

Synthesis and catalytic activity of perfluoroalkylated pyridine–palladium(II) complex toward olefin hydrogenation in scCO₂ and conventional organic solvents

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Abstract

The perfluoroalkylated pyridine, (*o*-COOCH₂(CF₂)₇CF₃-NC₅H₄), has been synthesized in two step from nicotinic acid and then the title compound, [Pd(*o*-COOCH₂-(CF₂)₇CF₃-NC₅H₄)₂(OAc)₂], obtained by reaction with Pd(OAc)₂. The catalytic activity of the Pd(II) complex examined for hydrogenation of styrene, 1-octene, *t*-2-octene and cyclohexene for both in supercritical carbon dioxide and in organic solvents. The effect of temperature and dihydrogen pressure, as well as the influence of the palladium and substrate concentrations have been studied ($T = 320\text{--}353\text{ K}$, $p(\text{H}_2) = 6\text{--}30\text{ bar}$, $[\text{Pd}] = (1.12\text{--}2.62) \times 10^{-5}\text{ M}$, $[\text{Styrene}] = (8.70\text{--}34.8) \times 10^{-3}\text{ M}$). The experimentally determined rate law is $r = k_{\text{cat}} [\text{Pd}]^a [\text{Styrene}]^b p(\text{H}_2)^c$ ($a = 1$, $b = 1$ and $c = 0.14$) where $k_{\text{cat}} = 4.4 \times 10^{-2}\text{ (mol}^{-1}\text{ s}^{-1})$ at 320 K. Activation parameters have been calculated at 320 K. Supercritical carbon dioxide is a more effective, green reaction medium for olefin hydrogenation compared with conventional organic solvents.

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1. Introduction

Supercritical fluids (SCF) are becoming increasingly important partly in response to the adverse environmental impact of solvent use and disposal for chemical synthesis. Among the diverse range of chemical reactions possible in SCF media both homogeneous and heterogeneous catalytic processes have been examined in some details [1,2]. Several reviews have been published explaining the fundamentals and the main advantages in this new field of the chemical synthesis [3,4]. Specifically, CO₂ has received special attention as a result of its easy replacement for organic solvents because its inexpensive, non-toxic, non-flammable and exhibit easy of recycle and disposal, capable of performing the duties of non-polar solvent while allowing manipulation of its solvent strength through a wide range of polarities [5,6]. Diffusivities in supercritical CO₂ (scCO₂) are higher and viscosities lower as compared to conventional organic solvents; therefore, a hydrogenation and hydroformylation reac-

tion that is diffusion limited in the solvent phase can be enhanced by carry out in SCF.

The modified palladium complexes with nitrogen containing bases (pyridine, ethylene diamine, quinoline) allows preparing of highly selective catalyst for alkynes and conjugated diene hydrogenation [7,8], enantio selective hydrogenation of α,β -unsaturated acid derivatives [9,10], chemoselective hydrogenation of unsaturated ketones and aldehydes [11,12]. Catalyst decomposition and poor reproducibility of the reaction was the major disadvantages of these catalytic systems in organic solvents. It has been found that some organometallic complexes are soluble in dense carbon dioxide to a certain extent but most metal complexes including commonly used phosphine compounds [13] are less soluble in scCO₂. To overcome this problem fluorinated compounds have been used because organofluorine compounds are well known to be highly soluble in scCO₂ [14]. The effectiveness of palladium complexes with various fluorinated phosphine compounds and fluorinated palladium sources like Pd(O-COCF₃)₂ and Pd(F₆-acac)₂ were investigated for carbon–carbon coupling reactions [15,16]. To date, unlike fluorinated phosphine compounds, fluorinated nitrogen compounds have not been studied in scCO₂. The present paper reports

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the first successful application of Pd(II) complex of perfluoroalkylated pyridine for the catalytic hydrogenation of styrene, 1-octene, *t*-2-octene and cyclohexene in scCO₂. The solubility behavior of synthesized ligand and Pd(II) complex has been estimated from visual observations of those reaction mixtures under studied conditions. The influence of some parameters such as H₂ pressure, CO₂ pressure, temperature, and reaction time has been investigated, and effectiveness of scCO₂ reaction medium has been compared with organic solvents. The catalyst recycling has also been examined in scCO₂.

2. Experimental

2.1. Synthesis of *o*-COOCH₂-(CF₂)₇CF₃-NC₅H₄

A mixture of nicotinic acid (1.23 g, 9.99 mmol) and thionyl chloride (5 mL, 68.50 mmol) was stirred at 90 °C. After 6 h reflux, the excess thionyl chloride was removed under reduced pressure and the resulting yellow-white solid was dissolved in CH₂Cl₂ (10.0 mL). Then, triethyl amine (1 mL) and heptadecafluorononanol (1.27 g, 2.82 mmol) were added to the mixture with stirring at 0 °C, and then mixture was allowed to warm room temperature and stirred for 15 h. After the solvent was removed under reduced pressure to dryness, the resulting white solid was washed with water and dried under vacuum. The pure compound was obtained after column chromatography on SiO₂ with hexane + ethyl acetate (6:1) as eluent. Yield: 76% (1.19 g), mp: 48–50 °C. Anal. Calc. for C₁₅H₆F₁₇O₂N: C 32.43; H 1.09; N 2.52. Found: C 31.38; H 1.03; N 2.69. FT-IR (cm⁻¹): 1738, 1600, 1338, 1290, 1203, 965, 845, 803, 740, 705, 663, 609, 561, 534. ¹H NMR (400 MHz, acetone-*d*₆) δ, 9.25 (1H, *J* = 1.8 Hz), dd, 8.84 (1H, *J*_{5,6} = 4.8 Hz, *J*_{4,6} = 1.5 Hz), quasi-dt, 8.34 (1H, *J*_{4,5} = 8.1 Hz, *J*_{4,6} = 1.5 Hz), dd, 7.46 (1H, *J*_{4,5} = 8.1 Hz, *J*_{5,6} = 4.8 Hz), t, 4.86 (1H, *J* = 13.2 Hz). ¹³C NMR (100 MHz, acetone-*d*₆) 163.8, 154.4, 151.3, 137.7, 124.7, 123.8, 109.4, 106.6, 94.1, 77.5, 60.84. ¹⁹F NMR –80.9 (s, 3F, CF₃), –119.3 (s, 2F, CF₂-CH₂), –121.9 (s, 2F, CF₂), –122.3 (s, 2F, CF₂), –122.8 (s, 2F, CF₂), 123.1 (s, 2F, CF₂), –123.6 (s, 2F, CF₂), –126.2 (s, 2F, CF₂) (Scheme 1).

2.2. Synthesis of [Pd(*o*-COOCH₂-(CF₂)₇CF₃-NC₅H₄)₂(OAc)₂]

Palladium(II) acetate (0.020 g, 0.09 mmol) (in 5 mL toluene) was added dropwise via syringe to a stirred solution of perfluoroalkylated pyridine (0.200 g, 0.36 mmol) in toluene (10 mL). The resulting mixture was stirred at room temperature for about 4 h. Then the volume of solution was removed by vacuum. The obtained yellow solid was washed with cold methanol and dried

under vacuum. The product is soluble in acetone, ether and chloroform. Yield: 81% (0.098 g), mp: 133–135 °C. Anal. Calc. for C₃₄H₁₈F₃₄O₈N₂Pd: C 30.59; H 1.36; N 2.10. Found: C 30.83; H 1.49; N 2.27. FT-IR (cm⁻¹): 1751, 1633, 1604, 1423, 1368, 1281, 1203, 1150, 1063, 1012, 965, 850, 779, 745, 700, 659, 617, 562, 537.

2.3. General

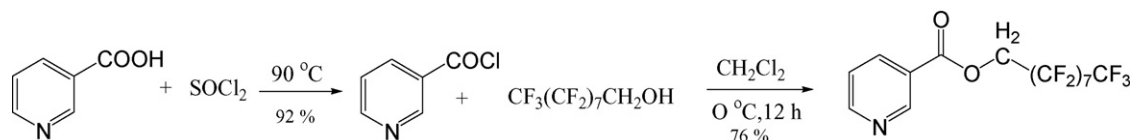
All the reactions were carried out under nitrogen atmosphere, by using standard Schlenk techniques; solvents were dried and purified according to literature methods. All reagents of commercial quality were used without further purification. Habas Company provided CO₂ at 99.9% minimum purity and hydrogen at 99.99% purity.

Elemental analysis of molecules was carried out using Elemental Vario EL III microanalyser. FT-IR spectra of compounds were recorded out on Jasco FT/IR-300 E spectrophotometer. ¹H, ¹³C, ³¹P and ¹⁹F NMR spectra were recorded at 25 °C on a Bruker (400 MHz) DPX FT spectrometer. Thermogravimetric analysis of catalyst was carried out on SETERAM-Labsys. Instrument at a heating rate of 10 °C min⁻¹ under argon atmosphere. The products obtained from catalytic hydrogenation reaction were carried out Thermo Finnigan Trace GC using Permabond SE-54-DF-0.25 25 m × 0.32 mm i.d. column attached to a flame ionization detector and He as carrier gas.

2.4. General procedure for hydrogenation reactions

The experimental equipment and procedure used for the experimentation have been described [17, 18]. A small visual cell reactor, 25 ml (Tharr Inc. Instruments, USA), was employed to visual check the solubility of the catalyst, the miscibility of the reactants and products and phase behavior of reaction medium in scCO₂ at studied conditions. Also, a 100 mL reactor (Parr Inc. 4590 micro Bench Top with 4842 process controller having a digital readout for measuring temperature and stirrer speed) with sampling online was installed to take samples at different times in order to determine the conversion and the selectivity profile against time (Fig. 1). All runs were repeated at least twice for reproducibility purposes. Before a typical experiment, blank reactions were performed to ensure the complete cleanness of the reactor (no conversion). The catalyst recycling experiments have been conducted as described at our previous work [19].

Hydrogenation reactions in organic solvents were also carried out in the 100 mL high-pressure reactor. The reactor was charged with substrate, catalyst and 10 mL solvent and was then sealed. It was flushed with H₂ three times to remove air inside the reactor



Scheme 1. Synthesis of perfluoroalkylated pyridine ligand.

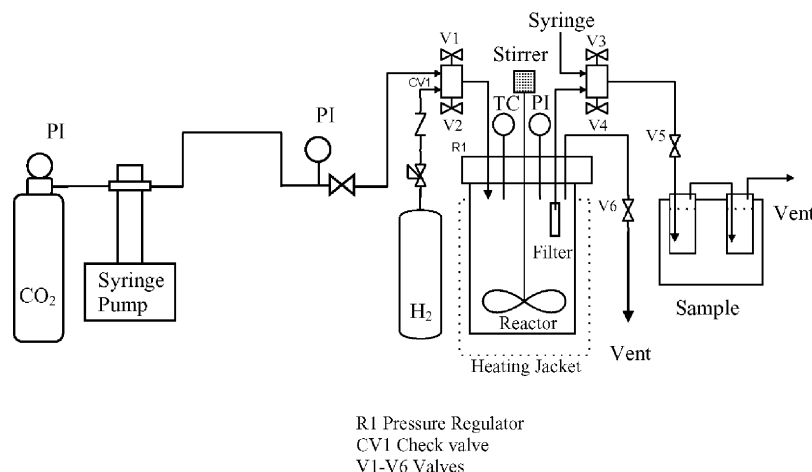


Fig. 1. Schematic diagram of the reactor system.

Table 1

Kinetic data for hydrogenation of styrene with $[\text{Pd}(o\text{-COOCH}_2\text{-(CF}_2\text{)}_7\text{CF}_3\text{-NC}_5\text{H}_4\text{)}_2(\text{OAc})_2]$ as the catalyst precursor

Entry	Pd ($\times 10^{-5}$ M)	Styrene (M)	pH ₂ (bar)	T (K)	r_1 (M s^{-1})
1	3.75	8.70×10^{-3}	6	353	0.75×10^{-5}
2	3.75	26.1×10^{-3}	6	353	2.41×10^{-5}
3	3.75	34.8×10^{-3}	6	353	3.74×10^{-5}
4	2.62	8.70×10^{-3}	6	353	8.69×10^{-5}
5	1.57	8.70×10^{-3}	6	353	6.63×10^{-6}
6	1.12	8.70×10^{-3}	6	353	3.68×10^{-6}
7	3.75	8.70×10^{-3}	6	353	7.48×10^{-6}
8	3.75	8.70×10^{-3}	10.5	353	7.95×10^{-6}
9	3.75	8.70×10^{-3}	20	353	8.94×10^{-6}
10	3.75	8.70×10^{-3}	30	353	9.29×10^{-6}
11	6.89	1.61×10^{-2}	11	320	8.61×10^{-6}
12	4.87	1.14×10^{-3}	7.7	330	9.30×10^{-6}
13	3.97	9.74×10^{-3}	6.7	340	9.20×10^{-6}

and heated up to studied temperature. After the introduction of H₂, the reaction was conducted as above.

The kinetics of styrene hydrogenation reaction was studied by following the ethyl benzene formation (or styrene conversion) in time at different catalyst and substrate concentrations, and at different temperatures and dihydrogen pressures. In all experiments it appeared that no induction period was needed to formation of actual catalyst. The conversion of styrene to ethyl benzene was low enough in the studied period of time, so that the initial rate method can be applied. The complete data are listed in Table 1. Initial rates were determined at 15th minute of the reaction. All the straight lines were fitted by use of conventional linear regression software to $R^2 > 0.96$.

3. Results and discussion

Characterization of the ligand and the complex were carried out on the basis of their physico-chemical properties, chemical analysis, FT-IR, TG and NMR spectral analysis. The melting point and analytical data of the Pd(II) complex suggest its formation and structure. The yellow color complex is stable in solid state at room temperature. TG analysis of the complex

showed that it is stable up to 130 °C and start to decompose after that temperature. The IR spectra of the perfluoroalkylated pyridine shows a large number of absorption bands in the range 1600–1370 cm^{-1} assigned to different vibration modes of the pyridine ring. The strong bands at about 1600 cm^{-1} for the highest-energy pyridine ring vibration (C=N) of the ligands are appreciably shifted by about 33 cm^{-1} to higher frequency after complexation. It indicates that the nitrogen atom of pyridine participates in the coordination [20,21]. The analogous Pd(II)-pyridine derivative compounds show the similar shifts [22,23]. Typical C–F vibrations were determined at about 1203–1150 cm^{-1} .

3.1. Phase behavior and solubility of compounds

The phase behavior examination is an important issue to study catalytic reactions in scCO₂; it is important to determine whether the reaction is occurring heterogeneously in two or more phase or homogeneously in a single phase. The solubility of ligand, catalyst and the phase behavior of the catalytic reaction in scCO₂ and H₂ mixture can be estimated by visual observation through window. In our study, it is not the purpose to determine the true solubility but to find conditions during reaction under studied conditions. Different amount of catalyst (1.48×10^{-3} to 5.93×10^{-3} mmol) were added in to the view cell and it was heated until desired temperature (310–353 K). After that, the cell was introduced with CO₂ (102–170 bar) and observed visually solubility behavior of the catalyst. The experiment was repeated as above in that case after heating process the cell was introduced with H₂ first, followed by introduction of CO₂ up to different pressures by syringe pump. Under the reaction conditions, no undissolved solid could be observed, but very small amount would have been difficult to detect owing to the reactor design.

3.2. Catalytic studies

In order to test the activity of Pd(II) catalyst towards hydrogenation of C=C double bonds in different chemical

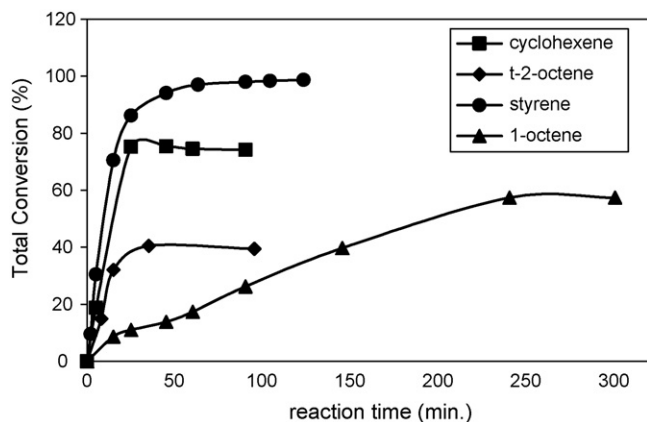


Fig. 2. Comparison of olefin hydrogenation in $scCO_2$. Reaction conditions: p_{H_2} 11 bar, $T=320$ K, substrate/catalyst=232.

environments, the hydrogenation of styrene, 1-octene, *t*-2-octene and cyclohexene was investigated in $scCO_2$. The results are presented in Fig. 2. It appeared that the hydrogenation rate of styrene was found to be fast compared to other studied olefins. Substrate as an examples of long-chain terminal, the hydrogenation of 1-octene and *t*-2-octene converts mainly to *n*-octane and mixture of isomers at 320 K. The hydrogenation of 1-octene has the slowest rate. Whereas the hydrogenation of internal C=C double (cyclohexene) bonds is very low and slow by molecular Pd catalyst as reported by van Laren and Elsevier [24] and Gade and coworkers [25], and also Wilkinson's catalyst [26], perfluoroalkylated pyridine–Pd(II) complex has good activity on the hydrogenation of cyclohexene to cyclohexane. Under the same reaction conditions, the maximum conversions reached to 98.7, 75, 57 and 40% for styrene, cyclohexene, 1-octene and *t*-2-octene, respectively.

3.3. Effect of parameters (styrene, catalyst, H_2 and T) on reaction rate of styrene hydrogenation

The effect of styrene concentration on the rate of hydrogenation was studied at 353 K, 6 bar H_2 pressure and 102 bar total pressure of CO_2 . The substrate concentration was varied in the 8.70 to 3.48×10^{-3} M range keeping constant the palladium, hydrogen and temperature (Table 1, entries 1–3). Fig. 3 shows a

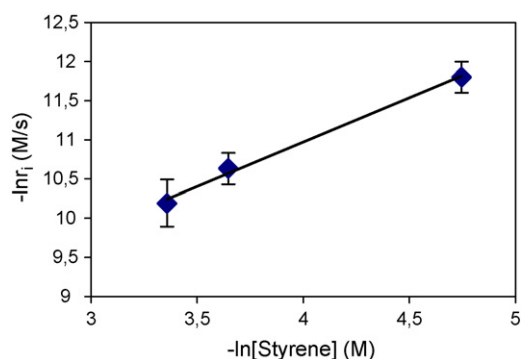


Fig. 3. Rate dependence on styrene hydrogenation with respect to substrate concentration. Conditions are given in Table 1.

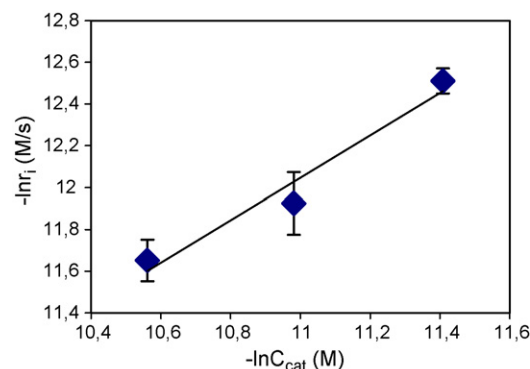


Fig. 4. Rate dependence on styrene hydrogenation with respect to catalyst concentration. Conditions are given in Table 1.

first-order dependence of the hydrogenation rate with respect to substrate concentration. The order of reaction calculated from the plot of $\log(\text{initial rate})$ versus $\ln[\text{styrene}]$ was found to be unity ($-\ln r_1 = -1.1314 \ln[\text{styrene}] + 6.4444$; $R^2 = 0.995$).

The effect of substrate to palladium molar ratio was carried out in 100 mL batch reactor 232, 554 and 776 while styrene, dihydrogen, CO_2 and temperature were kept constant. The experimental conditions were 353 K, 6 bar H_2 and 102 bar total pressure (Table 1, entries 4–6). The results are shown in Fig. 4. As expected, decrease the substrate catalyst molar ratio, the reaction rate increases. At each different S/C ratio the hydrogenation of styrene gives only one type of product (ethyl benzene). A plot of $-\ln r_1$ versus $-\ln[Pd]$ (Fig. 3a) yields a straight line ($-\ln r_1 = 1.0153 \ln[Pd] + 0.8779$; $R^2 = 0.960$), which is in agreement with first-order rate dependence.

The effect of hydrogen pressure on the reaction rate of styrene was investigated in the pressure range of 6–30 bar with palladium(II) complex. With the exception of hydrogen pressure all the experimental conditions remained constant. The data are given in Table 1 (entries 7–10) and Fig. 5. The initial rates show a direct dependence with respect to the hydrogen concentration as indicated with straight line plot of $-\ln r_1$ versus $-\ln H_2$ (Fig. 5). However, the order of the reaction is much lower than unity ($-\ln r_1 = 0.1412 \ln H_2 + 1.7541$; $R^2 = 0.987$). It is difficult to explain the hydrogen effect but the some factors can be consider such as the effect of changes in density in supercritical fluid consequent upon variation of the hydrogen pressure over

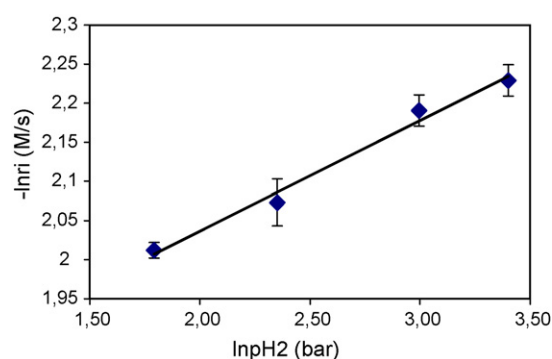


Fig. 5. Rate dependence on styrene hydrogenation with respect to hydrogen pressure. Conditions are given in Table 1.

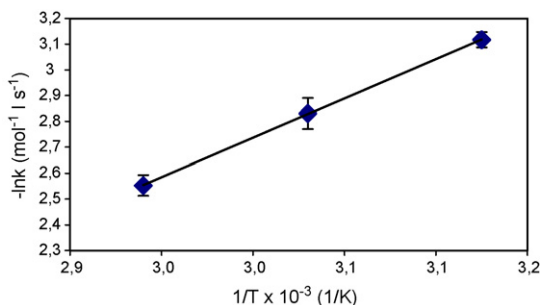


Fig. 6. Rate dependence on styrene hydrogenation with respect to temperature. Conditions are given in Table 1.

the range 6–30 bar, which might also influence the apparent reaction order.

The obtained results suggested that the hydrogenation of styrene by Pd(II) complex proceeds according to the experimental rate equation:

$$\text{rate} = k_{\text{cat}}[\text{Pd}]^a[\text{Styrene}]^b p[\text{H}_2]^c \quad (1)$$

where the hydrogenation is first-order in Pd, styrene concentration and independent of hydrogen partial pressure ($a = 1$, $b = 1$ and $c = 0.14$).

Experiments were performed at 320–340 K and the constant mole fraction of substrate, hydrogen and catalyst to determine the effect of temperature at a constant total pressure (102 bar) on reactivity and the selectivity of styrene. The mole ratio of substrate to catalyst was 232 and the mole fractions of styrene, hydrogen and CO_2 were 0.0017, 0.0491 and 0.9490, respectively. The effect of temperature variation has been shown in Fig. 6 and Table 1 (entries 11–13). The plot of $-\ln k_{\text{cat}}$ versus $1/T$, depicted in Fig. 6, yields straight line ($-\ln k_{\text{cat}} = 3050.7/T - 6.4156$; $R^2 = 0.996$), as expected from the Arrhenius equation (Eq. (2)):

$$k_{\text{cat}} = A \exp(-E_a/RT) \quad (2)$$

The satisfactory linearity of the Arrhenius plot is in agreement with the assumption that under the reaction conditions only one catalytic species is involved. The activation energy E_a can be calculated from the slope of the graph depicted in Fig. 6. The value of enthalpy, entropy and free energy of activation can be calculated (from the equations $\Delta H = E_a - RT$, $\Delta H = R \ln(hA/e^2 K_B T)$, and $\Delta G = \Delta H - T\Delta S$, respectively). The Arrhenius plot constructed from the obtained kinetic data is shown in Fig. 6 yielding the following activation parameters; $E_a = 25.5 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 22.8 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -208.3 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta G^\ddagger = 89.5 \text{ J K}^{-1} \text{ mol}^{-1}$. Similar values have been reported for ruthenium, nickel and palladium-catalyzed hydrogenation of alkenes in organic solvents [27–30]. The large negative value for the entropy of activation (ΔS^\ddagger) indicates a highly ordered transition state commensurate with the interaction of a dihydrogen molecule with the palladium center and also by the steric hindrance of the long-chain perfluoroalkylated pyridine groups.

In order to demonstrate the catalyst recycling, we used the catalyst which remained inside the reactor after depressuriza-

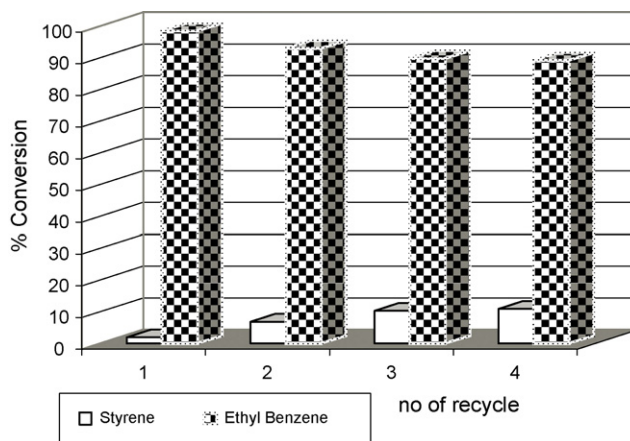


Fig. 7. Conversion of styrene as a function of cycle using Pd catalyst. Conditions are given in Table 1, entry 12.

tion. The cycle of hydrogenation were carried out at 330 K and 102 bar for 104 min. Fig. 7 presents the total conversion of these experiments. Four cycles were performed with slight decrease in activity of the catalyst. The maximum total conversion of styrene hydrogenation achieved was 98.5 and 89.2% in the first and fourth cycle, respectively.

3.4. Temperature effect on 1-octene hydrogenation

We also evaluated temperature effect on 1-octene hydrogenation in 100 mL reactor. Fig. 8 summarizes experiments at the three temperatures 320, 330 and 353 K. All experiments were carried out at the same pressure, 102 bar. The initial mole fractions of H_2 (0.048) and 1-octene (9.42×10^{-4}) were kept constant in all of the experiments, and the amount of catalyst in the system was changed according to the 1-octene concentration and the required substrate/catalyst molar ratio. Conversion increase with temperature and it levels off after 4 h at all temperatures. The maximum conversions reached at 320, 330 and 353 K were 52, 70 and 80%, respectively. As shown in Fig. 9, at 353 and 330 K, the initial selectivity (75%) of *n*-octane is very close and higher than 320 K. After 2.5 h, the *n*-octane selectivity remains constant at 353 K, but the selectivity at 330 K decrease slightly to 70% and it

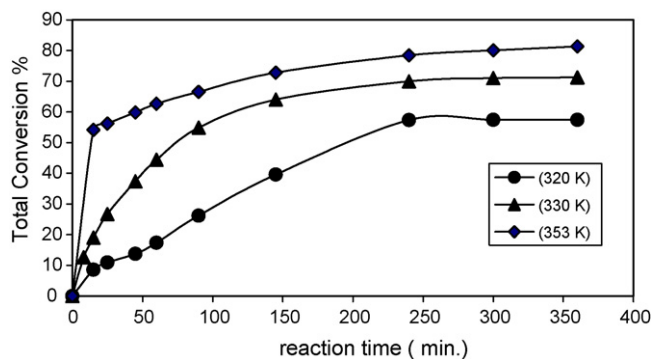


Fig. 8. 1-Octene hydrogenation at 320, 330 and 353 K at 102 bar total pressure. Mole fraction of $\text{H}_2 = 0.048$; 1-octene = 9.42×10^{-4} ; $\text{CO}_2 = 0.949$; substrate/catalyst = 232.

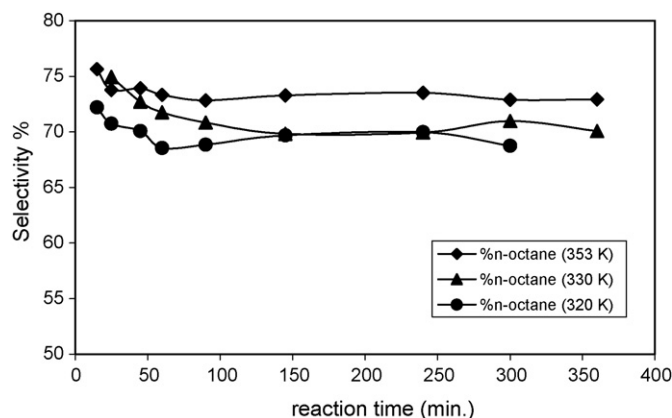


Fig. 9. Temperature effect on *n*-octane selectivity: 102 bar total pressure; mole fraction of $H_2 = 0.048$; 1-octene = 9.42×10^{-4} ; $CO_2 = 0.949$; substrate/catalyst = 232.

stayed at same value with 320 K till end of the reaction. The rate was found to be very dependent on the temperature and Arrhenius analysis of the resulting rate data yielded activation parameters: $E_a = 18.8 \text{ kJ mol}^{-1}$; $\Delta H^\ddagger = 16.2 \text{ kJ mol}^{-1}$; $\Delta S^\ddagger = -250 \text{ J K}^{-1} \text{ mol}^{-1}$; $\Delta G^\ddagger = 96.2 \text{ J K}^{-1} \text{ mol}^{-1}$. A comparison with the data reported to homogenous hydrogenation of 1-octene in dichloromethane/methanol mixture ($\Delta H = 36.4 \text{ kJ mol}^{-1}$, $\Delta S = -170.6 \text{ J K}^{-1} \text{ mol}^{-1}$) using Ni(*o*-MeO-dppp) [31] shows that Pd catalyst has similar behavior with Ni catalyst. The data reported by Khan et al. [32,33] for homogeneous hydrogenation of cyclohexene ($\Delta H = 4.4 \text{ kJ mol}^{-1}$, $\Delta S = 4.18 \text{ J K}^{-1} \text{ mol}^{-1}$) using $RhCl(PPh_3)_3$ and ($\Delta H = 1.1 \text{ kJ mol}^{-1}$, $\Delta S = -174.7 \text{ J K}^{-1} \text{ mol}^{-1}$) using [Pd(DPEA)-Cl]Cl indicates that Pd catalyst is associated with a higher energy of enthalpy and the entropy of activation, which could account for the more drastic conditions required to carry out the hydrogenation; however, a solvent effect might also be considered.

3.5. Total pressure effect

The total pressure effect on the hydrogenation of styrene and 1-octene has also been examined. As shown in Fig. 10, the conversion of styrene does not change with increasing the total

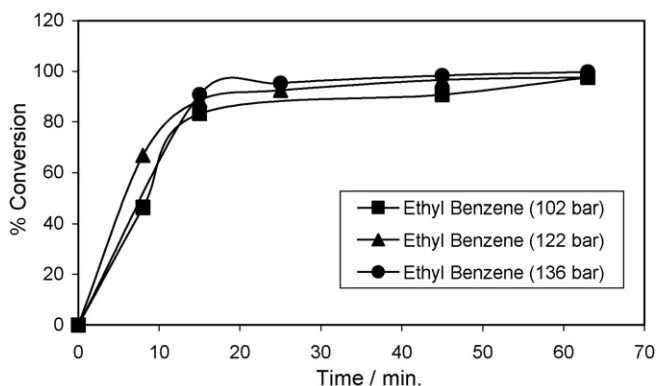


Fig. 10. Total pressure effect on styrene hydrogenation. Reaction conditions: $T = 353 \text{ K}$; substrate/catalyst = 232; mole fraction of $H_2 = 0.0491$.

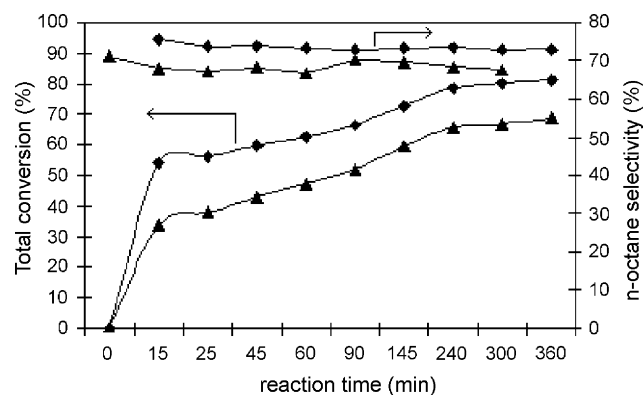


Fig. 11. Effect of CO_2 pressure on conversion and selectivity for hydrogenation of 1-octene in $scCO_2$ solvent at 353 K (\blacklozenge 102 bar; \blacktriangle 136 bar). Mole fraction of $H_2 = 0.048$; 1-octene = 9.42×10^{-4} ; $CO_2 = 0.949$; substrate/catalyst = 232.

pressure of CO_2 . However, the hydrogenation rate and selectivity of 1-octene was effected negatively compared to that of styrene (Fig. 11). By increasing pressure, the total conversion and selectivity to *n*-octane increased about 10%.

3.6. Solvent effect

The effect of solvent on the kinetics was investigated using toluene, acetone and methanol. The comparison of the hydrogenation rate of styrene in $scCO_2$ with respect conventional organic solvent is shown in Fig. 12. Under the conditions studied, the reaction was seen to be occurring in single homogeneous phase during the reaction in $scCO_2$ and heterogeneous reaction occurs in organic phase. We found that the palladium complex decomposes during the course of reaction leading to the precipitation of palladium black in organic solvents, which is active under the reaction conditions. We have not observed same behavior in supercritical conditions. Visual observation showed that no particle observed during the course of reaction. Turn over number (TON) for 60 min in $scCO_2$ is 232, which can be comparable with those in organic solvents for which TON is 150 in toluene, 170 in acetone, and 154 in methanol. As we can observe in Fig. 12, the polarity of organic the solvent does not

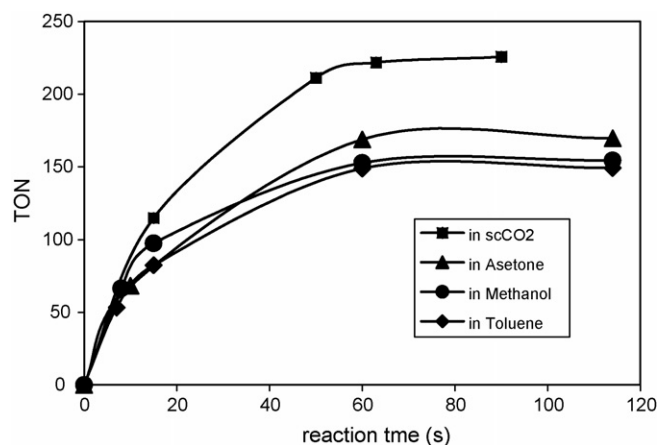


Fig. 12. Results for hydrogenation of styrene in $scCO_2$ and organic solvents. Reaction conditions: $pH_2 = 6 \text{ bar}$; $T = 320 \text{ K}$; substrate/catalyst = 232.

Table 2
Different substrates in the palladium-catalyzed hydrogenation^a

Substrate	Reaction medium	T (K)	Reaction time (min)	pH ₂ (bar)	Total conversion (%)	TON ^b	Main product
Styrene	scCO ₂ ^c	320	60	6	95.9	235	Ethyl benzene
	Toluene	320	60	6	87.7	151	Ethyl benzene
	Acetone	320	60	6	99.8	171	Ethyl benzene
	Methanol	320	60	6	90.0	155	Ethyl benzene
Cyclohexene	scCO ₂ ^c	320	60	11	74.5	166	Cyclohexane
	Acetone	320	90	11	100	223	Cyclohexane
	Chloroform	320	90	11	21	44	Cyclohexane
1-Octene	scCO ₂ ^c	320	90	11	26.2	60	<i>n</i> -Octane
	scCO ₂ ^c	330	90	8	55	128	<i>n</i> -Octane
	scCO ₂ ^c	353	90	6	66	278	<i>n</i> -Octane
	scCO ₂ ^c	353	240	6	78.4	367	<i>n</i> -Octane
<i>t</i> -2-Octene	scCO ₂ ^c	353	95	11	39.4	120	<i>n</i> -Octane

^a Reaction conditions: substrate/catalyst = 232.

^b TON = moles of styrene reacted/moles of palladium.

^c Total pressure = 102 bar.

notable affect the overall catalytic activity. TON values indicated that scCO₂ has a positive effect on the activity of the catalyst (Table 2). The miscibility of scCO₂ with hydrogen results in high diffusion rates, and provides the basis for achieving much higher reaction rates in conventional solvent.

4. Conclusion

In summary, the present work has demonstrated that the perfluoroalkylated pyridine–palladium complex is soluble and active for hydrogenation of olefins in pure scCO₂ at the reaction conditions studied. The results obtained in scCO₂ are comparable with those in toluene, acetone and methanol and it is suggested that scCO₂ has some positive effect in promoting the hydrogenation, due to the high diffusion and low viscosity of scCO₂, which can facilitate the collision of the reactant molecules and the separation of the resultant molecules from catalytic center. A kinetic study of the hydrogenation of styrene to ethyl benzene show that the experimental rate is first-order with respect to catalyst and styrene concentrations and zero order in hydrogen pressure.

Further work using similar rhodium and palladium complexes for kinetics and mechanistic study for the same reactions are in progress, and some extensions of this work with C–C coupling reactions in scCO₂.

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References

- [1] P.G. Jessop, F. Joo, C.-C. Tai, *Coord. Chem. Rev.* 248 (2004) 2425.
- [2] J.-D. Grunwald, R. Wandeler, A. Baiker, *Catal. Rev. Sci. Eng.* 45 (2003) 1.
- [3] E.J. Beckman, *J. Supercrit. Fluids* 28 (2003) 121.
- [4] R.G. Sheldon, *Green Chem.* 7 (2005) 267.
- [5] W. Leitner, *Acc. Chem. Res.* 35 (2002) 746.
- [6] P.G. Jessop, W. Leitner (Eds.), *Chemical Synthesis Using Supercrit Fluids*, Wiley–VCH, Weinheim, 1999.
- [7] H.-U. Blaser, A. Indolese, A. Schnyder, H. Steiner, N. Studer, *J. Mol. Catal. A: Chem.* 173 (2001) 3.
- [8] P. Espinet, K. Soulantica, *Coord. Chem. Rev.* 193–195 (1999) 499.
- [9] J.B. Arterborn, M. Pannala, A.M. Gonzales, R.M. Chamberlin, *Tetrahedron Lett.* 41 (2000) 7847.
- [10] P.J. Collier, T.J. Half, J.A. Iggo, P. Johnston, J.A. Slipszenko, P.B. Wells, R. Whyman, *Chem. Commun.* (1998) 1451.
- [11] C. Pham-Huu, N. Keller, G. Ehrer, L.J. Charbonniere, R. Ziessel, M.J. Ledoux, *J. Mol. Catal. A: Chem.* 170 (2001) 155.
- [12] G. Fogassy, L. Hegedus, A. Tungler, A. Levai, T. Mathe, *J. Mol. Catal. A* 154 (2000) 237.
- [13] F. Zhao, Y. Ikushima, M. Chatterjee, O. Sato, M. Arai, *J. Supercrit. Fluids* 13 (2003) 65.
- [14] S. Kainz, D. Koch, W. Bauman, E. Leitner, *Angew. Chem. Int. Ed. Engl.* 36 (1997) 1628.
- [15] N. Shezd, R.S. Oakes, A.A. Clifford, C.M. Rayner, *Tetrahedron Lett.* 40 (1999) 2221.
- [16] D. Prajapat, M. Gohain, *Tetrahedron* 60 (2004) 815.
- [17] I. Kani, M.A. Omary, M.A. Rawashdeh, Z.K. Lopez-Castillo, R. Flores, A. Akgerman, J.P. Fackler, *Tetrahedron* 58 (20) (2002) 3923.
- [18] I. Kani, R. Flores, J.P. Fackler, A. Akgerman, *J. Supercrit. Fluids* 31 (2004) 287.
- [19] Z.K. Lopez-Castello, R. Flores, I. Kani, J.P. Fackler Jr., A. Akgerman, *Ind. Eng. Chem. Res.* 42 (2003) 3893.
- [20] D.H. Williams, I. Fleming, *Spectroscopic Methods in Organic Chemistry*, McGraw-Hill, London, UK, 1995.
- [21] J. Kuduk-Jaworska, A. Puszko, M. Kubiak, M. Pełczyńska, *J. Inorg. Biochem.* 98 (2004) 1447.
- [22] R. Chen, J. Bacsa, S.F. Mapolie, *Polyhedron* 22 (2003) 2855.
- [23] U. Kalinowska, L. Chęcińska, M. Małecka, A. Erxleben, B. Lippert, J. Ochocki, *Inorg. Chim. Acta* 358 (2005) 2464.
- [24] M.W. van Laren, C.J. Elsevier, *Angew. Chem. Int. Ed.* 38 (1999) 3715.
- [25] B. Siggelkow, M.B. Meder, C.H. Galka, L.H. Gade, *Eur. J. Inorg. Chem.* (2004) 3242.
- [26] J.A. Osborn, F.H. Jardine, J.F. Young, G. Wilkinson, *J. Chem. Soc. A* (1966) 1711.
- [27] A.M. Kluwer, T.S. Koblenz, T. Jonischkeit, K. Woelk, C.J. Elsevier, *J. Am. Chem. Soc.* 127 (2005) 15470.

- [28] I.M. Angula, S.M. Lok, V.F. Quaroga Norabuena, M. Lutz, A.L. Spek, E. Bouwman, *J. Mol. Catal. A* 187 (2002) 55.
- [29] S. Huh, Y. Cho, M.J. Jun, *Polyhedron* 13 (1994) 1887.
- [30] R.A. Sanchez-Delgado, M. Rosales, *Coord. Chem. Rev.* 196 (2000) 249–280.
- [31] I.M. Angulo, A. Bouwman, *J. Mol. Catal. A: Chem.* 175 (2001) 65.
- [32] M.M.T. Khan, E. Rama Rao, M.R.H. Siddiqui, B.T. Khan, S. Begum, S.M. Ali, J. Reddy, *J. Mol. Catal.* 45 (1988) 35.
- [33] M.M.T. Khan, B.T. Khan, S. Begum, *J. Mol. Catal.* 45 (1988) 305.