# Oxidation of Acetaldehyde and Propionaldehyde on a V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> Catalyst

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# *VO<sub>x</sub>*-*TiO<sub>2</sub>* Catalyst / Partial Oxidation / Acetaldehyde / Propionaldehyde / Kinetics Modelling

The partial oxidation of acetaldehyde and propionaldehyde on a TiO<sub>2</sub> supported VO<sub>x</sub> catalyst in presence of water vapour was investigated in the temperature range from 120 to 280 °C. The selective oxidation to the appropriate carboxylic acids depended on the kind of aldehyde and the reaction temperature. An oxidative cleavage to lower carboxylic acids and CO<sub>x</sub> was also found. Furthermore, the kinetic model for the process of oxidation of acetaldehyde and propionaldehyde over the V<sub>2</sub>O<sub>5</sub>-TiO<sub>2</sub> catalyst was developed.

# **1. Introduction**

The vanadium-titanium oxide system has found a lot of applications in numerous partial oxidation processes including the selective oxidation [1-5] and oxidative dehydrogenation (ODH) [6, 7] of  $C_2$ – $C_4$  hydrocarbons. These oxides are reported to be selective catalysts for the oxidation of *n*-butenes to acetic acid, formerly by the Hüls AG [8] and recently by the Consortium für elektrochemische Industrie GmbH [9]. The presence of about 20 vol. % of water vapour in the feed has been shown to enhance the yields of acetic acid [9–11].

Kaneko *et al.* [3] and Seiyama *et al.* [11] developed fundamental details about the formation of acetic acid by catalytic oxidation of *n*-butene on  $V_2O_5$  containing catalysts. Both groups proposed the formation of a carbocation as the first step. According to Kaneko *et al.* [3], acetic acid is formed by reaction of oxygen with the carbocation leading to acetaldehyde further oxidized to acetic acid. On the contrary, Seiyama *et al.* [11] suggested that

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water reacts with the carbocation to form 2-butanol, followed by the oxidation to 2-butanone and its oxidative cleavage to acetic acid and acetaldehyde.

Furthermore, propionic acid has also been reported as a product of the 1-butene oxidation on a VO<sub>x</sub> containing catalyst [3, 9–12]. The formation of propionic acid was envisioned *via* the formation of propionaldehyde by asymmetric C–C scission of the chemisorbed 1-butene [12]. The C<sub>2</sub>, C<sub>3</sub> aldehydes and their further oxidation to carboxylic acids and/or to CO<sub>x</sub> products were also observed in the ODH of C<sub>2</sub>, C<sub>3</sub> hydrocarbons [4, 5]. However, the yields of C<sub>1</sub>–C<sub>3</sub> carboxylic acids were usually low (about 0.5–2.0%) and the total oxidation was favoured at temperatures above 300 °C and in absence of water vapour. According to Centi *et al.* [13], the selectivity to carboxylic acids by oxidation and/or ODH of hydrocarbons should depend on the reactivity of the intermediate C<sub>2</sub>, C<sub>3</sub> aldehyde species. Nevertheless, not much information is available for catalytic gas phase oxidation of C<sub>2</sub>–C<sub>3</sub> aldehydes.

A preliminary study on the oxidation of propional dehyde on VO<sub>x</sub> containing catalysts was carried out by Slavucha et al. [14]. The selectivity to propionic acid was found to be  $\sim 60\%$  on a VO<sub>x</sub>-MgO catalyst in the 250–300 °C temperature range in the presence of 20 vol. % water vapour. Ai et al. [15] investigated the partial oxidation of propionaldehyde on vanadium phosphate and iron phosphate at 400 °C in the presence of water. Propionic acid was formed with the 20% and 40% selectivity on  $P/FeO_v$  and  $P/VO_v$ , respectively. Quaranta et al. [16] reported on the partial oxidation of ethanol to acetaldehyde on VO<sub>x</sub> containing catalysts. The selectivity to acetic acid on  $V_2O_5/TiO_2$ ,  $V_2O_5/Al_2O_3$  and  $V_2O_5/SiO_2$  catalysts between 150–250 °C were about 2–5%. Erdöhelyi and Solymosi [17] and Iwamoto et al. [18] investigated the ODH of ethane on supported V<sub>2</sub>O<sub>5</sub> catalysts in presence of 20 vol. % water from 400 to 550 °C. The selectivity to ethylene was about 40% and to acetaldehyde about 4%; carboxylic acids could not be detected. Evnin et al. [19] reported for the oxidation of ethylene on Pd/V<sub>2</sub>O<sub>5</sub> catalysts in presence of water vapour between 110-180 °C the selectivities up to 65% and 25% for acetaldehyde and acetic acid, respectively. At high temperature the total oxidations of acetaldehyde are favoured.

It can be concluded that the selectivity to carboxylic acids during the oxidation of 1-butene and the ODH of hydrocarbons depends not only on the reactivity of 2-butanol or 2-butanone, but also on the reactivity of the intermediate  $C_2$  and  $C_3$  aldehyde species. Therefore, further investigations on the oxidative activity of  $C_2$ – $C_3$  aldehydes are necessary for a better understanding of the mechanism of the formation of carboxylic acids on VO<sub>x</sub> containing catalysts during the catalytic oxidation of *n*-butenes, the ODH of  $C_2$  and  $C_3$  hydrocarbons and the selective oxidation of ethanol. The present work deals with the role of temperature in the oxidation of acetaldehyde and propionaldehyde to different oxidation products on a VO<sub>x</sub>-TiO<sub>2</sub> catalyst in presence of water vapour.

# 2. Experimental

#### 2.1 Catalyst preparation and characterization

The VO<sub>x</sub>-TiO<sub>2</sub> catalyst was prepared by spray-drying of a slurry of TiO<sub>2</sub>-Anatase (Millenium GmbH) and V<sub>2</sub>O<sub>5</sub>. The catalyst synthesis is described in detail elsewhere [9, 10]. After calcination at 450 °C for 5 h, the sample was pressed and sieved. A fraction of 0.10–0.31 mm was used for the catalytic measurements. The catalyst contained 6.1 wt. % of vanadium and was characterised by BET surface area, temperature programmed desorption of ammonia and oxygen, temperature programmed reduction with hydrogen and X-ray photoelectron spectroscopy (XPS). The detailed results of the catalyst characterization are described elsewhere [12, 20]. The BET surface area was *ca*. 95 m<sup>2</sup>/g and the average pore size was *ca*. 90 Å.

#### 2.2 Catalytic reactions

The oxidation of aldehydes was performed in a catalytic test apparatus equipped with a continuous-flow quartz reactor (length: 29.0 cm; inner diameter: 0.6 cm), mass flow controllers for the feed gas and a liquid-flow evaporator to add water and the aldehydes to the feed. The catalytic reactions were carried out at atmospheric pressure in the temperature range from 120 to 280 °C using 200 mg of the catalyst mixed with 200 mg of corundum. The gaseous hourly space velocity (GHSV) was about 10 000 h<sup>-1</sup>. The feed gas consisted of 0.27 vol. % acetaldehyde or 0.14 vol. % propionaldehyde, 3.5 vol. % oxygen and 15.0 vol. % water vapour and helium (rest). Before the catalytic reaction, the catalyst sample was activated at 300 °C for about 12 h in a flow of 3.5 vol. % oxygen in helium. The reaction system was found to stabilise in 3 h. Therefore, all data in this work were measured after the initial time of 3 h.

The product gas was analysed by online mass spectrometry and infrared gas analysis. The mass spectrometer used was an Omnistar GSD 300 QMS 200 (1-200 amu) by Pfeiffer Vacuum. The gas passed to the mass spectrometer *via* a gas stream selector (GSS 300) which was kept at 393 K and time depending spectra were recorded for m/e values of 46 (formic acid), 60 (acetic acid), 74 (propionic acid). CO and CO<sub>2</sub> were determined by online FTIR-analysis (IR gas analyzer 1301; INNOVA). A detailed description of the apparatus is given in [20].

## 3. Results and discussion

#### 3.1 Catalytic reactions

*Oxidation of Acetaldehyde.* Acetic acid, formic acid, CO and  $CO_2$  were detected as main reaction products during the oxidation of acetaldehyde. The



Fig. 1. Conversion of acetaldehyde and yields of main oxidation products as function of reaction temperature in the oxidation of acetaldehyde on the  $VO_x$ -TiO<sub>2</sub> catalyst in presence of water vapour.

dependence of acetaldehyde conversion and the yield of the oxidation products on temperature are shown in Fig. 1. The oxidation of acetaldehyde started at temperatures as low as  $120 \,^{\circ}$ C with acetic acid as the major product.

With increasing reaction temperature the conversion of acetaldehyde and the yield of  $CO_x$  increased. At temperatures above 260 °C a nearly complete conversion was observed. The maximum yield of acetic acid (about 72%) was reached at reaction temperatures of about 200 °C. The yield of formic acid is significantly lower than that of acetic acid. The maximum yield of formic acid is in the same temperature range as for acetic acid. The decrease in the acetic acid and formic acid yield beyond this temperature can be attributed to the formation of the total oxidation products. This indicates that acetaldehyde is a very reactive compound and undergoes selective oxidation to acetic acid even at low reaction temperatures. Furthermore, small amounts of ethyl acetate and methane were detected. The yield of methane and ethyl acetate at 180 °C was about 0.5 and 0.3%, respectively.

*Oxidation of Propionaldehyde*. The products of the oxidation of propionaldehyde were propionic acid, acetic acid, formic acid and  $CO_x$ . The propionaldehyde conversion and the yield of the oxidation products in dependence of temperature are illustrated in Fig. 2. The conversion of propionaldehyde and the composition of the reaction product gas varied with increasing reaction temperature (Fig. 2a). The maximum yield of acetic acid (30–35%) was obtained between 180 and 220 °C (Fig. 2b).

The maximum yield of formic acid and propionic acid was found to be about 20% and 14% at 140 °C, respectively. Compared to the oxidation of acetaldehyde the maximum yield of acetic acid was only half as much but the



**Fig. 2.** Conversion of propionaldehyde and yields of  $CO_x$  (a); yields of  $C_1$ – $C_3$  carboxylic acids (b) as a function of reaction temperature in the oxidation of propionaldehyde on catalyst VO<sub>x</sub>-TiO<sub>2</sub> in presence of water vapour.

maximum yield of formic acid was twice as much. Contrary to the oxidation of propionaldehyde on P/VO<sub>x</sub> catalysts [15], the formation of acrolein was negligible (0.5%). At the temperature region of 220–280 °C, small amounts of ethylene were detected. The yield of ethylene at 220 and 280 °C was about 0.1 and 0.6%, respectively. It was observed that the yield of ethylene increased drastically with increasing temperature. At 320 °C the yield of ethylene was about 15%.

Comparison of the product formation from acetaldehyde and propionaldehyde. In order to compare the oxidation behaviour of two aldehydes, the selectivities to the oxidation products were calculated at various temperatures. The variation of selectivities for carboxylic acids and  $CO_x$  from oxidation of acetaldehyde and propionaldehyde with temperature are depicted in Fig. 3.



**Fig. 3.** Dependence of the selectivity to CO and  $CO_2$  (a) and  $C_1-C_3$  carboxylic acids (b) on temperature during the catalytic oxidation of acetaldehyde and propionaldehyde on catalyst  $VO_x$ -TiO<sub>2</sub>. Reactions conditions: see Figs. 1 and 2.

The selectivity for the catalytic oxidation of acetaldehyde and propionaldehyde to the corresponding carboxylic acids at temperatures in the range of 120–180 °C was observed to be about 80% and 20%, respectively. At temperatures above 220 °C the selectivity to acetic acid from acetaldehyde decreased rapidly, whereas the selectivity to  $CO_x$  increased. At 280 °C, the selectivity to acetic acid was only 10%, and the selectivity to  $CO_x$  was about 80–85%.

The main oxidation products during oxidation of propionaldehyde at lower temperature were acetic acid and formic acid. Contrary to the oxidation of acetaldehyde, the maximum selectivity to propionic acid during oxidation of propionaldehyde was only 20–15% between 120-160 °C. Moreover, the selectivity to formic acid and CO<sub>x</sub> in this temperature region is higher during oxidation of propionaldehyde compared to acetaldehyde.

Therefore, acetaldehyde appears to be oxidized to acetic acid more selectively than propionaldehyde to propionic acid. The low selectivity for propionic acid and also the formation of formic acid and  $CO_x$  even at 120 °C suggests a higher lability of propionaldehyde towards the oxidative cleavage. The propionaldehyde is more susceptible to the C–C bond cleavage compared to acetaldehyde due to difference in activity of the C–H bonds of CH<sub>2</sub> or CH<sub>3</sub> group in the both aldehydes. It can be expected that the secondary C–H bond



Fig. 4. The possible reaction pathways for the formation of oxidations products at the catalytic oxidation of acetaldehyde (a) and propionaldehyde (b).

on propional dehyde will be more activated and attacked on the surface of  $VO_x$ catalyst as compared to the primary C–H bond of acetal dehyde

#### 3.2 Kinetic modelling of the reactions pathway

According to the literature [13, 21] the formation of the carboxylic acid from the aldehyde proceeds *via* selective oxidation of the C–H bond of the carbonyl group by active lattice oxygen present on the surface of metal oxides (insertion of lattice oxygen). Total oxidation products, namely  $CO_x$  and formic acid, can be formed directly from the aldehyde by the decomposition and/or oxidative cleavage of intermediate species (formate, acetate, or propionate).

In order to appropriate the correct reaction pathways and the rate of formation of each oxidation product, a modelling of the reaction was carried out. Possible reactions describing the catalytic oxidation of acetaldehyde and propionaldehyde are shown in Fig. 4. The series-parallel reaction network was considered for this modelling. The formation of different products was based on the following assumptions: (a) formic acid, CO and CO<sub>2</sub> can be formed from starting aldehydes and from the carboxylic acids; (b) propionic acid can be formed only from propionaldehyde; (c) acetic acid can be formed from acetaldehyde and also from oxidative cleavage of propionic acid. For the modelling of oxidation process of both acetaldehyde and propionaldehyde, the experimental data for product distribution at different temperatures were used. Figure 4 summarises the possible reaction pathways for the oxidation of acetaldehyde and propionaldehyde.

Seven reaction products are possible for the oxidation of acetaldehyde, namely CO, CO<sub>2</sub>, formic acid, acetic acid, acetaldehyde, O<sub>2</sub> and H<sub>2</sub>O. Nevertheless, modelling reveals that the minimum of four reactions must take place for generation of the above-mentioned reaction products. Similarly to acetaldehyde, for the oxidation of propionaldehyde eight reaction products (CO, CO<sub>2</sub>, formic acid, acetic acid, propionic acid, propionaldehyde, O<sub>2</sub> and H<sub>2</sub>O) can be obtained by five key reactions. The range of element-species matrix is 3 for propionaldehyde oxidation reaction. Hence, the least of 5 keys reactions of independent linear key reactions are necessary for the description of the stoichiometric modelling.

From Fig. 4, a fixed set of reactions was selected to simulate the experimental data at the different temperatures. A one-dimensional pseudo-homogeneous plug-flow reactor model was used to describe the steady state under isothermal conditions. The pseudo-homogeneous mass balance for the key species, in terms of molar concentration, can be stated as a differential equation with an initial condition:

$$\frac{\mathrm{d}c_i}{\mathrm{d}z}=\frac{q_i}{u}\,,$$

where  $c_i$  (at z = 0) =  $c_{io}$  (measured); i = 1, ..., 5; and  $\frac{dc_i}{dz}$  = the change in concentration over the axial coordinate z of the reactor.

The concentration of the linearly dependent compounds was calculated by stoichiometric relation with the numerical procedure of non-linear regression analogue to [22]. A fourth-order Runge–Kutta–Mearson algorithm [23] was adapted for the simultaneous step length integration of all differential equations. For each temperature, partial mass balance equations with respect to the axial coordinate z were solved numerically and combined to calculate the concentration at the end of the catalyst bed. The reaction models were discriminated by the value of the sum-of-squared differences of model and experimental values.

$$\sum_{i=1}^{9} \sum_{j=1}^{3} \left( (c_{ij} - w_{ij})g \right)^2, \tag{1}$$

where  $c_{ij} = \text{concentration } (\text{mol/m}^3)$  of the species *i* at temperature *j*; *g* = weight of the sum-of-squared of all species; and  $w_{ij} = \text{experimental values}$ . The Simplex method of Nedler–Mead [24] was used to minimise the sum-of-squares by variation of the values of the frequency pre-factor and the activation energy.

Nr.	reaction	kinetical equation	$\lg k_o$ i	E (kJ/mol)
1	$CH_3CHO + 0.5O_2 \rightarrow CH_3COOH$	$r_1 = \frac{k_1 c_{\rm AcAl} c_{\rm O_2}}{1 + k_6 c_{\rm CO}}$	28.76	97.0
2	$\rm CH_3CHO + 2.5O_2 \rightarrow 2\rm CO_2 + 2\rm H_2O$	$r_2 = \frac{k_2 c_{\rm AcAl} c_{\rm O_2}}{1 + k_6 c_{\rm CO}}$	26.48	98.7
3	$\rm CH_3 CHO + 1.5O_2 \rightarrow 2HCOOH$	$r_3 = \frac{k_3 c_{\rm AcAl} c_{\rm O_2}}{1 + k_6 c_{\rm CO}}$	24.81	88.6
4	$\rm CH_3COOH + O_2 \rightarrow 2CO + 2H_2O$	$r_4 = k_4 c_{\rm AcOH} c_{\rm O_2}$	27.15	113.0
5	$\rm CH_3COOH + 2O_2 \rightarrow 2CO_2 + 2H_2O$	$r_5 = k_5 c_{\rm AcOH} c_{\rm O_2}$	30.79	133.1
6	Sorption of CO	$k_6 = \frac{K_{\rm CO}^{\rm ads}}{K_{\rm CO}^{\rm des}}$	9.05	0.1

**Table 1.** Optimal frequency factors and activation energy of the best schemes for the oxidation of acetaldehyde.

*Oxidation of Acetaldehyde*. The reaction rates for the formation of acetic acid, formic acid and  $CO_2$  from acetaldehyde are found to be of first order with respect to acetaldehyde and oxygen (Table 1). Similarly, the reaction rate for oxidative cleavage of acetic acid to CO and  $CO_2$  is also found to be of first order, with respect to the concentration of acetic acid and oxygen.

The dependence of the above-mentioned reaction rates on the oxygen concentration suggests that the reoxidation of the  $VO_x/TiO_2$  catalyst by oxygen from the gas phase might be the rate limiting step for the overall oxidation process. The kinetic equations for the formation of C1, C2 acid and CO2 contain term  $(1 + k_6 c_{CO})^{-1}$ , where  $k_6$  is the sorption rate coefficient for CO. This indicates that the rate for oxidation of acetaldehyde in the reactions 1, 2, and 3 (Table 1) is dependent on the sorption behaviour of CO on the catalyst surface. The selective oxidation of acetaldehyde  $(k_1)$  to acetic acid and their direct combustion to  $CO_2$  ( $k_2$ ) has similar activation energy of about 98 kJ/mol. It suggests that these two reactions proceed parallel and concurrently at the catalyst surface. Compared to that, the activation energy for the oxidative cleavage of acetic acid to CO and CO<sub>2</sub> is 113 and 133 kJ/mol, respectively. This indicates that combustion of acetic acid must be favoured at higher temperatures. The variation in the ratio of the reaction constants for the formation of  $CO_2$  from acetaldehyde and acetic acid and for formation of  $CO_2$ and CO from acetic acid in the temperature range of 120-280 °C is summarised in Fig. 5.

It is evident from the plot that, at low temperatures, CO<sub>2</sub> is primarily formed from direct oxidation of acetaldehyde. Further, it is evident with the sharp increase in the value of the  $k_5/k_4$  ratio at higher temperatures that CO<sub>2</sub>



**Fig. 5.** Dependencies of the ratio of the reaction constants for the formation of  $CO_2$  from acetaldehyde and acetic acid ( $k_2/k_5$ ), and for formation of  $CO_2$  and CO from acetic acid ( $k_5/k_4$ ) on the reaction temperature.

Nr.	reaction	kinetical equation	lg k <sub>o</sub> i	E (kJ/mol)
1	$C_2H_5CHO + 2.5O_2 \rightarrow 3HCOOH$	$r_1 = \frac{k_1 c_{\rm PrAl} c_{\rm O_2}}{1 + k_7 c_{\rm PrAl}}$	27.60	88.7
2	$\mathrm{C_2H_5CHO} + 0.5\mathrm{O_2} \rightarrow \mathrm{C_2H_5COOH}$	$r_2 = \frac{k_2 c_{\text{PrAI}} c_{\text{O}_2}}{1 + k_7 c_{\text{PrAI}}}$	24.08	75.1
3	$\mathrm{C_2H_5COOH} + \mathrm{O_2} \rightarrow \mathrm{CH_3COOH} + \mathrm{HCOOH}$	$r_3 = k_3 c_{\rm PrOH} c_{\rm O_2}$	10.59	28.9
4	$\rm HCOOH \rightarrow \rm CO + \rm H_{2}O$	$r_4 = k_4 c_{\mathrm{FA}}$	10.99	36.1
5	$\rm CH_3COOH + 2O_2 \rightarrow 2CO + 2H_2O$	$r_5 = k_5 c_{\rm AcOH} c_{\rm O_2}$	111.0	480
6	$\rm HCOOH + 0.5O_2 \rightarrow \rm CO_2 + \rm H_2O$	$r_6 = k_6 c_{\rm FA} c_{\rm O_2}$	27.76	75.9
7	Sorption of propionaldehyde (PrAl)	$k_7 = \frac{K_{\rm PrAl}^{\rm ads}}{K_{\rm PrAl}^{\rm des}}$	12.21	42.1

**Table 2.** Optimal frequency factors and activation energy of the best schemes for the oxidation of propionaldehyde.

is formed predominantly from the total oxidation of acetic acid under these reaction conditions.

*Oxidation of propionaldehyde.* The overall reaction can be proposed to involve the following six reactions. The reactions and the corresponding kinetical equations are listed in Table 2. This table also summarises the calculated values of the apparent frequency factors and the activation energy for optimal reaction



Fig. 6. Dependencies of ratio of the reaction constants for the formation of propionic acid, acetic acid, and formic acid and for their oxidative cleavage on the reaction temperature.

for oxidation of propionaldehyde. The selective oxidation of propionaldehyde to propionic acid, oxidative cleavage of propionaldehyde to formic acid and total oxidation of formic acid to  $CO_2$  (reactions 1, 2 and 6; see Table 2) proceed with comparable activation energies of about 75–88 kJ/mol. The oxidative cleavage of propionic acid to acetic acid and formic acid (reaction 3, see Table 2) is also found to proceed with even lower activation energy of about 29 kJ/mol.

Thus, the comparable values of activation parameters and frequency factors explain the observed lower selectivity for propionic acid during oxidation of propionaldehyde on the  $VO_x$ -TiO<sub>2</sub> catalyst. At the same time, the oxidative cleavage of acetic acid to  $CO_x$  is limited by the high activation energy of 480 kJ/mol for reaction 5. Therefore, the ratio of acetic acid production to

<i>T</i> (°C)	120	140	160	180	200	220	240	260	280
$\frac{(k_1 + k_2)_{\text{PrAl}}}{(k_1 + k_2 + k_3)_{\text{AcAl}}}$	8.72	6.95	5.69	4.76	4.06	3.52	3.11	2.78	2.50

**Table 3.** Ratio of sum of the reaction constants for the oxidation of acetaldehyde (AcAl) and propionaladehyde (PrAl) on  $VO_x$ -TiO<sub>2</sub> at various temperatures.

its consumption is very high at low temperatures. Hence, promoting its highly selective formation at temperatures lower than 200 °C.

Additional information about reaction behaviour of propionaldehyde can be obtained by analysing the reaction constants for the formation of oxygenates at various temperatures. The comparison of ratio of the reaction constants for the formation of propionic acid  $(k_2)$ , acetic acid  $(k_3)$ , and formic acid  $(k_1, k_3)$ with respect to that for the oxidative cleavage of propionic acid  $(k_3)$ , at different temperatures is depicted in Fig. 6.

It can be seen from Fig. 6a that at 120 °C the constant for the formation of propionic acid  $(k_2)$  is twice as high as that for the formation of formic acid  $(k_1)$ . With the temperature increase from 120 °C to 280 °C the ratio  $k_2/k_1$  decreased and the ratio  $k_2/k_3$  increased. This explains the improved selectivity observed for the formation of formic acid at higher temperatures. In Fig. 6b the curve representing the ratio between reaction rates for formation and consumption of formic acid

$$\frac{k_1+k_3}{k_4+k_6}\,,$$

rises sharply with the increase in temperature beyond 200 °C. This indicates that the formation of formic acid is favoured at high temperatures. Formic acid can be formed in two reaction ways: (i) directly from propionaldehyde  $(k_1)$  and (ii) *via* the oxidative cleavage of propionic acid  $(k_3)$ . Since the ratio of reaction rates for formation of formic acid *via* oxidative cleavage of propionic acid to its overall consumption

$$\frac{k_3}{k_4 + k_6}$$

decreases with temperature, it can be inferred that the selective formation of formic acid from the direct oxidation of propionaldehyde is the favoured step at temperatures above 200 °C.

Oxidation activity of acetaldehyde and propionaldehyde. In order to compare the activity of propionaldehyde and acetaldehyde for their oxidation on the  $VO_x$ -TiO<sub>2</sub> catalyst, the ratio of the reaction constants for their different reactions (as mentioned in Tables 1 and 2) was evaluated in detail for the temperature range of 120-280 °C. These data are summarised in Table 3. The ratio of the reaction constants decreased with increasing temperature indicating higher oxidation activity of propionaldehyde for the given reaction conditions, especially at lower temperatures. The activation energies for the direct oxidation of acetaldhyde (reactions 1, 2, and 3) given in Table 1 are about 10 kJ/mol higher compared to the activation energies for the direct oxidation of propionaldehyde (reactions 1 and 2) given in Table 2. From these results it can be concluded that the oxidation of acetaldehyde is favored at higher temperatures.

### 4. Conclusion

The oxidation of acetaldehyde and propionaldehyde follows two main routes: (1) selective oxidation to respective carboxylic acids, and (2) oxidative cleavage to lower carboxylic acids. The first route was favoured for both aldehydes under low temperature conditions, whereas the second route was favoured for temperatures above 200 °C. Though the routes followed remained the same, the following differences were observed in the oxidations pathways of propionaldehyde and acetaldehyde:

i) While the formation of  $CO_2$  from oxidation of acetaldehyde was found to proceed mainly through the total oxidation of acetaldehyde, the main reaction route for the formation of  $CO_2$  from propionaldehyde was through the oxidative cleavage of  $C_1$ ,  $C_2$  and  $C_3$  carboxylic acids.

ii) In the case of the oxidation of propionaldehyde the rate for the consumption of aldehyde was found to depend on terms related to concentration of aldehyde and oxygen and on term describing sorption behaviour of propionaldehyde. On the other hand, for oxidation of acetaldehyde the reaction rate was found to depend on terms related to the concentration of aldehyde and oxygen and the sorption's term for carbon monoxide.

The kinetic model confirmed the consecutive formation of  $C_1-C_3$  carboxylic acids. CO and CO<sub>2</sub> may be produced directly *via* decomposition of aldehydes on the catalyst surface and *via* total oxidation of carboxylic acids. The low selectivity for the formation of propionic acid from propionaldehyde can be attributed to the low stability of propionic acid and high activity of propionaldehyde towards the oxidative cleavage. These results are also relevant for explaining the low selectivity for carboxylic compounds during the ODH of  $C_2-C_4$  hydrocarbons at temperatures above 300 °C.

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