ELSEVIER

Catalysis Today 61 (2000) 9–17

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Partial oxidation of alkanes to oxygenates in supercritical carbon dioxide

B. Kerler, A. Martin*

Institut für Angewandte Chemie Berlin-Adlershof e.V., Richard-Willstätter-Str. 12, D-12489 Berlin, Germany

Abstract

The catalytic partial oxidation of propane in supercritical carbon dioxide has been investigated in a stirred batch reactor. Various metals (oxides) have been used as supported catalysts with respect to their activity and selectivity for the formation of oxygenates. The reactions run with a 1:2.3–2.9:68–108 molar ratio of propane:synthetic air:CO_2 at 453–573 K and 80–100 bar. Using a precipitated 2.4 wt.% Co_3O_4–SiO_2 catalyst at 573 K, a total oxygenate (i.e. acetic acid, acetone, acetaldehyde, methanol) selectivity of 59% and a propene selectivity of 21% were obtained at a propane conversion of 12 mol%. The same catalyst has been used to investigate the influence of the supercritical conditions and initial feed composition on the reaction, varying the density of CO_2 and the concentration of synthetic air, respectively. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Supercritical carbon dioxide; Partial oxidation; Propane; Oxygenates; Cobalt oxides; Heterogeneous catalyst

1. Introduction

Supercritical fluids (SCFs) have already been known for more than 150 years. But only in the last three decades this field was under more extensive study [1–3] and gained importance for some industrial applications besides expensive equipment. In general, substances and mixtures existing above their critical pressure (p_c) and temperature (T_c) are called supercritical fluids [4]. The critical data of some pure technically relevant compounds are listed in Table 1 [5]. It emerges that, especially supercritical CO_2 ($scCO_2$) surpasses other fluids in handling, because it provides 'benign' critical conditions (p_c=73.75 bar, T_c=304.05 K, ρ_c=0.468 g cm^{-3}); moreover, it is non-toxic, non-corrosive, non-flammable and available; a rather harmful effect may be the lack of a tuneable solvent polarity, e.g. in comparison to scH_2O.

A schematic pressure–temperature diagram including gaseous, liquid, solid, and supercritical state is shown for a pure compound in Fig. 1. In the subcritical region liquid and gaseous state are separated by the vapour–pressure curve, which ends at the critical point. Crossing this line by pressure increase at a given temperature, a phase transition occurs discretely altering the fluid properties (e.g. density) from gaseous to liquid. In contrast to that, above the critical point the phase boundary disappears and a homogeneous supercritical fluid phase exists. Its properties continuously change from 'gas-like' to 'liquid-like' as an extremely sensitive function of pressure and temperature with the highest slope close to the critical point. Thus, in this area SCFs bridge the gap between gases and liquids and combine the advantageous properties of both (Table 2) [6–8]. Their diffusivities and dynamic viscosities rather correspond with those of gases, whereas

---

* Corresponding author. Tel.: +49-30-6392-4306; fax: +49-30-6392-4350.
E-mail address: a.martin@aca-berlin.de (A. Martin).

PII: S0920-5861(00)00353-9

Table 1
Critical data of selected substances

	T_c (K)	p_c (bar)	ρ_c (g cm^{-3})
Ammonia	405.45	113.50	0.235
Carbon dioxide	304.05	73.75	0.468
Methanol	512.55	80.92	0.272
Sulphur hexafluoride	318.65	37.70	0.735
Water	647.05	220.60	0.322

Table 2
Typical properties of gases, SCFs and liquids

	Gas	SCF	Liquid
Density (g cm^{-3})	10^{-3}	10^{-1}	1
Dynamic viscosity (Pa s)	10^{-5}	10^{-4}–10^{-5}	10^{-3}
Kinematic viscosity (m^2 s^{-1})	10^{-5}	10^{-6}–10^{-7}	10^{-6}
Diffusion coefficient (cm^2 s^{-1})	10^{-1}	10^{-3}	10^{-5}
Thermal conductivity (W m^{-1} K^{-1})	10^{-2}	10^{-1}–10^{-2}	10^{-1}

densities and thermal conductivities are closer to liquids.

Considering this, the application of SCFs offers several promising opportunities to influence heterogeneously catalysed reactions: (i) As a consequence of the significant density change in the near-critical region, SCFs show an exponentially enhanced solubility for low-volatile compounds compared to the gaseous state [9]. Therefore, running gas phase reactions in the supercritical region result in easier desorption of intermediates/products or coke precursors from the catalyst surface, significantly improving catalyst lifetime and activity [10]. (ii) The miscibility of SCFs with ‘permanent’ gases like N_2 is nearly unlimited [11]. (iii) Furthermore, SCFs ensure catalyst stability by their high thermal conductivities [12]. Owing to an increased heat transfer in comparison with gases, catalysts are prevented from forming ‘hotspots’ and from possible damages in highly exothermic gas phase reactions. (iv) The high pressures, needed for the supercritical state, often have a different influence on the specific rate constants of parallel reactions due to their activation volumes [13]. So, the product selectivities and distribution in a reaction network can often be tuned in the desired direction by small changes in pressure [14]. (v) The high densities and diffusivities of SCFs entail a facilitated mass transfer between catalyst and fluid, which becomes apparent by larger Sherwood-numbers (as dimensionless mass-transfer coefficient) compared to those in the gas phase [8]. For that reason, mass transport controlled reactions should be accelerated under supercritical conditions.

There is not much literature on heterogeneously catalysed partial oxidations of hydrocarbons at supercritical conditions. The toluene partial oxidation on a CoO–Al_2O_3 catalyst under $scCO_2$ at 293–493 K was reported by Dooley and Knopf [15], whereas Zhou et al. [16] suggested Pd–Al_2O_3 at temperatures of

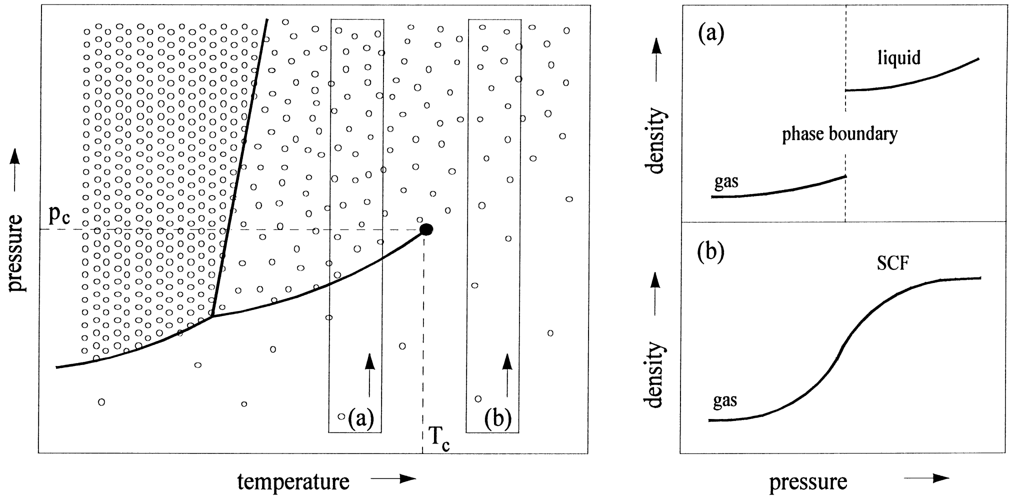

Fig. 1. Pressure–temperature diagram of a pure compound and density–pressure plots at subcritical (a) and supercritical state (b).

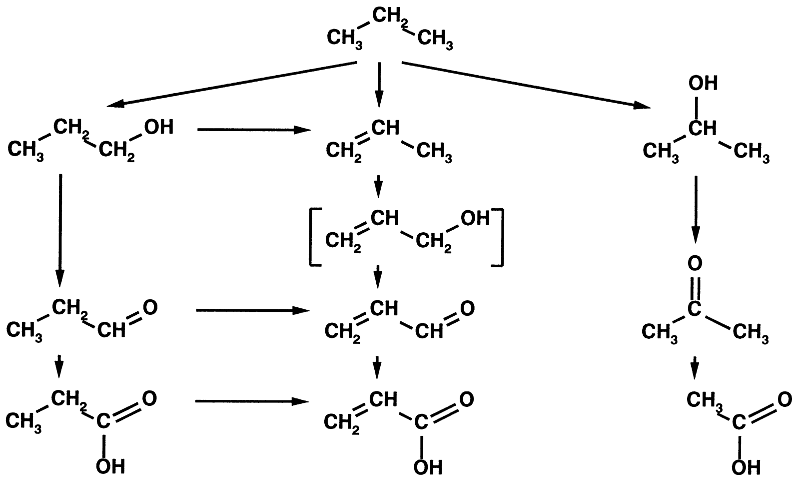

Fig. 2. Simplified reaction scheme and main oxygenate products of the partial oxidation of propane.

618–663 K for total oxidation. Zhou and Akgerman [17] also used a Pt–TiO_2 catalyst at 423–548 K for the total oxidation of ethanol and acetaldehyde in $scCO_2$. Fan et al. [18] reported on the partial oxidation of isobutane, directly using the hydrocarbon as SCF and a Pd–C catalyst at 426 K. Gaffney and Sofranko [19] proposed Cu-catalysts for the dihydroxylation of propene to propane-1,2-diol in $scCO_2$ at temperatures of 393–423 K.

Our research aims at applying these mentioned characteristic properties of SCFs to conventional gas phase oxidations. Among them, the direct catalytic selective oxidation of light alkanes (i.e. propane, Fig. 2, according to [20]) into their oxygenates (e.g. acetone, acrolein, acrylic acid) is of our special interest, because it may contribute to the extensive research to replace olefins as starting materials for the production of valuable chemicals. Until today, these reactions have often not led to sufficient high selectivities, e.g. the catalytic oxidation of propane to acrolein does not exceed selectivities of 60%, even at low conversions of 12 mol% [21]. These results are mainly caused by concurrent total oxidation of the formed reaction products (e.g. alkenes and oxygenates) under the rather severe alkane activation conditions. The intermediates remain adsorbed at the catalyst surface and are immediately subject to consecutive reactions, leading to the thermodynamically favoured final products CO_2 and H_2O.

It was the aim of the present work to investigate activity and selectivity of various catalysts for the partial oxidation of propane in $scCO_2$ atmosphere using a stirred batch reactor. Metal (oxide) catalysts containing CuO_2, Co_xO_y, Pd, and Pt, which had been reported in literature to work under supercritical conditions [15–19] were tested. Furthermore, the reaction conditions of the partial oxidation (i.e. the density of carbon dioxide and the partial pressure of synthetic air) were of special interest in this study.

2. Experimental

2.1. Catalyst preparation and characterisation

The catalyst samples were synthesised according to different methods: (i) Catalysts Co-1–Co-5, Cu-1, Mn-1 and Mo-1 (Table 3) were prepared by wet impregnation. The drying was carried out in a rotary evaporator (45 min, 333 K, 50 mbar) and subsequently in a vacuum oven (24 h, 303 K, 5 mbar). All samples were calcined in a muffle furnace. The Pt-1 catalyst was also prepared by impregnation. After drying the sample in a vacuum oven (14 h, 353 K, 5 mbar) the catalyst was reduced under a H_2 atmosphere in a tubular furnace. (ii) Catalysts Pd-1 and Co-6 were obtained by the precipitation method, adding dropwise 1 N KOH to a H_2PdCl_4–SiO_2 or $Co(NO_3)_2{\cdot}6H_2O$–SiO_2 suspen-

Table 3
Overview of the synthesised catalysts and some characterisation data supports: γ-Al_2O_3 spheres (Aluperl 1530; Solvay), SiO_2 powder (Type 62; Aldrich), ZrO_2 powder (Reachim); metal salt solutions for impregnation procedure: ($Co(NO_3)_2\cdot6H_2O$, $Cu(NO_3)_2\cdot3H_2O$, $Mn(NO_3)_2\cdot4H_2O$, $(NH_4)_2Mo_2O_7$, $H_2PtCl_6\cdot6H_2O$)

Catalyst		Preparation method	Calcination (T/K; t/h)	H_2 reduction (T/K; t/h)	Composition (wt.% metal)	BET surface area ($m^2\ g^{-1}$)	Particle size (nm)
Variation of active compound							
Co-1	Co_3O_4–γ-Al_2O_3	Impregnation	473; 6		5.3	134	n.d.[a]
Cu-1	CuO–γ-Al_2O_3	Impregnation	523; 14		4.3	139	n.d.
Mn-1	MnO_2–γ-Al_2O_3	Impregnation	523; 14		2.5	142	n.d.
Mo-1	MoO_3–γ-Al_2O_3	Impregnation	523; 14		5.5	136	n.d.
Pd-1	Pd–SiO_2	Precipitation		673; 2	8.4	130	n.d.
Pt-1	Pt–SiO_2	Impregnation		523; 2	4.8	340	n.d.
Variation of support							
Co-2	Co_3O_4–SiO_2	Impregnation	523; 14		3.8	310	50
Co-3	Co_3O_4–ZrO_2	Impregnation	523; 14		3.9	15	n.d.
Variation of Co content and preparation method							
Co-4	Co_3O_4–SiO_2	Impregnation	523; 14		0.7	328	50
Co-5	Co_3O_4–SiO_2	Impregnation	523; 14		7.4	293	n.d.
Co-6	Co_3O_4–SiO_2	Precipitation	523; 6+623; 6[b]		2.4	345	250
Co-7	Co_3O_4–SiO_2	Co-precipitation	523; 6+623; 6[b]		3.7	388	400

[a] Not determined.
[b] 6 h, 523 K and subsequently 6 h, 623 K.

sion until the pH value reached 9. The solid was centrifugated from the liquid (2 min, 10 000 rpm), washed twice with water and separated again. The sediments were dried in a vacuum oven (14–24 h, 373–383 K, 8 mbar). Subsequently, catalyst Pd-1 was reduced with H_2 in a tubular furnace, whereas catalyst Co-6 was calcined in a muffle oven. (iii) Catalyst Co-7 was synthesised by concurrent co-precipitation of support and active compound from a stirred aqueous solution of $Si(OC_2H_5)_4$, $Co(NO_3)_2\cdot6H_2O$, and C_2H_5OH as solubility promoter (4 days, 298 K). Again, the metal compound was precipitated by KOH. A rotary evaporator (45 min, 333 K, 50 mbar) and a vacuum oven (14 h, 383 K, 8 mbar) were used for drying and a muffle oven for calcining the samples. All catalysts were pressed (100 bar, 0.5 min), crushed, and classified into sieve fractions of 1.0–1.25 mm before testing them in the reaction.

The composition of the catalysts was determined by ICP emission spectroscopy (Optima 300 XL; Perkin-Elmer) using microwave pressure digestion (MDS 200; CEM) with hydrofluoric-acid or nitric acid at 8 bar. The surface area of fresh and used samples were analysed by the 5-point-BET method (Gemini III; Micromeritics). In order to determine particle size, some samples were additionally characterised by transmission electron microscopy (BS 500; Tesla) on carbon supported grids at 90 kV diffraction voltage. The crystallinity of several catalysts was investigated, recording X-ray diffraction patterns by a transmission powder diffractometer (STADIP; Stoe) with CuKα_1 radiation of 1.5406 Å using the inorganic powder data base ICSD. Table 3 summarises some of the obtained characterisation results.

2.2. Catalytic measurements

The catalytic experiments were performed in a stirred batch reactor (V=305 ml, maximum 623 K and 207 bar; Series 4560 Mini Reactors, Parr Instrument; Fig. 3) containing 2 ml of catalyst filling (diluted with 21 ml of glass beads) in a wire basket. The experiments were carried out according to different procedures: (i) For the catalyst screening, propane (98 vol.%; Aldrich) and synthetic air (20.5 vol.% of O_2 in N_2; Messer–Griesheim) were fed into the autoclave (R1) by depressurising corresponding 40 ml metering vessels (V1, V2). The liquid CO_2 was cooled by a cryostat (C1) and compressed up to the required density by means of a piston pump (P1;

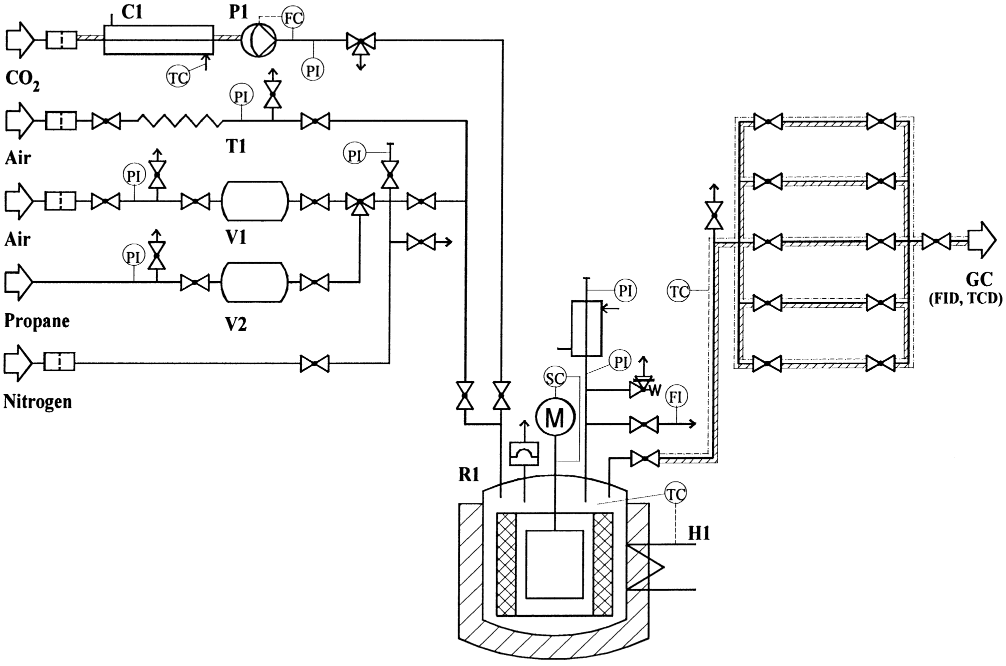

Fig. 3. Flow sheet of the apparatus for the catalytic measurements.

Model 305; Gilson). A heating jacket (H1) was used to increase temperature and, therefore, pressurise the autoclave content to the supercritical state. The reaction was carried out under the following conditions: Molar ratio of propane:air:CO_2=1:2.3–2.9:68–108 and p=80–100 bar. In order to identify exactly the beginning of the reaction, a step-like standard temperature–time program was applied, i.e. taking samples at 453 K (after 123 min, as reference), 478 K (173 min), 488 K (208 min), 498 K (243 min), 508 K (283 min), 518 K (318 min) and 573 K (353 min) during each run. (ii) For the investigation of the influence of the supercritical conditions on the reaction, a different procedure was used: Propane and CO_2 were fed into the reactor as before, whereas O_2 was added by depressurising a 25 ml pipe coil (T1) after reaction temperature had been reached in the autoclave. The reactions were run over 240 min at 553 K applying CO_2 densities 0.104–0.149 g cm^{-3} and molar ratios of propane:air:CO_2 of 1:6–9:103–107.

In all experiments hydrocarbons and oxygenates were analysed by online-capillary GC (Alumina, 50 m×0.53 mm and DB-FFAP, 50 m×0.32 mm; J&W) equipped with a flame ionisation detector. O_2 and N_2 were determined by a thermal conductivity detector (molecular sieve 5A, 30 m×0.32 mm; Quadrex) using the average of three parallel analyses.

3. Results and discussion

Conventional redox catalysts like BiMoO$_x$ [20,21] did not show a significant catalytic activity for the partial oxidation of propane at temperatures up to 623 K in plug flow reactors. However, the used stirred batch reactor can only be operated up to 623 K. Therefore, the experimental work necessarily consisted of two parts: a qualitative screening of catalysts, being active at low temperatures, followed by variation of the supercritical reaction conditions using one of the obtained suitable catalysts.

3.1. Catalyst screening

The first steps of our screening studies were based on catalyst compositions described in literature [15–19]. Before starting the catalytic investigations blank tests with empty catalyst basket and only sup-

Table 4
Feed composition, propane conversion ($X_{C_3H_8}$), total oxygenate selectivity (S_{Oxy}) and propene selectivity ($S_{C_3H_6}$) in the partial oxidation of propane on different metal (oxide) catalysts at 518–573 K (temperature–time program after 318–353 min, pressure 80–100 bar, $\rho(CO_2)=0.149\,g\,cm^{-3}$, 2 ml of catalyst)

Catalyst	Molar ratio (propane:air:CO_2)	Temperature (T/K, t/min)	Composition (wt.% metal)	$X_{C_3H_8}$ (mol%)	S_{Oxy} (%)	$S_{C_3H_6}$ (%)	Oxygenates
Variation of active compound							
Co-1	1:2.5:106	518; 318	5.3	14	2	2	Ace[a]
Cu-1	1:2.5:103	518; 318	4.3	14	0	Traces	None
Mn-1	1:2.5:104	518; 318	2.5	11	0	4	None
Mo-1	1:2.5:103	518; 318	5.5	3	0	2	None
Pd-1	1:2.3:107	518; 318	8.4	1	0	0	None
Pt-1	1:2.9:98	518; 318	4.8	10	0	0	None
Variation of support							
Co-2	1:2.5:101	518; 318	3.8	9	57	2	AA[b], Me[c], Ace[a], Aal[d], *i*Pr[e]
Co-3	1:2.5:105	518; 318	3.9	8	3	5	Ace[a]
Variation of Co content and preparation method							
Co-2	1:2.6:68	573; 353	3.8	11	13	10	AA[b], Me[c], Ace[a], Aal[d], *i*Pr[e]
Co-4	1:2.6:68	573; 353	0.7	8	52	15	AA[b], Me[c], Ace[a], AAl[d], *i*Pr[e], *n*Pr[f], Acr[g]
Co-5	1:2.6:69	573; 353	7.4	11	6	10	AA[b], Ace[a]
Co-2	1:2.5:101	573; 353	3.8	17	39	8	AA[b], Me[c], Ace[a], AAl[d], *i*Pr[e], *n*Pr[f], Acr[g], PrAl[h]
Co-6	1:2.5:112	573; 353	2.4	12	59	21	AA[b], Me[c], Ace[a], AAl[d]
Co-7	1:2.5:108	573; 353	3.7	6	20	3	AA[b], Ace[a]

[a] Ace=acetone.
[b] AA=acetic acid.
[c] Me=methanol.
[d] AAl=acetaldehyde.
[e] *i*Pr=*i*-propanol.
[f] *n*Pr=*n*-propanol.
[g] Acr=acrolein.
[h] PrAl=propionaldehyde.

port material, respectively, were carried out. No significant propane conversion and product formation, respectively, could be observed. The results of the conversion of propane in $scCO_2$ in the presence of catalysts at a temperature of 518 K are compared in Table 4. As expected, the use of the rather total oxidation catalyst Pt-1 did not result in the formation of oxygenates, but led to total oxidation of propane ($X_{C_3H_8} < 10$ mol%), which could be seen in a complete oxygen consumption without formation of oxygenates as well as other intermediates. Contrary to that, the other noble metal catalyst Pd-1, as well as the typical redox catalyst Mo-1, were nearly inactive up to 518 K, probably due to the low reaction temperature ($X_{C_3H_8} < 3$ mol%). Running the reaction with catalysts Cu-1 and Mn-1, a distinct total oxidation of propane ($X_{C_3H_8} < 14$ mol%) and slight formation of propene ($S_{C_3H_6} < 4\%$) occurred. Only the Co-1 (Co_3O_4–γ-Al_2O_3) catalyst produced traces of acetone ($X_{C_3H_8} = 14$ mol%, $S_{Oxy} = 2\%$) as a desired partial oxidation product of propane.

Based on these results, a support variation was carried out (Table 4). Replacing the γ-Al_2O_3 support by ZrO_2 the propane conversion declined, whereas the oxygenate selectivity slightly increased. A more significant rise could be noticed using a Co_3O_4–SiO_2 (Co-2) catalyst. The total oxygenate selectivity reached 57% at a propane conversion of 9 mol%. The product spectrum mainly consisted of acetic acid (S=37%), methanol (S=8%), acetone (S=6%), acetaldehyde (S=5%), *i*-propanol (S=1%) and propene (S=2%). This ranking may be attributed to the acid–base properties of the support: Strong acid sites (e.g. Al_2O_3) cause a firm adsorption of propane on the

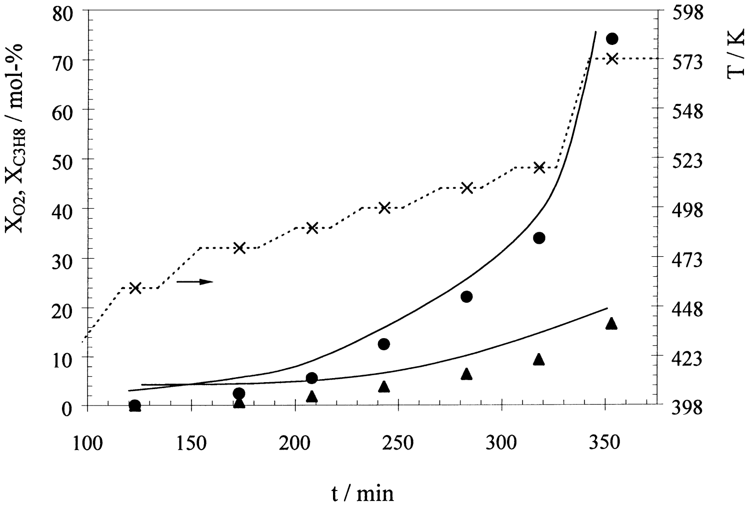

Fig. 4. Conversion of oxygen and propane vs. time and temperature ((×) sampling conditions) on the Co-2 catalyst (molar ratio of propane:air:CO_2=1:2.5:101, $\rho(CO_2)=0.149\,g\,cm^{-3}$, (●) oxygen, (▲) propane).

catalyst surface leading to total oxidation. A decrease in the strength of acid sites of the support (e.g. ZrO_2) towards a complete inert character (e.g. SiO_2) weakens the adsorption. Thus, the formed partial oxidation products can more easily desorb from the catalyst surface and the selectivity for oxygenates increases.

Figs. 4 and 5 show the course of reaction, i.e. the conversion of oxygen and propane (X_{O_2}, $X_{C_3H_8}$) as a function of the temperature–time program as well as the selectivities of desired products ($S_{C_3H_6}$, S_{Oxy}) depending on reaction temperature and time, i.e. at defined propane conversions using the Co-2 catalyst

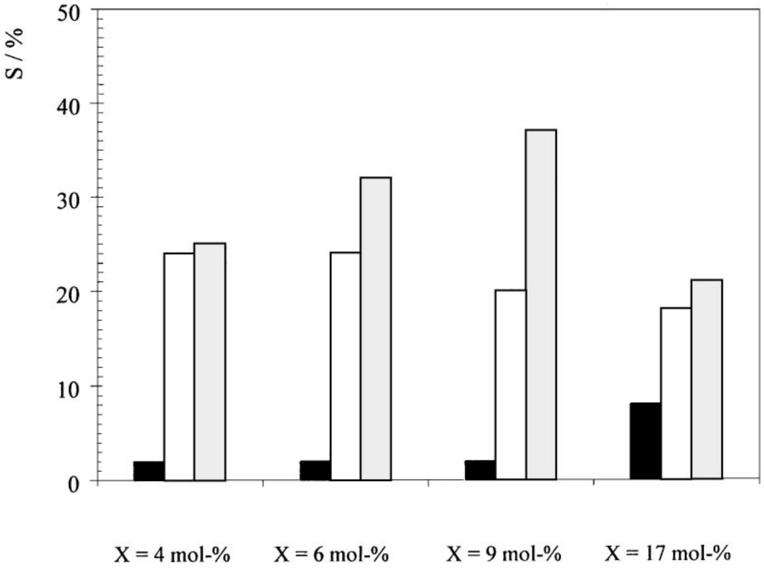

Fig. 5. Selectivity of propene (filled columns), acetic acid (shaded columns) and other oxygenates (acetone, methanol, *i*-propanol, acetaldehyde; blank columns) depending on propane conversion on the Co-2 catalyst (molar ratio of propane:air:CO_2=1:2.5:101, $\rho(CO_2)=0.149\,g\,cm^{-3}$).

(at a 1:2.5:101 molar ratio of propane:air:CO_2). As it can be seen, the optimum temperature is around 518 K, where the sum of the selectivities of oxygenates pass through a maximum, whereas higher temperatures promote the consecutive total oxidation of the formed intermediates (except propene). The reaction path to acetic acid via *i*-propanol and acetone seems to be favoured, considering the reaction scheme for propane oxidation (Fig. 2). Propionic acid as well as acrylic acid cannot be detected at all, whereas traces of their precursors *n*-propanol and acrolein were not found at temperatures lower than 573 K.

Furthermore, the influence of Co concentration and catalyst preparation on the partial oxidation were investigated at 573 K after 353 min (Table 4). Lowering the Co content of the catalyst (Co-5, Co-2, Co-4) at comparable BET surface areas led to increased total oxygenate selectivities at nearly constant propane conversions. Nevertheless, the particle sizes of the metal oxide of these samples, as far as they were roughly determined by TEM, seemed to be independent from the Co concentration and remained at quantities up to 50 nm. The product spectrum concurrently expanded, however acetic acid still significantly dominated other oxygenates.

Among differently prepared catalyst samples, the precipitated Co-6 showed the best results ($X_{C_3H_8}$ = 12 mol%, S_{Oxy} = 59%, referring to Table 4), although metal oxide particles could be detected up to 250 nm. In contrast, only poor oxygenate selectivities and propane conversions were found for co-precipitated Co-7. Its catalytic behaviour may be explained by the inhomogeneously dispersed, large metal oxide particles (up to 400 nm). Furthermore, it may also be concluded, that the cobalt oxide had partly been enclosed by the supporting material during the preparation and was no longer available for the reactants. So, co-precipitation was — against expectations — even a less suitable method for the preparation of Co_3O_4–SiO_2 than impregnation.

3.2. Varying supercritical conditions

Within the screening studies the precipitated Co-6 turned out to be most suitable for further investigations of the influence of the supercritical conditions on the reaction. Therefore, this catalyst was used for a first variation of the propane:air:CO_2 molar ratio from 1:7:106 (●) to 1:9:107 (○) at a constant reaction temperature of 553 K and a CO_2 density of 0.149 g cm^{-3} (Fig. 6). The propane conversion significantly increased with the slightly higher concentration of air in the initial feed composition, whereas the selectivity of oxygenates and propene nearly kept

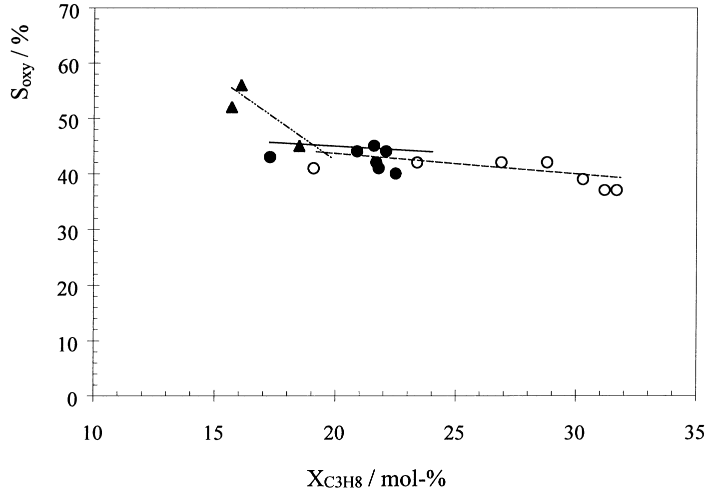

Fig. 6. Selectivity of oxygenates vs. propane conversion on the Co-6 catalyst at T=553 K ($\rho(CO_2)$=0.149 g cm^{-3}, molar ratio of propane:air:CO_2=1:7:106, (●) $\rho(CO_2)$=0.149 g cm^{-3}, molar ratio of propane:air:CO_2=1:9:107, (○) $\rho(CO_2)$=0.104 g cm^{-3}, molar ratio of propane:air:CO_2=1:6:103, (▲)).

constant. The yield of formed oxygenates rose from 9 up to 12%.

Additionally, the effect of CO_2 density was also studied in first experiments on Co-6 at a constant oxygen proportion (Fig. 6). The lowering of the CO_2 density from $\rho(CO_2)=0.149\,g\,cm^{-3}$ ((●) reaction pressure: 112 bar) to $0.104\,g\,cm^{-3}$ ((▲) reaction pressure: 79 bar) caused a decrease in propane conversion at significantly higher oxygenate selectivities. However, the obtained results may only be seen as first indications of the influence of oxygen partial pressure and CO_2 density, respectively, on the propane conversion at supercritical conditions; further experiments are needed for a more extensive investigation.

4. Conclusions

In summary, cobalt-containing catalysts lead to the best results for the partial oxidation of propane to oxygenates in $scCO_2$ using a stirred batch reactor. Furthermore, less-acidic supports and low contents of the metal oxide significantly improve the partial oxidation. A precipitated 2.4 wt.% Co_3O_4–SiO_2 showed a propane conversion of 12 mol% and a total oxygenate selectivity of 59%, surpassing similar catalysts which have been obtained by impregnation as well as co-precipitation. First experiments concerning the variation of the supercritical reaction conditions indicate that the decrease of the CO_2 density results in a higher selectivity of oxygenates.

For a better understanding of the influence of $scCO_2$ on the partial oxidation of propane further experiments are in progress in the batch reactor. Especially, the investigations concerning the variation of CO_2 density and propane:air:CO_2 molar ratio shall be extended to validate the effects reported in this work. Additionally, a recently set-up continuous flow-reactor, which can be operated up to 200 bar and 923 K, will be used for further investigations. Thereby, the examination of conventional redox catalysts, which had to be neglected in the past due to the temperature limit of the batch reactor, is of our special interest in order to enable comparisons with published data for gas phase oxidations.

Acknowledgements

The authors like to thank Prof. Dr. M. Baerns for the central idea of this work and stimulating discussions, Mrs. M. Hartelt and Mr. A. Krepel for the experimental assistance, Dr. U. Schülke for the helpful advice concerning the catalyst preparation and the Federal Ministry of Education and Research, Germany, as well as the Senate of Berlin for the financial support of this work (Project No. 03 C3012 0).

References

[1] M.A. McHugh, V.J. Krukonis, Supercritical Fluid Extraction — Principles and Practice, Butterworth/Heinemann, Boston, MA, 1994.
[2] M.E. Paulaitis, Chemical Engineering at Supercritical Fluid Conditions, Ann Arbor Science, Ann Arbor, MI, 1983.
[3] L.T. Taylor, Supercritical Fluid Extraction, Wiley, New York, 1996.
[4] P.E. Savage, S. Gopalan, T.I. Mizan, C.J. Martino, E.E. Brock, AIChE J. 41 (7) (1995) 1723.
[5] D. Ambrose, in: D.R. Lide (Ed.), Handbook of Chemistry and Physics, 72nd edition. CRC Press, Boca Raton, FL, 1991.
[6] T.G. Squires, C.G. Venier, T. Aida, Fluid Phase Equilibria 10 (1983) 261.
[7] S.A. Ulybin, S.S. Bakulin, Thermal Eng. 24 (1) (1977) 68.
[8] H. Tiltscher, H. Hofmann, Chem. Eng. Sci. 42 (5) (1987) 959.
[9] J. Chrastil, J. Phys. Chem. 86 (15) (1982) 3016.
[10] H. Tiltscher, H. Wolf, J. Schelchshorn, Ber. Bunsenges. Phys. Chem. 88 (1984) 897.
[11] M. Poliakoff, M.W. George, S.M. Howdle, in: R. van Eldik, C.D. Hubbard (Eds.), Chemistry Under Extreme or Non-classical Conditions, Wiley Spektrum Akademischer Verlag co-publication, New York, 1997.
[12] A. Baiker, Chem. Rev. 99 (1999) 453.
[13] J.W. Moore, R.G. Pearsons, Kinetics and Mechanism, Wiley, New York 1981.
[14] B.J. Hrnjez, A.J. Mehta, M.A. Fox, K.P. Johnston, J. Am. Chem. Soc. 111 (1989) 2662.
[15] K.M. Dooley, F.C. Knopf, Ind. Eng. Chem. Res. 26 (1987) 1910.
[16] L. Zhou, C. Erkey, A. Akgerman, AIChE J. 41 (1995) 2122.
[17] L. Zhou, A. Akgerman, Ind. Eng. Chem. Res. 34 (1995) 1588.
[18] L. Fan, T. Watanabe, K. Fujimoto, Appl. Catal. A 158 (1997) 141.
[19] A.M. Gaffney, J.A. Sofranko, in: Proceedings of the Symposium on Catalytic Selective Oxidation, Washington, DC, August 23–28, 1992, p. 1273.
[20] M.M. Bettahar, G. Costentin, L. Savary, J.C. Lavalley, Appl. Catal. A 145 (1996) 1.
[21] M. Baerns, O.V. Buyevskaya, M. Kubik, G. Maiti, O. Ovitser, O. Seel, Catal. Today 33 (1997) 85.