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Membrane reactor for homogeneous catalysis in supercritical carbon dioxide

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Abstract

A membrane reactor is presented for homogeneous catalysis in supercritical carbon dioxide with in situ catalyst separation. This concept offers the advantages of benign high-density gases, i.e., the possibility of achieving a high concentration of gaseous reactants in the same phase as the substrates and catalyst as well as easy catalyst localization by means of a membrane. For the separation of the homogeneous catalyst from the products an inorganic microporous membrane is used. The concept is demonstrated for the hydrogenation of 1-butene using a fluorous derivative of Wilkinson's catalyst [RhCl{P–(C_6H_4-p-$SiMe_2CH_2CH_2C_8F_{17}$)$_3$}$_3$]. The size of Wilkinson's catalyst, 2–4 nm, is clearly larger than the pore diameter, 0.5–0.8 nm, of the silica membrane. The membrane will, therefore, retain the catalyst, while the substrates and products diffuse through the membrane. Stable operation and continuous production of n-butane has been achieved at a temperature of 353 K and a pressure of 20 MPa. A turnover number of 1.2×10^5 has been obtained during 32 h of reaction. The retention of the catalyst was checked using UV–vis spectroscopy and ICP-AAS; no rhodium or phosphorous species were detected at the permeate side of the membrane.
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1. Introduction

For a large number of reactions homogeneous catalysts have better activity and (enantio)selectivity, as compared to heterogeneous catalysts. There are, however, two main disadvantages related to the use of homogeneous catalysis. The first drawback is caused by the organic solvent used for the reaction medium, and the second drawback is the difficult separation of the catalyst from the products. With respect to the first drawback, increasing concern regarding the dissemination of volatile organic compounds, chloro–fluorocarbons, and aqueous waste streams into the environment has prompted the chemical industry to conform to more environmentally sound practices in the manufac-

ture and processing of products. It is generally thought that the use of supercritical solvents provides a powerful means to achieve these goals [1,2]. High-density carbon dioxide has some clear advantages for both extraction and reaction purposes [3]. This is due to the fact that supercritical carbon dioxide ($scCO_2$) has a low viscosity and that most species have a high diffusivity in $scCO_2$ [4]. Carbon dioxide has also a reasonable low critical temperature and pressure ($T_c = 304$ K and $P_c = 7.4$ MPa), is a cheap substance (approximately 0.05 US \$/kg), is nonflammable, and is nontoxic.

Use of supercritical fluids (SCFs) can lead to innovating processes utilizing the unique features of high-density gases. The complete miscibility of SCFs with other gases is one of the most interesting features [1]. This means that it is possible to obtain high concentrations of gases like hydrogen, oxygen, or carbon monoxide in a single phase with the substrates, as opposed to most liquids, which can only

solubilize a limited amount of gaseous species. Therefore, reactions in SCFs can be much faster than reactions in liquids, which is especially important for reactions with mass transfer limitations [5]. Furthermore, negative partial molar volumes in supercritical systems can be exploited to adjust rate constants of various reactions [6,7]. These aspects in combination with the high mass transfer rates observed for SCFs means that these solvents offer some specific advantages for homogeneous catalysis.

To resolve the second disadvantage of homogeneous catalysis, it is crucial to reuse and recycle the catalyst. In this study, a microporous membrane is used to immobilize a fluorous version of Wilkinson's catalyst. Wilkinson's catalyst is used for a homogeneous reaction in scCO$_2$. In this way the two major drawbacks associated with homogeneous catalysis are circumvented.

At the moment, mainly organic membranes are being used in carbon dioxide applications. However, organic membranes have several disadvantages for use in carbon dioxide, like swelling and stability. A number of different types of inorganic membranes are now becoming available which can be used for high-pressure applications [8–12]. Inorganic membranes exhibit physical and chemical properties that are not, or only partially, shown by organic membranes, including a better structural stability without the problems of swelling or compaction. Generally, they can withstand harsh chemical environments and high temperatures [13,14].

A group of inorganic membranes with favorable characteristics for use in supercritical applications are silica membranes. Brunner and co-workers [15] have used silica composite membranes with a fluorinated polymer selective top layer for extraction purposes. Silica has a high affinity for hydrophilic organic compounds while carbon dioxide does not adsorb too well on microporous silica, as compared to silicalite-1 zeolite and microporous carbons.

There are a number of examples of a homogeneous catalytic reaction carried out in a membrane reactor [16–19] or in supercritical media using gaseous reactants [20–23]. Most of the existing homogeneous catalysts have low solubility in scCO$_2$. The solubility can be increased by attaching groups with low cohesive energy density, like perfluoroalkyl tails, to the ligands of catalyst. For example, a fluorous version of Wilkinson's catalyst has been used for hydrogenation and hydroformulation reactions in scCO$_2$ [5].

Recently, fluorous triphenylphosphine containing a –SiMe$_2$CH$_2$CH$_2$–spacer has been used in the synthesis of a fluorous derivative of Wilkinson's catalyst for the hydrogenation of 1-octene under fluorous biphasic conditions [24,25]. This fluorinated version of Wilkinson's catalyst, **1**, using fluorous triarylphosphines P[C$_6$H$_4$-p-SiMe$_2$(CH$_2$)$_2$C$_n$F$_{2n+1}$]$_3$ makes it possible to fine-tune the catalyst with respect to catalytic activity, the solubility in scCO$_2$, and its size. When the perfluoroalkyl groups are attached, the solubility in scCO$_2$ as well as the size of Wilkinson's catalyst increase considerably.
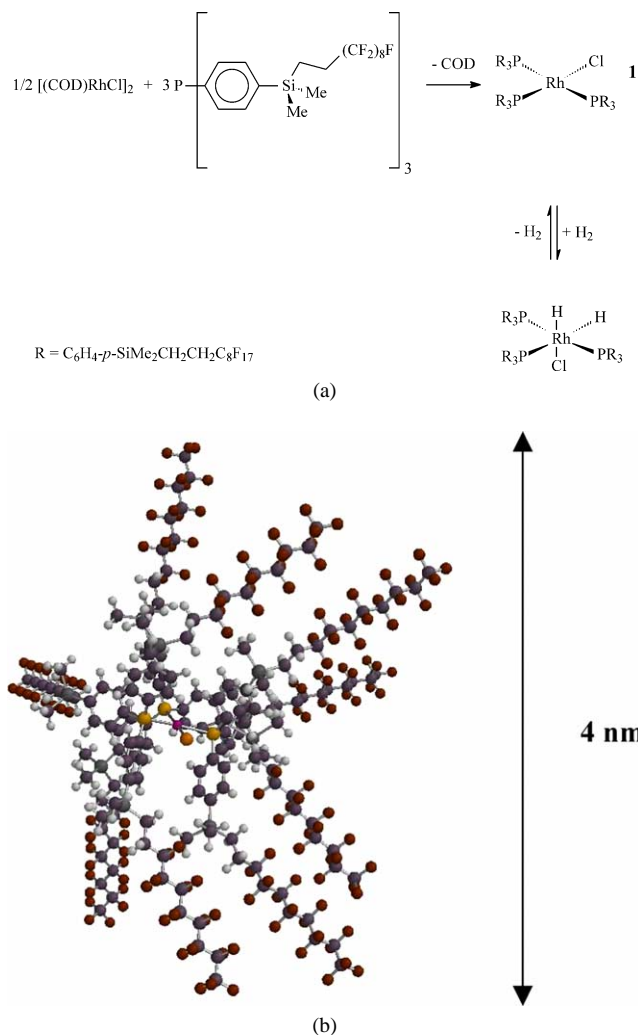

Fig. 1. (a) Synthesis of the fluorous derivative of Wilkinson's catalyst, **1**, containing a –SiMe$_2$CH$_2$CH$_2$–spacer. (b) Computational structure of **1** (MM94, Spartan 5.1.1. (SGI)).

The (idealized) synthesis route and the catalyst, **1**, are given in Figs. 1a and 1b, respectively. The size of **1**, obtained from computer modeling (molecular mechanics structural optimization using MM94, Spartan 5.1.1, SGI) and verified by dynamic light scattering experiments using a fluorous solvent, is between 2 and 4 nm. This means that a microporous membrane will reject Wilkinson's catalyst. According to the IUPAC definition, microporous materials have pore diameters smaller than 2 nm [26]. Furthermore, due to the hydrophilic nature of the membrane, the hydrophobic catalyst is not likely to adsorb on the surface of the membrane material. The membrane has a high affinity for water, while the catalyst has a high affinity for carbon dioxide.

In this work, a membrane reactor is described using scCO$_2$ as the solvent. The homogeneous catalyzed hydrogenation of 1-butene to n-butane with a fluorous derivative of Wilkinson's catalyst is carried out in scCO$_2$ using a microporous silica membrane to immobilize the catalyst. The
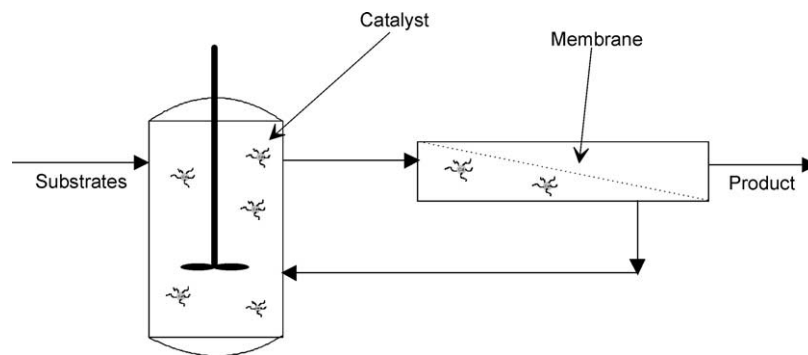
Fig. 2. Membrane reactor for continuous homogeneously catalyzed reactions in supercritical carbon dioxide.

principle of the membrane reactor is shown schematically in Fig. 2.

2. Experimental

2.1. Materials

Hydrogen (grade 5.0), carbon dioxide (grade 5.0), and 1-butene (grade 2.5) were obtained from HoekLoos (Amsterdam, The Netherlands).

The membrane permeation experiments and the continuous membrane reactor experiments were performed with a tubular microporous silica membrane provided by ECN (Petten, The Netherlands). The membrane consists of several support layers of α- and γ-alumina, and the selective top layer at the outer wall of the tube is made of amorphous silica [27]. The silica layer has a thickness of 200 nm. The silica top layer has a small pore size distribution with pores between 0.5 and 0.8 nm, with an average pore diameter of 0.6 nm. The membrane is 0.30-m long and has a diameter of 14 mm.

2.2. In situ catalyst preparation

A fluorous version of Wilkinson's catalyst was prepared in situ from 1 eq. of [RhCl(COD)]$_2$ (COD = *cis,cis*-1,5-cyclooctadiene) and 6 eq. of P[C$_6$H$_4$-*p*-SiMe$_2$(CH$_2$)$_2$ C$_8$F$_{17}$]$_3$. The fluorous phosphine ligand was synthesized as reported by Richter et al. [24]. The amounts used in the synthesis are given in Table 1. The two precursors were added to the reactor in a 1:6 molar ratio, i.e., one rhodium atom per three fluorous ligand molecules. The idealized reaction scheme for the synthesis of the fluorinated catalyst is given

in Fig. 1a. The reactor was flushed with carbon dioxide to remove the oxygen. The catalyst was formed, at a temperature of 353 K, from the precursors by pressurizing the reactor with a mixture of carbon dioxide and hydrogen. During the first 2 h of the assembly of the catalyst the pressure was equal to 10 MPa. After 2 h the pressure was increased to 20 MPa to solubilize Wilkinson's catalyst. During the formation of the catalyst and during the hydrogenation of 1-butene, the concentration of Wilkinson's catalyst was measured with a Spectronic Genesys 5 spectrophotometer by following the absorption at 410 nm.

2.3. Batch reactor

The homogeneously catalyzed hydrogenation of 1-butene in supercritical carbon dioxide was first performed in a high-pressure batch setup depicted in Fig. 3. The volume of the reactor was varied with a piston between 16 and 31 mL. The reactor is equipped with two opposite sapphire windows, a heater, and a Pt100 thermometer. The reactor was pressurized using a LKB HPLC pump, and the pressure was monitored by a Meyvis 802-C pressure module. Samples were taken at a constant pressure provided by the piston. After the formation of the catalyst (1 μM) the hydrogenation was started by the addition of 1-butene (0.02 M) and hydrogen (0.08 M). To determine the yield of the reaction, the samples were analyzed by GC and GC-MS. The GC (Chrompack CP 9001) had a TCD detector equipped with a PoraPLOT Q packed column with a length of 1.9 m. The GC-MS was equipped with a 50-m CP-Al$_2$O$_3$/KCl column.

2.4. Permeation of supercritical carbon dioxide

The membrane permeability for high-density carbon dioxide was measured at 353 K with the high-pressure setup depicted in Fig. 4. The ceramic membrane was placed in an oven (Heraeus) and the temperature was controlled with a Pt100 thermometer. The membrane setup can be pressurized at the feed and permeate side up to 20 MPa. For a flux measurement, the needle valve at the permeate side of the membrane was opened until a trans-membrane pressure was reached varying between 1 and 3 MPa. After the permeate needle valve was closed, the trans-membrane pressure

Table 1
Amounts used in the synthesis of **1**

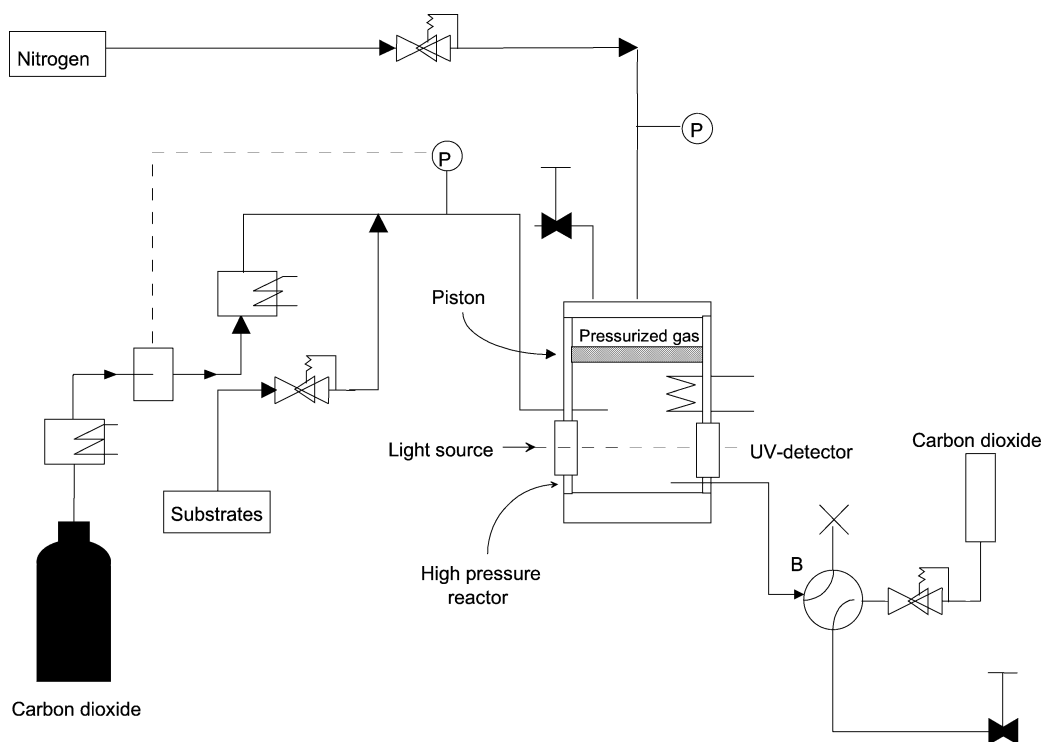|	P-(C$_6$H$_4$-*p*-SiMe$_2$CH$_2$CH$_2$C$_8$F$_{17}$)$_3$		[RhCl(COD)]$_2$	
	m (g)	*m* (mol)	*m* (g)	*m* (mol)
Batch reactor	1.9×10^{-3}	1.1×10^{-6}	9.0×10^{-5}	2.2×10^{-7}
Membrane reactor	1.7×10^{-3}	1.0×10^{-6}	1.0×10^{-4}	1.8×10^{-7}

Fig. 3. High-pressure setup for homogeneous catalyzed batch reactions.

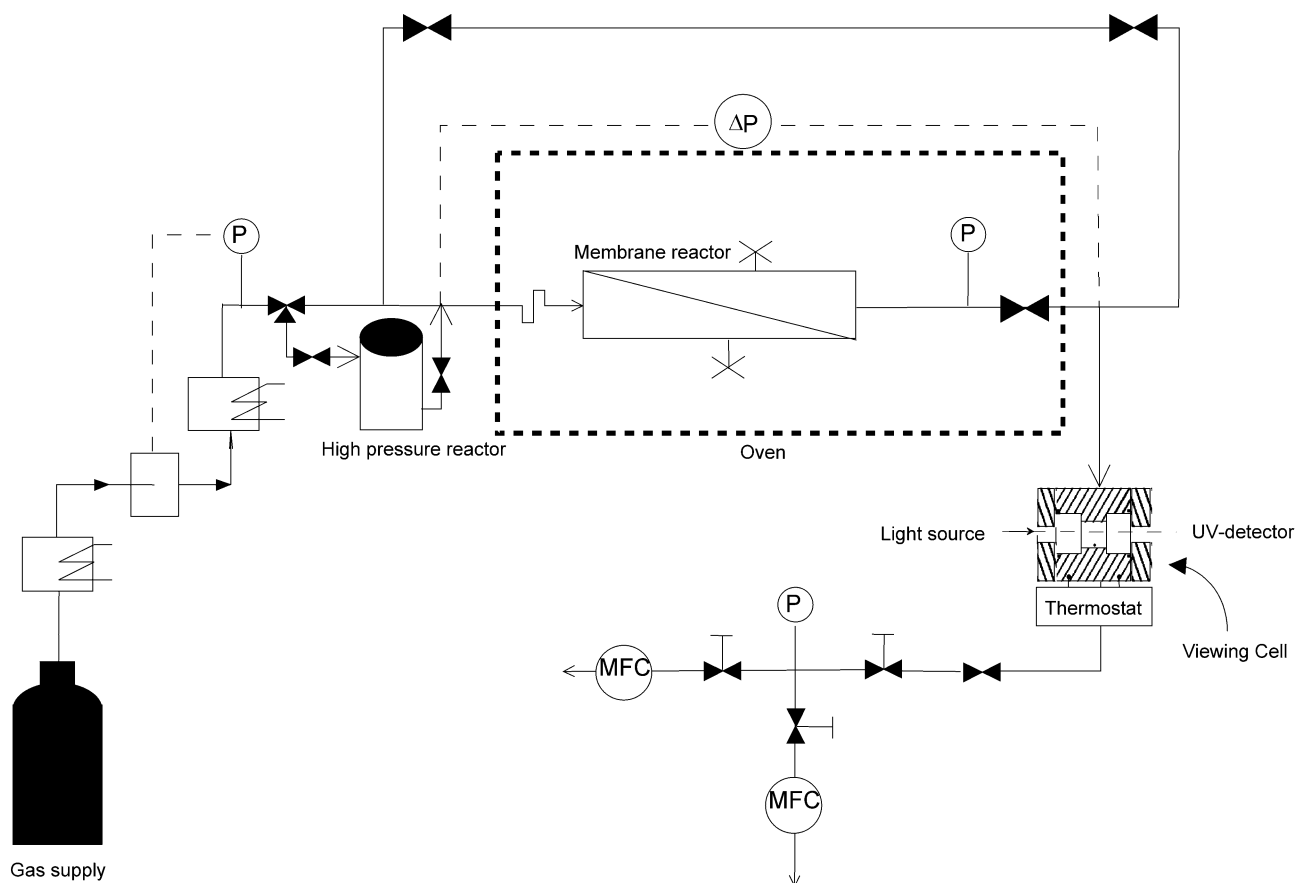Fig. 4. High-pressure membrane reactor set-up.

was measured with a pressure-difference meter from Druck (Smart Pressure Transmitter STX 2100).

2.5. Continuous membrane reactor

The continuous hydrogenation reaction in supercritical carbon dioxide (353 K, 20 MPa) with the membrane reactor was performed in the same high-pressure setup as used for the permeation experiments; see Fig. 4. The catalyst was first synthesized in situ in the high-pressure reactor, as described above. The reaction was started by the addition of the 1-butene and hydrogen in a molar ratio of 1:4. The catalyst concentration was equal to 1.0×10^{-6} mol/L. The concentration of 1-butene and hydrogen in the feed was equal to 0.02 and 0.08 mol/L, respectively, at a total pressure of 20 MPa.

The substrates and the carbon dioxide were continuously supplied to the membrane module from a gas cylinder. The membrane was pressurized at the feed and permeate side up to 20 MPa with the reaction mixture, using a LKB HPLC pump. The pressure was monitored by a Meyvis 802-C pressure module. The permeate needle valve was opened to create a trans-membrane pressure varying between 0.05 and 1 MPa. The catalyst was brought in the system by flushing the feed mixture (H_2, 1-butene, and CO_2) through the high-pressure reactor. To assure that no leaching of the catalyst and/or of the free ligand through the membrane occurred, the permeate stream was led through a high-pressure viewing cell of 2.2 mL, which was placed in a Spectronic Genesys 5 spectrophotometer. The absorption was measured at 410 nm. Leaching of the catalyst and the ligand was studied in detail in a separate retention measurement using ICP-AAS because of the limited accuracy of UV–vis spectroscopy.

To obtain the flux through the membrane, the permeate stream was led through mass flow controllers (Bronkhorst). The permeate stream was analyzed using GC and GC-MS. The analytical apparatuses were the same as described in the section "Batch reactor." All the data of the pressures, the absorbance, and the permeate mass flow were recorded on a PC.
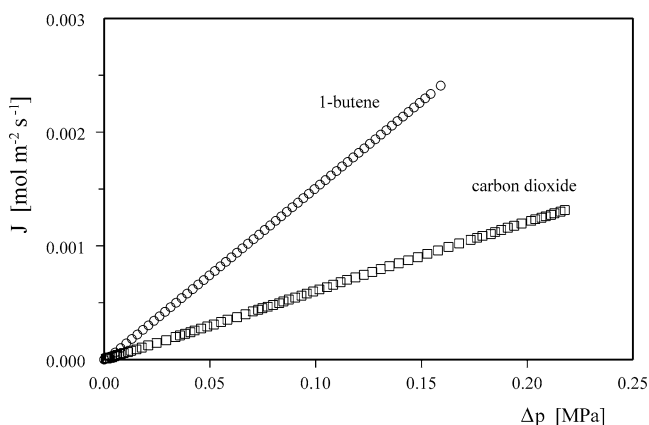
3. Results and discussion

3.1. Permeation of supercritical carbon dioxide

In Fig. 5 a comparison is made between the flux of gaseous carbon dioxide and 1-butene, at a temperature of 353 K and a feed pressure of 0.3 MPa, and for a pressure difference across the membrane up to 0.2 MPa. Both species permeate through the microporous membrane, and both fluxes show a linear dependency on the pressure difference across the membrane. The flux of 1-butene is a factor of 3 higher than the flux of carbon dioxide. This is mainly due to a difference in equilibrium adsorption. Carbon dioxide is smaller than 1-butene with a size of 0.33 and 0.45 nm, respectively [28]. However, 1-butene adsorbs more strongly than carbon dioxide on silica. As a result, 1-butene will have a higher flux than carbon dioxide through the microporous silica membrane.

Transient profiles of supercritical carbon dioxide, at different feed pressures, are given in Fig. 6. All the profiles are obtained for carbon dioxide in the supercritical state, i.e., pressures above 7.4 MPa. With an increase in the feed pressure the approach to equilibrium becomes faster. So even at high pressures in combination with a low-pressure difference across the membrane there is still a driving force for carbon dioxide to permeate. Consequently, at the reaction conditions of 20 MPa the substrates, hydrogen and 1-butene, the solvent, and the product, *n*-butane, will permeate through the silica membrane.

3.2. Batch reactor

In the high-pressure reactor the precursors of Wilkinson's catalyst are added in a molar ratio of one rhodium atom per three fluorous ligand molecules, until a concentration of 1.3×10^{-6} mol/L of Wilkinson's catalyst is obtained. The reactor is heated until 353 K and all air is slowly removed with carbon dioxide. For the formation of the catalyst, at $t = 0$ h, the reactor is pressurized with carbon dioxide up to 10 MPa at 353 K.

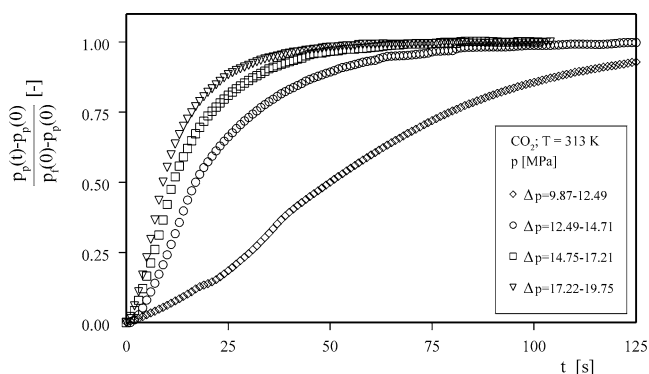Fig. 5. Flux of gaseous carbon dioxide and 1-butene, at different trans-membrane pressures.

Fig. 6. Transient profiles of supercritical carbon dioxide through the silica membrane for different feed pressures, with p_f and p_p the pressure at the feed and the permeate side.
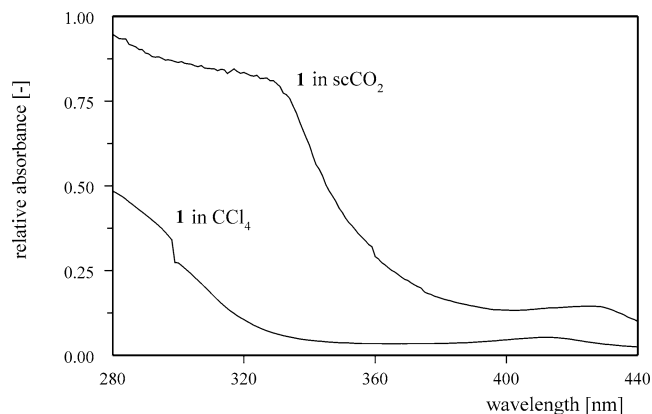
Fig. 7. UV–vis spectrum of **1** in supercritical carbon dioxide and tetrachlorocarbon, obtained in the batch system.
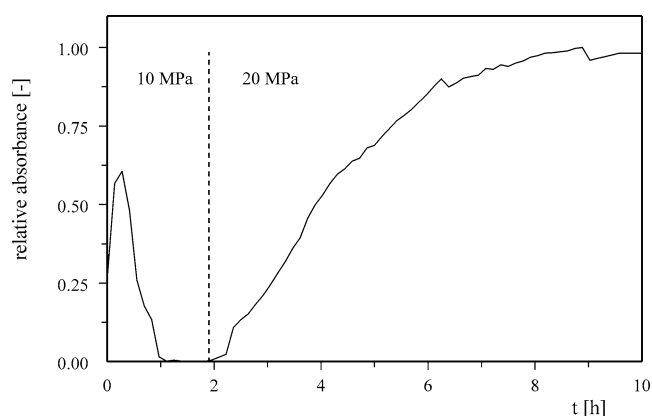

Fig. 8. Absorbance at 410 nm of **1** in supercritical carbon dioxide as a function of time, indicating the formation of **1**.

Fig. 7 shows the UV–vis spectrum of Wilkinson's catalyst in scCO$_2$ and tetrachlorocarbon as a reference. The solubilized catalyst has a specific yellow color and a clear absorbance maximum at 410 nm. From the spectra it follows that **1** has been synthesized in situ in scCO$_2$.

Fig. 8 shows the absorption at 410 nm during the formation of fluorous Wilkinson's catalyst. The two most likely species that are formed are the catalysts or the precursor of the catalysts. The ligand has only a benzene ring that has one UV peak, and this peak lies between 200 and 300 nm. The spectrum at 410 nm is the result of the formation of a complex between rhodium-containing species and phosphine-containing species. From the fact that at 10 and 20 MPa the same spectrum is observed it can be concluded that the catalyst is the most likely species that is formed. From the absorption it can be seen that the catalyst is formed in scCO$_2$ during the first 2 h, while the pressure is equal to 10 MPa. After the formation the catalyst precipitates. By pressurization up to 20 MPa, after the first 2 h, the catalyst dissolves again and is completely dissolved in the scCO$_2$ after 8 h. After complete solubilization of the catalyst the 1-butene and hydrogen are added in a molar ratio of 1:4, using 0.02 mol/L 1-butene.
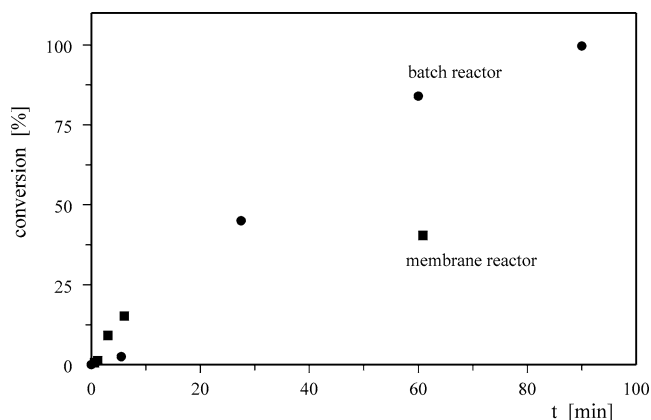

Fig. 9. Conversion of 1-butene obtained in the batch and the membrane reactor, as a function of time. For the continuous experiment *t* denotes the residence time.

In Fig. 9 a comparison is made between the conversion of 1-butene to *n*-butane obtained in the batch setup and in the membrane reactor. In the batch reactor complete conversion is obtained after 100 min, and this corresponds to a turnover frequency (TOF) of 9.4×10^3 h^{-1}. For comparison, Deelman and co-workers [20,21] have performed hydrogenation reactions using the same catalyst in a fluorous biphasic system containing c-CF$_3$C$_6$F$_{11}$. The advantage of the high solubility of hydrogen in scCO$_2$, as compared to the solubility of hydrogen in conventional solvents (2.7 mM in toluene at 298 K and 1×10^5 Pa) or in fluorous solvents (6.1 mM in c-CF$_3$C$_6$F$_{11}$ at 298 K and 1×10^5 Pa) has lead to an increase in reaction rate by at least a factor of 10. This is still rather low as compared to the ratio of hydrogen present in scCO$_2$ and c-CF$_3$C$_6$F$_{11}$. At high hydrogen concentrations, however, it is known that the reaction rate becomes zero order in hydrogen [29].

3.3. Continuous membrane reactor

For the experiments in the continuous membrane reactor the catalyst is also prepared in situ. The feed mixture was used to pressurize the system. The residence time is defined as the volume of the membrane module divided by the total flux through the membrane. This means that when the pressure difference is changed across the membrane, the residence time in the membrane module can be varied. The pressure difference has been varied between 0.05 and 1 MPa. The flux through the membrane increases with an increase in trans-membrane pressures, and a higher flux leads to a shorter residence time.

The conversion obtained in the membrane reactor, as a function of the residence time, is also given in Fig. 9. For the membrane reactor the conversion increases with an increase in residence time, which is a result of the lower fluxes.

For both cases an increasing trend is seen, as a function of the (residence) time, although the conversion obtained in the membrane reactor is somewhat lower than the conversion obtained in the batch reactor. The difference may be a result
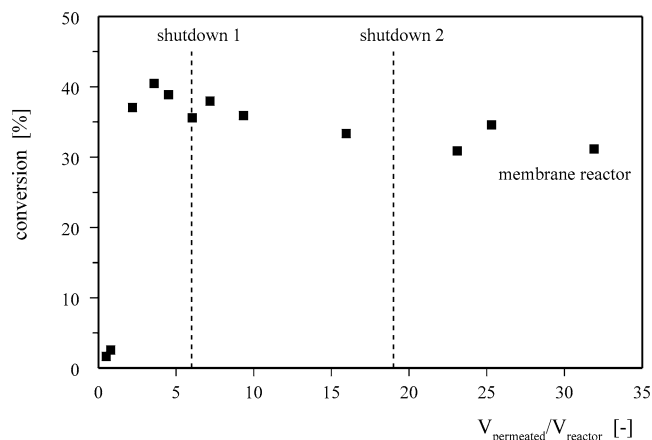
Fig. 10. Conversion of 1-butene in a continuous membrane reactor, as a function of the number of reactor volumes permeated.

of a lower catalyst concentration in the membrane reactor, in combination with a difference between the residence time of hydrogen and 1-butene in the membrane reactor. In the membrane reactor also some of the unreacted hydrogen and 1-butane will permeate through the membrane.

In Fig. 10 the conversion of the hydrogenation of 1-butene, performed in the membrane reactor, is depicted as a function of the number of reactor volumes permeated. During the reaction, which is performed at 353 K and 20 MPa, a pressure difference of 0.3 MPa has been applied. This resulted in a total flux of 9.0×10^{-8} mol m^{-2} s^{-1} Pa^{-1}. For these conditions the residence time equals 62 min. After 3 h a constant conversion of 40% with a TOF of 4×10^3 h^{-1} is obtained.

Overnight, the pressure of the system is reduced to 6 MPa, and the needle valve at the permeate side is closed. During depressurization the catalyst precipitates in the membrane reactor and no reaction occurs. The precipitated catalyst can be used for a new cycle by pressurization of the membrane reactor. During the second and the third run the system is first pressurized to 20 MPa for 2 h. As a result, the catalyst dissolves again in the high-density carbon dioxide phase. At the end of the third run the conversion is about 33%, with a TOF of 3×10^3 h^{-1}. This is about 60% lower than the conversion obtained during the batch experiment (TOF $= 9.4 \times 10^3$ h^{-1}). For the experiments performed in the continuous membrane reactor a turnover number of 1.2×10^5, in 32 h, is obtained.

If the decrease in conversion would have been caused by leaching of the catalyst, the retention of the catalyst would still be well over 99%. Analysis of the permeate stream with UV–vis spectrophotometry showed, however, no flux of the catalyst or free ligand through the membrane. Additional ICP-AAS analysis of the permeate stream indicates that complete retention of the catalyst occurred. This confirms that the size of the catalysts is considerably larger than the pore diameter of 0.5–0.8 nm of the silica membrane. The size of **1** dissolved in a c-C$_6$F$_{11}$CF$_3$ solution, obtained by dynamic light scattering, is 2–4 nm, which is similar to the size

obtained from a computer modeling study. With respect to the decrease in conversion, it is well known that the catalyst is susceptible to oxidation [20,21]. Possible traces of oxygen present in the carbon dioxide or the feed may be responsible for deactivation of the catalyst.

4. Conclusions

A methodology for homogeneous catalysis in supercritical carbon dioxide operated continuously has been presented. A fluorous version of Wilkinson's catalyst is used for the hydrogenation of 1-butene, at a pressure of 20 MPa carbon dioxide and a temperature of 353 K. The catalyst is completely retained at the feed side of a microporous silica membrane. The retention of the catalyst and the possible free ligand is higher than 99.9%, as shown by UV–vis spectroscopy and ICP-AAS.

The silica membrane investigated has some clear advantages over the polymeric membranes reported in the literature. One of the main advantages is that it is not necessary to have a high-pressure difference across the membrane to obtain a carbon dioxide flux. High fluxes of carbon dioxide have been obtained for feed pressures up to 20 MPa.

After 32 h of continuous operation a turnover number of 1.2×10^5 has been obtained. The turnover frequencies obtained for the reaction carried out in carbon dioxide using the batch reactor and the membrane reactor, 4.0×10^3 h^{-1} and 9.4×10^3 h^{-1}, respectively, are significantly higher than the turnover frequency obtained in an organic solvent (TOF $= 100$–1000 h^{-1}).

After two shutdown and start-up procedures, by changing the pressure, the catalyst shows a small decrease in activity. This means that flexible processes are possible using homogeneous catalysis in supercritical media, with in situ separation of the products from the catalyst. It can be concluded that the methodology of using a membrane with pore sizes smaller than the size of the catalyst, but larger than the diameter of the products, will lead to various new opportunities of homogeneous catalysis in supercritical fluids.

References

[1] M.A. McHugh, V.J. Krukonis, Supercritical Fluid Extraction: Principles and Practice, 2nd ed., Butterworth, Stoneham, MA, 1994.
[2] K.P. Johnston, R.M. Lemert, Supercritical fluid technology: theory and application, in: J.J. McKetta, G.E. Weismantel (Eds.), Encyclopedia of Chemical Processes and Design, Dekker, New York, 1996.
[3] P.E. Savage, S. Gopalan, T.I. Mizan, C.J. Martino, E.E. Brock, AIChE J. 41 (1995) 1723.
[4] C.-H. He, AIChE J. 43 (1997) 2944.

[5] S. Kainz, D. Koch, W. Baumann, W. Leitner, Angew. Chem. Int. Ed. 6 (1997) 1628.

[6] A.A. Chialvo, P.T. Cummings, Y.V. Kalyuzhnyi, AIChE J. 44 (1998) 667.

[7] P.G. Jessop, W. Leitner (Eds.), Chemical Synthesis using Supercritical Fluids, Wiley–VCH, Weinheim, 1999.

[8] T. Bein, Chem. Mater. 8 (1996) 1636.

[9] A.F. Ismail, L.I.B. David, J. Membr. Sci. 193 (2001) 1.

[10] F.K. Katsaros, T.A. Steriotis, A.K. Stubos, A. Mitropoulos, N.K. Kanellopoulos, S. Tennison, Microporous Mater. 8 (1994) 171.

[11] W.J. Koros, R. Mahajan, J. Membr. Sci. 175 (2000) 181.

[12] Y. Tokunaga, T. Fujii, K. Nakamura, Biosci. Biotechnol. Biochem. 61 (1997) 1024.

[13] H.P. Hsieh, R.R. Bhave, H.L. Fleming, J. Membr. Sci. 39 (1988) 221.

[14] A. Tavolaro, E. Drioli, Adv. Mater. 11 (1999) 975.

[15] L. Sartorelli, G. Brunner, in: Proceedings 5th International Symposium on Supercritical Fluids, Atlanta, GA, 2000, Cd-rom.

[16] N. Brinkman, D. Giebel, G. Lohmer, M.T. Reetz, U. Kragl, J. Catal. 183 (1999) 163.

[17] D. Turlan, E.P. Urriolabeitia, R. Navarro, C. Royo, M. Menendez, J. Santamaria, Chem. Commun. (2001) 2608.

[18] D.E. de Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalysts Immobilization and Recycling, Wiley–VCH, Weinheim, 2000.

[19] L.J.P. Van den Broeke, E.L.V. Goetheer, A.W. Verkerk, E. De Wolf, B.-J. Deelman, G. Van Koten, J.T.F. Keurentjes, Angew. Chem. Int. Ed. 40 (2001) 4473.

[20] P.G. Jessop, T. Ikariya, R. Noyori, Chem. Rev. 99 (1999) 475.

[21] J.R. Hyde, P. Licence, D. Carter, M. Poliakoff, Appl. Catal. A 222 (2001) 119.

[22] D. Koch, W. Leitner, J. Am. Chem. Soc. 120 (1998) 13398.

[23] D.R. Palo, C. Erkey, Ind. Eng. Chem. Res. 37 (1998) 4203.

[24] B. Richter, E. de Wolf, G. van Koten, B.-J. Deelman, J. Org. Chem. 65 (2000) 3385.

[25] B. Richter, A.L. Spek, G. van Koten, B.-J. Deelman, J. Am. Chem. Soc. 122 (2000) 3945.

[26] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.

[27] M.K. Koukou, N. Papyannakos, N.C. Markatos, M. Bracht, H.M. van Veen, A. Roskam, J. Membr. Sci. 155 (1999) 241.

[28] D.W. Breck, Zeolite Molecular Sieves, Wiley, New York, 1974.

[29] J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, J. Chem. Soc. A 12 (1966) 1711.