$(VO)_2P_2O_7$ catalysed partial oxidation of propane in dense CO_2

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The aim of this study was to elucidate the catalytic partial oxidation of propane to oxygenates on vanadyl pyrophosphate ($(VO)_2P_2O_7$) in dense carbon dioxide acting as a solvent. The reaction was carried out in continuous flow experiments at 673 K at a molar ratio of CO_2 : synthetic air : propane of 86 : 13 : 1, a residence time of 19 s and sub- to supercritical pressures ranging from 2.4 to 9.7 MPa. The catalytic tests revealed the formation of acrylic and acetic acid besides total oxidation products. The selectivity to acetic acid increased with rising pressure, whereas that of acrylic acid decreased. These results may be attributed to a diverging adsorption of both the oxygenates with pressure, which was investigated by supercritical fluid chromatography. Additionally, critical data of both the reaction feed and the product mixture were determined in a high-pressure optical cell by the opalescence method.

KEY WORDS: dense carbon dioxide; vanadyl pyrophosphate; propane partial oxidation; oxygenates; critical data; supercritical fluid chromatography; opalescence method

1. Introduction

The heterogeneously catalysed direct oxidation of propane to oxygenates (*e.g.*, acrolein and/or acrylic acid) is one of the demanding and challenging objectives in present oxidation catalysis research [1–7]. In general, this reaction is suffering from low yields at gas-phase conditions: either the formed intermediates are subject to consecutive total oxidation owing to their strong adsorption at the catalytic sites or propane is directly converted in a non-selective reaction to the undesired total oxidation products parallel to the selective pathway. However, recent patents report acrylic acid yields up to *ca.* 50 mol% [8,9]. Furthermore, to suppress total oxidation, numerous efforts have been reported in the literature [1,2], for example by using two reaction zones in series containing two different catalysts for dehydrogenation and subsequent oxygen insertion [3]. New innovative concepts may also help to solve this problem, *e.g.*, by using membrane reactors to remove the products very quickly from the reaction mixture or to limit oxygen concentration at the catalytic sites [*e.g.*, 10,11].

Another promising mode seems to be given by the application of supercritical fluids (SCF) as an alternative reaction medium due to their unusual physico-chemical properties [*e.g.*, 12–15] such as (i) "liquid-like" density with high solubility for organic compounds; (ii) "gas-like" low dynamic viscosity and high diffusivity; (iii) high compressibility and thermal conductivity; and (iv) complete miscibility with permanent gases. Especially, supercritical carbon dioxide ($scCO_2$; $p_c = 7.37$ MPa, $T_c = 304$ K) is an environmentally benign fluid, non-toxic, non-flammable and non-corrosive. Thereby, SCF are supposed to overcome the limitations of heterogeneously catalysed gas-phase reactions in several respects. Reaction intermediates and coke-precursors may desorb faster from the solid catalyst surface due to their higher solubility in a dense solvent compared to the gas-phase [16]. Damages of the catalyst by "hot-spots" in exothermic reactions are reduced as a consequence of enhanced heat transfer [13]. The mass transport of both reactants and products between the catalyst and the surrounding reaction medium is improved [17]. Additionally, rate constants and selectivities of parallel reactions may show a different dependence on pressure owing to their activation volumes [13,18]. Furthermore, the local density and composition of the supercritical fluid can drastically be changed by a clustering of solvent molecules around those of the solute [19,20].

Compared to the well-known extraction [21] with $scCO_2$, its application as an alternative reaction medium in catalysis has gained significance only during the last few years [*e.g.*, 12–14]. In recent literature the heterogeneously catalysed alkylation of naphthalene [22] and the hydrogenation of various organic compounds [23] were reported. However, only rare literature exists on the partial oxidation of hydrocarbons in $scCO_2$, *e.g.*, oxidation of toluene [24] as well as benzyl alcohol [25] to benzaldehyde or propylene dihydroxylation [26] to propylene glycol. In our previous work [27] on the partial oxidation of propane in dense CO_2, precipitated CoO_x on SiO_2 was found to be most active and selective in batch experiments ($p = 8$–10 MPa, $T = 518$–573 K) compared to other supported metal (oxide) catalysts known for

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oxidation reactions in SCF [24–26]. The main products were acetic acid, methanol, acetone and acetaldehyde besides the formation of propylene. Performing the reaction batchwise under gaseous as well as supercritical conditions ($t = 2\,h$, $T = 553\,K$), a significant rise in the cumulative oxygenate selectivity (S) could be observed at elevated pressures ($p = 2.5\,MPa$: $S < 1\%$; $p = 11.3\,MPa$: $S = 44\%$) [28,29]. Analogous results ($p = 2.6\,MPa$: $S < 1\%$; $p = 11.1\,MPa$: $S = 40\%$) were obtained in continuous flow experiments under similar conditions ($\tau = 2\,s$, $T = 623\,K$) [30]. It was supposed that the CoO_x-catalysed reaction proceeds *via* a radical mechanism initiated on the solid surface. The application of redox catalysts may lead to a change in product distribution towards desired acrolein or acrylic acid due to other mechanistic pathways. However, such redox catalysts, *e.g.*, $(VO)_2P_2O_7$, had not been tested under supercritical conditions earlier.

Vanadium phosphates are well known as catalysts for selective O- and N-insertion reactions of aliphatics and methyl aromatics [*e.g.*, 31–33]. This class of catalysts has been intensively investigated in the last decade because of its immense significance in the partial oxidation of *n*-butane to maleic anhydride [*e.g.*, 31,34]. Vanadyl pyrophosphate $(VO)_2P_2O_7$ (VPP) is the outstanding specimen of these materials [*e.g.*, 31,34]. Some efforts have also been reported to use VPP catalysts in partial oxidation of other alkanes: *e.g.*, Quandt [35] reported on the application of VPP catalysts for the partial oxidation of propane, leading to yields (Y) of acrylic acid of *ca.* 9 mol% and of acetic acid of *ca.* 5 mol% at a propane conversion (X) of 48 mol%. Similar results were found by Ai earlier (*e.g.*, Y (acrylic acid) = 10.5 mol%, X ~ 42 mol% [5] or Y (acrylic acid) = 7 mol%, Y (acetic acid) = 7 mol%, X ~ 50 mol% [6]).

It was the aim of the present work to elucidate fundamental aspects of supercritical engineering related to heterogeneous catalysis. For that, the partial oxidation of propane was studied in continuous flow experiments under a dense CO_2 atmosphere using VPP as catalyst. Since information on the phase behaviour is essential for performing reactions in pressurised fluids, critical points of the ternary reaction feed and those of the multi-component product mixture were additionally determined by the opalescence method. Moreover, the effect of sorption behaviour of oxygenates in dense CO_2 on the catalytic results was followed by supercritical fluid chromatography (SFC) experiments.

2. Experimental

2.1. Catalyst preparation and characterisation

VPP was obtained by the established dehydration procedure of a $VOHPO_4{\cdot}0.5\,H_2O$ precursor, synthesised by the aqueous route [*e.g.*, 36]. 73 g V_2O_5 (0.4 mole) were added to a hot mixture (353 K) of 102 g H_3PO_4 (85%, 1.04 mole) and 76 g $(COOH)_2$ (0.84 mol) in 160 ml distilled H_2O under vigorous stirring for 18 h. The solution was cooled, filtered and the light-blue residue was dried for 14 h at 423 K. Precursor treatment under inert gas (6 h at 873 K) led to the VPP catalyst. Before the catalytic tests, the synthesised VPP was pressed to tablets (10 MPa, 0.5 min), crushed and classified by sieving into a fraction of 1.0–1.25 mm.

The composition of fresh and used catalyst samples was determined by ICP emission spectroscopy (Optima 300 XL, Perkin Elmer). BET surface areas of the solids were obtained by N_2-adsorption (Gemini III, Micromeritics). To analyse the morphology of the VPP samples, scanning electron microscopy (SEM; 1000B, Amray) was used. Furthermore, the crystallinity of fresh and used samples was characterised by recording X-ray diffraction patterns by transmission powder diffractometry (XRD; STADIP, Stoe). For the detection of coke or carbonate species formed, X-ray photoelectron spectroscopy (XPS; ESCALAB 220 iXL, Fisons Instruments) and electron spin resonance measurements (ESR; ELEXSYS 500-10/12, Bruker) were applied. Additionally, the surface composition of fresh and spent probes was analysed by XPS.

2.2. Opalescence measurements

Phase equilibrium measurements were conducted in a 35 ml high-pressure optical cell with sapphire windows (PH 251–500, Sitec), which has been described previously [30,37]. The critical curves of the ternary CO_2–synthetic air–propane reaction feed (x(synthetic air) = 21–25 mol%) as well as of a characteristic multi-component product mixture (additionally containing ~0.1 mol% of acetic and acrylic acid each) were determined by the opalescence method [30,37,38]. The concentrations of acetic and acrylic acid were derived from the dosed volume of each. The mole fraction of CO_2, N_2, O_2 and propane was determined via off line-GC using a TCD and a combination of two packed columns (Molecular sieve 13X, 3 m × 0.75 mm and Porapak N, 1 m × 0.75 mm). A maximum GC calibration error of ±4% was observed, whereas the dosing error of small amounts of the oxygenates reached *ca.* ±5%. The standard deviation of the measurements was less than 1%. CO_2 (purity: 99.95 vol%), synthetic air (79.5 vol% N_2, 20.5 vol% O_2 (purity: 99.999 vol%)) and propane (purity: 98 vol%) were supplied by Messer; acetic acid was delivered by Merck (purity: pro analysis) and acrylic acid by Fluka (purity: >99.0%).

2.3. Catalytic testing

The synthesised catalyst was tested for the partial oxidation of propane to oxygenates in dense CO_2 using a commercial 5 ml fixed-bed continuous flow-reactor

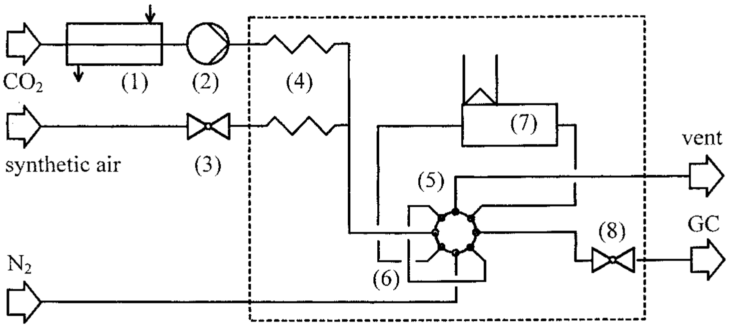


Figure 1. Experimental set-up for catalytic testing: 1, cryostat; 2, HPLC pump; 3, mass flow controller; 4, preheater and mixer; 5, multi-port valve; 6, bypass; 7, reactor (containing the fixed bed of $(VO)_2P_2O_7$ catalyst); 8, manually driven back pressure regulator, reactor oven module --- ($T_{max} = 553$ K).

(BTRS Junior, Autoclave Engineers Inc.). The high-pressure apparatus is shown in figure 1 and has been described elsewhere in more detail [30]. An on-line capillary GC (Alumina, 50 m × 0.53 mm and DB-FFAP, 50 m × 0.32 mm) equipped with FID was used for the analysis of hydrocarbons and partial oxygenates, whereas O_2, N_2 and CO were detected by TCD (Molecular sieve 5A, 30 m × 0.32 mm). A GC calibration error of ±2% was observed, whereas the determination of GC factors led to an accuracy of *ca.* ±7%. CO_2 formed as total oxidation product could not be determined due to its use as excess solvent and, therefore, neither carbon nor oxygen balances could be derived. The reactants (premixed 1 mol% of propane in liquid CO_2; synthetic air: 79.5 vol% N_2, 20.5 vol% O_2 (purity: 99.999 vol%)) as well as N_2 (purity: 99.996 vol%) were delivered by Messer.

Conversion of propane is calculated as the ratio of reacted moles related to the basic concentration in the feed. Selectivities are defined as moles of formed product divided by moles of reacted compound, multiplied by the carbon number of product and divided by that of the reactant, to get stoichiometric values. Yield of reaction products is calculated as the product of conversion and selectivity. Residence time τ is defined as the ratio of catalyst volume and flow under reaction conditions.

2.4. Supercritical fluid chromatography

The effect of sorption behaviour of oxygenates on VPP catalyst on the catalytic results in dense CO_2 was followed by several SFC experiments [39,40] using a modified GC (figure 2). Liquid CO_2 was directly dosed from a gas cylinder (at $p < p_c$) *via* a cryostat (1) and a HPLC pump (2; at $p > p_c$). The dense fluid was continuously fed through a tube (3; $L = 35$ mm, i.d. = 2 mm) that contained the catalyst ($d = 0.5$–1.0 mm, $m = 16$ mg). Finally, CO_2 was expanded to ambient pressure *via* a restrictor (4; Macherey and Nagel) in the FID. A CO_2 side stream was depressurised and saturated with acetic or acrylic acid (5); then it was continuously run through the injection loop (6; T (injection) = 373–393 K, V (injection) = 140 μl). By switching the injection valves, acrylic or acetic acid were pulsed into the CO_2 stream. Elution times for the acids through both the catalyst bed and the empty tube for comparison were determined at different CO_2 pressures. The standard deviation of the elution times was less than *ca.* ±5%. CO_2 was delivered by Messer (purity: 99.95 vol%); acetic acid was supported by Merck (purity: pro analysis) and acrylic acid by Fluka (purity: >99.0%).

3. Results and discussion

3.1. Determination of critical lines

Before the catalytic testing, the phase behaviour of the reaction system had to be investigated in more detail. Figures 3 and 4 compare the critical curves of a binary CO_2–propane system [38] with that of the ternary reaction feed (CO_2–synthetic air–propane) and the multi-component product mixture (additionally containing acetic and acrylic acid). These investigations

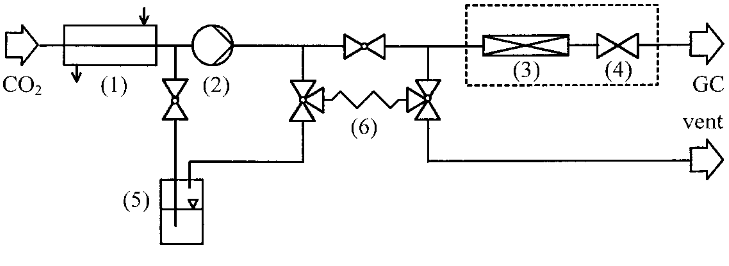


Figure 2. Experimental set-up for supercritical fluid chromatography measurements: 1, cryostat; 2, HPLC pump; 3, fixed bed of $(VO)_2P_2O_7$/empty tube; 4, restrictor; 5, oxygenate saturator; 6, injection loop, GC oven module --- ($T = 473$ K).

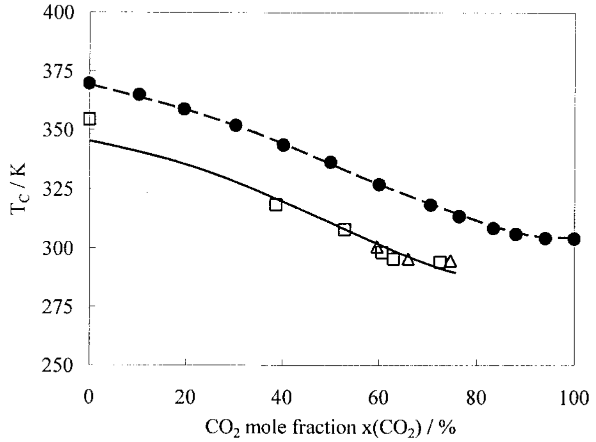


Figure 3. Dependence of critical temperature (T_c) on the mole fraction of CO_2 ($x(CO_2)$) for binary, ternary and multi-component mixtures, determined by the opalescence method: (●) CO_2–propane [38], (□) CO_2–synthetic air (21–25 mol%)-propane [30], (△) CO_2–synthetic air (21–23 mol%)–propane–acetic acid (0.1 mol%)–acrylic acid (0.1 mol%).

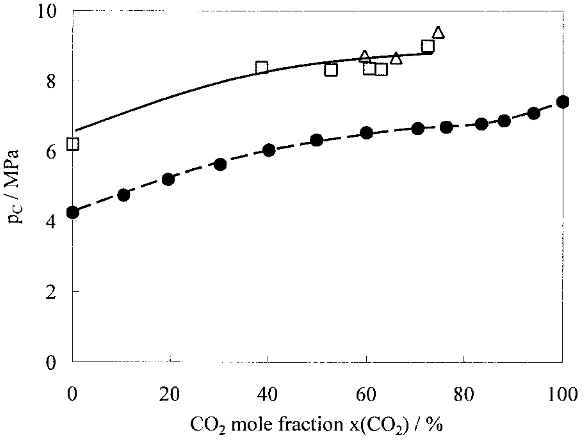


Figure 4. Dependence of critical pressure (p_c) on the mole fraction of CO_2 ($x(CO_2)$) for binary, ternary and multi-component mixtures, determined by the opalescence method: (●) CO_2–propane [38], (□) CO_2–synthetic air (21–25 mol%)–propane [30], (△) CO_2–synthetic air (21–23 mol%)–propane–acetic acid (0.1 mol%)–acrylic acid (0.1 mol%).

gave significance to the following: (i) adding 21–25 mol% synthetic air to the CO_2–propane mixture, critical temperatures shifted to lower values ($\Delta T > -12\,K$), whereas critical pressures markedly increased ($\Delta p > 2\,MPa$). Similar effects have already been reported in the literature on a CO_2–N_2–isopropyl benzene system [41]. (ii) Due to their low concentration, the influence of acetic and acrylic acid on critical data seems to be negligible compared to that of air. The observed minor deviations between critical lines of the ternary and the multi-component system (see figures 3 and 4) were only attributed to slight differences in concentrations of the synthetic air proportions of each. (iii) Despite the admixture of three additional compounds to the binary CO_2–propane mixture, its critical behaviour could still be classified as analogue type I according to the nomenclature of van Konynenburg and Scott [42]. Therefore, phase separations, coexisting liquid–liquid phases or azeotrope formation should not occur during propane oxidation at any applied pressure. Thus, the catalytic reaction is supposed to run under homogeneous gaseous ($p < 8.9\,MPa$) or under homogeneous supercritical conditions ($p > 8.9\,MPa$) using a feed consisting approximately of $x(CO_2) = 86$ mol%, $x(\text{air}) = 13$ mol% and $x(\text{propane}) = 1$ mol%.

3.2. Optimisation of reaction conditions

Optimum reaction conditions were determined for the partial oxidation of propane on VPP at a constant pressure of 8.0 MPa (table 1), before studying potential differences between sub- (*i.e.*, gas-phase) and supercritical reaction processing. Varying the temperature, at 673 K a maximum yield of oxygenates was found (Y (acetic acid) = 2.0 mol%, Y (acrylic acid) = 0.2 mol%, X = *ca.* 80 mol%, besides formation of methanol, acetone, acrolein and acetaldehyde). According to the reactivity of propane and its partial oxidation products (acrolein > propylene > acetic acid > acrylic acid > propane [5]), higher reaction temperatures resulted in enhanced consecutive total oxidation of oxygenates. As known for VPP [35] and for other V_2O_5-P_2O_5-based catalysts [5,6] under gas-phase conditions, higher concentrations of oxygen favoured propane conversion and the formation of acetic as well as of acrylic acid. A similar influence was observed in dense CO_2, when the yield of oxygenates could be markedly improved on raising the concentration of air from 4 mol% to 15 mol% (Y (acetic acid) = 0.3 mol%, Y (acrylic acid) = 0 mol%, X = 50 mol% to Y (acetic acid) = 2.6 mol%, Y (acrylic acid) = 0.4 mol%, X = 73 mol%). However,

Table 1
Variation of reaction temperature (T), molar ratio of CO_2 : synthetic air : propane = $99 - x(\text{air}) : x(\text{air}) : 1$ and residence time (τ) at constant pressure (p) for optimisation of reaction conditions using $(VO)_2P_2O_7$ as catalyst

Variation of	T (K)	x (air) (mol%)	τ (s)	p (MPa)
Temperature	573–723	14	2	8.0
Molar ratio of air	673	4–15	2	8.0
Residence time	673	14	2–33	8.0

the concentration of air for the oxidation of propane in dense CO_2 was limited to a maximum value of 15 mol% for safety reasons [43,44]. The variation of residence times led to a maximum yield of oxygenates at $\tau = 19\,s$ (Y (acetic acid) = 2.2 mol%, Y (acrylic acid) = 1.0 mol%, X = 73 mol%). Thus, optimum reaction conditions for the partial oxidation of propane in dense CO_2 were found to be $T = 673\,K$, feed proportion of synthetic air = *ca.* 15 mol% and a residence time of $\tau = 19\,s$.

Compared to previously reported yields [5,6,35] of acrylic acid under gas-phase conditions on vanadium phosphate catalysts (*e.g.*, Y (acrylic acid) = 10.5 mol%, X = 42 mol% [5]), the results in dense CO_2 have to be seen on the following background: (i) in the gas-phase, the yield of acrylic acid can be significantly increased by higher oxygen concentrations. Thereby, acrylic acid yield was more than doubled from *ca.* 3 mol% (X = 6 mol%) up to *ca.* 7.5 mol% (X = 26 mol%) by enhancing the molar oxygen concentration in the feed from 6 mol% to 82 mol% [5]. However, in this study the oxygen content was limited to 3.9 mol% (= 15 mol% air) as mentioned above. (ii) The addition of water vapour has also been reported to favour markedly the formation of acrylic acid (from *ca.* 5 mol% up to 9 mol% by adding 36 vol% water at X = *ca.* 28 mol% [5]), as it seems to play a crucial role in removing quickly the formed acrylic acid from the surface [6]. However, the dosing of water as additional compound to the dense CO_2–air–propane feed could not be realised due to phase separation (water: $T_c = 647\,K$, $P_c = 22.1\,MPa$).

3.3. *Influence of compressed CO_2-phase on the propane oxidation*

Figure 5 demonstrates the catalytic performance of VPP in dependence on reaction pressure. The propane conversion continuously increased with pressure (X (2.4 MPa) = 71 mol%; X (9.7 MPa) = 82 mol%), whereas the selectivities of both of the formed intermediates showed a diverging behaviour. The selectivity of acetic acid was markedly favoured at higher pressures (S (2.4 MPa) = 1%; S (9.7 MPa) = *ca.* 3%). In contrast, that of acrylic acid continuously declined with increasing pressure (S (2.4 MPa) = 2.5%; S (9.7 MPa) < 1%).

The characterisation of fresh and used VPP samples revealed significant differences in their morphology: Whereas the elemental composition in the bulk and on the surface remained nearly unchanged during reaction according to ICP and XPS analysis, the BET surface of a catalyst tested under supercritical conditions ($4.0\,m^2/g$) has been diminished by 38% compared to the fresh probe ($6.4\,m^2/g$). Concurrently, SEM images revealed a favoured growing of well-defined crystalline particles of the catalyst with increasing pressure (figure 6). The XRD patterns of fresh and spent samples depicted crystalline $(VO)_2P_2O_7$ specimens as shown in figure 7. However, slight differences could be observed at $2\theta = 22.9$ (040) and $2\theta = 47.03$ (020) pointing to changed orientation to the "010" direction that correlates to the formation of the more plate-like habit as observed by SEM. The deposition of coke or carbonaceous compounds on the catalyst could be neglected under gas-phase as well as supercritical conditions. Signals of C-radicals, as an indication of coke deposits on the surface, were not observed by ESR measurements for any of the spent catalysts.

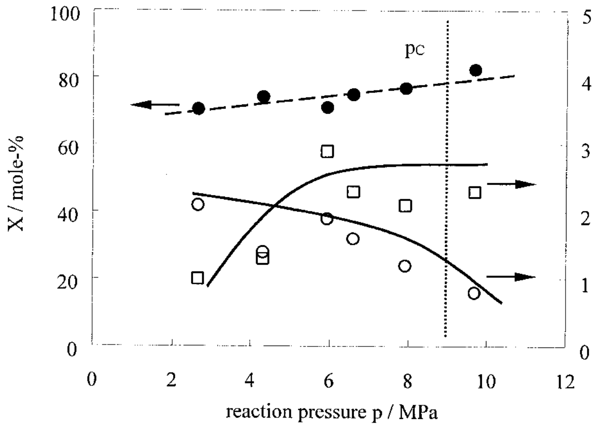
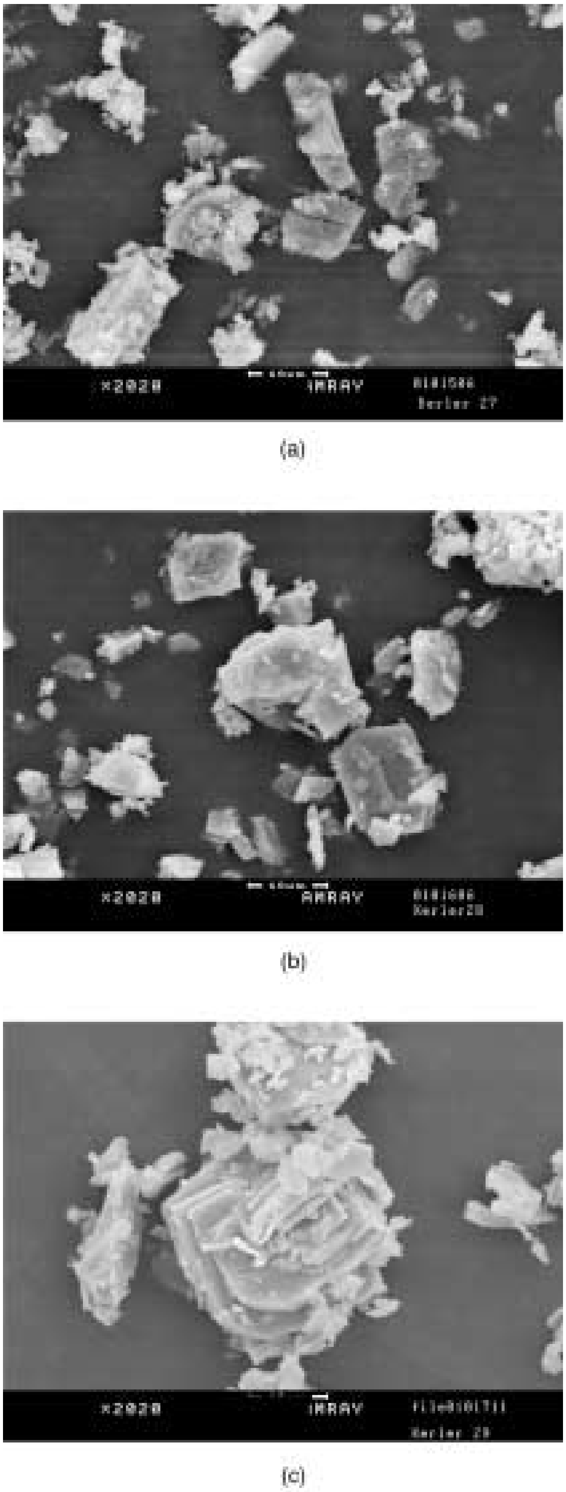


Figure 5. Dependence of propane conversion (X; ●), selectivity of acetic acid (S; □) as well as of acrylic acid (S; ○) on reaction pressure (*p*) using a $(VO)_2P_2O_7$ catalyst ($T = 673\,K$, CO_2 : synthetic air : propane molar ratio = 86 : 13 : 1, $\tau = 19\,s$).

Figure 8 depicts the results of the SFC measurements, *i.e.*, the changes in the normalised elution times of acrylic acid and acetic acid on VPP in dense CO_2 at conditions comparable to that of propane oxidation. For both the oxygenates, elution times rose with increasing pressure compared to subcritical conditions. However, acrylic acid seemed to be more strongly adsorbed on the catalyst than acetic acid under supercritical conditions (acrylic acid: $t_R(11.0\,MPa)/t_R(2.5\,MPa) = 1.75$, acetic acid: $t_R(11.0\,MPa)/t_R(2.5\,MPa) = 1.54$).

The conversion behaviour of the partial oxidation of propane (see figure 5) may be caused by an increase in the reaction rate due to a higher partial pressure of propane at constant feed composition. Similar results have also been found in dense reaction mixtures for the heterogeneously catalysed alkylation of naphthalene [22] as well as in our previous investigations on the partial oxidation of propane on silica-supported CoO_x catalysts [30]. The diverging dependence of acetic and acrylic acid selectivity on pressure may be discussed as follows: According to the results of opalescence measurements (see figures 3 and 4) thermodynamic effects (*e.g.*, the existence of phase separations or formation of azeotropes during the reaction) can be excluded. Moreover, common features of SCF, *e.g.*, clustering effects or the influence of activation volumes on parallel reactions [18–20], are strongly related to the proximity of the critical point (*i.e.*, to a reduced temperature


(a)

(b)

(c)

Figure 6. SEM photographs of $(VO)_2P_2O_7$: (a) fresh probe; (b) used in gas-phase ($p = 2.4$ MPa); and (c) in supercritical propane oxidation ($p = 9.7$ MPa).

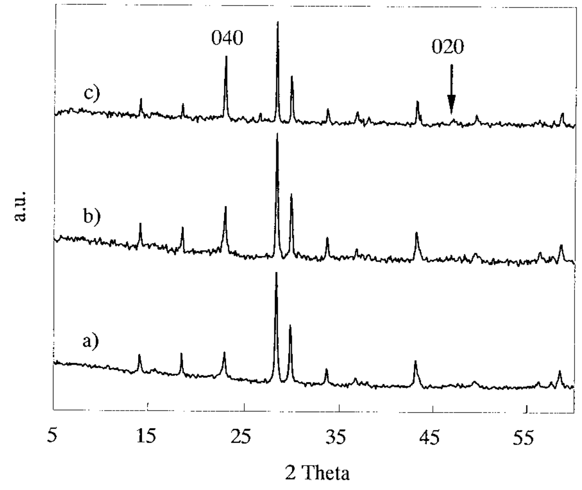


Figure 7. XRD patterns of $(VO)_2P_2O_7$: (a) fresh probe; (b) used in gas-phase ($p = 2.4$ MPa) and (c) in supercritical propane oxidation ($p = 9.7$ MPa).

$T_R = T$ (reaction)$/T_c \sim 1$) [22]. However, the partial oxidation of propane was performed at a reaction temperature of 673 K ($T_R = 2.2$). Thus, these characteristics of supercritical reaction engineering should also not be taken into account for the observed behaviour of oxygenate selectivity with pressure. A more reasonable explanation for the catalytic results may be seen in the different sorption of acetic and acrylic acid on the catalyst surface. The SFC measurements (see figure 8) generally indicate a stronger oxygenate adsorption with higher pressure, compensating the enhanced solvent power of supercritical CO_2. However, this effect is more pronounced for acrylic acid than for acetic acid. As a consequence, the first is supposed to be oxidised more readily than the latter resulting in lower selectivity in the catalytic run. Furthermore, due to catalyst characterisation (see figures 6 and 7), it seems also very likely that the reaction pressure has a significant impact on its structural properties, which may additionally attribute to the diverging pressure dependence of the selectivity of acetic and acrylic acid.

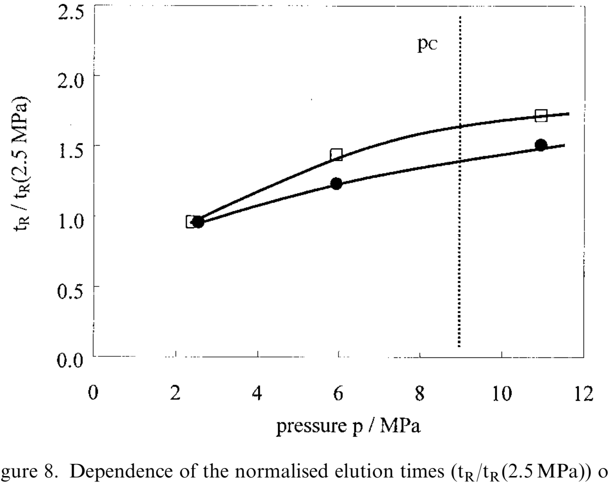


Figure 8. Dependence of the normalised elution times (t_R/t_R(2.5 MPa)) on the pressure (p): (●) acetic acid, (☐) acrylic acid (m($(VO)_2P_2O_7$) = 16 mg, T (oven) = 473 K, T (injection) = 373–393, V (injection) = 140 μl).

4. Conclusions

The partial oxidation of propane was studied in dense CO_2 using $(VO)_2P_2O_7$ as catalyst. A maximum selectivity of *ca.* 3% ($p = 9.7$ MPa) and 2.5% ($p = 2.4$ MPa) was reached for acetic and acrylic acid, respectively, at propane conversion of *ca.* 70–80%. It seems likely that the insufficient selectivities were mainly caused by the limited maximum concentrations of both oxygen and water vapour in the feed. The formation of acetic acid was favoured with increasing reaction pressure, whereas that of acrylic acid continuously decreased. According to the results obtained by supercritical fluid chromatography, acrylic acid remained more strongly adsorbed on the catalyst surface than acetic acid at higher pressures. Thereby, acrylic acid may more readily undergo total oxidation processes, resulting in decreased selectivities at supercritical conditions in contrast to that of acetic acid. Moreover, alterations in catalyst morphology may also contribute to the catalytic results.

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