

Palladium-catalysed dehydrogenation of 1-phenylethanol in dense carbon dioxide

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Abstract

The feasibility of the heterogeneous catalytic dehydrogenation of alcohols in dense (sub- and supercritical) carbon dioxide is shown by the transformation of 1-phenylethanol in a continuous flow fixed-bed reactor. A 0.5 wt.% Pd/Al₂O₃ catalyst afforded reasonably good activity (turnover frequency (TOF): 15 h⁻¹ at 155 °C) and up to 100% selectivity to acetophenone. An interesting feature of the reaction is that the conversion and selectivity varied parallel under conditions investigated (80–165 °C, 30–190 bar, CO₂/alcohol molar ratio: 30–360). Reaction rate and ketone selectivity were favored at high temperature (around 150 °C), low total pressure (favourably in the subcritical region), high CO₂ and low alcohol flow rates. Under these conditions, interfacial mass transport and removal of the co-product hydrogen is enhanced. No catalyst deactivation was observed within about 300 h on stream.

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Keywords: Dehydrogenation of 1-phenylethanol; Supercritical carbon dioxide; Acetophenone; Pd/Al₂O₃

1. Introduction

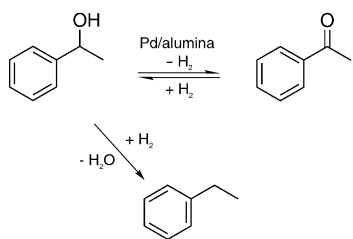
Dehydrogenation of alcohols in solid/gas type reactors is a well established method for the production of simple, thermally resistant aldehydes and ketones [1–3]. The reaction is endothermic and reversible; the equilibrium is limited by the formation of two moles of products from one mole of alcohol. In order to achieve high yields, the equilibrium has to be shifted by applying high reaction temperature (usually 200–450 °C), low total pressure, or an inert diluent. Major limitation of the method is that at the necessary high temperature dehydration and polymerization, or degradation of more complex molecules, may dominate the transformation.

The aim of the present work was to investigate this reaction in supercritical fluids that would allow the application of relatively low temperature and the transformation of more complex, non-volatile alcohols. Supercritical fluids have numer-

ous advantages compared to conventional organic solvents, including the easy separation of the solvent and the enhanced mass transfer [4–10]. Carbon dioxide is an environmentally benign reaction medium that has a critical point at mild conditions ($T_c = 30.9$ °C, $p_c = 73.8$ bar). It is non-flammable, relatively inert, and available at low cost. Note that in chemistry the expression “supercritical” is generally used for multi-component systems being beyond the critical point of the solvent or the mixture. In fluid theory, however, the term is defined only for a single-component system and has no meaning concerning phase behavior of multi-component systems [11,12].

Supercritical solvents have found numerous applications in homogeneous [9,13,14] and heterogeneous catalysis [8,12], but reports on dehydrogenation in supercritical fluids are rare. The catalytic dehydrogenation of C₁₀–C₁₄ paraffins showed that the thermodynamic equilibrium was strongly shifted when the reactants were in a supercritical phase [15]. Dehydrogenation of ethanol and 2-propanol was carried out in supercritical water at elevated temperature [16,17].

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Scheme 1. Palladium-catalyzed dehydrogenation and hydrogenolysis of 1-phenylethanol.

Here, we have chosen the transformation of 1-phenylethanol to acetophenone to test the feasibility of alcohol dehydrogenation in supercritical carbon dioxide (Scheme 1). Dehydrogenation of 1-phenylethanol in the gas phase has already been studied over various oxides [18,19] and supported Cu [20] at 200 °C, and on NaZnPO₄ [21] at 350 °C. In the latter case, high selectivities were obtained. When the reaction was carried out in refluxing toluene over Raney-Ni, a 1:1 mixture of acetophenone and ethylbenzene formed and the selectivity to acetophenone could be improved only by addition of an olefin as hydrogen acceptor [22].

2. Experimental

2.1. Materials

1-Phenylethanol (98%, Aldrich), ethyl acetate (99.5%, Merck) and carbon dioxide (99.9%, PanGas) were used as delivered. A sieved fraction (ca. 0.5–1.4 mm) of a shell-impregnated 0.5 wt.% Pd/Al₂O₃ catalyst was used for the hydrogenation reactions (Engelhard 99812, metal dispersion: 0.29 determined by hydrogen chemisorption).

2.2. Continuous high pressure reactor system

The dehydrogenation experiments were carried out in a computer-controlled continuous flow stainless steel reactor system designed for pressures up to 300 bar and temperatures up to 200 °C. The apparatus, which essentially consisted of a dosing system for the reactant (1-phenylethanol, PE) and the solvent (CO₂), a tubular reactor, pressure and temperature control and automatic sampling, is shown in Fig. 1. The liquid reactant was being fed into the system through an HPLC pump (Jasco PU-980). The carbon dioxide flow was controlled by a combination of a flow meter (HI-Tec Bronkhorst; El-Flow) and a needle valve (Kämmer). In the mixing chamber, equipped with a mechanical Teflon stirrer and a rupture disk (300 bar), all feed streams were combined before entering the vertically mounted reactor section (RS: i.d. = 25 mm; length = 125 mm). The reactor section consisted of an inner stainless-steel tube with an i.d. of 25 mm closed by steel frits towards both ends. Tem-

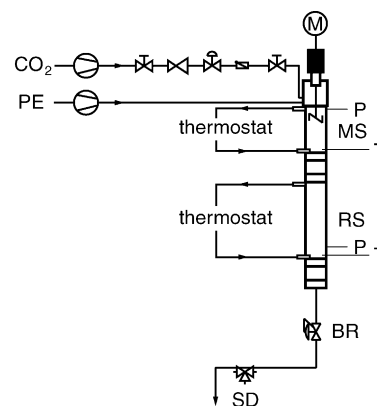


Fig. 1. Schematic illustration of the high pressure continuous fixed-bed reactor. MS: mixing section; RS: reactor section; BR: back pressure regulator; SD: sampling device; T: temperature measurement and P: pressure measurement; PE: 1-phenylethanol.

perature of the mixing chamber and the reactor section was regulated with two independent thermostats (Julabo type HD-4 and type F32-HD). The pressure in the reactor was controlled with a backpressure regulator (Tescom Series 26-1700) located right after the reactor section. The valve was wrapped with a strip heater to prevent the backpressure regulator from freezing due the expansion of carbon dioxide. The samples were branched off from the product stream at intervals of 60 min by a computer-controlled three-way valve placed after the backpressure regulator. The complete setup was controlled by an automatic process computer (Eurotherm). A more detailed description of the reactor system has been reported elsewhere [23].

The samples were analyzed gas-chromatographically (HP 6890) after dilution with ethyl acetate. The chromatograph was equipped with an auto sampling device (HP 7683) a split/splitless injector (1 μ l sample volume), a capillary column (HP-FFAP; 0.25 μ m, 30 m, 0.32 mm), and a flame ionization detector. Helium was used as carrier gas. Selectivity was defined as Y_i/X_i (Y_i , yield of a product; X_i , conversion of 1-phenylethanol), in percentage.

2.3. Catalytic studies

The reaction section was filled with 5 g 0.5 wt.% shell-impregnated and crushed Pd/Al₂O₃ (particle size, d_p ; in the range, 0.5–1.4 mm) resulting in a catalyst bed length L of approximately 85 mm (plus quartz wool plugs) and a ratio $L/d_p = 90$. Under standard reaction conditions, at 145 °C, the 1-phenylethanol flow was 5.47 g h⁻¹ and the carbon dioxide flow 180 NL h⁻¹, corresponding to a molar ratio of 1-phenylethanol:CO₂ = 1:180. The space time related quantity W/F was 112 g h mol⁻¹ (W : catalyst mass, F : molar feed rate). The values presented in Table 1 and the figures are the average of those measured after 1 and 2 h time-on-stream (after setting the specified parameters).

Table 1
Influence of temperature on the conversion of 1-phenylethanol (PE) and selectivity to acetophenone^a

Temperature (°C)	Pressure (bar)	CO ₂ :PE (molar ratio)	Conversion (%)	Selectivity (%)
80	50	100:1	6	70
90	50	160:1	12	100
100	50	160:1	13	100
115	50	160:1	21	100
135	50	160:1	42	96
145	50	180:1	60	97
155	40	210:1	59	99
165	40	210:1	59	99

^a Other conditions as specified in Section 2.

The average turnover frequencies related to the number of surface Pd sites were estimated using Eq. (1):

$$\text{TOF} = \frac{X F_{\text{PE}} M_{\text{Pd}}}{m_{\text{cat}} \text{Pd}_{\text{loading}} D} \quad (1)$$

where X is the conversion of 1-phenylethanol; F_{PE} , molar 1-phenylethanol flow; M_{Pd} , the atomic mass of Pd (106.4 g mol⁻¹); m_{cat} , the amount of catalyst (g), and D represents the Pd dispersion (ratio of surface to total number of metal atoms, 0.29, determined by hydrogen chemisorption).

3. Results and discussion

Preliminary experiments revealed that below 90 °C the activity of the 0.5 wt.% Pd/Al₂O₃ catalyst was low and the selectivity to acetophenone poor. Some selected values are collected in Table 1 for illustration. At lower temperatures the formation of hydrogen and its removal from the surface were slow, resulting in extensive hydrogenolysis of the aromatic alcohol reactant to the corresponding hydrocarbon (Scheme 1). Other noble metal catalysts (e.g. supported Pt) were even less active, in agreement with an earlier study of the transfer dehydrogenation of alcohols in refluxing cyclohexane with supported noble metal catalysts [24].

The selected Pd/Al₂O₃ catalyst was very robust and stable: steady state in conversion and selectivities was obtained within 1 h and no deactivation was observed during the whole study (ca. 300 h on stream). The following investigation of the role of some important reaction parameters was carried out at 145 °C.

The influence of total pressure on the conversion and selectivity at constant flow rates of 1-phenylethanol and carbon dioxide is shown in Fig. 2. The lower alcohol conversion achieved at high pressure is in agreement with the formation of two moles of products from 1 mole reactant. The selectivity to acetophenone was high, 95–98% in the whole pressure range. Under the reaction conditions, at 145 °C, the system was far from the critical density of carbon dioxide (466 kg/m). On the basis of the T_s diagram of carbon dioxide [25] and the phase equilibrium of the carbon dioxide–2-phenylethanol mixture at 40–50 °C [26], we estimate that pressures in the range 250–300 bar would be necessary to reach the one-phase region at 145 °C.

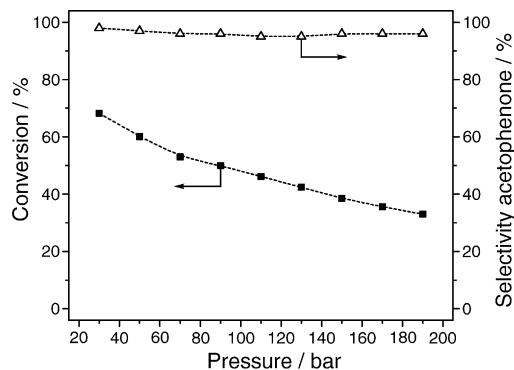


Fig. 2. Influence of total pressure on the conversion of 1-phenylethanol and selectivity to acetophenone; other conditions as specified in Section 2 (standard conditions).

Next, the mass flow rate of 1-phenylethanol was varied while the total pressure and the carbon dioxide flow rate were kept constant (Fig. 3). The conversion decreased with increasing flow rate, as expected, because higher reactant mass flow corresponds to lower residence time. The best selectivity to acetophenone (100%) was obtained at the lowest 1-phenylethanol flow rate but the selectivity remained excellent (97%) even at the highest flow rate.

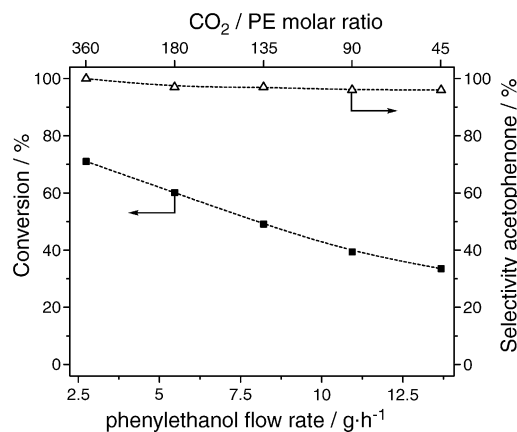


Fig. 3. Influence of the variation of 1-phenylethanol mass flow rate on the conversion and selectivity; standard conditions, 50 bar. The corresponding carbon dioxide/1-phenylethanol (PE) molar ratio is indicated at the top.

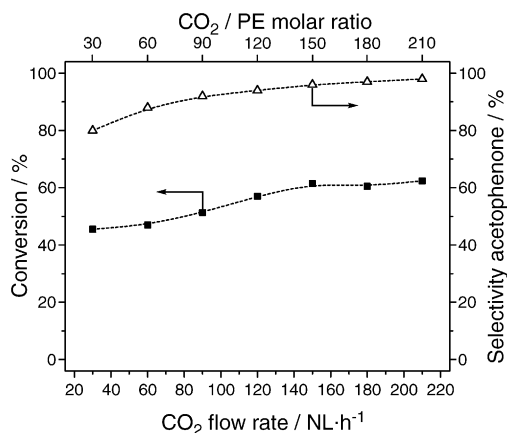


Fig. 4. Influence of the CO₂ flow rate on the conversion and selectivity; standard conditions, 50 bar. Variation of the corresponding carbon dioxide/1-phenylethanol (PE) molar ratio is indicated at the top.

A partly different correlation was obtained when the carbon dioxide/1-phenylethanol molar ratio was changed by variation of the carbon dioxide flow rate at constant total pressure and 1-phenylethanol flow rate (i.e. at constant residence time, Fig. 4). Both conversion and selectivity improved significantly with increasing carbon dioxide mass flow rate, though the conversion reached its limit at a carbon dioxide/1-phenylethanol molar ratio of 150. The probable explanation for these changes is that high CO₂ flow reduces the thickness of the stagnant liquid film around the catalyst particles and thus diminishes the external film diffusion resistance. Besides, high carbon dioxide flow rate facilitates the removal of the coproduct hydrogen and suppresses the hydrogenolysis of 1-phenylethanol to ethyl benzene. Higher dilution by carbon dioxide is expected also to shift the equilibrium towards the ketone (thermodynamic control).

Though optimization of the reaction conditions to achieve the highest acetophenone yield has not been attempted yet, during the study, we found several sets of parameters that allow the formation of acetophenone without any detectable byproduct. Among them, the highest conversion of 88% was measured at 155 °C, 25 bar, and a carbon dioxide/1-phenylethanol molar ratio of 675. Under these conditions, the average turnover frequency (TOF) was 15.4 h⁻¹. The conversion can be further increased by decreasing the flow rate or increasing the amount of catalyst.

It is also interesting to compare our results to the very few data available on the gas phase and liquid phase dehydrogenation of 1-phenylethanol. The reaction over NaZnPO₄ afforded similar selectivity (97–99%) at lower conversion (56–71%) [21]. The reaction temperature was, however, remarkably higher (350 °C). That condition renders the process unattractive for the transformation of more complex, thermally labile alcohols. In the liquid phase in apolar solvents, reasonable selectivity could be achieved only by addition of a hydrogen acceptor, such as an olefin [22,24,27] or molecular oxygen [28].

4. Conclusions

The present study shows that the heterogeneous catalytic dehydrogenation of alcohols in supercritical carbon dioxide is a feasible process. In the model reaction, the transformation of 1-phenylethanol to acetophenone, the 0.5 wt.% Pd/Al₂O₃ catalyst afforded up to 100% selectivity at 88% conversion, at relatively low temperature of around 150 °C. The only byproduct detected was ethyl benzene that formed by hydrogenolysis of the reactant under conditions where the removal of the coproduct hydrogen was too slow. No dehydration or oligomerization type side reactions occurred that are typical for the vapor phase dehydrogenation of alcohols carried out at elevated temperatures. A further important advantage of the process is the excellent stability of the catalyst during the whole period of this study, about 300 h on stream.

Acknowledgement

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