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# Fluid phase equilibria of the reaction mixture during the selective hydrogenation of 2-butenal in dense carbon dioxide

Nikolai E. Musko<sup>a,b,d</sup>, Anker Degn Jensen<sup>b</sup>, Alfons Baiker<sup>c</sup>, Georgios M. Kontogeorgis<sup>a,\*</sup>, Jan-Dierk Grunwaldt<sup>d,\*\*</sup>

<sup>a</sup> Department of Chemical and Biochemical Engineering, Centre for Energy Resources Engineering (CERE), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
 <sup>b</sup> Department of Chemical and Biochemical Engineering, Combustion and Harmful Emission Control Centre (CHEC), Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark
 <sup>c</sup> Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Hönggerberg, HCI, CH 8093 Zurich, Switzerland
 <sup>d</sup> Institute for Chemical Technology and Polymer Chemistry (ITCP) and Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany

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# ABSTRACT

Knowledge of the phase behaviour and composition is of paramount importance for understanding multiphase reactions. We have investigated the effect of the phase behaviour in the palladium-catalysed selective hydrogenation of 2-butenal to saturated butanal in dense carbon dioxide. The reactions were performed using a 5 wt% Pd on activated carbon in custom-designed high pressure autoclaves at 323 K. The Cubic-Plus-Association (CPA) equation of state was employed to model the phase behaviour of the experimentally studied systems. CPA binary interaction parameters were estimated based on the experimental vapour-liquid or liquid-liquid equilibria data available in the literature. No experimental data for the  $CO_2$ -2-butenal binary system were available in the literature; therefore, the bubble points of this mixture of varying composition at three different temperatures were measured in a high-pressure view cell. The results of the catalytic experiments showed that small amounts of carbon dioxide added to the system significantly decrease the conversion, whereas at higher loadings of CO<sub>2</sub> the reaction rate gradually increases reaching a maximum. The CPA calculations revealed that this maximum is achieved in the so-called "expanded liquid" region, which is located near the critical point of the reacting mixture. It was also found that in this point the hydrogen concentration achieved its maximum in the CO<sub>2</sub>-expanded phase. Furthermore, the pressure - temperature regions where the multicomponent reaction system exists in one single phase and in multiphase were calculated.

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# 1. Introduction

Hydrogenation reactions in general are widely used in the chemical industry [1]. Particularly, the selective hydrogenation of  $\alpha,\beta$ -unsaturated aldehydes has been extensively studied over the past decades, because the products – saturated aldehydes and  $\alpha,\beta$ -unsaturated alcohols – have many applications, especially in the synthesis of various fine chemicals [2]. The scope of the present study comprises the selective hydrogenation of 2-butenal to butanal (Scheme 1). Recent findings on bifunctional catalysts have shown that it is the first step of the "one-pot" synthesis with the consecutive second step of the aldol reaction of the saturated aldehydes [3]. The present study is planned to be extended to those

\*\* Corresponding author. Tel.: +49 721 60842120.

systems as well, and some exploration in that direction has already been done [4–6].

In molecules of  $\alpha$ , $\beta$ -unsaturated aldehydes with two types of double bonds, C=C and C=O, the former unsaturated bond is thermodynamically more prone to hydrogenation than the latter. However, depending on the catalyst used in the process one or the other product can be selectively produced. Thus, platinum catalysts doped with different additives favours mainly C=O hydrogenation [7–15], whereas palladium catalysts are typically used for C=C hydrogenation. For example, using a 10 wt% Pd/C catalyst, 2-butenal was easily hydrogenated into butanal with almost 100% selectivity [16]. Also over 1 wt% Pd/Amberlyst-15 and 1 wt% Pd/C in carbon dioxide as reaction medium selective hydrogenation of the double bond was found [3]. Similarly, the C=C double bond in 2-hexenal is selectively converted with hydrogen on a 1 wt% Pd/Amberlyst-15 catalyst [17].

Heterogeneous catalysis combined with the use of dense and/or supercritical carbon dioxide provides additional opportunities to optimise and intensify the process [18–21]. This is particularly

<sup>\*</sup> Corresponding author. Tel.: +45 45252859.

*E-mail addresses:* gk@kt.dtu.dk (G.M. Kontogeorgis), grunwaldt@kit.edu (J.-D. Grunwaldt).

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List of	sym	bols
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$a_0$	CPA fluid specific parameter
b	CPA fluid specific parameter
C1	CPA fluid specific parameter
g.	$g(\rho)$ radial distribution function
k <sub>i</sub>	binary interaction parameter
'n	number of experimental points
Р	pressure
$P^{s}$	t vapour pressure
R	gas constant
Т	temperature
Te	critical temperature
T <sub>r</sub>	reduced temperature
$V^l$	liquid volume
х.	mole fraction
X,	fraction of free sites A belonging to molecule <i>i</i>
G	eek letters
α	fluid specific parameter in CPA
ß	$_{i}B_{j}$ association volume for the hydrogen bond between
'	sites A and B belonging in molecules i and j, respec-
	tively
Δ	$A_{iB_{j}}$ association strength between two sites A and B
	belonging in molecules <i>i</i> and <i>i</i> , respectively

interesting for gas-liquid reactions like selective hydrogenation [22,23]. Thus, it has been shown that the reaction rate of the selective hydrogenation of 2-butenal to butanal is higher in supercritical fluids than in conventional liquid phase with or without addition of a solvent [3,16,17]. Burgener et al. [24] studied the hydrogenation of citral in supercritical CO<sub>2</sub> and conventional solvents in continuous and batch reactors. It was shown that the reaction rate and selectivity were greatly influenced by the type of the reactor, solvent, total pressure, and feed composition. In many cases both conversion and selectivity in CO<sub>2</sub> were higher than those in conventional solvents, and both depended on the CO<sub>2</sub> pressure, whereas hydrogen pressure mainly accelerated the reaction rate [24]. An interesting trend was observed when different H<sub>2</sub>: feed ratios were used. The highest conversion was observed when the system was changing from single phase to two phases at a moderate H<sub>2</sub> concentration. The authors claimed that these changes might be attributed to the changes in the phase behaviour of the reaction mixture. All aforementioned reactions have been performed in carbon dioxide media but the phase behaviour during the reaction progress with its changing composition was not studied systematically. Note, however, that the phase behaviour for a number of other systems has been investigated experimentally [25].

Phase behaviour plays an important role in chemical reactions in dense and/or supercritical carbon dioxide media. It is very demanding to study it experimentally, especially *in situ* during the reaction, however theoretical thermodynamic calculations may be very useful in this regard. A large number of thermodynamic models have been developed in order to predict many thermodynamic properties of mixtures, including their phase behaviour with satisfactory accuracy [26]. The challenge for applying them to catalysis is to provide examples that demonstrate that they are capable of predicting multicomponent mixtures at varying composition, as occurring during reaction.



Scheme 1. Selective hydrogenation of 2-butenal in dense carbon dioxide.

For this purpose, an advanced thermodynamic model, the Cubic-Plus-Association (CPA) equation of state [27], is used in the present study. CPA is one of the models that takes into account strong crossassociation between components, i.e. hydrogen bonding; and it has been proven to be a powerful tool for predicting various properties of complex multicomponent systems at elevated temperatures and pressures [28,29]. The CPA equation of state consists of two parts – the Soave–Redlich–Kwong (SRK) equation of state and an association term based on Wertheim's first order thermodynamic perturbation theory [30]. In the case when no hydrogen-bonding components are present in the mixture, the association term vanishes and CPA reduces to the SRK functionality.

In the present reaction, all the components comprising the reaction mixture – 2-butenal, hydrogen, butanal and carbon dioxide – are non-associating, i.e. they do not form hydrogen bonds between themselves and/or each other. For such a simple system the original Soave–Redlich–Kwong equation of state might be used [31], instead of CPA. However, the original SRK uses critical temperature  $T_c$ , critical pressure  $P_c$ , and acentric factor  $\omega$  as pure fluid parameters. On the other hand, the estimation of pure fluid parameters for CPA is based on experimental vapour pressure and liquid density data, which means that the temperature dependency of those important properties is captured by the model. Therefore, CPA gives better results when describing vapour pressure dependencies with temperature.

In order to account for intermolecular interactions one interaction parameter  $k_{ij}$  is typically used in the model. It is estimated on the basis of experimental vapour–liquid, liquid–liquid or vapour–liquid–liquid equilibria data (VLE, LLE or VLLE) for the binary mixtures of the components comprising the reaction system. In many cases such data are available in the literature for binary systems; however, no experimental data were found for the CO<sub>2</sub>–2butenal binary system. Therefore, the bubble point pressures of the CO<sub>2</sub>–2-butenal binary mixture of various compositions at the different temperatures were measured experimentally. Based on the obtained data the binary interaction parameter of CPA for this system was estimated.

In summary, the present study aims at the following aspects: (1) the elucidation of the influence of the carbon dioxide amount on the catalyst performance, (2) the measurement of the phase equilibrium of the  $CO_2$ -2-butenal binary mixture, and finally, (3) the application of the CPA equation of state and the parameters obtained for predicting the phase equilibrium of the multicomponent reaction systems.

#### 2. Experimental

#### 2.1. Catalyst preparation

A 5 wt% Pd/C catalyst was prepared using the incipient wetness impregnation technique as follows. 0.1282 g of  $[Pd(NH_3)_4]Cl_2$  (Sigma–Aldrich) as a precursor was dissolved in 1.69 ml of deionised water – the amount required for the complete impregnation of 0.988 g of activated carbon (Sigma–Aldrich, ground fraction 125–250  $\mu$ m). The sample was dried at room temperature overnight, then in an oven at 373 K for 24 h, and subsequently activated in nitrogen flow containing 10 vol% of hydrogen at 383 K for 2 h. The final catalyst sample was stored in dry atmosphere.

#### 2.2. Catalyst characterisation

The specific surface areas of the as-prepared 5 wt% Pd/C catalyst was determined using BET isotherms recorded on a BEL Japan surface area analyser at a nitrogen adsorption temperature of 77 K. The specific surface of the sample was measured to be  $994 \text{ m}^2/\text{g}$ .



Fig. 1. Typical TEM image of 5 wt% Pd/C catalyst.

The as-prepared catalyst was analysed using X-ray diffraction (Bruker D8-Advance Diffractometer with a Cu K $\alpha$ -Anode source,  $\lambda = 1.54$  nm, angle range 20–80° 2 $\theta$ ). The obtained diffractograms did not reveal any significant reflections, which indicates that the palladium particles are well dispersed and fairly small.

In order to support this finding, the transmission electron microscopy images (TEM) were obtained on a FEI Technai TEM operating at 200 kV (Centre of Electron Nanoscopy, DTU). A typical TEM image is depicted in Fig. 1. It can be seen that the palladium particles are evenly distributed on the carbon surface, and the average particle size falls below 4 nm.

Temperature-programmed reduction (TPR) of the impregnated catalyst was performed as follows: 500 mg of the fresh sample was placed into a quartz tube (10 mm in diameter) heated in flowing N<sub>2</sub> (air liquid, 50 ml/min) to 393 K, and held for 10 min. The tube was then cooled in flowing nitrogen to room temperature, N<sub>2</sub> was replaced by the carrier gas, and the TPR run was started using the following conditions: carrier gas 5 vol%. H<sub>2</sub> in N<sub>2</sub> (air liquid) with a flow rate of 50 ml/min; initial temperature 308 K; ramp rate 5 K/min; and final temperature 433 K. The concentration of hydrogen was detected with a GC-14A chromatograph (Shimadzu GmbH). The TPR experiments indicate that the palladium in the temperature range 363 and 383 K.

#### 2.3. Catalytic hydrogenation of 2-butenal

The catalyst performance was tested in the selective hydrogenation of 2-butenal using homemade stainless steel autoclaves with magnetic stirring bars ( $T_{max} = 250 \circ C$ ,  $P_{max} = 200$  bar, inner volume ~ 125 ml). Before use, the reactors were thoroughly washed with organic solvents and dried with compressed air. Required amounts of the catalyst and 2-butenal were loaded into the autoclaves which then were tightly closed. After that, the reactors were carefully flushed with hydrogen several times and pressurised up to the desired pressure. Hydrogen was supplied directly from the hydrogen cylinder via an interconnected reduction valve. As a next step, carbon dioxide was added using a CO<sub>2</sub>-compressor (NWA, PM-101, Loerrach, Germany), and its amount was measured by weighing the autoclaves before and after loading. Pressure and temperature were monitored with installed manometers and thermocouples, respectively.

After the reaction, the autoclaves were quickly cooled down to room temperature in a water bath, slowly and carefully depressurised, and opened.

Samples of the reaction mixture were taken out, diluted with toluene and analysed employing a gas chromatograph (Shimadzu, GC 2010+, polar column), which had been previously calibrated for the reactant and possible products.

All catalytic experiments were performed at least twice. The conversion of 2-butenal in two identical experiments by maximum deviated by 7% relative.

## 2.4. Phase behaviour measurements

Phase behaviour was visually monitored in a high pressure view cell (15–65 ml, SITEC, Switzerland) with a sapphire window (26 mm diameter). The pressure was adjusted by changing the volume of the cell by means of a screw-type manual pump. The set up principle is based on the so-called synthetic method [32], where the phase transition is directly observed through the window without taking samples. The flow chart and the set up description can be found in Ref. [33–35]. Temperature and pressure were monitored with a thermocouple and a Dynisco pressure sensor, respectively. Stirring was performed by a magnetic stirrer with a stirring bar placed inside the cell. Temperature was controlled by means of an oil-containing heating jacket connected to a thermo/cryostat.

Before every experiment the view cell was thoroughly cleaned with acetone and CO<sub>2</sub>, dried with an air jet, and left open heated up to 323 K in the air for a minimum of 2 h. After cooling it down to room temperature, the desired amount of 2-butenal (Aldrich, 99.8%+) was loaded into the cell. Its mass was calculated by weighing the syringe before and after loading. After charging the cell with the liquid, it was closed, tightened, and flushed slowly and carefully with gaseous CO<sub>2</sub> in order to substitute the air. CO<sub>2</sub> was added using a CO<sub>2</sub>-compressor (NWA, PM-101, Loerrach, Germany), and its quantity was measured by a mass flow transmitter (Rheonik Messgeraete GmbH, Germany) at a constant pressure of 100 bar, which was controlled by means of an interconnected reduction valve. The view cell was further heated up to a desired temperature and pressurised to a pressure higher than the expected bubble point pressure. At this stage the cell was left for equilibrating for at least 2 h. A first rough estimation of the bubble point was made by stepwise depressurising the system (4-6 bar). After the first bubbles appeared in the top part of the cell, it was pressurised again and left for equilibration. Small stepwise pressure drop (0.2-1 bar) with subsequent equilibration after each step was applied to determine the bubble point pressure of the specific system. Since the first bubble of gas phase usually appeared in the highest point of the cell, the latter was slightly tilted to make this point more visible. The pressure at which the first bubble of the second phase appeared was noted. All the experimental points were measured at least three times. The difference between these points was generally less than 0.2–0.4 bar, which was within the accuracy range of the pressure gauge. The temperature was measured with a precision of 0.5 K.

# 3. Experimental results

#### 3.1. Catalyst performance

A series of catalytic experiments were carried out in order to investigate the influence of the carbon dioxide content on the catalytic performance. Blind tests without a catalyst were also performed, and no detectable catalytic activity was observed. The results are presented in Table 1.

The results showed that the conversion, and corresponding turnover frequency (TOF) reached a minimum when the amount

Table I	
Selective hydrogenation of 2-butenal to b	outanal over 5 wt% Pd/C catalyst.

Amount of CO <sub>2</sub> , g	Mole ratio CO <sub>2</sub> :2-butenal	Total pressure, bar	Conversion, %	TOF, h <sup>-1</sup> a
0	0.0:1	22	34.3	730
4	2.3:1	34	27.6	580
10	5.7:1	50	10.7	230
28	15.9:1	70	14.6	310
34	19.3:1	98	17.1	360
45	25.6:1	111	20.2	430
60	34.1:1	126	39.1	840
70	39.8:1	138	39.7	840
82	46.6:1	150	26.6	560
92	52.3:1	185	24.6	520

*Conditions*: Substrate 0.04 mol, H<sub>2</sub>:2-butenal molar ratio 2.5:1 (corresponding to a pressure of 20 bar at room temperature),  $m_{cat} = 0.01$  g, temp = 323.2 K, reaction time 60 min.

<sup>a</sup> TOF[h<sup>-1</sup>] =  $(n_{sub} \times Conv.)/((m_{cat} \times wt_{Pd})/(Mr_{Pd}) \times t)$ , where  $n_{sub}$  – amount of 2-butenal, mol; Conv. – conversion of 2-butenal, %;  $m_{cat}$  – catalyst mass, g;  $wt_{Pd}$  – palladium loading, wt%;  $Mr_{Pd}$  – molecular weight of Pd, g/mol; t – time, h.

of carbon dioxide approached 10 g, i.e. when the mole ratio  $CO_2$ :2butenal was 5.7:1. When this ratio was increased, the conversion also went up reaching a maximum of almost 40% at a mole ratio  $CO_2$ : substrate of 35–40:1. The total pressure of the reaction system, however, was almost linearly dependent on the amount of  $CO_2$ used in the reaction. Note that in the present case the turnover frequency was referred to the total number of Pd atoms: in reality only the surface palladium atoms or even special sites will contribute to the reaction.

## 3.2. Phase behaviour measurements

The bubble point pressures for the  $CO_2$ -2-butenal binary mixture at four different compositions were measured at three different temperatures using the aforementioned setup and experimental procedure. The results are presented in Table 2.

#### 4. Modelling with the CPA equation of state

Modelling of the reaction mixture, also during the progress of the reaction, was based here on the CPA EoS which combines the classical Soave–Redlich–Kwong (SRK) equation of state with an advanced association term [27]. The CPA EoS can be expressed for mixtures in terms of pressure *P* as follows [26]:

$$P = \frac{RT}{\nu_m - b} - \frac{a_o \left[1 + c_1 \left(1 - \sqrt{T_r}\right)\right]^2}{\nu_m \left(\nu_m + b\right)} - \frac{1}{2} \frac{RT}{\nu_m} \left(1 + \rho \frac{\partial \ln g}{\partial \rho}\right) \sum_i x_i \sum_{A_i} (1 - X_{A_i})$$
(1)

The key element in the association term is  $X_{A_i}$  – the fraction of sites type *A* on molecule *i* that do not form hydrogen bonds with other active sites. It is related to the association strength  $\Delta^{A_iB_j}$ between two sites belonging to two different molecules, e.g. site *A* 

Table 2Experimental bubble point pressures for CO2-2-butenal.

CO <sub>2</sub> mole fraction	Pressure, bar		
	313.2 K	331.9 K	350.2 K
0.3899	28.8	38.2	48.4
0.4580	34.9	46.5	59.2
0.5429	41.5	55.2	70.3
0.7081	57.4	77.6	98.8

on molecule *i* and site *B* on molecule *j*. This parameter is determined from:

$$X_{A_i} = \frac{1}{1 + \rho \sum_j x_j \sum_B B_j x_{B_j} \Delta^{A_j B_j}}$$
(2)

The association strength  $\Delta^{A_i B_j}$ , in its turn, can be expressed as:

$$\Delta^{A_i B_j} = g(\rho) \left[ \exp\left(\frac{\varepsilon^{A_i B_j}}{RT}\right) - 1 \right] b_{ij} \beta^{A_i B_j}$$
(3)

where  $g(\rho) = 1/1 - 1.9(b\rho/4)$  – the radial distribution function, while  $b_{ij} = (b_i + b_j)/2$ .  $b_i$  is the temperature independent co-volume parameter of the component *i*, and  $\rho$  is the molar density.  $T_r = T/T_c$ is the reduced temperature, and  $T_c$  is the experimental critical temperature.

In the expression for the association term (Eq. (3)), the parameters  $\varepsilon^{A_iB_j}$  and  $\beta^{A_iB_j}$  are called the association energy and association volume, respectively. These two parameters are only used for associating components, and together with the three additional parameters from the SRK part ( $a_0$ , b,  $c_1$ ) are the five pure fluid parameters of the CPA model.

When the CPA is used for mixtures, the conventional mixing rules are employed in the physical term (SRK) for the energy and co-volume parameters. The geometric mean rule is used for the energy parameter  $a_{ij}$ . The interaction parameter  $k_{ij}$  is the only binary adjustable parameter of CPA:

$$a = \sum_{i} \sum_{j} x_i x_j a_{ij}, \text{ where } a_{ij} = \sqrt{a_i a_j} (1 - k_{ij})$$

$$\tag{4}$$

$$b = \sum_{i} x_i b_i \tag{5}$$

#### 4.1. Pure fluids

The CPA pure fluid parameters ( $a_0$ , b,  $c_1$ ) were estimated using saturated liquid density  $V^{liq}$  and vapour pressure  $P^{sat}$  data from DIPPR [36] or, when it was possible, they were obtained from the literature (Table 3). Due to the fact that all the components are nonassociating, the association energy and volume ( $\varepsilon^{A_iB_j}$  and  $\beta^{A_iB_j}$ ) are equal to zero. The pure fluid parameters are presented in Table 3.

#### 4.2. Binary mixtures

The reaction mixture consists of four components (CO<sub>2</sub>, hydrogen, 2-butenal, and butanal) therefore, six interaction parameters are required for the six binaries occurring in the system. As it was previously mentioned, for estimating  $k_{ij}$  parameters some experimental data are required.

Unfortunately, the experimental data were not available for all the binaries, specifically, for the binaries with 2-butenal no data were found in the literature. However, due to the strong similarities between the structure of 2-butenal and butanal, the following assumptions were made: (1) the  $k_{ij}$  for the hydrogen–2-butenal binary was assumed to be equal to that of hydrogen–butanal, and (2) for the 2-butenal–butanal system  $k_{ij}$  was set to zero. The binary interaction parameters are presented in Table 4.

The CPA model describes quite satisfactorily the phase behaviour of the  $CO_2$ -hydrogen binary mixture, however, slight deviations between the model predictions and experimental data are observed at higher hydrogen concentrations, as shown in Fig. 2.

For the CO<sub>2</sub>-butanal binary mixture a temperature independent  $k_{ij}$  parameter was estimated based on the experimental VLE data. The first attempt to measure and predict the phase behaviour of this system was made by da Silva et al. [37]. In their work the authors used the SRK and Peng–Robinson (PR) equations of state, in both cases employing the quadratic mixing rules with two

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#### Table 3

CPA parameters for pure fluids.

<i>Т</i> <sub>с</sub> , К	$a_0$ , L <sup>2</sup> bar mol <sup>-2</sup>	b, L mol <sup>-1</sup>	<i>c</i> <sub>1</sub>	%AAD <sup>a</sup> in P <sup>sat</sup>	%AAD in V <sup>liq</sup>	Ref.
Carbon dioxide $(T_m - 0.9T_c)$						
304.2	3.5079	0.0272	0.7602	0.2	0.8	[47]
Hydrogen ( $0.5T_c - 0.9T_c$ )						
33.19	0.2664	0.0194	0.0474	1.6	4.4	This work
2-Butenal ( $0.4T_c - 0.9T_c$ )						
565.0	18.9939	0.0728	0.8140	4.8	1.9	This work
Butanal $(0.4T_c - 0.9T_c)$						
537.2	16.6777	0.0758	0.8803	2.2	0.8	This work
vcal vexp						

<sup>a</sup> %AAD =  $\frac{1}{n} \sum_{i} \left| \frac{A_{i}^{n-A_{i}}}{X_{i}^{exp}} \right| \times 100$ , where X stands for  $P^{sat}$  or  $V^{tiq}$  and n is the number of experimental data points.

#### Table 4

CPA binary interaction parameters for binary mixtures. All k<sub>ij</sub> are independent of temperature.

System	Temperature range, K	k <sub>ij</sub>	%AAD in P	%AAD in y <sub>1</sub>	Data ref.
CO <sub>2</sub> -H <sub>2</sub>	278.15-290.15	-0.0323	6.9	17.9	[48]
CO <sub>2</sub> -butanal	303.2-313.2	-0.2859	10.0	0.6	[37]
CO <sub>2</sub> -2-butenal	313.2-350.2	-0.0180	1.4	_ a	This work
H <sub>2</sub> -butanal	293.15-393.15	-0.0436	7.3	_ a	[49]
H <sub>2</sub> -2-butenal	-	-0.0436 <sup>b</sup>	_	_	No lit. data
2-Butenal-butanal	-	0	-	_	No lit. data

<sup>a</sup> Calculations based on experimental P-x-T data, therefore, %AAD in  $y_1$  were not estimated.

<sup>b</sup> The interaction parameter for this binary mixture is set equal to the interaction parameter of the H<sub>2</sub>-butanal binary.



**Fig. 2.** Hydrogen–CO<sub>2</sub> VLE. Experimental data (points) at different temperatures and CPA calculations (lines) with a temperature independent  $k_{ij} = -0.0323$ .

adjustable parameters, i.e.  $k_{ij}$  for the energy parameter and  $l_{ij}$  for the co-volume. The authors report that the employed equations of state quite accurately described the experimental data. However, at higher concentrations of carbon dioxide in the mixture (0.9–1.0

 $CO_2$  molar fraction) a large difference between the model prediction and experimental data is observed. This might be due to the fact that the experimental data in this range are not accurate enough. One of the sets of data was measured at a temperature of 303.2 K, which is very close to the critical temperature of pure  $CO_2$  (304.2 K [36]). This means that at high concentrations of  $CO_2$  the vapour pressure of the mixtures should be close to its critical pressure (73.83 bar [36]), however, it is nearly 20 bar lower than that. Moreover, the second data set was measured at 313.2 K, which is 9 K higher than the critical point of  $CO_2$ , but the vapour pressures of the mixtures with a significant excess of  $CO_2$  are still lower than its critical pressure.

Note, however, that the CPA model predictions account for this behaviour and show reasonable vapour pressures for the CO<sub>2</sub>-rich mixtures. This is due to the fact that the CPA pure fluid parameters are fitted to the pure compound vapour pressure. In the present work only one adjustable parameter  $k_{ij}$  is considered for the CO<sub>2</sub>-butanal binary, as shown in Fig. 3.

The temperature independent binary interaction parameter was estimated for the  $CO_2$ -2-butenal system based on the *P*-*x*-*T* experimental data obtained in the present study. The CPA model



**Fig. 3.** CO<sub>2</sub>-butanal VLE. Experimental data (points) at different temperatures and CPA calculations (lines) with a temperature independent  $k_{ij}$  = -0.2859. On the right: carbon dioxide-butanal VLE in the CO<sub>2</sub>-rich region.



**Fig. 4.**  $CO_2$ -2-butenal VLE. Experimental data (points) at different temperatures and CPA calculations (lines) with a temperature independent  $k_{ij} = -0.0180$ .

predictions are in good agreement with the bubble point pressures of the binary mixtures of different composition at three different temperatures, as shown in Fig. 4.

The phase behaviour of  $CO_2$ -2-butenal resembles that of the  $CO_2$ -butanal binary mixture. However, the vapour pressures of the  $CO_2$  binaries with butanal are lower than those with 2-butenal at the same composition. This might be explained by the fact that 2-butenal is more polar than butanal, dipole moment 3.66 versus 2.72 D, respectively [36]. Carbon dioxide, in turn, is a non-polar compound, and therefore, less polar components, such as butanal, are more soluble in it, which explains the lower vapour pressures of binary mixtures.

The  $k_{ij}$  parameter for the hydrogen–butanal system was estimated using available P–x–T data at different temperatures. The H<sub>2</sub>–butanal mixture had been previously investigated by Ke et al. [38], where the authors used the Peng–Robinson equation of state which required a temperature dependent  $k_{ij}$ . However, due to its small value they set it to zero in their further calculations. When using the CPA model one temperature independent parameter is sufficient, as shown in Fig. 5. Again, due to the similarity of CPA with SRK for non-associating components, this improvement is attributed to the inclusion of vapour pressure data in the pure compound parameter estimation.

#### 4.3. CPA predictions for the multicomponent reaction system

The catalytic results have shown that the conversion of 2butenal is dependent on the amount of  $CO_2$  loaded into the reactor (Table 1). There are multiple effects caused by the addition of  $CO_2$  to the system. Firstly, the more carbon dioxide is used in a batch autoclave the higher the reaction pressure. The partial pressures of the reacting components, however, do not change and, therefore, the thermodynamic equilibrium is not affected by the increasing pressure, as seen in Scheme 1. What possibly happens is that the amount



**Fig. 5.** Hydrogen–butanal VLE. Experimental data (points) at different temperatures and CPA calculations (lines) with a temperature independent interaction parameter  $k_{ij} = -0.0436$ .

of  $CO_2$  determines the number and composition of the phases coexisting in the reactor as well as the dissolution power of hydrogen in the  $CO_2$ -expanded liquid reactant phase. The liquid (or more general, the denser phase) is of particular interest, because it is in direct contact with the solid catalyst at the bottom of the autoclave and, therefore, the reaction occurs in this dense fluid. In order to determine the initial concentrations of the components in the 2-butenal hydrogenation reaction, the CPA equation of state together with the binary interaction parameters estimated in the present work were used. The concentrations of the components and the number of phases present in the reactor before reaction are presented in Table 5 and underline the presence of a  $CO_2$ -expanded reactant phase. The amount of  $CO_2$  increases with pressure, whereas for hydrogen in only increases between 70 and 138 bar.

Table 5 shows that in most cases the reaction started at biphasic conditions and only when a large excess of  $CO_2$  was used, the reaction ran in the single phase regime.

However, at this point another question arises, i.e. whether the number of phases changes as the reaction proceeds. In this regard, P-T regions where the multicomponent reaction mixture exists in one or two phases depending on the conversion were calculated with CPA. It was assumed that the mole ratio of the components in the initial mixture was CO<sub>2</sub>:H<sub>2</sub>:2-butenal = 25:2.5:1. No conversion, 20, 40, 60, 80% and full conversion were considered. The corresponding compositions of the mixtures are presented in Table 6, and the obtained P-T diagrams are shown in Fig. 6. According to this figure and the phase behaviour calculations, if the mentioned above initial reaction mixture starts to react, for instance, at 313 K and 175 bar, it means that before the reaction (t=0) it exists in one single phase, and it will stay in one phase even after all 2-butenal has converted. If the reaction occurs under the same conditions but at a pressure in the system of around 130 bar, the predictions imply that the initial system is bi-phasic, however,

Table 5
Phase composition of the reaction mixture before reaction.

<i>Т</i> , К	P, bar	Feed composition, mol		Number of phases	Compositio	n of the liquid (de	nse) phase, mole fraction	
		CO <sub>2</sub>	H <sub>2</sub>	2-Butenal		CO <sub>2</sub>	H <sub>2</sub>	2-Butenal
323	22	0.00	0.1	0.04	2	0.000	0.007	0.993
323	34	0.09	0.1	0.04	2	0.178	0.006	0.816
323	50	0.23	0.1	0.04	2	0.367	0.006	0.627
323	70	0.64	0.1	0.04	2	0.604	0.006	0.390
323	98	0.77	0.1	0.04	2	0.770	0.014	0.216
323	111	1.02	0.1	0.04	2	0.817	0.021	0.162
323	126	1.36	0.1	0.04	2	0.911	0.043	0.045
323	138	1.59	0.1	0.04	1	0.919	0.057	0.024
323	150	1.86	0.1	0.04	1	0.930	0.050	0.020
323	185	2.09	0.1	0.04	1	0.937	0.045	0.018

#### Table 6

Composition of a reaction mixture with a ratio  $\text{CO}_2$ :H<sub>2</sub>:2-butenal:butanal at different conversion.

Mixture	Conversion, %	Composition of the reaction mixture, mol				
		CO <sub>2</sub>	$H_2$	2-Butenal	Butanal	
1	0	25	2.5	1.0	0	
2	20	25	2.3	0.8	0.2	
3	40	25	2.1	0.6	0.4	
4	60	25	1.9	0.4	0.6	
5	80	25	1.7	0.2	0.8	
6	100	25	1.5	0.0	1.0	

as the reaction proceeds, at some point the phase transition will occur and the system will become mono-phasic. Finally, if the reaction pressure is 90 bar, the reaction will begin in the two phase region and it will stay like this even after all substrate has reacted.

#### 5. Discussion

The results of the catalytic studies (Table 1) show that the presence of small amounts of carbon dioxide in the reacting system deteriorates catalytic performance; however, higher amounts of carbon dioxide added to the system leads to higher conversion. As mentioned above, this might be due to the concentration and phase behaviour effects arising when more  $CO_2$  is added to the system. The calculations performed with CPA show that the amount of  $CO_2$  used in the reaction determines the number of phases, their composition and total pressure in the reaction, as shown in Table 5.

Most of the time, the reactions occurred in the biphasic region. This means that the initial reaction kinetics was determined by the initial concentrations of the components in the liquid phase, which is in direct contact with the catalyst. The reaction pathway in the biphasic region might be easily impeded by mass transfer limitations, i.e. diffusion of the components (particularly hydrogen) from the gas phase to the liquid and further to the catalyst surface. Under single phase conditions, the concentration of all the components was constant in the whole volume of the reaction mixture due to intense stirring, therefore, possible external mass transfer limitations were minimised. However, as it was shown by the calculations the maximum catalyst activity was observed at a CO<sub>2</sub>:2-butenal ratio near the critical point of the reaction mixture, where the phase transition occurred. Further dilution of the system with CO<sub>2</sub> caused a decrease of catalytic activity. In other words, even though the reaction conditions were in favour of higher conversion, i.e. minimised mass transfer effects, the opposite was observed.

A similar observation was made by Burgener et al. [24], where they found that at higher hydrogen concentrations the



**Fig. 6.** CPA predictions of the bubble and dew point curves for the reaction mixtures during the selective hydrogenation of 2-butenal in carbon dioxide. The composition of every mixture is shown in Table 6.

catalytic performance decreased, which was against the expectation from reaction thermodynamics and kinetics. A significant change occurred when the system moved to an "expanded liquid" where maximal conversion was obtained. Unlike in the present study, this phase transition occurred due to the fact that hydrogen decreased the dissolution power of carbon dioxide, and as a consequence, the one phase system split into two phases. Furthermore, in an earlier study by Tschan et al. [39], the authors investigated the selective semi-hydrogenation of propargyl alcohol in supercritical carbon dioxide. They concluded that in the two phase region excessive amounts of hydrogen are required in order to maintain a sufficient supply through the liquid layer to the catalyst surface, whereas when working in a single phase lower hydrogen concentrations are needed for the selective semi-hydrogenation of propargyl alcohol due to the minimised mass transport limitations. In both studies the concentrations of hydrogen in the reaction phase was speculated to be crucial.

In the present study, thermodynamic calculations were used to provide insight into the behaviour during the hydrogenation of 2-butenal. Table 5 suggests that the concentration of 2-butenal gradually decreased when more CO<sub>2</sub> was added to the system, whereas the concentration of hydrogen was more or less stable at the very beginning and after a certain point it started to rise to the point where the phase transition occurred, as shown in Fig. 7. At this point the concentration of hydrogen in the dense layer was maximal, and then it started to decrease gradually. The maximum concentration of hydrogen coincides with the maximum catalytic activity. Interestingly, only C=C-hydrogenation and not carbonyl hydrogenation was observed despite the group of Arai and co-workers [40,41] have shown that there is a strong interaction between CO<sub>2</sub> and unsaturated aldehydes such as cinnamaldehyde, which affects the selectivity. Therefore, due to the fact that the concentration of 2-butenal was decreasing at the beginning while the concentration of hydrogen in the liquid layer was constant the reaction rate was decreasing as well. After the point where the concentration of hydrogen started to increase, the reaction rate increased as well. These observations are in line with the conclusions for the abovementioned reactions studied by Burgener et al. [24] and Tschan et al. [39]. Fig. 7 further shows that in the one phase region the concentration of hydrogen decreases while the concentration of the substrate stays almost unchanged; thereby possibly explaining the decrease in the catalytic activity. Furthermore, the excessive amounts of carbon dioxide at high reaction pressures may



**Fig. 7.** Mole fractions (CPA lines) of hydrogen and 2-butenal in the liquid (dense) phase which is in contact with the catalyst and conversion of 2-butenal (bars) depending on the initial CO<sub>2</sub>:2-butenal mole ratio. *Conditions*: 2-butenal 0.04 mol, H<sub>2</sub>:2-butenal mole ratio 2.5:1,  $m_{cat}$  = 0.01 g, T = 323.2 K, reaction time 60 min. Shaded area – one phase region.

cause its strong adsorption on the catalyst surface, which competes with the adsorption of hydrogen and 2-butenal. In addition, both Zhao et al. [42] and Burgener et al. [43] found reaction of  $CO_2$  and hydrogen under single phase conditions on noble metal particles.

Further CPA calculations of the P-T regions of co-existing phases (Fig. 6) showed that the system phase transition at a constant temperature and elevated pressures decreases towards lower pressures as the reaction proceeds. This means that if the initial reaction mixture (at t = 0) was in a single phase it stayed in one phase even after all the 2-butenal had reacted. However, depending on the composition, T and P, in some cases the reaction may begin in the two phase region, but at a certain conversion the phase transition may occur and the system will become single phase. These changes of the phase behaviour as a result of concentration changes during reaction have to be considered for proper interpretation of reaction kinetics and the CPA calculations proved to be an elegant tool for this task.

Usually, carbon dioxide is considered as an inert reaction medium, however, some recent findings revealed that under certain conditions, i.e. in the presence of hydrogen and noble metals already at relatively low temperatures, CO<sub>2</sub> can react with hydrogen in the so-called reverse water-gas shift reaction and form carbon monoxide and water [43,44]. The former acts as catalyst poison especially for low coordinated metal sites [45], and thereby sometimes changes the catalyst selectivity [46]. Despite poisoning by CO might be the case in the present study, this is hardly the main reason because of the too strong drop in conversion when excessively large amounts of CO<sub>2</sub> were used. As it was pointed out by Burgener et al. [43], the reverse water-gas shift reaction takes place in many hydrogenation reactions and under hydrogenation conditions metal surfaces are partially covered with CO, however, this effect is mostly restricted to low coordinated Pt-sites.

Another type of intermolecular interactions can play an important role when reactions are performed in scCO<sub>2</sub>. Carbon dioxide, possessing electron-accepting properties, can easily interact with other functional groups in organic molecules, such as aldehydes, ketones, esters, etc. Such interactions and their pressure dependency have been studied using high-pressure FT-infrared spectroscopy [40,41]. It was found that CO<sub>2</sub> is capable of activating of carbonyl groups in organic aldehydes and this effect is different for saturated and unsaturated ones [41]. Thus, in the hydrogenation of benzaldehyde the conversion into benzyl alcohol is merely decreasing with increasing CO<sub>2</sub> pressure due to dilution of the system, whereas for cinnamaldehyde conversion reaches a maximum. The authors attribute it to the activation of C=O bond in cinnamaldehyde by CO2 at low pressures, and at elevated pressures this effect disappears and conversion decreases due to the dilution of the system. Despite in the present study another type of hydrogenation is relevant, i.e. C=C bond saturation, the presence of intermolecular forces between CO<sub>2</sub> and aldehydes is indirectly indicated by binary interaction parameters  $k_{ij}$  (Table 4), which is attributed to the non-ideality of the binary systems. The significance of such interactions is that they determine the phase behaviour of the system, which in turn determines the catalyst performance as it was discussed above.

#### 6. Conclusion

The influence of the phase behaviour on the palladium-catalysed selective hydrogenation of 2-butenal to butanal was investigated. For this purpose the CPA equation of state was successfully used and directly provided a correlation between the concentrations of the reactants in the fluid phase and the reaction rate. The interaction parameters for three binaries were estimated using

experimental data from the literature. The binary mixture carbon dioxide-2-butenal was experimentally studied in order to find the bubble point pressures at different temperatures. Based on this experimental data the binary interaction parameter was obtained.

The CPA model is shown to be a powerful tool allowing thermodynamic calculations with high precision and accuracy. Using CPA the number of co-existing phases was predicted, and the concentrations of the reacting components in coexisting phases were calculated. These data are very important and useful for further kinetic studies where knowledge of concentrations in individual phases is a key element.

Furthermore, calculations using CPA gave insight into the phase behaviour during the reaction, showing that the pressures and temperatures at which a one phase region exists are decreasing as the reaction proceeds.

The catalytic studies showed that maximum conversion was achieved when the reaction mixture changed from one-phase to the two-phase regions, near the critical point of the system. The concentrations of the components in the reaction mixture, calculated with CPA, were shown to cause such behaviour.

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