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Review

Selective oxidation of propane to acrylic acid with molecular oxygen

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Abstract

This review covers the recent developments and the present state of selective oxidation of propane to acrylic acid with molecular oxygen. The current commercial manufacturing process of acrylic acid, as well as the possible oxidation pathways of propane are included as background information. Special attention is given to three classes of leading catalysts: vanadium pyrophosphate, heteropoly acids and salts and mixed metal oxides. Topics covered include the development and the effectiveness of the catalyst systems, the oxidation pathways, and some structural aspects. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propane; Catalyst; Vanadium pyrophosphate; Heteropoly compounds; Mixed metal oxides; Selective oxidation; Acrylic acid

1. Introduction

The global abundance of low alkanes and the huge economic incentives of converting them to various highly desirable petrochemicals or feedstocks for more valuable chemicals have stimulated an enormous amount of interests to explore selective oxidation processes to accomplish such conversions [1,2]. These processes include oxidative dehydrogenation, ammoxidation and selective oxidation.

Oxidative dehydrogenation of low alkanes to the corresponding alkenes with molecular oxygen over heterogeneous catalysts is an exothermic process, which is not subjected to the same thermodynamic limitations as the conventional, endothermic dehydrogenation process. Many vanadium oxide-based catalysts [3–7], molybdate-based catalysts [1] as well as rare-earth element-based catalysts [2] are reasonably effective for low-alkane activation. However, their selectivity to the corresponding alkenes is generally low, especially at higher reaction temperatures necessary for high conversions. Some promising research directions, such as those concerning the cooperation effects between active phases, as well as the concept of spillover oxygen have been suggested [8]. Nonetheless, the technology breakthrough in this area has yet to occur.

Ammoxidation of low alkanes, especially propane, is another process that has received much attention [9–12]. Fairly high yields of acrylonitrile from propane have been reported on a V-Sb-W-M-O-based catalyst [13] since the 1980s and on a Mo-V-Te-Nb-O catalyst [14] since the early 1990s. However, neither catalyst has been commercialized. Apparently, the new propane ammoxidation processes have yet to be successful in challenging the existing commercial process, which utilizes propylene as the starting material and is very efficient [1,15].

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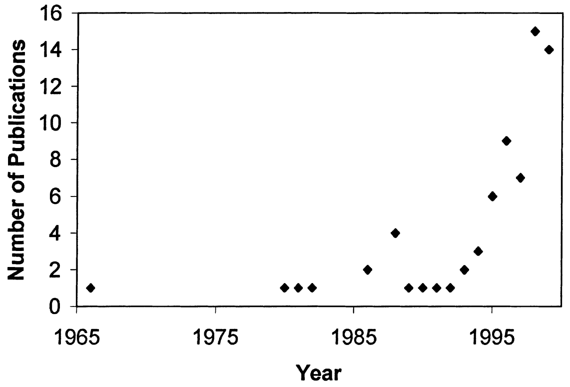

Fig. 1. Publications on propane selective oxidation to acrylic acid.

For the selective oxidation of alkanes, there has been one successful commercial example since the 1970s; *n*-butane replacing benzene as the starting material to produce maleic anhydride over a V-P-O catalyst [16]. This process is well established but the catalytic mechanism, especially the nature and structure of the active sites, is still under intense study [17–19]. Although the excellent performance of V-P-O catalyst in the selective oxidation of *n*-butane has not yet been transferred to that of propane, the success of V-P-O in *n*-butane oxidation has stimulated great interests in propane selective oxidation to acrylic acid. This is clearly revealed in Fig. 1, which shows the rapid increase of the number of annual publications, including journals and patents, on propane oxidation to acrylic acid in the past few years. However, aside from some brief coverage in several related reviews [1,2,20–22], there has appeared to be no focused review on this fast growing research area. This review intends to cover the recent progress in the research of propane selective oxidation to acrylic acid. The currently used commercial process for the production of acrylic acid will be briefly discussed as background information.

2. Current manufacturing process of acrylic acid

Acrylic acid and its esters are important industrial chemicals. The annual world capacity of crude acrylic acid production reached 6 billion pounds in 1997 [23]. With a reactive α,β-unsaturated carboxyl moiety, these versatile monomers undergo polymerization, sometimes with other functional monomers as co-polymers, to produce various important polymers which have many commercial applications, such as super absorbents, detergent, textile, paper additives, adhesives, plastics and coating materials, etc. Currently, the commercial process used worldwide for making acrylic acid is a two-step process [24]. This process starts with propylene and goes through acrolein as the intermediate to make acrylic acid in the two steps shown as follows:

Step 1:

$$\mathrm{H_2C{=}CH{-}CH_3} + \mathrm{O_2} \rightarrow \mathrm{H_2C{=}CH{-}CHO} + \mathrm{H_2O}, \quad \Delta H = -81.4\,\mathrm{kcal/mol} \tag{1}$$

Step 2:

$$\mathrm{H_2C{=}CH{-}CHO} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2C{=}CH{-}COOH}, \quad \Delta H = -60.7\,\mathrm{kcal/mol} \tag{2}$$

Several multi-component metal oxide catalysts developed for this process have achieved excellent product selectivity with a high conversion of propylene. As shown in Table 1, several catalysts for the first step can offer >90% acrolein yields while several for the second step can lead to >97% acrylic acid yields. Thus, in theory, the overall acrylic acid yield from propylene can be as high as 87% via this two-step process.

Alternatively, acrylic acid can also be produced from a one-step oxidation of propylene, as described in Eq. (3)

$$\mathrm{H_2C{=}CH{-}CH_3} + 1\tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{H_2C{=}CH{-}COOH} + \mathrm{H_2O}, \quad \Delta H = -142.1\,\mathrm{kcal/mol} \tag{3}$$

However, the best-achieved overall acrylic acid yield via the one-step oxidation is significantly lower than that of the two-step process as data suggested in Table 1 [24]. These data not only reveal the compositional difference in these catalysts, they also reveal the difference of optimal reaction temperatures for the oxidation of propylene and acrolein. The optimal temperatures for the two-step process are around 320–330°C for the first step and 210–255°C for the second step. Apparently, the activation of propylene requires a higher reaction temperature than that of acrolein. In the one-step reaction, the operating temperature has to be around 325–350°C to afford a

Table 1
Catalysts for one or two-step propylene oxidation to acrylic acid

Company	Catalyst components	Reaction	Temperature (°C)	Product yield (%)	Reference
Nippon Shokubai	Mo-Bi-Fe-W-Co-K-Si-O	Propylene→acrolein	320	90.2	[25]
Ube Industries	Mo-Bi-Fe-Co-V-K-O	Propylene→acrolein	330	90.3	[26]
Nippon Kayaku	Mo-V-Cu-Fe-Mn-Mg-P-O	Acrolein→acrylic acid	210	97.5	[27]
Nippon Shokubai	Mo-V-W-Cu-Sr-Al-O	Acrolein→acrylic acid	255	97.5	[28]
Nippon Shokubai	Mo-W-Te-Sn-Co-O	Propylene→acrylic acid	350	65	[29]
Nippon Shokubai	Nb-W-Co-Ni-Bi-Fe-Mn-Si-Z-O	Propylene→acrylic acid	325	73	[30]

sufficient propylene conversion. However, under such temperatures, not only the desired reaction of acrolein to acrylic acid takes place, further deep-oxidation of acrolein or acrylic acid are also likely to occur. Thus, the overall acrylic acid yield is lower than the two-step process. It is likely that such a temperature requirement for the one-step oxidation of propylene limits the total yield achievable. As a result, the one-step process has not been a choice for commercial production.

3. Oxidation of propane

The oxidation of propane can take place via many different pathways, as illustrated in Fig. 2. A saturated hydrocarbon, propane is much less reactive than its partial oxidation products [31–33]. When left uncontrolled at temperatures sufficient to activate propane, all its partial oxidation products can easily be further oxidized to carbon oxides while releasing large quantities of heat. As a result, without proper catalysts, propane is either unreacted, or totally oxidized to CO_x while generating large quantity of heat. The total oxidation, or combustion, as a fuel to generate heat is the primary use of propane today.

As a saturated hydrocarbon, propane has low reactivity under most reaction conditions. This low reactivity can be understood in view of the high strength of C–H bonds of propane, especially those in the terminal methyl groups. As a result, substantial amount of energy is required to selectively activate the methylene C–H bonds, and even more is needed for the methyl C–H bonds of propane, since the former is weaker than the latter. In fact, such energy is more than sufficient to break the carbon–carbon bonds of many of the C3 partial oxidation products of propane shown in Fig. 2, thus, leading to lower value C1 or C2 molecules. Therefore, one is faced with serious challenges in attempts to partially oxidize propane and 'stop' the oxidation at certain valuable C3 intermediates. These challenges include activating the inert propane while preserving the active C3 intermediates at the same time. To overcome these challenges and produce some meaningful amount of C3 partial oxidation intermediates, it is quite apparent that a catalytic process is the only path to pursue. Such a process should selectively activate the strong C–H bonds of propane while avoiding the breaking of any weaker C–C bonds.

There are other challenges. Acrylic acid is only one of several C3 partial oxidation products of propane, as outlined in Fig. 2. Among these C3 products, some, such as propylene or acrolein, can be further oxidized and lead to acrylic acid, while others, such as acetone, once formed, will not lead to acrylic acid [32,33]. To achieve a high selectivity to acrylic acid, the undesirable pathways, such as the one leading to acetone, must be blocked or suppressed. Despite these seemingly formidable technical challenges, converting an abundant fuel into a highly valuable chemical feedstock holds promise due to the lower cost of propane relative to propylene.

The one-step oxidation of propane in gas phase with molecular oxygen to acrylic acid follows Eq. (4):

$$C_3H_8 + 2O_2 \overset{\text{catalyst}}{\rightarrow} CH_2{=}CH\text{–}COOH(g) + 2H_2O(g), \quad \Delta H = -171\,\text{kcal} \tag{4}$$

This catalyzed reaction, which involves the transfer of eight electrons, most likely requires the coordinated efforts of several active sites, as well as balanced

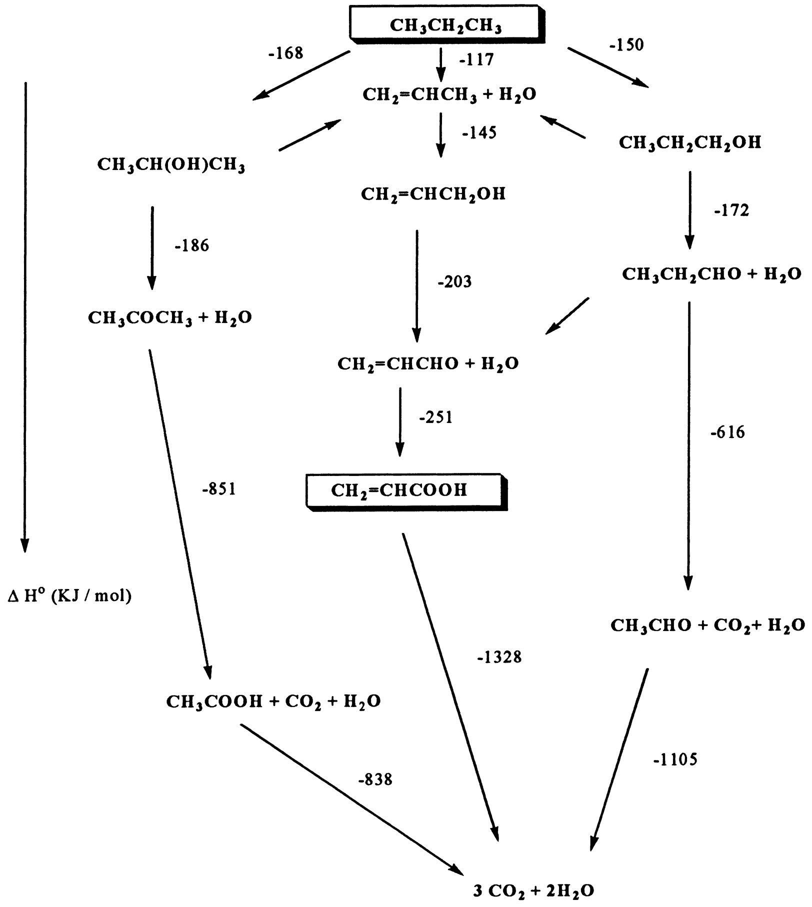

Fig. 2. Propane oxidation pathways and calculated standard reaction enthalpies.

reduction–oxidation properties of the catalyst to complete the catalytic cycle. Compared to the propylene oxidative dehydrogenation, this reaction requires the transfer of more electrons or oxygen atoms. In terms of product stability, acrylic acid, the desired product in propane oxidation, is less stable and more prone to further oxidation than acrylonitrile and maleic anhydride, the desired products in propane ammoxidation and *n*-butane oxidation, respectively. Part of the instability of acrylic acid is likely to be related to the additional adsorptive ability of its acid functional group onto the catalyst surface, which renders it susceptible to further oxidation. Overall, there has been a perception that it is very difficult to achieve a high acrylic acid yield in a one-step propane oxidation [1,34].

4. Catalysts for propane oxidation to acrylic acid

Typically, catalysis research for a new reaction starts with scouting systems effective for similar reactions. In the case of propane, selective oxidation to acrylic acid, there exist three potential leading systems. The most obvious one is the vanadium pyrophosphate (VPO) type catalysts, which have been used successfully in the industrial process of *n*-butane oxidation to maleic anhydride. Another is the class of heteropoly acids and salts, which are effective in alkane oxidative dehydrogenation. The third are the multi-component mixed metal oxides, which are utilized in propylene oxidation to acrylic acid, and are effective in propane ammoxidation and alkane oxidative dehydrogenation. To date, most of the effective catalysts developed for propane oxidation to acrylic acid belong to these three systems and significant progress has been made in all of the three, especially the mixed metal oxide catalysts.

4.1. VPO type catalysts

4.1.1. Effectiveness of VPO for propane oxidation

VPO catalysts have been used in the industrial process to manufacture maleic anhydride from *n*-butane since the 1970s. The reported yields of maleic anhydride vary from 45 to 61% with the *n*-butane conversion at about 65% and selectivity to maleic anhydride ranging from 65% [35,36] to as high as 97% [37]. VPO catalysts are very effective in *n*-butane oxidation as reflected by the high conversion and high selectivity to maleic anhydride, although the performance varies somewhat depending on the catalyst preparation and modifiers, and some results are sometimes difficult to reproduce. However, VPO catalysts are not very effective in propane selective oxidation to acrylic acid, despite the fact that propane is a homologue of *n*-butane with only one less CH_2. Table 2 lists the composition and performance of various VPO type catalysts tested for the selective oxidation of propane to acrylic acid. None of them offered an acrylic acid yield >15%. Such a significant performance difference of VPO catalysts for propane oxidation versus *n*-butane oxidation may suggest that VPO type catalysts is rather structure specific towards the length of hydrocarbon chain. On the other hand, the performance difference may simply reflect the relative stability of the partial oxidation products. Maleic anhydride is fairly stable while acrolein and acrylic acid are more prone to further oxidation.

The properties of VPO-based catalysts for selective oxidation of propane were first reported in 1986 [31]. The VPO type catalysts were found to be active with molecular oxygen as the oxidant and acrylic acid was reported to be the sole product, besides carbon oxides. The effects of P:V ratio were investigated and the catalyst with a P:V ratio of 1.15 was found to have the highest selectivity for acrylic acid over a wide range of propane conversion rates. It was also found that the addition of a small amount of TeO_2 further increased the selectivity and yield to acrylic acid. Thus, an acrylic acid yield up to 10.5% was achieved with the $V_1P_{1.15}Te_{0.1-0.15}O$ catalyst while only 7 to 3% yields were achieved with the $V_1P_{1.15}O$ and $V_1P_{0.9}O$ catalysts, respectively. It was also reported that higher concentrations of oxygen and water vapor in the feeds, and lower reaction temperatures favored the formation of acrylic acid.

Contrary to the above results, some later studies of the application of VPO in propane oxidation only led to poor or no yield of acrylic acid [38,39]. In one example, with a $V_1P_{0.96}O$ catalyst, which is fairly effective for the conversion of *n*-butane to maleic anhydride, only trace amount of acrylic acid was obtained from propane oxidation, while the major partial oxidation product was propylene [38]. Although this catalyst does not contain Te and is not as effective as the VP-Te-O catalysts, its composition, nonetheless, is within the composition range of the VPO type catalysts reported to achieve up to 7% acrylic acid [31]. One likely explanation for such a difference in acrylic

Table 2
Vanadium pyrophosphate type catalysts for propane oxidation to acrylic acid

Catalyst	Feed (C3=propane)	Temperature (°C)	Propane conversion (%)	AA yield (%)	Selectivity (%)	Reference
$V_1P_{1.15}Te_{0.1-0.15}O$	$C3/O_2/H_2O$	390	30	10.5	30	[31]
$V_{1.04}P_1O$	$C3/O_2/He$	300	24	Trace	38 (propylene)	[38]
V_1P_1O	$C3/O_2/H_2O$	400	6	None	Only to other oxygenates	[39]
$V_1P_{1.05}O$	$C3/O_2/H_2O$	385	37	14.4	39	[40]
$V_1P_{1.1}O$	$C3/O_2/H_2O$	420	46	14.7	32	[41]
VPO/TiO_2-SiO_2	$C3/air/H_2O$	300	22	13.3	61	[42]
VPO	$C3/air/H_2O$	300	15	7	47	[42]
VPO	$C3/air/H_2O$	400	23	11.2	48	[43]
$VPZr_{0.5}O$	$C3/air/H_2O$	340	18	14.8	81	[43]
Ce/VPO	$C3/air/H_2O$	390	28	18.8	68	[44]

acid yield is the difference in reaction conditions. Up to 36 vol.% of water vapor was used when 7% acrylic acid was produced in one case, while no water was added to the feed and no acrylic acid was produced in the other case. Therefore, water seems to play a critical role. On the other hand, although up to 30 vol.% of water was included in the feed with propane over a VPO catalyst in yet another example [39], acrylic acid was still not detected. Instead, acrolein and propylene were detected as the major C3 partial oxidation products. In this later case, other preparative variables may be the sources of the performance differences. The preparative variables in making VPO catalysts include the source of vanadium (oxides or salts), the solvent (aqueous or organic), the reducing agent and amount used, etc.

More recently, several independent research groups have confirmed the effectiveness of VPO type catalysts for propane oxidation to acrylic acid [40–43]. Surprisingly, these recent results have very different implications regarding the function of Te. It is now suggested that Te is not a necessary component for an effective VPO catalyst. In fact, higher yields to acrylic acid were achieved using catalysts containing no Te [40–44].

As shown in Table 2, low propane conversion or low acrylic acid selectivity at higher propane conversion contribute to the lower yields of acrylic acid for these catalysts. Although propane conversion increased as temperature increased, it was reported that higher temperature is not favorable for acrylic acid yield [31]. The observed selectivity to acrylic acid is a combined measure of its formation and its further reaction. The relative order of reactivity for propane and its partial oxidation products over the VPTeO catalyst was proposed as: propane<acrylic acid<acetic acid<propylene<acrolein [31]. Thus, temperature increase would have a greater impact to reactions of acrylic acid and acrolein than to propane conversion. Therefore, it is fairly safe to conclude that increasing acrylic acid yields could not be achieved by simply raising the reaction temperature.

4.1.2. Chemical modification of VPO

Some interest has been directed to the chemical modification of VPO catalysts. Wang et al. [41] studied the effects of several promoters M (Co, Bi, Mo, Te, Nd, B) on M-VPO systems, and concluded that none of these promoters enhanced acrylic acid selectivity. However, Deng et al. found [43] that the addition of Zr could significantly enhanced acrylic acid selectivity. Recently, a cerium-doped vanadium phosphorous oxide catalyst was also reported to further improve the overall performance. With only 0.01% of cerium doping on the VPO catalyst, acrylic acid yield of 18.8% was achieved [44]. To date, this is the highest acrylic acid yield reported on VPO type catalysts.

While most of the studies were conducted on bulk VPO catalysts, the oxidation behavior of VPO on TiO_2-SiO_2 support was also investigated [42]. With only 16.7% of VPO on a TiO_2-SiO_2 support, higher propane conversion (22%) and higher acrylic acid selectivity (61%) were achieved.

4.1.3. Reaction pathways and reaction conditions

Although acrylic acid was reported to be the sole product besides carbon oxides, Ai proposed the following reaction pathways (Fig. 3) including acrylic acid as well as acetone and acetic acid on the Te modified VPO catalyst [31].

Propane is first oxidized to propylene, which is further oxidized to acrylic acid through acrolein as the intermediate, or is oxidized to acetone through isopropanol as the intermediate. The existence of the acetone pathway to acetic acid and CO_x was suggested although acetic acid was not reported in the product stream in the above study [31]. However, in addition to acrylic acid and CO_x, significant amounts of acetic acid were indeed observed on Te-free VPO catalysts by Zhao et al. [40] and Wang et al. [41], which is consistent with the pathways proposed in Fig. 3.

Although not included in the pathways, water seems to play an important role in the reaction. When water was not fed to the reaction, propylene and CO_x

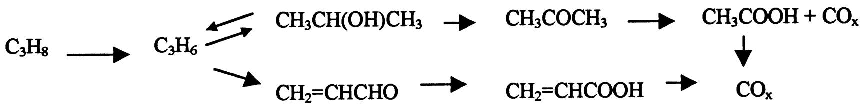

Fig. 3. Propane oxidation pathways over a Te-VPO catalyst [31].

were observed as the major product while only trace amounts of acrylic acid was obtained [38]. Thus, water may enhance the further oxidation of propylene, and when absent or present in very small quantities, most of the propylene produced is released to the product stream. Water may increase the concentration of hydroxyl groups on the catalyst surface and facilitate the reaction between the adsorbed acryloyl species and hydroxyl groups to form acrylic acid. Water may also enhance the desorption of acrylic or acetic acids from the surface of VPO catalysts to prevent them from being further oxidized to CO_x. Again, when water was absent or only present in very small quantities, these adsorbed acids could have stayed longer on the catalyst surface, thus increasing the chance of being further oxidized to CO_x.

It was found that propane conversion and selectivity to acrylic acid over VPO catalyst were sensitive to propane concentration in the feed and that propane conversion decreased with the increase of propane concentration [31]. This observation may suggest that saturation of active sites by propane can occur at relatively low propane concentration. Thus, increasing the surface density of active sites may be a direction for the future development of VPO type catalysts. This may not be an easy task since the quantitative determination of the number or density of active sites on the surface of solid oxide catalysts has been difficult [45] and quite often, the measurement of BET surface area of oxide catalysts can be misleading.

4.1.4. *Structural aspects of VPO catalysts*

Most of the published studies of VPO catalysts for propane oxidation did not delve into the structural aspects. However, the needed improvements have to rely heavily on a good understanding of the catalyst structures. On the other hand, many structural aspects such as crystal phases or active sites of VPO catalysts have been extensively investigated for *n*-butane oxidation [46–48] and some of the conclusions may be applicable to VPO catalysts for propane oxidation.

$(VO)_2P_2O_7$ was found to be the major crystal phase in VPO catalysts active in *n*-butane oxidation [47,48] and propane oxidation [42,43]. In the crystallites of $(VO)_2P_2O_7$, the preferential exposure of crystal planes parallel to the (1 0 0) planes [47,48] was proposed by many to be involved in the transformation of *n*-butane to maleic anhydride [47,49]. However, it was recently proposed that the oxidation of *n*-butane to maleic anhydride takes place over the amorphous surface of VPO catalyst [50]. An amorphous VPO/SiO_2 sample was compared to a crystalline VPO catalyst for *n*-butane oxidation. It was found through EXAFS that these two samples had strong resemblance in catalyst selectivity, yield, as well as local structure around vanadium.

A recent study in propane oxidation [42] may also lead to the proposition that transformation of propane to acrylic acid takes place on the amorphous phases of the VPO catalysts. As shown in Table 3, the transformation of propane to acrylic and acetic acid was not related to the presence or absence of $(VO)_2P_2O_7$ crystal phase. In fact, the amorphous catalysts (with lower VPO loading and little or no $(VO)_2P_2O_7$ crystal phase) is more effective than the bulk VPO catalysts, which contain mostly $(VO)_2P_2O_7$ crystal phase. If the amorphous phases were truly the active phase, supported VPO could have advantages over bulk VPO as catalysts. Note that there could be many different amorphous phases present with various composition, density or surface components, etc.

Additionally, there have also been interesting discussions about the role of active species in VPO catalysts. As pointed out by an earlier review on

Table 3
VPO/TiO_2-SiO_2 catalyst in propane oxidation [42]

Composition VPO/TiO_2-SiO_2	XRD peaks of $(VO)_2P_2O_7$ phase	Propane conversion (%)	Acid selectivity (%) (acrylic and acetic acid)
100/0	Strong	15	47
23/77	Medium	21	44
17/83	Weak	22	61
11/89	Not detected	18	55
8/92	Not detected	16	52
0/100	Not detected	0	–

VPO in *n*-butane oxidation [46], extensive analysis of VPO samples identified a single crystal phase of $(VO)_2P_2O_7$, which implied that the corresponding V^{4+} species to be the active species. But more recent studies revealed that the active phases of VPO catalyst are more complex than the simple $(VO)_2P_2O_7$ model [51]. Although in low concentration, $VOPO_4$ phases with V^{5+} species were found on the surface of VPO catalysts, acting as centers of oxidation for activating *n*-butane [35,51]. Regarding the kinetic significance of V^{5+} species for *n*-butane oxidation, a recent study [52] with time-resolved in situ X-ray absorption spectroscopy showed that the rate of maleic anhydride formation is proportional to the rate of decay of V^{5+} species in the VPO catalysts. This result suggests that V^{5+} species is significant for the production of maleic anhydride. Furthermore, it was suggested that V^{5+} species also play a role in the hydrogen abstraction from *n*-butane. More interestingly, V^{4+} was suggested to be responsible for the by-product formation.

It is yet to be confirmed whether these conclusions regarding active phases or species of VPO catalysts in *n*-butane oxidation can be applied partially or completely in propane oxidation. A recent study has started to look into the structural aspects of VPO in propane oxidation. It was reported that a minor $VOPO_4$ (V^{5+}) phase and a major $(VO)_2P_2O_7$ (V^{4+}) phase were observed in VPO catalysts effective for propane oxidation [43].

4.1.5. Outlooks of VPO catalyst for propane oxidation

Based on the excellent performance of VPO catalysts for converting *n*-butane to maleic anhydride, it is reasonable to believe that VPO type catalysts have real potential for converting propane to acrylic acid effectively. The future of VPO catalysis research for propane oxidation need to rely on a good understanding and systematic studies of the structural origin, such as active phases and active species. Once the active phases or active sites of catalysts are identified, whether amorphous or crystal phases, it would be a challenge for catalyst preparation to increase the density of such sites.

On the other hand, systematic studies of the effects of promoters may generate leads for more effective catalysts. Several promoters, such as Te for increasing selectivity to acrylic acid [31] and Zr and Ce for propane activation [43,44], are good examples of promoters enhancing the overall performance of VPO catalysts. The mechanism of how these promoters function is still not clear, although changing surface acidity or redox properties are among the possibilities. The study of the roles of promoters and how they impact the structural aspects of VPO catalysts will certainly provide guidance for further improvement.

In the catalyst testing, attention should also be paid to isolate the effects of reaction conditions from those of the intrinsic properties of catalysts to be tested. The study of possible reaction pathways and product distributions could offer some guidance for the optimization of reaction conditions.

4.2. Heteropoly compounds (HPC)

HPC refer to inorganic, heteropoly acids and the corresponding salts. HPC have well defined cage-like structures with a central cation and surrounding polyanions. The central cation can be cations of heteroatoms, such as P, As, Si, Ge, B, etc. and the surrounding polyanions are often oxoanions of Mo or W [53]. HPC can be formed through the polymerization of oxoanions around central cations in aqueous solutions at low pH. A variety of cage-like structures, such as Keggin, Dawson, and Anderson type structures, are known and well characterized with IR or XRD [54]. Among these, the most studied as oxidation catalysts are the Keggin type compounds. The general formula of a unit Keggin structure is $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ consisting of a central cation X^{n+} surrounded by twelve edge- and corner-sharing MO_6 octahedral polyanions. Most often, M can be Mo or W, and X can be P, Si, As, or Ge [53]. Fig. 4 shows the primary structure of $PW_{12}O_{40}{}^{3-}$ Keggin ion.

4.2.1. Effectiveness in propane oxidation

Unlike VPO or other metal oxide catalysts, heteropolyacids catalysts can contain acidic protons and have strong acidity. In fact, these compounds have long been used as acid catalysts in solution for dehydration, esterification and alkylation, due in part to this strong acidity. Heteropoly-anions are multi-electron oxidants, especially those containing Mo and V. The redox properties of HPC compounds enable them to be used as catalysts for dehydrogenation of alcohols

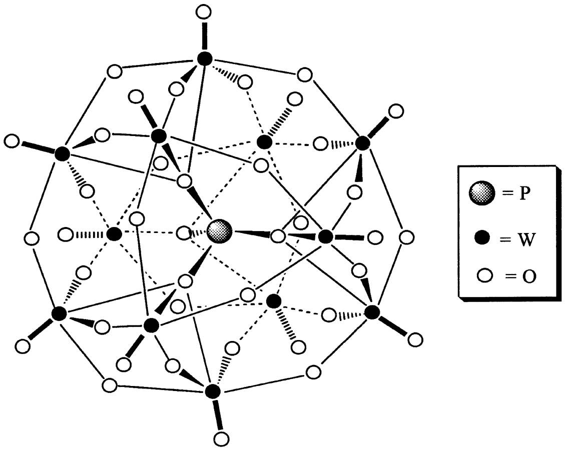

Fig. 4. Primary structure of $PW_{12}O_{40}^{3-}$ Keggin ion.

or amines, and for allylic oxidative dehydrogenation of aldehydes, aids, ketones and nitriles [54].

The Keggin type HPCs have long been known as effective catalysts for the oxidative dehydrogenation of alkane (Table 4), such as for propane to propylene [55] and ethane to ethylene [56].

Recently, increasing efforts have been devoted to the study of HPCs as catalysts for one-step conversion of propane to acrylic acid with molecular oxygen as the oxidant. Table 5 lists the application of several HPCs as catalysts for propane oxidation to acrylic acid.

Although the actual acrylic acid yield was relatively low and there was no follow-up for more than a decade, the first application of HPCs in one-step oxidation of propane to acrylic acid was actually conducted in the early 1980s by researchers in Rohm and Haas company [57]. In the early 1990s, Centi and Trifiro reported a $H_5PV_2Mo_{10}O_{40}$ catalyst, which showed reasonable initial activity and selectivity. It was found, however, that the sample rapidly deactivated (in about 1–2 h) due to deep reduction with decomposition of the Keggin anion structure [58]. This observation is consistent with the understanding that Keggin type structures lack thermal stability and structural decomposition could occur in air at below 400°C [54].

4.2.2. Improvement by structural modification

According to Ueda and co-workers, the simple form of Keggin compound $H_3PMo_{12}O_{40}$ is inactive for converting propane when tested at 340°C [59,60]. By neutralizing the acidic sites with ammonia, the catalyst showed some activity. When the acidic sites were neutralized with pyridine, the propane conversion further improved and the selectivity to acrylic acid also greatly increased. However, the overall yield to acrylic acid was still low, mainly due to the low conversion. Apparently, the adsorbed pyridine blocked the Brönsted acid sites on the surface, which was believed to affect the activation and selectivity. However, there was

Table 4
HPCs in the ODH of alkane

Catalyst composition	Feed	Temperature (°C)	Conversion (%)	Selectivity to alkene (%)	Reference
$CrPMo_{12}O_{40}$	propane/O_2/He	400	<10	55 (propylene)	[55]
$K_3PsbMo_{11}FeCe_{0.25}Cr_{0.5}O_n$	ethane/O_2/He	540	26	74 (ethylene)	[56]

Table 5
Heteropoly compounds for propane oxidation to AA

Catalyst composition	Feed (C3=propane)	Temperature (°C)	Conversion (%)	AA yield (%)	AA selectivity (%)	Reference
$H_{3-n}Sb_nP_1Mo_{12}O_{40}$	C3/O_2/H_2O/N_2	340	10	2	19	[57]
$H_5PV2Mo_{10}O_{40}$	C3/O_2/N_2	–	41	9	22	[58]
$H_3PMo_{12}O_{40}$	C3/O_2/H_2O/N_2	340	0	–	–	[59,60]
$(NH_4)_3PMo_{12}O_{40}$	C3/O_2/H_2O/N_2	340	4.5	–	6	[59,60]
$(PyH)_3PMo_{12}O_{40}$	C3/O_2/H_2O/N_2	340	7.5	2	29	[59,60]
$H_{1.26}Cs_{2.5}$ $Fe_{0.08}P_1V_1Mo_{11}O_{40}$	C3/O_2/N_2	380	47	13	28	[61]
$H_{3+n}PV_nMo_{12-n}O_{40}/Cs_3PMo_{12}O_{40}$	C3/air/H_2O/N_2	<400	50.4	10.8	21.5	[62,63]

no information about the length of time pyridine can remain on the catalyst.

Unlike other catalyst systems, the preparation of HPCs usually does not involve a calcination step and the catalytic activity and the thermal properties of the HPCs depend almost entirely on the formation of certain cage structures through the proper arrangement of the constituent elements of polyanion and counter-cations. To date, the highest acrylic acid yield (13%) achieved on this type of catalyst is reported to be a substituted $H_3PMo_{12}O_{40}$ compound. By partially substituting the H^+ with Fe^{3+} and one Mo^{6+} with one V^{5+} in $Cs_{2.5}H_{1.5}PMo_{12}O_{40}$, Mizuno and co-workers obtained $Cs_{2.5}Fe_{0.08}H_{1.26}PVMo_{11}O_{40}$, the most active and selective HPC catalyst for the conversion of propane to acrylic acid reported to date [61]. In addition to the improved activity and selectivity, the substitutions also improved structural stability of the catalyst. Based on IR and XRD data of the catalyst, the authors suggested that the Keggin structure was retained during the reaction within the temperature range of 300–400°C.

Another example of improved thermal stability by substituting protons with appropriate metal ions is the catalyst $K_3PSbMo_{11}FeCe_{0.25}Cr_{0.5}O_n$ for oxidative dehydrogenation of ethane, which was reported to be stable even at 540°C [56]. Performance improvements were also reported by supporting a heteropolyacid on the corresponding Cs-salt which is thermally more stable and have high surface area [62]. According to the authors, the active component of the catalyst is the corresponding heteropolyacid phase. However, the surface characteristics of the acid phase are difficult to control and reproduce. To overcome these difficulties, the high surface area salt was used to support and stabilize the acid form.

4.2.3. *Outlooks of HPCs for propane oxidation*

The major advantage of the HPC type of compounds over the VPO or other metal oxide catalysts is their well-defined cage type of structures, which allow well controlled structural modifications, such as the partial substitution of the protons in heteropolyacid with metal cations, which allows the control of surface acidity. Further modifications of surface or bulk redox properties of HPCs are also conceivable with controlled ion exchanges of HPC.

One major disadvantage of HPC type of catalysts is their general lack of thermal stability. Thermal stability is critically required for catalysts for propane oxidation, since propane activation calls for high temperatures. Furthermore, hot spots can be generated in a catalyst bed. Although substitution of protons with metal ions can substantially improve the thermal stability of heteropolyacids, a complete substitution of all protons appeared to lead to less active or even inactive salts [62]. Further improvement of thermal stability through other means will certainly be one of the future directions for HPCs.

4.3. *Multi-component metal oxides (MMO)*

MMO catalysts for propane oxidation are primarily mixed oxides of transition metals. Some MMO catalysts also contain V and P, the essential elements of the VPO type catalysts. In general, MMOs do not have a well-defined primary structure as HPC do. Rather, MMOs contain a mix of multiple crystal and amorphous phases. MMOs are generally prepared through calcination at high temperatures and thus have excellent thermal stability.

4.3.1. *Effectiveness of MMOs for propane oxidation*

The applications of MMO type catalysts in propane oxidation to AA only started in the 1990s, although Mo-V-Nb mixed oxides, the basis for these high performing propane selective oxidation catalysts was initially developed in the 1970s for the oxidation of ethane to ethene and acetic acid [64]. This Mo-V-Nb mixed oxide catalyst was also reported to be capable of activating propane at 300°C but producing only acetic acid, acetaldehyde and carbon oxides. To date, most of the applications of MMO type catalysts are mentioned in patents. Table 6 lists some of these applications of MMO catalysts for propane oxidation to acrylic acid.

All of these MMO catalysts are Mo-based and most of them also contain V as a major component. As seen in Table 1, Mo is the essential element of most commercial catalysts for propylene oxidation to acrolein and acrolein oxidation to acrylic acid while V is another essential element used as commercial catalysts for acrolein oxidation to acrylic acid. Although mixed oxide catalysts lacking V are very active for propylene oxidation [25,29,30], they are not very active for propane oxidation [66,67].

Table 6
Mixed metal oxide type catalysts for propane oxidation to acrylic acid

Catalyst examples	Feed (C3=propane)	Temperature (°C)	Conversion (%)	Yield (%)	Selectivity (%)	Reference
$Mo_1V_{0.4}Nb_{0.04}Bi_{0.08}Sb_{0.08}K_{0.08}O_n$	$C3/O_2/H_2O$	400	19	6	29	[65]
$MoSnO_n$	$C3/O_2/N_2$	360	4	2	48	[66]
$Mo_{1.51}Ni_1Te_{0.01}P_{0.02}O_n$	$C3/O_2/H_2O/He$	460	12	3	23	[67]
$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	$C3/air/H_2O$	380	80	48	60	[68]
$Mo_1V_{0.3}Sb_{0.16}Nb_{0.05}O_n$	$C3/air/H_2O$	380	50	16	32	[69]
$Mo_1V_{0.3}Sb_{0.25}Nb_{0.11}O_n$	$C3/O_2/H_2O/N_2$	400	21	12	61	[70]
$Mo_1V_{0.3}Sb_{0.25}Nb_{0.12}K_{0.013}O_n$	$C3/O_2/H_2O/N_2$	420	39	25	64	[71]
$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	$C3/air/H_2O$	390	71	42	59	[72]
$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	$C3/O_2/H_2O/He$	350	23	14	61	[73]

The potential of Mo- and V-based mixed oxides in propane oxidation was reported by Bartek et al. [65]. However, the most effective catalysts to date for propane to acrylic acid are those Mo-V-Te-Nb-O catalysts reported by Ushikubo et al. [68] and Lin and Linsen [72]. In fact, a catalyst with the same four components was first found to be very effective for propane ammoxidation to acrylonitrile [74]. It may have been quite unexpected that the same catalyst can function so well in two different reactions without the need of any compositional modification. Although the two reactions, propane oxidation and propane ammoxidation, may share some fundamental reaction steps, such as propane activation and propane oxidative dehydrogenation, there are significant differences between the two. For instance, ammonia activation and addition steps for nitrile formation are unique to propane ammoxidation to acrylonitrile and do not exist in propane oxidation. Furthermore, acrylonitrile and acrylic acid differ significantly with respect to the acidity and thermal stability. Nonetheless, this Mo-V-Te-Nb-O catalyst was shown to be remarkably robust and efficient for both reactions (Table 7).

The performance of this Mo-V-Te-Nb-O catalyst for propane oxidation to acrylic acid has been shown to be significantly better than that of any other MMO type of catalysts, or any VPO or HPC type of catalysts reported to date. However, others have found it rather difficult to prepare active Mo-V-Te-Nb-O catalysts that exhibit the claimed performance in either propane ammoxidation to acrylonitrile or propane oxidation to acrylic acid [1]. Recently, several reports have indicated that not only the composition of the catalyst is of importance, the preparation methods also greatly affect the effectiveness of the catalysts of essentially the same compositions. For example, the performance of $Mo_1V_{0.3}Te_{0.23}Nb_{0.1}O_n$ catalysts can vary from very poor (no yield) [72,75], mediocre (14% acrylic acid yield) [73], to excellent (>40% acrylic acid yield) [72,75]. As will be discussed later in more details, these performance differences reflect the structural differences of the catalysts prepared under different preparation conditions [72,75,76].

By substituting Te of Mo-V-Te-Nb-O with Sb, Ushikubo and co-workers further reported a Mo-V-Sb-Nb-O catalyst for propane selective oxidation to acrylic acid [69]. Although this Sb catalyst is less active and less selective than the corresponding Te-containing analogue, its overall performance is still quite good. The application of Mo-V-Sb-Nb-O catalyst for the conversion of propane to acrylic acid was also investigated independently by Takahashi and

Table 7
Mo-V-Te-Nb catalyst in propane (Amm) oxidation

Catalyst	Reaction	Temperature (°C)	Conversion (%)	Selectivity (%)	Yield (%)	Reference
$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	Oxidation	380	80	60 (acrylic acid)	48 (acrylic acid)	[68]
$Mo_1V_{0.3}Te_{0.23}Nb_{0.12}O_n$	Ammoxidation	420	89	64 (acrylonitrile)	58 (acrylonitrile)	[74]

coworkers [70]. It was further reported that by incorporating K into the Mo-V-Sb-Nb-O catalyst, a higher propane conversion was achieved [71].

4.3.2. Compositional and structural aspects

As discussed above, Mo-V-Nb mixed oxides, which are the basis for these high performing propane selective oxidation catalysts, were found by Thorsteinson et al. to be capable of activating propane at 300°C, but produced only acetic acid, acetaldehyde and carbon oxides as the products [64]. An analogous catalyst was recently tested by Ushikubo and co-workers for propane oxidation, and was found incapable of producing any acrylic acid [68]. Also reported was a Mo-V-Te mixed oxide catalyst, which achieved a 48% propane conversion but again produced no acrylic acid. The function of niobium in these mixed oxide catalysts was believed to stabilize the structure of Mo-V oxides against over-oxidation or reduction and permit a strongly oxidized or reduced catalyst to return more readily to its original state in ethane oxidation [64]. While the $Mo_1V_{0.37}Nb_{0.12}O_n$ catalyst was structurally stable, it failed to produce any C3 oxygenates in propane oxidation. Apparently, the addition of Te or Sb to Mo-V-Nb mixed oxides can contribute to certain structural changes leading to the formation of acrylic acid [68–70]. These results support the suggestion that Mo and V are responsible for the activation of propane while Nb and Te are part of the active sites responsible for the formation or release of C3 oxygenates. This suggestion is in agreement with the report that two component Mo-V oxides can effectively active ethane [64].

While not much has been discussed about the structures of Mo-V-Te-Nb oxides catalysts for propane oxidation the key X-ray diffraction angles of the catalysts were reported [68,72]. On the other hand, more details were discussed regarding the structural features of an analogous catalyst for propane ammoxidation [77–79]. It was speculated that at least two crystal phases participate in the ammoxidation of propane. One phase with XRD angles at 9.0, 22.1, 27.2, 29.2 and 35.4° is believed to relate to the activation of propane and the other phase with XRD angles at 22.2, 28.2, 36.3, 45.2 and 50.5° to the formation of acrylonitrile. Furthermore, the existence of certain metal–oxygen layer structures in these catalysts was recently proposed [76]. These layer structures are believed to be associated with XRD angles of 22 and 45° commonly observed in several Mo-V-M oxides effective for ethane oxidation, where M is Cr, Fe, Bi, Al or Co [80]. Since propane oxidation and ammoxidation may share some common features and reaction steps, the propane activation phase identified in propane ammoxidation reaction is likely to function in a similar manner in propane oxidation.

As mentioned above, several recent reports revealed that not only the elemental composition affects the structure and performance of Mo-V-Te-Nb oxide catalysts, preparative variables can also affect them greatly. Among the preparative variables, methods for precursor preparation appear to be critical [75,76]. In one example [75], two Mo-V-Te-Nb oxide catalysts were prepared for propane oxidation from two precursors of identical composition but via different drying methods. The two catalysts obtained have very different crystal structures as revealed by XRD (Fig. 5). The XRD results suggest a strong dependence of crystal structures on drying methods in catalyst precursor preparation. Reflecting the structure difference, the propane conversion vary from 1% (sample a) to 21% (sample b). In another example [76], several different methods were used to prepare the precursors of Mo-V-Te-Nb oxide catalysts for propane ammoxidation. The XRD patterns (Fig. 6) again indicate that the crystal structures of Mo-V-Te-Nb oxides are very sensitive to the preparation methods. As a result of

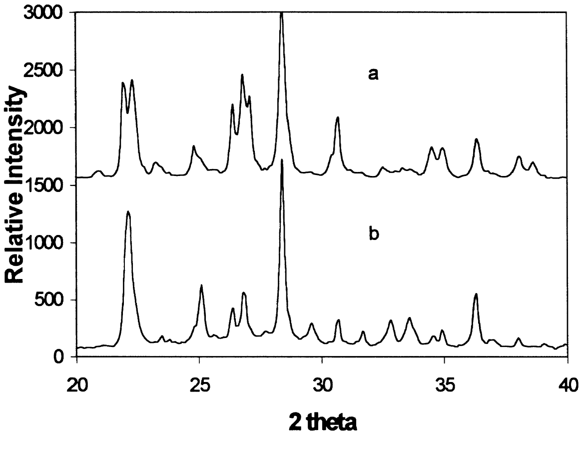

Fig. 5. XRD spectra of Mo-V-Te-Nb oxides from precursors obtained via different drying methods: (a) heat evaporation; (b) freeze-dry [75].

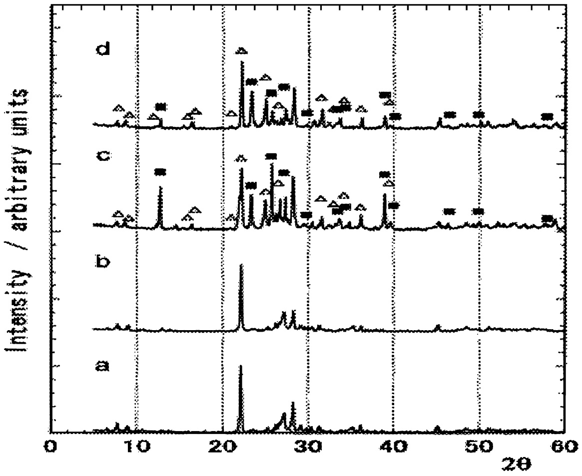

Fig. 6. XRD spectra of Mo-V-Te-Nb oxides: (a) dry-up method, (b) hydrothermal method, (c) and (d) solid state method ((Δ) $(Mo\text{-}X)_5O_{14}$, (■) MoO_3). (Courtesy of Y. Koyasu) [76].

the structural differences, propane conversion varies from 0% with one sample (d) to 91% with another (sample b).

The catalyst calcination condition is another critical preparative variable having a great impact on the structure of Mo-V-Te-Nb oxide catalysts [72,75]. Starting from one precursor, two catalysts of very different crystal phases (Fig. 7) were obtained under different calcination atmosphere [75]. As a result of the structure differences, propane conversion ranged from 0% (sample a) to 71% (sample b).

While the crystal phases may appear to be critical in Mo-V-Te-Nb oxide catalysts for propane oxidation and ammoxidation reactions as discussed above, there were also some stimulating discussions about the nature of the active phases in Mo-V-Nb oxide catalysts for ethane partial oxidation. Thorsteinson and co-workers suggested the importance of crystal phases of Mo-V-Nb-O catalysts for ethane as well as propane oxidation in the 1970s [64]. Recently, Ruth and co-workers further suggested that an amorphous phase may also play crucial roles in these oxide catalysts in ethane oxidation [81,82]. If these suggestions can be substantiated, it is possible that certain amorphous phases of Mo-V-Nb-Te-O catalysts may also play a similarly critical role in propane oxidation.

4.3.3. *Reaction pathways*

As shown in Fig. 8, oxidation pathways of propane oxidation over a Mo-V-Te-Nb-O catalyst was recently proposed [32,33]. With the exception of 2-propanol, the existence of all other partial oxidation products is supported by the experimental findings. In this view, propane is partially oxidized to acrylic acid with molecular oxygen via propylene and acrolein as intermediates. Oxidative dehydrogenation of propane to propylene and allylic oxidation of propylene are the two key steps which determine the selectivity to acrylic acid. Other than carbon oxides, acetic acid is the major by-product, which is formed mostly through an undesirable pathway with acetone as intermediate. Further oxidation of acrylic acid and undesirable

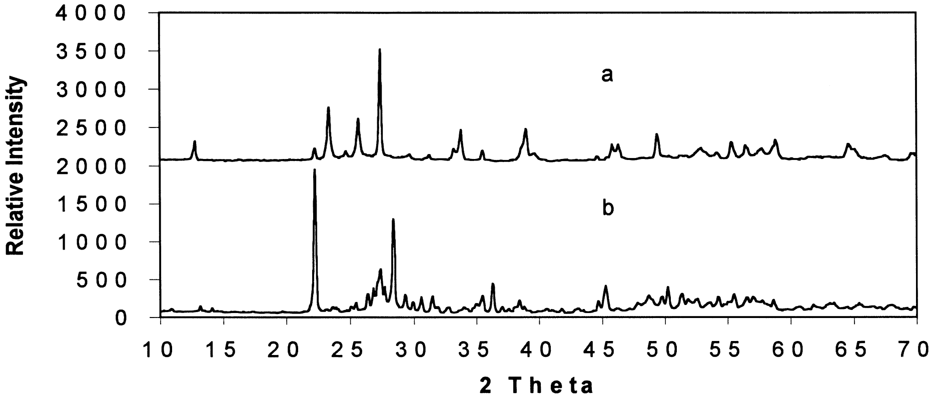

Fig. 7. XRD spectra of Mo-V-Te-Nb oxides: (a) calcined in air; (b) calcined in nitrogen [75].

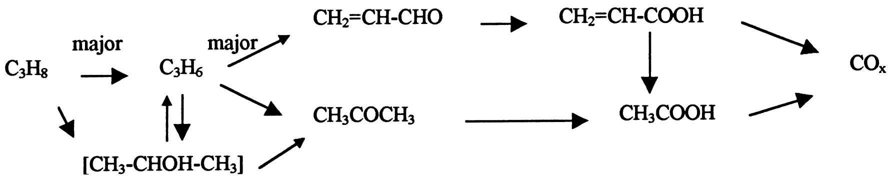

Fig. 8. Proposed oxidation pathway over a Mo-V-Te-Nb-O catalyst [32,33].

acetone pathway are the two major factors negatively impacting the selectivity to acrylic acid. In addition, the direct C–C breakage of acrolein or propylene to C1 and C2 molecules without going through acrylic acid may also compete with the selectivity to acrylic acid.

The major pathway from propane to acrylic acid over this Mo-V-Te-Nb-O catalyst is similar to that proposed over the Te/VPO system (Fig. 3). However, this type of similarity may not always hold. Recently, different propane oxidation pathways, as shown in Fig. 9, were proposed [83] for $Mo_{1.51}Ni_1Te_{0.01}P_{0.02}O_n$ mixed oxide catalyst (Table 6).

Over this catalyst, direct oxidation of propylene to CH_3CHO or CO_x was proposed. Aldehyde intermediates were observed experimentally in the product stream while acetic acid was not detected. These differences between the Te-P/Ni-Mo-O and Mo-V-Te-Nb-O catalysts could be attributed to both chemical and structural differences of the catalyst systems involved, despite the fact that major path from propane to acrylic acid contains the common intermediates propylene and acrolein. Here, the competition among the desirable and undesirable pathways could dictate the product distribution, while the catalytic activity, which is independent of the product distribution, could greatly affect the overall performance.

4.3.4. *Outlooks of mixed metal oxide catalysts for propane oxidation*

Although the history of the application of mixed metal oxides in propane oxidation to acrylic acid is relatively short, these catalysts, especially Mo-V-based, have afforded excellent propane conversion and acrylic acid selectivity. It should be pointed out that while the high acrylic acid selectivity achieved may be partly attributed to the specific properties of the catalysts, one should not overlook the contribution by the relatively low reaction temperatures at which high propane conversions were achievable. Since studies have shown that the further oxidation of acrylic acid increased greatly as the reaction temperature increased [32,33], highly active catalysts have the advantage of allowing a lower operation temperature, thus minimizing the further oxidation of acrylic acid after its formation.

In addition to the excellent catalytic properties, mixed metal oxide catalysts generally are found to be thermally stable under the reaction conditions, since they are usually prepared via calcination at much higher temperatures. One of the major drawbacks of the mixed metal oxide catalysts appears to be the difficulties in controlling the preparation parameters. The catalytic properties can be very sensitive to the preparation conditions which determine the catalyst structures, such as the formation of the active phases or sites. The development of synthetic methods which allow a better control of oxide structures should be an important research direction. Additionally, while very little has been achieved, a good understanding of structural aspects could also guide the design and preparation of mixed oxide catalysts. The progress in structural understanding

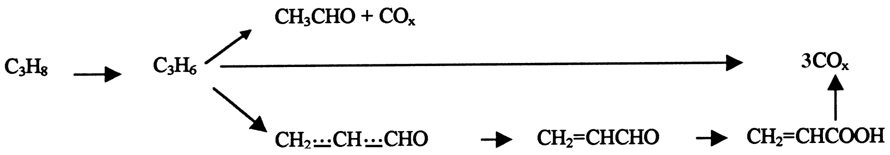

Fig. 9. Propane oxidation pathways over a Te-P/Ni-Mo-O catalyst [83].

can greatly impact the future of mixed metal oxide catalysts.

5. Concluding remarks

While the discovery and development of catalyst systems for the selective oxidation of propane to acrylic acid is still at an early stage, reasonable propane conversion and acrylic acid selectivity have been demonstrated in vanadium pyrophosphate, HPC and mixed metal oxides systems in laboratory scales. Currently, the most effective catalysts are those of Mo- and V-based mixed metal oxide catalysts. Possible oxidation pathways have been studied for several VPO and metal oxide catalysts and propylene and acrolein are found to be the major reaction intermediates for the formation of acrylic acid from propane. For Mo-V-Te-Nb oxides, further oxidation of acrylic acid after its formation and the undesirable acetone pathway are the two major factors negatively impacting the selectivity to acrylic acid. However, very little has been reported concerning the catalyst active phases or active sites, as well as the long-term stability of the catalyst activity in these systems.

Based on the performance of catalysts discussed in this review, it is likely that one or more effective and stable catalysts for the one-step propane oxidation to acrylic acid will be developed in due time, although much more fundamental research still remains to be done. Furthermore, there are tougher challenges for the eventual commercialization of propane-based processes as alternatives to the current propylene process, since the latter, which is extremely efficient, has set a very high standard.

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