

# Advances in Selective C<sub>3</sub> and C<sub>4</sub> Oxidations

by Robert Karl Grasselli

*One quarter of the most important organic chemicals and intermediates are produced by selective heterogeneous catalysis. The upgrading of C<sub>3</sub> and C<sub>4</sub> hydrocarbons to useful industrial products such as acrylonitrile, acrylic acid, propylene oxide, methacrylic acid and maleic anhydride are reviewed with emphasis on the nature and behaviour of the catalysts most suited for these processes and how these can be further improved. Catalyst efficiency is emphasised which translates to "green chemistry" or "green processes".*

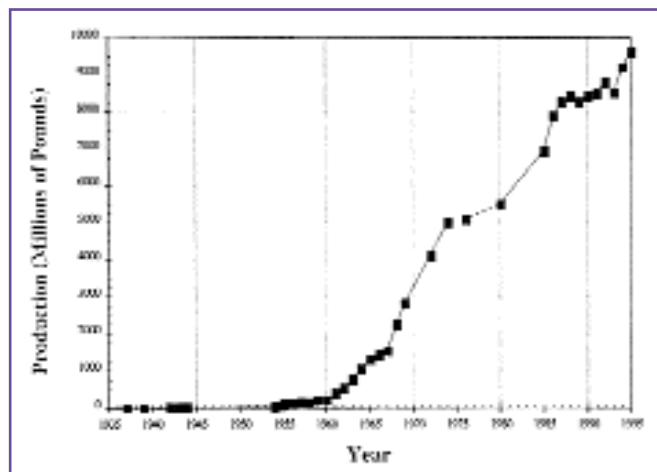


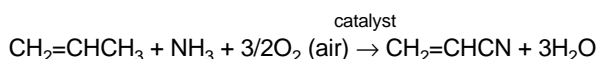
Figure - World production of acrylonitrile

As is well known, selective heterogeneous oxidation catalysis is of vital importance to the well-being of mankind, producing about 25% of the most important industrial organic chemicals and intermediates used in the manufacture of industrial products and consumer goods. Within this group, the selective oxidation of C<sub>3</sub> and C<sub>4</sub> hydrocarbons commands an important place, since products derived from them include such strategic intermediates as acrolein, acrylic acid, acrylonitrile, methacrylic acid, MTBE, maleic anhydride, and propylene oxide, to mention just a few. Over the past fifty years great efforts have been expended, particularly by industrial researchers, to make the selective oxidation processes and catalysts ever more efficient and environmentally friendlier. The very term "selective oxidation catalysis" implies efficiency, preservation of matter, and thereby also environmental responsibility. The recently coined term "green chemistry" has been practiced already for the past fifty years by researchers active in the area of selective oxidation catalysis, and with ever-greater prowess as time went on and the fundamental understanding of catalyst behavior on an atomic and molecular level improved. For example the inefficient and expensive process of IG Farben (HCN + acetylene) to produce acrylonitrile was totally replaced in the early 1960's by the highly efficient and environmentally friendly Sohio process (propylene + ammonia + air). The yield of acrylonitrile was raised over the past forty years from 50% to over 80%, through the discovery and development of five gen-

erations of improved and ever more efficient catalysts. The current world production of acrylonitrile using the Sohio/BP process exceeds 5 billion kg per year. Another early example of green chemistry is the Chevron discovered process in the late 1970's for the selective oxidation of *n*-butane to maleic anhydride, replacing the carbon inefficient process of oxidizing benzene to maleic anhydride. Essentially all maleic anhydride (about 1 billion kg/year) is currently produced from *n*-butane.

It is the objective of this paper to give a brief overview of the status and advances achieved in the selective oxidation of C<sub>3</sub> and C<sub>4</sub> hydrocarbons particularly from the standpoint of the catalysts effective in this area, and to point out some possible improvements for the future.

## Ammoxidation of propylene



This process was invented by Sohio (now BP America) and was commercialized in the early 1960's [1, 2]. It completely displaced the earlier and inefficient IG Farben process, which used the expensive and environmentally unfriendly starting materials HCN and acetylene. The process is a 6 electron oxidation and uses, as catalysts, mixed metal oxides selected from either molybdates or antimonates. The process is carried out in fluid bed reactors >10 m in diameter, at 400 to 460 °C,

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*This paper was presented as plenary lecture at the Deutsche Wissenschaftliche Gesellschaft für Erdoel, Erdgas und Kohle in Hamburg October 12, 2001.*

atmospheric pressure and contact times between 3-12 seconds. The world production of acrylonitrile stands currently at approximately 5 billion kg/year; utilizing 20 world size plants, each operating two fluid bed reactors, containing approximately 50,000 kg of catalyst/reactor and each reactor producing about half a million kg of acrylonitrile/day. The main uses of this key petrochemical intermediate are in acrylic fibers, resins, rubbers and many specialty products.

Over the past forty years, the in tank yield of acrylonitrile has been raised from the low 50's to now exceeding 80% [3]. The improvement stems mostly because of the discovery of ever more efficient catalysts (Table 1). All of these catalysts have been discovered, developed and commercialized by Sohio. Figure shows the increase in the world production over time and the dramatic increase in production with the introduction of the Sohio process in 1960; each new generation of catalysts further accelerates the world production. The molybdate catalysts all contain bismuth, from the first to the latest generation. Bismuth happens to be the best  $\alpha$ -hydrogen abstracting element in a molybdate structure, second best is tellurium, but the latter suffers from volatility problems under redox conditions of the ammoxidation process. The other worthy comment to make about the more advanced multicomponent molybdates (MCM) is that they all are at least biphasic, with two or more phases cooperating with each other. For example the system  $K_aNi_bCo_cFe_dBi-Mo_{12}O_x$  [4] derives its superior catalytic properties through the cooperation of the Scheelite-based  $\alpha$ -Bi-molybdate phase (the actual catalytic phase), which contains also some Fe, and the  $\beta$ -Fe-molybdate phase, (the co-catalytic reoxidation phase). The latter phase contains, and is structurally stabilized by, Ni and Co to maintain the bulk of the iron in the  $Fe^{2+}$  oxidation state, comprising centers for easy dioxygen dissociation and its re-incorporation into the catalytic cycle. For phase cooperation to be effective, it is imperative that the two phases be in intimate contact with each other, in order to facilitate their cooperation on an atomic scale. This condition is readily met when the two phases contain at least one lattice plane each that is structurally closely matched, thereby facilitating the formation of coherent interfaces (epitaxy) between the two phases. In the above example, the two phases are in registry, with less than a 2% mismatch at their respective {010} lattice face.

The antimonate catalysts (Table 2) all contain at least one element, which has a reduction potential above that of antimony [2, 3]. These elements are U, Fe, Mn, Cr, Ce, V, to mention a few. Their function is to keep the antimony in its highest oxidation state, 5+, preventing it to permanently slip to 3+, which would make the catalyst ineffective (some  $Sb^{3+}$  is however needed for the  $\alpha$ -hydrogen abstraction to proceed, thus a bal-

ance must be provided through compositional choices). In commercial operation, antimonates notoriously drift to lower oxidation states with catalyst deactivation. This problem can be overcome by an engineering expedient of incorporating into the fluid reactor an autoregeneration zone at the bottom of the reactor (propylene and ammonia spargers are placed well above the air sparger). A more elegant way is to introduce into the antimonate a reoxidation co-catalyst, making this system also at least biphasic. For example among the more advanced multicomponent antimonates (MCA) the composition  $Na_{0.3}(Cu,Mg,Zn,Ni)_{0.4}(V,W)_{0.05-1}Mo_{0.1-2.5}Te_{0.2-5}Fe_{10}Sb_{13-20}O_x$ , the two phases that cooperate with each other are the actual catalytic phase  $FeSbO_4$  and the reoxidation co-catalyst  $Fe_xMo_yO_z$ . The latter prevents the antimonite from deep reduction during the catalytic process. Because of the fickle nature of the antimonate catalysts, the molybdates are commercially the preferred ones. The last two generations of molybdate catalysts (Table 1) are designed to be practically indestructible and well able to withstand serious abuse in plant upsets [2, 3]. These systems have been known to operate continuously for 10 years and more in the plant, with only periodic addition of small amounts of  $MoO_3$ , which slowly oozes out of the catalyst because during the redox process of the catalytic reaction, the volatile compound  $MoO(OH)_2$  is formed, which leaves the reactor. A great deal of the inherent  $MoO_3$  loss is however already foiled by steam coil rotation. What improvements can still be made in the ammoxidation of propylene? First of all, there is no a priori reason why a 100% acrylonitrile yield (or nearly so) should not be attainable. There is no thermodynamic barrier. Probably the first thing to try to accomplish is to devise catalysts, which would be capable of lower temperature operation. One can take a hint from the selective oxidation of propylene, which proceeds with a better than 90% yield to acrolein, and the catalysts for the two reactions are related. Of course the difference is that the oxidation to acrolein is carried out 100 °C lower, at about 320 °C. Therefore, one of the approaches to take is to find a way to activate the ammonia at a lower temperature than what is possible with the current catalytic compositions. Another improvement, which might be possible with the compositions as they stand, is to optimize the texture of the active phase. Not much effort has been expended thus far in this direction. Modification of the  $SiO_2$  support, or a totally different support, could also bring a few points. Compositional changes of the catalyst to reduce the  $MoO_3$  loss would also be of some value. Finally, engineering innovations might enhance acrylonitrile yields, such as the operation at lower pressures or by staging the air supply; even the use of oxygen and steam/ $CO_2$ , instead of air might be of some benefit.

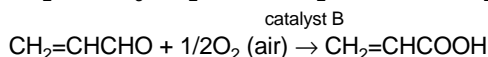
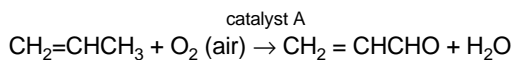
**Table 1 - Propylene ammoxidation catalysts (molybdates)**

| <i>Early catalysts</i>  | <i>Acrylonitrile in-tank yields</i> |
|---|-------------------------------------|
| $Bi_9PMo_{12}O_{52}-SiO_2$                                      | ~55%                                |
| $Fe_{4.5}Bi_{4.5}PMo_{12}O_{52}-SiO_2$                          | ~65%                                |
| <i>Advanced Multicomponent Catalysts (MCM)</i>                  |                                     |
| $K_a(Ni,Co)_9Fe_3BiPMo_{12}O_x-SiO_2$                           | ~75%                                |
| $(K,Cs)_a(Ni,Co,Mn)_{9.5}(Fe,Cr)_{2.5}BiMo_{12}O_x-SiO_2$       | ~78-80%                             |
| $(K,Cs)_a(Ni,Mg,Mn)_{7.5}(Fe,Cr)_{2.3}Bi_{0.5}Mo_{12}O_x-SiO_2$ | >80%                                |

**Table 2 - Propylene ammoxidation catalysts (antimonates)**

| <i>Early catalysts</i>  | <i>Acrylonitrile in-tank yields</i> |
|---|-------------------------------------|
| $FeSb_{8.6}O_x-SiO_2$   | ~65%                                |
| $USb_{4.6}O_x-SiO_2$  | ~70%                                |
| <i>Advanced Multicomponent Catalysts (MCA)</i>  |                                     |
| $Na_{0.3}(Cu,Mg,Zn,Ni)_{0.4}(V,W)_{0.05-1}Mo_{0.1-2.5}Te_{0.2-5}Fe_{10}Sb_{13-20}O_x-SiO_2$ | ~75%                                |

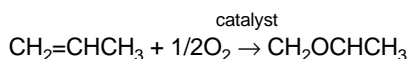
### Oxidation of propylene to acrolein and acrylic acid



The oxidation of propylene to acrolein is a 4 electron oxidation. The reaction is carried out commercially in shell and tube fixed bed reactors, with >10,000 tubes/reactor and tubes of approximately 2 to 2.5 cm in diameter and 3-5 meters in length. The reaction is carried out at 330-370 °C, atmospheric pressure, and 1-3 sec. contact time. The world production is modest, estimated at about 100 million kg per year. The product is used as an intermediate for specialty products. The bulk of the acrolein (about 2,5 billion kg/year) is not isolated, but passes uncondensed on to a second stage reactor where it is converted to acrylic acid. The catalysts, which are employed for the selective oxidation of propylene to acrolein are very similar to those used in the production of acrylonitrile from propylene and are summarized in Table 3. All of them are based on Bi-molybdates, the majority having been developed by Sohio, Nippon Kayaku, Nippon Shokubay and Basf. The oxidation of acrolein to acrylic acid is also carried out in shell and tube fixed bed reactors of the same type as those used for the acrolein production. The reaction is carried out at 230-300 °C, atmospheric pressure and 1-3 sec. contact time. The world production exceeds 2,5 billion kg per year and is rapidly growing. The major uses of acrylic acid are in the production of polyesters, coatings, paints, adhesives, and super-absorbents (disposable diapers). The catalysts are all molybdates, derivatives of heteropoly acids (two dimensional surface acids) containing phosphorous or vanadium as key elements (Table 3). The advanced multicomponent catalysts contain also Cu as a redox element, allowing for higher activity of the catalyst and Sb, which enhances the selectivity of the catalyst. The acrylic acid catalysts have been developed mainly by the same major players who developed the acrolein catalysts (see above). As can be seen from the impressive yields, about 95% in both stages, respectively, for an overall acrylic acid yield of about 90%, there is hardly much room for catalyst innovation. Selective doping might squeeze out another

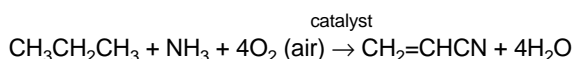
point or so, as might a careful optimization of texture. An improvement of MoO<sub>3</sub> loss in both catalyst stages would be desirable. This might be attainable by selective doping of the existing catalysts, whereby a combinatorial chemistry approach might be useful. The rest must come from engineering innovations, such as oxygen staging, catalyst gradation along the bed, and improvement of the hotspot distribution.

### Epoxidation of propylene to propylene oxide



The epoxidation of propylene to propylene oxide (PO) is a 2 electron oxidation. PO is manufactured by two basic processes: the traditional chlorohydrin (Dow) process, with CaCl<sub>2</sub> as a stoichiometric byproduct, and the hydroperoxide (Arco) process, where *t*-butanol or styrene are coproducts [5]. Both of these processes have obvious drawbacks because of their byproduct formation and for being environmentally hostile. For these reasons, much research has been expanded towards a direct selective oxidation process. Propylene oxide is an important organic intermediate for the production of propylene glycol, polyether polyols, glycol ethers, alkanolamines and many specialty products. The world production of PO is in the range of 6 billion kg per year. Direct selective oxidation of propylene with dioxygen or air has met with little success thus far. The use of H<sub>2</sub>O<sub>2</sub> as the oxidizing agent, or in situ produced peroxydic species from cofed H<sub>2</sub> and O<sub>2</sub> has shown some promise. Eni has succeeded to epoxidize propylene in good yields using H<sub>2</sub>O<sub>2</sub> as the oxidizing agent and TS-1 as catalyst. More recently there has been a flurry of activity surrounding the use of Au based catalysts (particularly those supported on TiO<sub>2</sub>) and H<sub>2</sub>+O<sub>2</sub> cofed with propylene [6, 7]. Although the yields of PO are still modest (about 3%), the selectivities are very high, in the range of about 95%. One of the key factors appears to be the dispersion of Au and the stability of the dispersion. Surely improvements will be achieved in this area by doping the Au with appropriate elements to achieve increased yields and catalyst stability. It is apparent from the research conducted thus far, that the catalysts active for the epoxidation of propylene are vastly different from those effective in the selective allylic oxidation. The latter use lattice oxygen as oxidizing moieties, the former peroxy species.

### Ammoxidation of propane



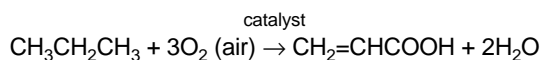
The ammoxidation of propane is an 8 electron oxidation. The process has not as yet been commercialized, although it has been pilot planted by BP America, Mitsubishi and Asahi. It is only a matter of time until it becomes commercial. The reaction will most probably be run in fluid bed reactors, when commercialized, and in a temperature range between 350 and 520 °C, atmospheric pressure and 3-12 sec. contact time. While an array of catalysts has been investigated for this reaction (Table 4), all of the best candidates thus far contain vanadium, whether they are molybdate or antimony based systems. The most promising thus far are the Sohio VSb<sub>5</sub>W<sub>0.5</sub>Te<sub>0.5</sub>Sn<sub>0.5</sub>O<sub>x</sub> [3], the Eni (Cr,Sn,Ti,Ni,Mn,Fe)<sub>x</sub>VSb<sub>y</sub>O<sub>z</sub> [8], and the Mitsubishi

Table 3 - Propylene oxidation catalysts

| <i>Propylene→Acrolein</i>   | <i>Acrolein &amp; Acrylic acid yields</i> |
|---|---|
| <i>Early catalysts</i>  |   |
| Bi <sub>9</sub> PMo <sub>12</sub> O <sub>52</sub> -SiO <sub>2</sub>   | ~50%                                      |
| Fe <sub>4.5</sub> Bi <sub>4.5</sub> PMo <sub>12</sub> O <sub>52</sub> -SiO <sub>2</sub>   | ~60%                                      |
| <i>Advanced Multicomponent Catalysts</i>  |   |
| K <sub>a</sub> (Ni, Co) <sub>9</sub> Fe <sub>3</sub> BiPMo <sub>12</sub> O <sub>x</sub> -SiO <sub>2</sub>                                       | ~85%                                      |
| (Na, K) <sub>a</sub> (Ni, Mg, Zn) <sub>b</sub> Fe <sub>c</sub> Bi <sub>d</sub> W <sub>e</sub> Mo <sub>12</sub> O <sub>x</sub> -SiO <sub>2</sub> | ~93%                                      |
| <i>Acrolein→Acrylic acid</i>  | <i>Acrylic acid yields</i>                |
| <i>Early catalysts</i>  |   |
| PMo <sub>12</sub> O <sub>x</sub> -SiO <sub>2</sub>  | ~60%                                      |
| V <sub>a</sub> (P) <sub>b</sub> Mo <sub>12</sub> O <sub>x</sub> -SiO <sub>2</sub>   | ~80%                                      |
| <i>Advanced Multicomponent Catalysts</i>  |   |
| Cu <sub>a</sub> V <sub>b</sub> (Sn, Sb) <sub>c</sub> W <sub>d</sub> Mo <sub>12</sub> O <sub>x</sub> -SiO <sub>2</sub>                           | ~95%                                      |

$V_{0.3}Te_{0.23}Nb_{0.12}MoO_x$  [9] systems (the Asahi catalyst is a variation of the Mitsubishi one, with replacement of the Te by Sb). The highest yield of acrylonitrile is produced by the Mitsubishi system. One drawback of this system is its difficult synthesis (although it can be successfully mastered with some extra effort) and most of all its Te content, which will be difficult to maintain during the operation of the process. In the redox reaction of the ammoxidation process, the Te gets steadily reduced to the 4+ oxidation state, which is volatile and will ultimately be lost out of the reactor. While the yields of acrylonitrile produced from propane are becoming of commercial interest, there is still ample room for improvement. All three of the above contenders can be further improved, each in its own unique way. Some of the systems lack components to more effectively convert the intermediate propylene product to acrylonitrile, others operate at too high a temperature and need redox components or ammonia activators, and still others need to be made more redox stable. The area is ripe for a breakthrough, which will ultimately challenge the well established ammoxidation process.

#### Oxidation of propane to acrylic acid



The process is a 6 electron process. Thus far it has not been commercialized, because of the lack of appropriately effective catalysts. Once the catalyst is found, the process could be carried out either in fixed bed, transfer-line or fluid beds. Since grass root plants would probably be built for this purpose, fluid bed technology might hold an advantage. Many catalysts have been studied for this reaction; by far the best among them is the Mitsubishi system, which has about the same composition as that for the ammoxidation of propane,  $V_{0.3}Te_{0.23}Nb_{0.12}MoO_x$  [9]. As already mentioned, the Te poses a certain problem which needs to be addressed. One intriguing aspect of this catalyst system is its structure and how it is formed. At this juncture it is not entirely certain whether two and possibly three phases cooperate with each other to give the rather respectable acrylic acid yields obtained (~40%). However, currently evidence is mounting, that a unique single phase is the catalytically active and selective phase operating in this system [10-12]. If this postulate ultimately prevails, the structure will lend itself ideally for alteration through molecular design manipulation. This should ultimately lead to higher acrylic acid yields, and also to higher acrylonitrile yields under ammoxidation conditions. This area is ripe for additional innovation and ultimately a major breakthrough.

**Table 4 - Paraffin ammoxidation catalysts**

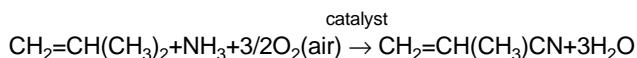
##### Molybdates

- a)  $VMo_xM_yO_z$  where M=Bi, Te, Ga, Nb, Ta, Ce,  
 b)  $V_{0.3}Te_{0.23}Nb_{0.12}MoO_x$  Ag. 55.1% AN yield (86.7 conv.,  
 63.5 sel.) (Microreactor)

##### Antimonates

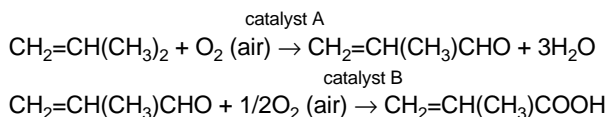
- a)  $VSb_xM_yO_z$  where M=W, Te, Nb, Sn, B, Bi, Al,  
 b)  $VSb_5W_{0.5}TeSn_{0.5}O_x$  Ti. 39.1% AN yield (68.8 conv.,  
 56.7 sel.) (Microreactor)

#### Ammoxidation of *i*-butylene to methacrylonitrile



The ammoxidation of *i*-butylene is a 6 electron oxidation. The process has never been commercialized, although Sohio ran a commercial propylene ammoxidation plant in the 1970's for about a week on *i*-butylene, ammonia and air and  $USb_{4.6}O_x/SiO_2$  as the catalyst. The run was successful, the in-tank yield of methacrylonitrile about 60%. Since the demand for methacrylonitrile is modest, the approach was not further pursued on a commercial scale. Since the above plant test, research developed much more efficient catalysts, one of the best being  $Cs_{0.5}Ni_{4.5}Co_{4.5}Fe_3BiSbMo_{12}O_x/SiO_2$  [13], giving methacrylonitrile yields of about 85% with better than 90% selectivity (microreactor scale). This catalyst is already an excellent one, but could most probably be further optimized, if the demand for methacrylonitrile were to significantly increase.

#### Oxidation of *i*-butylene to methacrolein and methacrylic acid



The oxidation of *i*-butylene to methacrolein is a 4 electron oxidation and the oxidation of methacrolein to methacrylic acid a 2 electron oxidation.

As in the oxidation of propylene, the oxidation of *i*-butylene to methacrylic acid would be produced in two consecutive fixed bed reactors, without interstage condensation of products. Current demand for methacrolein is too low to be of commercial interest. Methacrylic acid is currently produced by the well established acetone-cyanhydride (ACH) route which uses the toxic HCN as one of the starting materials and produces one mole of  $NH_4HSO_4$  for each mole of methacrylic acid produced; an environmental nightmare. An improvement of this process has recently been claimed by Mitsubishi, which proceeds via the methylester of 2-hydroxyisobutyric acid and dehydration via a Na-Y zeolite, thus circumventing the production of sulfate. Nonetheless, the incentive is high to replace the ACH process and the selective oxidation of *i*-butylene stands high on that list. Methacrylic acid is produced world wide on a 2 Billion pound per year scale, with its major uses being acrylic sheet (Plexiglas/Lucite), surface coating resins, water based paints, molding and extrusion compounds, biomedical appliances and optical products. The catalysts for the first stage oxidation of the *i*-butylene to methacrolein are essentially the same as those for the production of methacrylonitrile, namely  $Cs_{0.5}Ni_{4.5}Co_{4.5}Fe_3BiSbMo_{12}O_x/SiO_2$  [13] and are cousins of the propylene selective oxidation catalysts.

The second stage catalysts for the oxidation of the methacrolein are substantially different from those used for the second stage acrolein oxidation; they are derived from heteropolyacids with partial replacement of the acidic hydrogen by cesium. Some of the best catalysts have the empirical formula of  $Cs_{2.5}H_{0.5}[PMo_{12}O_{40}]$  and may be doped with Cu, V, Fe, As and Sb [14]. What further improvements can be done? The first stage catalyst is quite good and optimization studies would



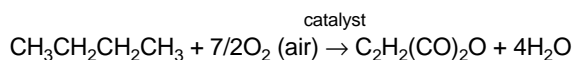
likely improve the yields of methacrolein further. The second stage catalyst could use further improvement. Here, fundamental studies, including kinetics, to better understand the individual mechanistic steps on a molecular level would be welcome. Also, the catalyst must be improved in its long-term stability. All of these shortcomings could be also addressed by computational chemistry approaches, which might also lead to entirely new catalytic systems. Further improvements could also be achieved by innovative engineering approaches.

#### Oxidation and ammoxidation of *i*-butane to methacrylic acid and methacrylonitrile

There is an incentive to directly oxidize *i*-butane to methacrylic acid, and less so to methacrylonitrile. At this juncture there exists no commercial process for these reactions.

Research has been expanded in the selective oxidation of *i*-butane to methacrylic acid, with the majority of the catalysts being of the heteropoly acid type, with intact Keggin structures:  $H_mX_{0.5-1.5}Y_{0.2-1.5}Z_{0-3}P_{1-1.2}Mo_{12}O_n$ , where  $X=V, As, Cu$   $Y=alkali$ ,  $Z=Sb, Sn$ , group VIII elements [15]. The P is the central heteropoly atom and needed for the overall stability of the catalytic structure, the V, presumably to activate the paraffin, as is the case in most paraffin selective oxidation catalysts and the role of the Sb is to reduce some of the  $Mo^{6+}$  to  $Mo^{5+}$ . Higher activities are presumably obtained with partially reduced catalysts and the Cu helps bring down the reaction temperature through its favorable redox potential. Nonetheless, the yields of methacrylonitrile are meager and stand below 10%, and the catalysts lack long-term stability under reaction conditions. They reduce too readily, too far. For these reasons, additional research is needed to enhance the effectiveness of the catalysts. The area is wide open.

#### Oxidation of *n*-butane to maleic anhydride



The oxidation of *n*-butane to maleic anhydride is a 14 electron oxidation. It is the most commercially most successful light paraffin selective oxidation to date. The unique, and most used catalyst, which is essentially  $(VO)_2P_2O_7$  was first invented by Chevron Corporation [16]. Since then commercial processes have come on stream using the VPO catalyst, that include BP-UCB, Alma, DuPont-Monsanto, and Mitsubishi Denka-Scientific Design. The reaction is carried out at 320-360 °C, atmospheric pressure and a contact time of between 1-10 sec. The reactors are either fluid bed or riser reactors. World production of maleic anhydride amounts to about 1 billion kg/year. Major uses are for alkyd resins, laquers, plasticizers, lubricants, and intermediates for THF and butanediol. The  $(VO)_2P_2O_7$  catalyst is one of the most studied systems in the catalytic community [17, 18]. Recently, the Lonza group published an improvement of their Almax fluid bed catalyst [19], claiming that better yields are obtained when the catalyst was calcined in a fluidized bed calciner in a mixture of air and steam. The morphology is changed, from the usual  $N_2$  treated samples, leading to a lesser exposure of the basal {100} crystal faces, and allegedly higher selectivity at comparable conversion. The results and the interpretation of them are unfortunately not very clear. Optimization of preparation methods could lead to higher yields.

Selective doping might also help bring down the waste products. It is indeed amazing, that thus far only the VPO system has been found effective in this area of catalysis. One would think, that there must be other systems. Perhaps here an intelligent combinatorial chemistry approach might be rewarding.

#### Conclusions

Selective oxidation and ammoxidation of  $C_3$  and  $C_4$  hydrocarbons is an important endeavor for the petrochemical industry and of great benefit to society through the products which it produces for personal use, whether it be for building materials, carpeting, motor vehicles, tires, consumer products or luxury items. The major processes and their catalysts for the selective oxidation of  $C_3$  and  $C_4$  hydrocarbons were briefly reviewed, their current status pointed out and some suggestions were made, where and how improvements may be forthcoming.

The key to the success of selective oxidation is, the various catalysts that have been developed over the years, their continual improvement and potential for still newer systems to be discovered. The deep understanding on an atomic level of the structural, surface and dynamic behavior of mixed metal oxides which comprise the bulk of the most effective catalytic systems, the application of modern and classical bulk and surface spectroscopic techniques, as well as the use of molecular probes and well placed combinatorial chemistry, will lead to the design and discovery of many new and more efficient, as well as environmentally friendlier selective oxidation catalysts. The time is nearing, when we will be able to introduce all of the desired catalytic functions into selected crystalline phases and space them in an optimum way for optimum product yield. The field is progressing rapidly.

In addition to developing new and more effective catalysts, engineering innovations are also going to help improve the desired product yields and selectivities, and help make the processes more efficient and environmentally friendlier.

#### References

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