.g., V) as well as elements of olefin activating properties (e.g., Bi, Te), and O and/or NH-inserting properties (e.g., Sb, Mo). What is missing is the mechanistic cognoscence, that these functions should not simply be tossed at random into a pot, but that a rational approach needs to be worked out to sequence these functionalities either in a single phase if possible, in a solid solution as the next best possibility, or lastly by utilizing the two distinct functionalities in two separate catalytic phases and bringing them into spatial proximity, best through the choice of phases having at least one epitaxially similar plane. The two phases must be also temperature matched, that means that their respective conversion efficiencies must be optimized to a common compromise operating temperature. A third requirement is that the two phases be chemically compatible with each other, so that neither poisons the other. (For example, both are either antimonates or molybdates; it is generally unwise to mix antimonates with molybdates and vice versa, because they cross poison each other. There are a few exceptions to this general rule.) Rather than using two physically distinct particles, it might be possible to prepare the two phases separately in two pots, and combining their ingredients in a paste state or at some convenient intermediate step during the drying and/or calcination.

A rational catalyst design along the lines outlined should result in improved paraffin ammoxidation catalysts. It will be also necessary to keep the concentration of the propylene intermediate low during the process to prevent its destruction by the paraffin activating catalyst. This means, the paraffin activating catalyst must be surrounded by ample olefin ammoxidation catalyst (or its function) and/or the efficiency of the latter one must be increased at the temperature of operation. Ultimately, it will be desirable to invent catalysts capable of activating the paraffin as well as the ammonia at lower temperatures, resulting in higher useful product selectivities.

Another possible approach might be to generate propyl radicals in the gas phase in a pre-reactor and quenching them by an olefin ammoxidation catalyst in a subsequent reactor. Several studies are underway in this direction to produce propylene and/or oxygenates from propane. This approach could be adopted to the propane to acrylonitrile reaction.

2.3. *Oxydehydrogenation of paraffins*

Conventionally practiced dehydrogenations of paraffins, particularly those for the dehydrogenation of propane and isobutane to the respective olefins, are commercially well established. They are endothermic processes and are thermodynamically limited. Best known are the Star (Phillips Petroleum), Catofin (Lummus), Oleflex (UOP), Linde-BASF and Snamprogetti-Yarsintez processes. The Star process uses a supported Pt catalyst and a fixed bed, the Catofin a chromia–alumina catalyst and a fixed bed, the Oleflex a supported Pt catalyst and a moving bed, the Linde-BASF a chromia–alumina catalyst and a fixed bed, and the Snamprogetti-Yarsintez a doped chromia–alumina catalyst and a fluid bed.

Among these, the Oleflex, Catofin and Snamprogetti-Yarsintez processes are commercially practiced. The greatest advantage of these processes is that they are net producers of byproduct hydrogen. Their greatest disadvantages are their thermodynamically limited olefin yields, high frequency of regeneration to burn off coke from the catalyst surface, and the high energy input requirements because of the inherent endothermicity of the process.

For these reasons it would be desired to invent an oxydehydrogenation process, which is inherently not thermodynamically limited for the production of olefins from paraffins. An illustrative example would be the two electron conversion of propane to propylene:

$$CH_3CH_2CH_3 + \tfrac{1}{2}O_2\ (\text{air}) \overset{\text{catalyst}}{\rightarrow} CH_2{=}CHCH_3 + H_2O$$

A large number of catalysts have been investigated for this reaction, with the results being rather halting thus far and no large breakthrough looming immediately on the horizon.

A large majority of the catalysts studied are based on the chemistry of vanadium oxides. V_2O_5-based catalysts give propylene yields between 8% and 20% and are greatly dependent on the loading and the support. The upper yield range is attained with MgO supported catalysts [35], while SiO_2, Al_2O_3, TiO_2, La_2O_3, Sm_2O_3 or Bi_2O_3 supported systems are inferior [36]. Magnesium vanadates have been also investigated [37,38] giving similar yields as V_2O_5 on MgO, $Mg_2V_2O_7$ is implicated as the active phase in the former systems and might also play a role in the latter systems. Recently, a study was reported on the system $MgV_xSb_yO_z$ [39–41].

V_2O_5/Nb_2O_5 catalysts have been also investigated, with $V_2Nb_{23}O_{62}$ presumed to be the active phase [42,43]. Propylene yields of 12% at a relatively high selectivity of 70%, and at high productivity were reported; no partially oxidized products were observed. V-ZSM-5 has also been reported to yield allegedly 25% propylene from propane, however, at very low productivity.

The most noteworthy propane oxydehydrogenation catalysts not based on vanadium chemistry are those based on Co–molybdate and Ni–molybdate. $CoMoO_4/SiO_2$ variously doped with P, Ni, Mg, and/or Fe are reported to yield 15% propylene [44] with high productivity and no production of undesirable partial oxidation byproducts. Unsupported Ni–molybdates were studied as monophases, with β-$NiMoO_4$ yielding 13.2% propylene (20.9% conv., 63.1% sel.) and α-$NiMoO_4$ yielding 9.3% propylene (24% conv., 37.5% sel.) [45,46]. In the latter systems, the β-phase appears to be the more selective and overall preferred catalytic phase.

Recently, a comprehensive study of propane oxydehydrogenation over silica supported molybdate based catalysts of the formula $AMoO_4$, where A=Ni, Co, Mg, Mn, and Zn, has been reported [47]. The reaction network and kinetics of a $Ni_{0.5}Co_{0.5}MoO_4/SiO_2$ system [48] reveal that propylene is the sole primary product of the reaction, that based on isotope studies the abstraction of a methylene hydrogen from propane is the rate limiting step, and that the maximum yield obtained is 16% propylene (34% conv.,

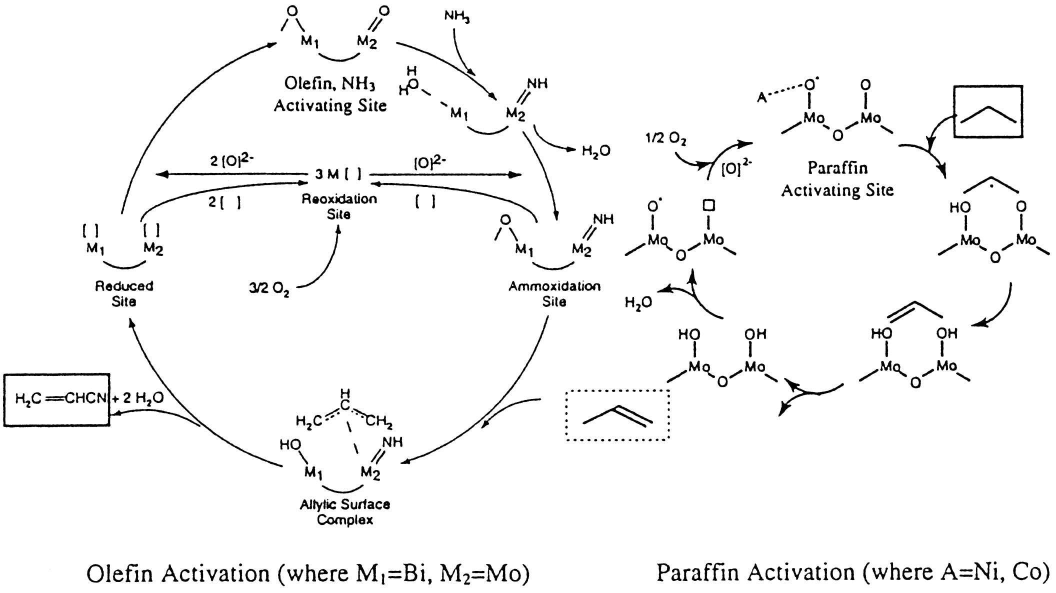

Fig. 5. Proposed mechanism of propane ammoxidation using a paraffin activating catalyst, e.g., $Ni_aCo_bM_cMoM_x$; and a multicomponent mixed metal molybdate olefin ammoxidation catalyst, e.g., $Cs_aK_bNi_cMg_dM_eBi_fSb_gMo_hO_x$; where M=Ce, Cr, and/or Fe [47–49].

47% sel.). These catalysts convert also effectively the first formed propylene product to acrolein ($k_{\mathrm{propylene}}/k_{\mathrm{propane}}=3.5$), but even more efficiently the acrolein on to CO_x ($k_{\mathrm{acrolein}}/k_{\mathrm{propylene}}=13$). For these reasons it is proposed [49] that Ni–Co–molybdates are more likely to find utility as paraffin activation catalysts in combination with known selective olefin conversion catalysts for the direct production of oxygen (e.g., acrylic acid) or nitrogen (e.g., acrylonitrile) containing products, rather than as oxydehydrogenation catalysts for the production of olefins (e.g., propylene). A schematic representation of this concept is illustrated in Fig. 5.

Future trends: VO_x/MgO and $MgVSbO_x$ based systems, as well as Ni–Co–molybdate systems hold some promise as paraffin oxydehydrogenation catalysts. However, because in addition to their paraffin activating properties they also posses oxygen inserting properties, their utility will be better harnessed by combining them with established olefin conversion catalysts to produce unsaturated acids or nitriles. Matching of operating temperature and chemical compatibility of these two catalyst systems needs still to be optimized, as well as the desire to contain the two distinct functionalities in a single solid state structure or solid solution. Ideas along these lines have been developed in Section 2.

To achieve selective oxydehydrogenation of paraffins without the production of undesirable partial oxidation products, it might be useful to turn to noble metal catalysts, e.g., Pt based catalysts, and to carry out the reaction at very short contact times. Some attempts along these lines have already surfaced in [50].

2.4. *Dehydrogenation with selective hydrogen oxidation*

An alternative to paraffin oxydehydrogenation is a compromise between conventional dehydrogenation and oxydehydrogenation; it is dehydrogenation with concomitant selective hydrogen oxidation, illustrated for propane as follows:

$$CH_3CH_2CH_3 \overset{\text{catalyst-A}}{\rightarrow} CH_2{=}CHCH_3 + H_2$$

$$H_2 + \tfrac{1}{2}O_2 \overset{\text{catalyst-B}}{\rightarrow} H_2O$$

A similar concept has been worked out for the ethylbenzene conversion to styrene by UOP in their Smart process.

Suitable catalysts for the first step (catalyst-A) are those selected from Group VIII noble metals, e.g., Pt; while those effective for the second step (catalyst-B) are those selected from selectively poisoned Group VIII metals, e.g., Cs_xPt or Bi_xPt, where x is a small fraction of one. Such catalysts are generally supported on Al_2O_3, sometimes additionally doped with Sn, to make the catalyst steam stable and claimed to have a 95%+ hydrogen combustion selectivity to H_2O [51,52].

More recently, base metal catalysts containing elements selected from the metals Bi, In, W, Mo, etc. have been reported to be effective for the selective combustion of hydrogen (90–99% selectivity), without attacking and combusting the produced olefin [53–56].

High yields of olefins, well in excess of equilibrium, are attainable by staging dehydrogenation/selective hydrogen combustion/dehydrogenation reactors; or zones. The oxygen driven combustion of hydrogen overcomes the conventional dehydrogenation limitation. This process has also appeal by the possibility of a perfect heat balance of the overall process (essentially isothermal).

Future trends. The dehydrogenation/selective hydrogen combustion process has potential until an effective oxydehydrogenation process is discovered. Engineering innovations are desired to optimize heat balancing (sheet and tube reactors are possibilities). Base metal oxides commingled with dehydrogenation catalysts or functionalities therefrom, wherein the oxygen for the hydrogen combustion is carried out by the metal oxide as lattice oxygen, would be desirable innovations. No oxygen plant would be required with such a catalyst system, resulting in substantial savings. The catalyst system would be simply regenerated periodically with air.

2.5. *Oxydehydrogenation of n-butane to maleic anhydride*

The commercially most successful paraffin oxidation process is the 14-electron oxidation of *n*-butane to maleic anhydride:

$$CH_3CH_2CH_2CH_3 + 7/2O_2 \text{ (air)} \xrightarrow{\text{catalyst}} C_4H_2O_3 + 4H_2O$$

Several companies, e.g., BP-UCB, ALMA, DuPont–Monsanto, Misubishi, Denka-Scientific Design, have commercialized the process. Interestingly, all of the companies use essentially the same catalyst, vanadyl pyrophosphate $(VO)_2P_2O_7$, which was originally invented by Chevron [57]. Various improvements are claimed through selective doping, however, the improvements appear minor compared to the effectiveness of the base catalyst.

The catalyst is most frequently used unsupported even in fluid bed reactors, because virtually all supports studied lower the selectivity of the catalyst. An elaborate calcination process is required to attain sufficient hardness and attrition resistance of the unsupported catalyst. The only exception appears to be the silica (di-silicic acid) coated system developed by DuPont.

Reactors used for the process are fixed bed, fluid bed and riser reactors. While the latter, used by DuPont, is claimed to give the highest maleic anhydride selectivities, the complexity of the reactor and the large amount of solids handling are less than desirable in practice. For these reasons, the ease of operation of a simple fluid bed makes it the preferred choice of industry.

The solid state structure of $(VO)_2P_2O_7$ and its redox mechanism in *n*-butane oxidation have been studied extensively by many researchers in the past 10 years [58–62]. Recently, a molecular level mechanism [63] has been worked out which stresses the site isolation (an important concept developed some 35 years ago for achieving selectivity in oxidation catalysts [64]). Site isolation is also innate to the VPO structure, where four V–O–V dimers form domains, isolated structurally from other domains by phosphate groups, so that each domain can operate independently from neighboring domains, is itself self-sufficient to produce one molecule of maleic anhydride, before it needs to be regenerated, and the process can start all over again (Fig. 6). These dimeric V–O–V sites can assume interchangeably four different electronic configurations, wherein the formal valance of the vanadium can assume a 5^+, 4^+ and/or 3^+ state. The relative ratios of the four possible electronic states are dictated by the feed and product ratios of reductants and oxidants, and the reaction conditions. The proposed mechanism constitutes a good basis for contemplating future catalyst improvements.

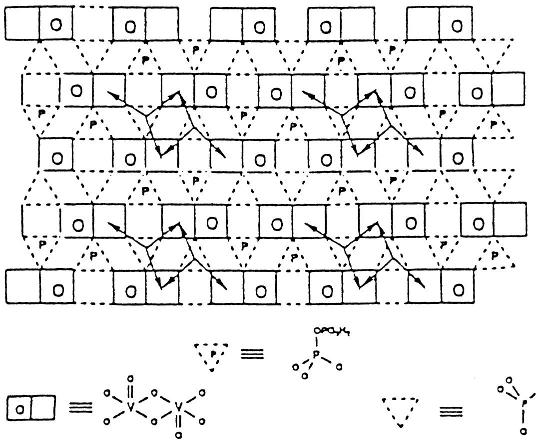

Fig. 6. Schematic representation of $(VO)_2P_2O_7$ surface structure. The arrows represent the possible pathways for facile exchange of surface bound oxygen, either monoatomic or diatomic, between the active sites. The "site isolation" [64] due to the diffusion barrier created by the pyrophosphate group is clearly shown by these arrows [63].

Future trends. It appears that VPOs unique structure and redox properties make it a difficult system to be displaced by a newer and more efficient system. Selective doping of the parent compound is in vogue and might lead to marginal improvements. A radically different approach is to search for alternative structures which might yield to rational catalyst design. Such an approach has been taken recently and some encouraging preliminary results have materialized therefrom [65–67]. This field has just begun to attract interest and is deemed to have excellent potential for innovative catalyst design, leading ultimately to commercially viable catalytic processes.

2.6. *Oxidation of propane to acrylic acid*

Many attempts have been made to convert propane directly to acrylic acid. The catalysts developed until now fall far short of the requirements needed to build a commercial plant. There is no competition to the well-established two-stage fixed bed process to convert propylene to acrolein, and further, without separation in a second catalytic stage to acrylic acid.

Catalysts studied for the direct conversion of propane to acrylic acid include V–P oxides [68], Mn–P oxides [69], Bi–V–Mo oxides [70], Bi–V–Nb–Sb–Mo oxides [71]. None of these catalysts give acrylic acid yields in excess of about 10%. An exception appears to be the Mitsubishi reported catalyst of the empirical composition $MoV_{0.3}Te_{0.23}Nb_{0.12}O_x$ [72], which is claimed by the patentees to yield 48% acrylic acid (80.1% conv., 60.5% sel.). Unfortunately, several independent laboratories in the US and in Europe have had difficulties duplicating the results claimed by Mitsubishi, primarily because of the difficulties encountered with the exact selection of catalyst starting materials and its involved preparation.

Future trends. If the claims of Mitsubishi can be verified, the yields are impressive and would serve as a basis for an eventual commercial process to convert propane to acrylic acid. In the absence of such a verification the field is wide open. Some claims are being made that useful leads towards this goal are being made using heteropoly acids and/or salts thereof as catalysts, as are specifically doped VPO catalysts. No doubt the incentive exists to discover a catalyst or a combination of catalysts for the conversion of propane to acrylic acid. The driving force is the much lower price of propane and its abundance, the same scenario as that for the ammoxidation of propane to acrylonitrile. As an aside, the ambient temperature functionalization of propane to isopropanol using Cu–chlorophthalocyanines encapsulated in X and Y zeolites [46] shows promise to attack paraffins in a selective manner at low temperatures and might be a lead for further pursuit.

2.7. *Oxidation of i-butane to methacrylic acid*

The direct oxidation of *i*-butane to methacrylic acid is a desirable goal. Thus far, no suitable catalysts have been discovered, as is the case with propane oxidation.

The majority of the studied catalysts are based on heteropoly acids or salts thereof [73–75], e.g.,

$$H_mX_{0.5-1.5}Y_{0.2-1.5}Z_{0-3}P_{1-1.2}Mo_{12}O_n$$

where X = V, As, Cu, Y = alkali, Z = Sb, Sn, Group VIII elements.

It is presumed that heteropoly compounds having intact Keggin structures are the active components of these catalysts. The yields of acrylic acid obtained with these catalysts lie below 10%, hence well below commercially attractive levels.

Future trends. The field is wide open.

2.8. (Amm)oxidation of xylenes

In the well-established area of selective *o*-xylene oxidation to phthalic anhydride, catalyst research continues along both compositional and preparational lines. The prevailing compositions are still based on V oxides supported on TiO_2 (anatase), but are strongly doped, particularly with elements such as Sb, Nb, and Cs. As an illustrative example, Nippon Shokubai [76] discloses among others compositions of the following empirical formula: $VSb_{0.1–1}Nb_{0.05–0.5}P_{0–0.2}Cs_{0–0.2}O_x/TiO_2$, with active phase loadings in the vicinity of a monolayer. Improved selectivities, longer catalyst life and catalyst ruggedness against plant upsets are claimed. From the composition one can surmise that $VSbO_4$ is formed as one of the phases and hence modifies the base V_2O_5/TiO_2 composition. The modification has both electronic, as well as, structural consequences. Electronically, the addition of Sb lowers the oxidation state of vanadium; structurally, it interposes itself between V–O–V chains and thus helps to isolate V–O moieties from each other (site isolation at work). When excess antimony is present, the presence of supra-surface antimony sites [29] can be postulated on top of the V_2O_5/TiO_2 or $VSbO_4/TiO_2$ active phase. The result is a more selective catalyst.

These solid state dopings and their catalytic consequences are another manifestation of the importance of the concept of site isolation in selective (amm)oxidation catalysis. This concept, first conceived in the early 1960s [64], continues to pervade modern approaches to catalyst design and their improvement in efficiency. It is amply practiced in industrial as well as in fundamental studies of selective catalytic (amm)oxidation.

Recent studies indicate that *p*-xylene can be preferentially oxidized from a mixture of xylenes to terephthalic acid (or precursors thereof), or ammoxidized to terephthalic nitrile (or its precursors) using ZSM-5-based catalysts.

Amoco [77,78] reports preferential selective oxidation of *p*-xylene over *o*- and *m*-isomers, using an Fe–Mo oxide modified, partially deborinated B-ZSM-5. Yields are reasonably good.

German researchers [79] report that *p*-xylene can be ammoxidized with large preference over the other two isomers to terephthalonitrile, using a Cu-ZSM-5.

Both results constitute good leads for future research.

Future trends. Catalyst compositions capable of (amm)oxidizing preferentially *p*-xylene over the other two isomers will be hotly pursued. Current results are not sufficient for commercialization. Also, materials other than ZSM-5, materials which are more steam stable, will have to be utilized as the basis to achieve preferential isomer selectivity. The utilization of fluid beds has never gained favor in xylene oxidation although there is actually no fundamental reason to stay away from them. Perhaps, some clever new engineering innovation in fluid beds might find applicability.

3. Summary

An overview of the current status of several commercially important heterogeneous catalytic (amm)-oxidation processes reveals that catalysts for these reactions are rather complex in chemical composition and physical makeup. It reveals further that the understanding of their functions is being ever better understood, and because of this better understanding, the catalytic systems are becoming even more complex in nature as they also become more efficient. Future trends aim greatly towards the discovery and development of paraffin activation catalysts and their use towards producing useful functionalized chemical intermediates. Catalysts towards this end are composed of paraffin activating elements contained in a common structure with selective olefin oxidation components, or they are composed of two distinct phases, best situated in intimate proximity of each other (preferably epitaxially matched), or as a worst case scenario in two physically separate phases; again best when in proximity of each other. Site isolation pays an important role within both of the respective phases, their mutual cooperation is imperative, and their relative placement to each other and/or respective spatial sequencing is paramount to high catalytic overall efficiency; and a subject matter which needs further study. The application of combinatorial chemistry also shows promise.

(Amm)oxidation catalysis of light hydrocarbons remains a lucrative field of study and continues to hold exceptionally good future commercial rewards in the conversion of olefins, aromatics, and in particular paraffins to useful functionalized end products.

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