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# The partial oxidation of $C_4$–$C_6$ alkanes to maleic anhydride, 2-methyl maleic anhydride, and acetic acid over MoVO catalysts

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Alkanes such as *iso*-butane, *n*-pentane, and cyclohexane have been converted effectively to maleic anhydride, 2-methyl maleic anhydride, and acetic acid over MoVO catalysts below 330 °C. In order to explore the possible reaction pathways, the oxidation of *iso*-butene, cyclohexene, 2-methyl-1-propanol, tert-butanol, and 2-methylacrylic acid were examined over the catalysts. In *iso*-butene oxidation, acetic acid and 2-methyl maleic anhydride were detected but not maleic anhydride. In cyclohexene oxidation, benzene and phenol were detected as major products but it was not the case in cyclohexane oxidation. The results of our investigation indicate that the oxidation pathway of *iso*-butane is different from that of *iso*-butene, 2-methyl-1-propanol, tert-butanol, and 2-methylacrylic acid, whereas the oxidation pathway of cyclohexane is different from that of cyclohexene.

**KEY WORDS:** *iso*-butane oxidation catalysts; alkane oxidation; acetic acid; 2-methyl maleic anhydride; maleic anhydride.

## 1. Introduction

Alkanes are major components of oil and natural gas, and are generated as major components in oil and natural gas processing. Especially, propane and butanes are formed in large amount in petroleum refinery. Because alkanes are much more stable than olefins, their direct applications in synthesis chemistry are very limited. It is hence desirable to convert alkanes to synthesis intermediates such as olefins [1,2] and oxygenates [3–6]. Extensive researches have been conducted for the activation of alkanes, such as alkane selective oxidation [7–10] and alkane metathesis reaction over silica-supported transition metal hydrides [11]. In alkane selective oxidation, due to the relatively high reaction temperature [9,12], it is common to have low selectivity to the targeted products [3–13], and the scale-up process is not only difficult but also economically unacceptable. For example, in propane oxidation, the selectivity of propylene and/or acrylic acid [14–16] was low.

In *iso*-butane oxidation, *iso*-butene [17] and 2-methylacrylic acid [18–21] were reported as products. *Iso*-butene could be used as feedstock for the synthesis of methyl tert-butyl ether. The direct oxidation of *iso*-butane to methacrolein and 2-methylacrylic acid have received much attention. If a new process could be developed to meet the industrial requirements, it would be an alternative to the currently adopted acetone-cyanohydrin route. It was reported that the catalytic oxidation of pentane would lead to the formation of maleic anhydride [22] or both maleic anhydride and phthalic anhydride [23]. Maleic anhydride and phthalic anhydride are important monomers in polymer chemistry. The efforts made on the selective oxidation of cyclohexane were for the production of cyclohexanol, cyclohexanone, and adipic acid [24–26]. Currently, the catalytic process of cyclohexane oxidation has not been commercialised because the selectivity to the desired products are not high. There are lots of by-products and separation is difficult. We have recently reported the oxidation of propane to acetic acid and maleic anhydride [27]. The work reported in this paper is an investigation on the reaction pathways of alkanes oxidation.

## 2. Experimental

### 2.1. Catalysts preparation

The C1–C7 catalysts were prepared by first dissolving $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ in water or in an aqueous $H_2C_2O_4\cdot 2H_2O$ solution to obtain Solution A, and dissolving $NH_4VO_3$ in deionized water to obtain Solution B as depicted in Table 1. Then solution B was added into Solution A under stirring. The pH values of the mixtures are listed in Table 1. To obtain the C1–C7 catalysts, the mixtures were dried in an oven with a temperature profile of heating from room temperature to 120 °C within 1 h and then kept at 120 °C for 12 h. The dried samples were heated from room temperature to 400 °C within 2 h and followed by calcination in air at 400 °C for 10 h.

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Table 1
List of prepared catalysts

| Catalyst | Precursors | | | |
|---|---|---|---|---|
| | $(NH_4)_6Mo_7O_{24}\cdot 4H_2O/H_2C_2O_4\cdot 2H_2O$ /$H_2$ (g/g/mL) | $NH_4VO_3/H_2O$ (g/mL) | pH | Composition |
| C1 | 9.32/0/100 | 0.68/50 | 5.13 | $Mo_{90\%}V_{10\%}O_x$ |
| C2 | 8.96/0/100 | 1.06/50 | 5.48 | $Mo_{85\%}V_{15\%}O_x$ |
| C3 | 8.57/0/100 | 1.42/50 | 5.52 | $Mo_{80\%}V_{20\%}O_x$ |
| C4 | 9.68/20.45/100 | 0.35/50 | 0.84 | $Mo_{95\%}V_{5\%}$ $O_x$ |
| C5 | 9.32/19.54/100 | 0.68/50 | 0.80 | $Mo_{90\%}V_{10\%}O_x$ |
| C6 | 8.96/19.18/100 | 1.06/50 | 0.81 | $Mo_{85\%}V_{15\%}O_x$ |
| C7 | 8.57/18.30/100 | 1.42/50 | 0.78 | $Mo_{80\%}V_{20\%}O_x$ |

### 2.2. Catalyst testing

All of the catalysts were tested for the selective oxidation of *iso*-butane, and a number of them were tested for the selective oxidation of *n*-pentane and cyclohexane. For mechanistic investigation, catalyst C6 was tested for the oxidation reaction of *iso*-butene, 2-methyl-1-propanol, tert-butanol, 2-methyl acrylic acid, and cyclohexene. For every reaction, 1.000 g of catalyst was used. The empty spaces on both sides of the catalyst bed were filled with quartz sand. Oxygen and *iso*-butane (or *iso*-butene) was fed into the reactor via a mass flow controller. The flow rate of oxygen was 10.0 mL/min whereas that of *iso*-butane (or *iso*-butene) was 2.5 mL/min. The liquid reactant *n*-pentane, cyclohexane, cyclohexene, 2-methyl-1-propanol, tert-butanol, or 2-methylacrylic acid was fed into the reactor at a flow rate of 0.91 mL/h by the use of a syringe pump. The reaction was carried out in a glass tube reactor (OD 1.0 cm, ID 0.8 cm) at 280–320 °C and at 1.0 atm pressure. In the reactor, there was a heating zone before the catalyst bed where oxygen mixed with the organic reactant. Other reaction conditions would be described later in the corresponding sections. All activity data were collected after three days of on-line reaction. The liquid effluent was collected in a receiver chilled in an ice bath. The gas phase effluent was analyzed separately. The reaction products were identified using an Agilent GC/MS (HP6890N)/MS(5973N). The quantification of reaction effluents was conducted using an Agilent HP 6890N GC equipped with a thermal conductivity detector (TCD); a 30 m HP-MOL SIV column and a 50 m AT FFAP column were adopted for the analysis of gas and liquid effluent, respectively. The conversion was calculated based on the mole of carbon-containing reactants. The selectivity of a product was calculated based on a molar basis of the compound.

The control experiment for *iso*-butane oxidation was conducted on the same reaction system with the whole reactor tube being filled with quartz sands (40–80 mesh). The reaction was carried out at 300, 310, and 320 °C at oxygen and *iso*-butane flow of 10.0 mL/min and 2.5 mL/min, respectively. Under such reaction condition, we did not detect any oxidation products.

The XRD examination of samples was performed over a Philips PW3040/60 X-ray diffraction spectrometer with Cu K-$\alpha$ irradiation.

## 3. Results

### 3.1. XRD measurement

The XRD measurements show that the C1–C3 catalysts prepared without the involvement of oxalic acid contain phases of orthorhombic $MoO_3$ and hexagonal $V_{0.12}Mo_{0.88}O_{2.94}$ (Figure 1). Over the C4–C7 catalysts prepared with oxalic acid involvement, only the orthorhombic $MoO_3$ phase was detected (Figure 1).

### 3.2. Iso-butane oxidation

The VMoO catalysts were tested for the oxidation of *iso*-butane. Over the catalysts, $CO_x$, acetic acid, maleic anhydride, and 2-methyl maleic anhydride were detected (Table 2). Our results reveal that over catalysts C1–C3, deep oxidation of reactant to $CO_x$ (i.e. CO and $CO_2$) was common. Over catalysts C4–C7, acetic acid and 2-methyl maleic anhydride were the major products, whereas maleic anhydride, acrylic acid, CO, and $CO_2$ were by-products. We detected trace amount of phthalic anhydride and benzoic acid over some of the catalysts. The amount of phthalic anhydride and benzoic acid was below the detection limit of a GC thermal conductivity detector and had to be detected by GC/MS. On the basis of the overall yield of acetic acid, maleic anhydride, and 2-methyl maleic anhydride, C5 (containing 10% of V) was catalytically the most active. The C6 catalyst (containing 15% of V) showed the highest total selectivity of acetic acid, maleic anhydride, and 2-methyl maleic anhydride.

The products obtained in *iso*-butane oxidation were different from those reported in the literature, where *iso*-butene, methacrolein, 2-methylacrylic acid, acetic acid,

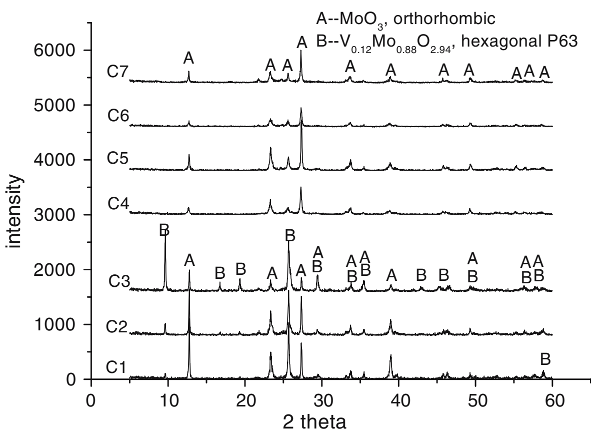

Figure 1. The XRD spectra of catalysts.

Table 2
Performance of catalysts in *iso*-butane oxidation

| Catalyst | T (°C) | X (%) | $S_1$ (%) | $S_2$ (%) | $S_3$ (%) | $S_4$ (%) | $S_5$ (%) | $S_6$ (%) | $S_3/(S_1+S_2)$ |
|---|---|---|---|---|---|---|---|---|---|
| C1 | 300 | 10.3 | 34.4 | 30.1 | 17.8 | 0.03 | 2.4 | 15.2 | 0.3 |
| C2 | 300 | 12.1 | 34.4 | 34.5 | 15.5 | 0.004 | 2.8 | 12.9 | 0.2 |
| C3 | 300 | 8.6 | 28.7 | 49.5 | 14.5 | 0.02 | 1.0 | 6.2 | 0.2 |
| C4 | 300 | 21.6 | 24.0 | 0 | 45.6 | 0 | 2.9 | 27.4 | 1.9 |
| C5 | 300 | 34.9 | 16.4 | 1.2 | 57.4 | 0 | 3.1 | 21.8 | 3.3 |
| C6 | 300 | 28.2 | 15.0 | 0 | 48.9 | 0 | 5.7 | 30.3 | 3.3 |
| C7 | 300 | 21.3 | 18.6 | 5.6 | 42.2 | 0.1 | 3.2 | 30.4 | 1.7 |

*Note*: T denotes reaction temperature; X denotes *iso*-butane conversion. For selectivity: $S_1$ CO, $S_2$ $CO_2$, $S_3$ acetic acid, $S_4$ acrylic acid, $S_5$ maleic anhydride, $S_6$ 2-methyl maleic anhydride.

CO, and $CO_2$ were the usual products [28,29]. At room temperature, maleic anhydride and methyl maleic anhydride will be in solid form. If online analysis system were used without proper heating, these products would condense readily inside the tubes and the connection junctions. This could be the reason why they were not detected in most cases. In our reaction, we paid particular attention to this problem and collected the products directly at the exit of the reactor. In our cases, acetic acid and 2-methyl maleic anhydride were obtained as major products.

### 3.3. *Search for iso-butane oxidation intermediates*

To our understanding, 2-methyl propanol and tert-butanol have not been reported as reaction intermediates in the literature, whereas *iso*-butene was suggested to be a reaction intermediate in *iso*-butane oxidation [30,31]. Although we did not detect *iso*-butene, 2-methyl propanol, *tert*-butanol, and 2-methyl acrylic acid as products in *iso*-butane oxidation, they could be transient intermediates undetected in the experiments. In order to investigate whether *iso*-butene, 2-methyl-1-propanol, tert-butanol, and 2-methylacrylic acid were intermediate species in *iso*-butane oxidation, we conducted the oxidation reaction of these compounds over the C6 catalyst.

### 3.4. *Iso-butene oxidation*

The oxidation of *iso*-butene was carried out at 300 °C with oxygen and *iso*-butene flows of 10.0 mL/min and 2.5 mL/min, respectively. A single pass *iso*-butene conversion of 27.2% was obtained. The products were acetic acid, 2-methyl maleic anhydride, 2-methylpropanoic acid, 2-methylacrylic acid, phthalic anhydride, CO, and $CO_2$, and the corresponding selectivity were 40.6%, 37.3%, 3.3%, 4.7%, 0.3%, 10.6%, and 3.2%. It can be seen that in both cases of *iso*-butane and *iso*-butene oxidation, acetic acid, 2-methyl maleic anhydride, phthalic anhydride, CO, and $CO_2$ were detected. The differences between the two oxidation reactions are that 2-methylpropanoic acid and 2-methylacrylic acid were detected in *iso*-butene oxidation but not in *iso*-butane oxidation, while maleic anhydride and acrylic acid were detected in *iso*-butane oxidation but not in *iso*-butene oxidation.

### 3.5. *Methyl-1-propanol oxidation*

In 2-methyl-1-propanol oxidation, the flow of 2-methyl-1-propanol and oxygen was 0.91 mL (liquid)/h and 10.0 mL (gas)/min, respectively. The 2-methyl-1-propanol single-pass conversion at 300 °C was 22.2% over catalyst C6. The products were CO (30.8%), $CO_2$ (3.0%), acetaldehyde (5.0%), acetic acid (9.2%), *iso*-butene (4.7%), 2-methyl-propanal (8.7%), methacrolein (10.0%), 3-methyl-2-butanone (8.0%), 2-methylpropyl acetate (0.31%), 2-methyl-propanoic acid (4.2%), 2-methylacrylic acid (3.4%), 2,4-dimethyl-benzene (1.0%), 2-methylpropyl 2-methyl-propanate (2.0%), 1,1'-[ethylidenebis(oxy)]bis[2-methyl-propane] (1.4%), 1,1-diisobutoxy-isobutane (2.0%), and 1,2-benzenedicarboxylic acid bis(2-methylpropyl) ester (9.9%), with the corresponding selectivity bracketed.

### 3.6. *Tert-butanol oxidation*

The oxidation of tert-butanol was carried out over catalyst C6 at 300 °C with a tert-butanol flow of 0.91 mL (liquid)/h and an oxygen flow of 10.0 mL/min. A single-pass tert-butanol conversion of 53.1% was obtained. In the reaction, CO (2.2%), $CO_2$ (18.4%), *iso*-butene (4.0%), 2-methyl-propanal (16.8%), methacrolein (23.2%), 2,3-butanedione (17.0%), acetic acid (9.4%), 2-methylpropanoic acid (7.4%), and 1,3-dimethylbenzene (0.8%) were detected as products (shown in bracket is the corresponding selectivity). Beside CO and $CO_2$, 2-methyl-propanal, methacrolein, and 2,3-butanedione were the major products.

### 3.7. *2-Methylacrylic acid oxidation*

Since acrylic acid and acetic acid were obtained in *iso*-butane oxidation, we wondered if 2-methylacrylic acid was an intermediate for acetic acid and acrylic acid formation. We carried out the oxidation reaction of 2-methylacrylic acid over catalyst C6. In the reaction, the flow of 2-methylacrylic acid and oxygen were 0.91 mL(liquid)/h and 10.0 mL/min, respectively, and the reaction was conducted at 300 °C. We observed very low 2-methylacrylic acid conversion (below 0.2%), and the products were CO, $CO_2$, acetic acid, acrylic acid, vinyl 2-methylacrylate, 2-methylacrylic anhydride, and benzoic acid. Comparing to the conversion of *iso*-butane, *iso*-butene, 2-methyl-1-propanol, and *tert*-butanol in the oxidation reaction, the conversion of 2-methylacrylic acid was trivial. Relatively speaking, the adsorption of 2-methylacylic acid on the catalyst surface and/or the oxidation of the acid is unfavorable. In *iso*-butane oxidation, compounds such as acetic acid and acrylic acid were detected but 2-methylacrylic acid was not. Apparently, 2-methylacylic acid is unlikely to be an intermediate or once it was formed, it was converted to CO, $CO_2$, acetic acid, and acrylic acid in *iso*-butane oxidation. Nevertheless, the formation of acetic acid and vinyl 2-methylacrylate indicates that there are $C_2$ species formed in the reaction.

### 3.8. *n-Pentane oxidation*

In *n*-pentane oxidation, CO, $CO_2$, $CH_3COOH$, acrylic acid, maleic anhydride, 2-methyl maleic anhydride, benzoic acid, and phthalic anhydride were products (Table 3). The major products were CO, $CO_2$, $CH_3COOH$, maleic anhydride, and 2-methyl maleic anhydride. The phenomena observed in *n*-pentane oxidation are similar to those observed in *iso*-butane oxidation: very high total selectivity of acetic acid and maleic anhydride, and the generation of 2-methyl maleic anhydride. Comparing to the case of *iso*-butane oxidation,*n*-pentane oxidation showed higher maleic anhydride selectivity as well as higher yield of benzoic acid and phthalic anhydride. In *iso*-butane oxidation, benzoic acid and phthalic anhydride were only in trace amounts.

### 3.9. *Cyclohexane oxidation*

In the oxidation reaction of *iso*-butane, *iso*-butene, and *n*-pentane, we found that the branched *iso*-butane and *iso*-butene produced more 2-methyl maleic anhydride (branched), whereas the unbranched *n*-pentane produced more maleic anhydride (unbranched). We observed no generation of maleic anhydride in the oxidation of *iso*-butene. The result is in consistent with the fact that maleic anhydride selectivity was high in propane oxidation [27]. In order to explore the influence of alkane structure on product distribution in alkane oxidation, we carried out oxidation reaction of cyclohexane over the C1-C7 catalysts (Table 4). Besides the products detected in the oxidation of *iso*-butane and *n*-pentane, we obtained significant amount of phenol and benzene. It is clear that phenol and benzene are products of the oxidative dehydrogenation of cyclohexane. In cyclohexane oxidation, the selectivity of maleic anhydride was higher than that of 2-methyl maleic anhydride. The results indicate that the formation of maleic anhydride is favourable in the oxidation of unbranched alkanes and cycloalkane while 2-methyl maleic anhydride is a likely product in the oxidation of branched alkanes. It is possible that unbranched alkane such as *n*-pentane could isomerise to branched species and then forming 2-methyl maleic anhydride in oxidation reaction. In the case of cyclohexane, isomerization to branched species is a multi-step process and is difficult to occur. Hence, maleic anhydride rather than 2-methyl maleic anhydride was produced in cyclohexane oxidation. In other words, by adopting cyclohexane as the starting reactant, one can avoid products of branched carbon skeleton.

### 3.10. *Cyclohexene oxidation*

Phenol and benzene were produced in cyclohexane oxidation. They could be from the direct oxidative dehydrogenation of cyclohexane or generated via a cyclohexene intermediate. However, we did not detect cyclohexene amidst the products by GC. In order to find out whether cyclohexane oxidation proceeds with a cyclohexene intermediate, we conducted the cyclohexene oxidation reaction over catalyst C6. In the reaction, the flows of cyclohexene and oxygen were 0.91 mL (liquid)/h and 10.0 mL/min, respectively. In the gas phase, CO and $CO_2$ were detected. The composition of liquid products was 82.8% of cyclohexene, 14.9% of benzene, 0.26% of cyclopentanone, 0.32% of cyclopentanecarboxaldehyde, 0.21% of cyclohexanone, 0.12% of $\beta$-benzoquinone, 1.1% of phenol, 0.13% of cyclopentanecarboxic acid,

Table 3
Oxidation of *n*-pentane over MoVO catalysts C1, C2, and C3

| Catalyst | T (°C) | X (%) | $S_1$ (%) | $S_2$ (%) | $S_3$ (%) | $S_4$ (%) | $S_5$ (%) | $S_6$ (%) | $S_7$ (%) | $S_8$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|
| C1 | 290 | 42.3 | 8.3 | 2.1 | 41.4 | 1.9 | 27.5 | 16.7 | 0.3 | 1.9 |
| C1 | 300 | 48.9 | 9.6 | 0.9 | 41.7 | 2.0 | 32.6 | 10.3 | 0.3 | 2.9 |
| C1 | 310 | 51.9 | 12.1 | 3.6 | 39.3 | 2.2 | 30.2 | 9.5 | 0.3 | 2.8 |
| C2 | 300 | 42.1 | 24.2 | 5.9 | 29.1 | 1.0 | 27.6 | 8.2 | 0.7 | 3.5 |
| C2 | 310 | 52.5 | 22.1 | 6.7 | 27.0 | 1.5 | 32.1 | 9.5 | 0.3 | 0.9 |
| C3 | 290 | 45.4 | 8.7 | 2.9 | 32.1 | 1.9 | 36.3 | 16.3 | 0.4 | 1.4 |
| C3 | 300 | 56.9 | 14.3 | 6.6 | 29.6 | 2.6 | 34.7 | 9.8 | 0.5 | 1.9 |

Note: T denotes reaction temperature; X denotes *n*-pentane conversion. For selectivity: $S_1$ CO, $S_2$ $CO_2$, $S_3$ acetic acid, $S_4$ acrylic acid, $S_5$ maleic anhydride, $S_6$ 2-methyl maleic anhydride, $S_7$ benzoic acid, $S_8$ phthalic anhydride.

Table 4
Oxidation of cyclohexane over MoVO catalysts

| Catalyst | T (°C) | X (%) | $S_1$ (%) | $S_2$ (%) | $S_3$ (%) | $S_4$ (%) | $S_5$ (%) | $S_6$ (%) | $S_7$ (%) | $S_8$ (%) | $S_9$ (%) | $S_{10}$ (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C1 | 310 | 28.3 | 9.0 | 15.7 | 6.3 | 0.09 | 52.7 | 8.5 | 2.7 | 0.7 | 2.4 | 2.4 |
| C2 | 310 | 21.5 | 17.0 | 19.6 | 6.9 | 0.1 | 35.6 | 8.2 | 3.8 | 0.2 | 3.4 | 5.0 |
| C3 | 310 | 33.8 | 7.8 | 13.1 | 15.9 | 0.07 | 25.6 | 18.7 | 13.3 | 0.4 | 1.0 | 4.7 |
| C5 | 290 | 38.7 | 3.0 | 0.3 | 5.6 | 0.1 | 59.2 | 16.4 | 3.2 | 0.4 | 9.5 | 2.3 |
| C5 | 300 | 41.4 | 3.9 | 1.4 | 3.4 | 0.07 | 70.8 | 5.0 | 1.4 | 0.5 | 10.4 | 3.0 |
| C6 | 310 | 30.8 | 6.7 | 8.7 | 12.2 | 0.24 | 36.1 | 10.3 | 4.8 | 0.6 | 14.1 | 6.2 |
| C7 | 310 | 52.2 | 3.5 | 10.4 | 10.9 | 0.08 | 54.4 | 3.9 | 1.0 | 1.0 | 11.3 | 3.7 |

*Note*: T denotes reaction temperature; X denotes cyclohexane conversion. For selectivity: $S_1$ CO, $S_2$ $CO_2$, $S_3$ acetic acid, $S_4$ acrylic acid, $S_5$ maleic anhydride, $S_6$ 2-methyl maleic anhydride, $S_7$ phenol, $S_8$ benzoic acid, $S_9$ phthalic anhydride, $S_{10}$ benzene.

0.13% of benzoic acid, and trace amounts of cyclohexyl-benzene, bi-2-cyclohexen-1-yl, biphenyl, and dibenzofuran.

## 4. Discussion

The results of Figure 1 and Table 2 indicate that the vanadium-containing orthorhombic $MoO_3$ phase of the C4–C7 catalysts favors the formation of acetic acid and 2-methyl maleic anhydride and the selectivity to CO and $CO_2$ were relatively low. Over the C1–C3 catalysts where both the orthorhombic $MoO_3$ and hexagonal $V_{0.12}Mo_{0.88}O_{2.94}$ phases were present, most of the *iso*-butane was deeply oxidized and the selectivity to acetic acid and 2-methyl maleic anhydride were low. We propose that the vanadium-containing orthorhombic $MoO_3$ phase is the active phase for the generation of acetic acid and 2-methyl maleic anhydride.

We calculated the selectivity ratios of acetic acid to $CO_x$ ($x = 1$ or 2), i.e. $S_3/(S_1+S_2)$, and compiled the results in Table 2. The data show that over most of the catalysts, the ratio is higher than 2/1. If acetic acid were formed through the deep oxidation of *iso*-butane, one mole of *iso*-butane would be oxidized to one mole of acetic acid and two moles of $CO_x$, the maximum $S_3/(S_1+S_2)$ ratio should be 2/1. To obtain a $S_3/(S_1+S_2)$ ratio higher than 2/1, there must involve the cracking of carbon-carbon bonds and the formation of new carbon–carbon bonds. There are two possible ways of reaching such an end. One is to have *iso*-butane isomerised to a non-branched $C_4$ species. The $C_4$ species could then be oxidized to maleic anhydride or crack into two $C_2$ species, which could be oxidized to acetic acid or recombine back to $C_4$ species. The other possibility is to have *iso*-butane cracked on active sites to form $C_1$, $C_2$, and $C_3$ species, then a $C_1$ species could combine with a $C_1$, $C_2$ or $C_3$ species to form surface $C_2$, $C_3$, and unbranched $C_4$ species; similarly, $C_2$ species could combine with $C_3$ species to form unbranched $C_5$. With the oxidation of $C_2$, $C_3$, $C_4$, and $C_5$ species, there would be the generation of acetic acid, acrylic acid, maleic anhydride, and 2-methyl maleic anhydride. If a $C_3$ species combined with $C_4$, and $C_4$ combined with another $C_4$ species, $C_7$ and $C_8$ species could be formed. The oxidative aromatization of $C_7$ and $C_8$ species would result in the formation of benzoic acid and phthalic anhydride; this could be the reason for the detection of a trace amount of benzoic acid and phthalic anhydride. In both cases, since there is no formation of $CO_x$ while acetic acid is being formed, one can obtain a $S_3/(S_1+S_2)$ ratio higher than 2/1, such as that over C5 and C6 (Table 2).

In *iso*-butene oxidation, the ratio of acetic acid selectivity to $CO_x$ selectivity is 2.94/1, which is again higher than 2/1. The results indicate that acetic acid is not formed from one mole of *iso*-butene with the wasting of two moles of carbon in $CO_x$ formation. In other words, reaction steps such as intramolecular isomerization, carbon–carbon bond cracking and adspecies recombination must have occurred. If reaction steps were as suggested, one would expect the formation of hydrocarbon species with two to eight skeleton carbons; the existence of $C_2$–$C_8$ species should lead to high acetic acid selectivity as well as products of high skeleton-carbon such as 2-methyl maleic anhydride and phthalic anhydride. However, we did not observe any acrylic acid and maleic anhydride in*iso*-butene oxidation. If unbranched $C_4$ species were formed through intramolecular isomerization of *iso*-butene, *iso*-butene should be a better candidate than *iso*-butane for the formation of maleic anhydride. It is because the conversion of *iso*-butene to a cationic species on an acid site occurs more readily than the conversion of *iso*-butane. We deduce that the intramolecular isomerization step of forming unbranched $C_4$ is not a major reaction pathway in both *iso*-butane and *iso*-butene oxidation reaction over the C6 catalyst. However, there should be similarities in reaction pathways in the oxidation of *iso*-butane and *iso*-butene because acetic acid and 2-methyl maleic anhydride were major products in the reactions.

Despite further experimental works are needed for the establishment of the mechanism involved in alkanes oxidation, the concept of "carbon–carbon cracking and adspecies recombination" can provide explanation for the formation of acetic acid, acrylic acid, maleic anhydride, and 2-methyl maleic anhydride in the oxidation of*iso*-butane, iso-butene, pentanes, and cyclohexane. There was no maleic anhydride formation in *iso*-butene oxidation whereas maleic anhydride was formed in *iso*-butane oxidation, we suggest that the discrepancy is due to the structural difference between adsorbed *iso*-butane and *iso*-butene. When *iso*-butane loses a methyl group to form adsorbed $C_3$ species, at least two of the carbons of the $C_3$ species are still saturated with hydrogen. The $C_3$ species can continue to crack into $C_1$ and $C_2$ species or crack a C–H bond to form allyl species on the surface, and a $C_2$ species can combine with a $C_3$ species to form branched or non-branched $C_5$ species. The branched $C_5$ species are potential reactant for 2-methyl maleic anhydride formation. It is generally accepted that an adsorbed allyl entity is much more stable than a $C_3$ species with two methyl groups. In *iso*-butene oxidation, after losing a hydrogen atom, adsorbed 2-methyl allyl species (branched $C_4$) can be formed directly. Of course, the adsorbed 2-methyl allyl species can also forsake a methyl group, resulting in the generation of $C_3$ species and $C_1$ species. The stable branched $C_4$ allyl species is relatively less likely to break down. It is possible that a branched $C_5$ species could be formed in the combination of $C_1$ and branched $C_4$ allyl species. This could be the reason for maleic anhydride not being formed in *iso*-butene oxidation. Based on the product distribution in the oxidation of 2-methyl-1-propanol, *tert*-butanol, and 2-Methylacrylic acid, we believe that these compounds are not major intermediates in *iso*-butane oxidation.

The recombination of hydrocarbon species to form new carbon-carbon bond is unusual under oxidation conditions. Nevertheless, Labinger and coworkers reported carbon-carbon bond formation in propane oxidation over NbPMo11V(pyr) [32] and similar observation was reported by us in propane oxidation [27]. The concept of "carbon–carbon cracking and adspecies recombination" can also be adopted to explain the oxidation of *n*-pentane and cyclohexane over the VMoO catalysts. Since acetic acid and maleic anhydride are major products, there must be the generation of $C_2$ and $C_4$ species in the cracking of *n*-pentane and cyclohexane. The existence of acrylic acid by-product indicates that $C_3$ species were formed. The combination and oxidation of $C_3$ and $C_4$ species or $C_4$ and $C_4$ species could lead to the formation of benzoic acid and phthalic anhydride as observed in the reactions. Haber and coworkers proposed that phthalic anhydride can be produced in *n*-pentane oxidation when maleic anhydride reacts with 1,3-butandiene via the Diels–Alder reaction and then followed by an oxidative dehydrogenation process [22]. In a similar manner, benzoic acid can be formed between 1,3-butandiene and acrylic acid. In the oxidation of cyclohexane with the occurrence of the oxidative dehydrogenation reaction, phenol and benzene were formed. In this study, the products of the oxidation of cyclohexene are different from those of the oxidation of cyclohexane. The oxidative dehydrogenation of cyclohexene does not lead to significant carbon–carbon bond cracking. Hence, cyclohexene should not be an intermediate of cyclohexane oxidation.

## 5. Conclusion

In the oxidation of *iso*-butane, *iso*-butene, *n*-pentane, and cyclohexane, there is the cracking of skeleton carbon-carbon bond and recombination of hydrocarbon adspecies. The hydrocarbon adspecies generated in the cracking steps are essential for the formation of acetic acid, maleic anhydride, 2-methyl maleic anhydride, and other minor by-products such as benzoic acid and phthalic anhydride. The results of the current study indicate that the reaction pathway of *iso*-butane oxidation is different from that of *iso*-butene oxidation. In the oxidation of 2-methyl-1-propanol, tert-butanol, and 2-methylacrylic acid, the oxidation of terminal carbon and isomerization of carbon skeleton appear to be the major steps. We purpose that 2-methyl-1-propanol, tert-butanol, and 2-methylacrylic acid are unlikely to be the reaction intermediates of *iso*-butane oxidation. Based on the discrepancy in the oxidation of cyclohexane and cyclohexene, we deduce that the cracking of hydrocarbon skeleton and recombination of hydrocarbon species are the major reaction pathways for the formation of acetic acid, maleic anhydride, and 2-methyl maleic anhydride in cyclohexane oxidation. In cyclohexene oxidation, the oxidative dehydrogenation reaction dominates and leads to the formation of benzene and phenol. The results demonstrate that through this type of oxidation reaction, unbranched alkanes such as propane, *n*-pentane, and cyclohexane can be converted to maleic anhydride and acetic acid with high conversion and good selectivity, whereas branched alkanes can be oxidized to acetic acid and 2-methyl maleic anhydride with high selectivity.

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