Available online at www.sciencedirect.com

ScienceDirect

Journal of Catalysis 254 (2008) 374–382

JOURNAL OF CATALYSIS

www.elsevier.com/locate/jcat

Hydrogenation of dienes by a recyclable poly(ethylene oxide)–rhodium phosphineless catalytic system

Aline Tavares, Silvana I. Wolke [1], Ricardo Gomes da Rosa [*]

Instituto de Química, Universidade Federal do Rio Grande do Sul, Av. Bento Gonçalves, 9500, P.O. Box 15003, 1501-970, Porto Alegre-RS, Brazil

Received 17 October 2007; revised 12 January 2008; accepted 14 January 2008

Abstract

The monocationic complex $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ in poly(ethylene oxide) (PEO) 3350/MeOH has proven to be a very efficient catalyst for 1,7-octadiene, 1,9-decadiene, and 1,5-cyclooctadiene hydrogenation. This system allows perfect product separation and catalyst phase recycling, resulting in thousands of catalytic cycles (TON ≈ 9000). Even at room temperature, turnover frequencies as high as 5000 h^{-1} are attained (50 bar), which makes this one of the most active catalytic systems for diene hydrogenation. Kinetic studies reveal that the reaction rate is second-order in H_2 pressure and first-order in both rhodium and diene concentrations. Typical tests suggest that, despite the reductive reaction conditions, which could lead to colloidal metal dispersion, the reduction of dienes is catalyzed by molecular species.

Keywords: Diene hydrogenation; Phosphineless rhodium-based system; Poly(ethylene oxide) (PEO); Catalyst recycle; Cyclopentadienyl–rhodium complex

1. Introduction

One of the most important challenges in organometallic catalysis is to develop an efficient and ecologically catalytic system that allows a facile product separation, catalyst recovery, and recycling [1]. The first studies of these systems used water as the polar phase and hydrosoluble phosphine as ligands [2]. More recently, fluorinated solvents [3] and ionic liquids [4–6] have replaced water. Other alternatives to address catalyst availability and recycling problems included using thermosensitive polymers [7] or poly(acrylamides) as homogeneous catalyst supports [8].

Our initial research on biphasic catalysis systems studied olefin hydrogenation [9] using a ternary system formed by two organic solvents with different polarities and poly(ethylene oxide) (PEO) 3350 [10–12]. Using the systems heptane/CH_2Cl_2 (or MeOH)/PEO 3350 + $RhCl(PPh_3)_3$ (or $[Rh(1,5\text{-COD})(dppe)]PF_6$, where 1,5-COD = 1,5-cyclooctadiene and dppe = diphenylphosphineethane), in the hydrogenation of hex-1-ene, we obtained excellent results in terms of phase separation, catalyst segregation to the polar phase, and catalytic performance. However, limits of four recyclings in the case of Wilkinson's complex and 10 recyclings for the cationic rhodium complex bearing a chelating diphosphine was observed. These limits were understood to be related to deactivation of the catalytic species due to phosphine leaching during the recycling process.

The literature contains many other applications of PEO or PEG (poly(ethylene glycol)) in catalysis. Important reactions include olefin hydrogenation using PEO/CO_2(sc) [13], olefin epoxidation [14], the Suzuki reaction [15–17], the Heck reaction [18], Sonogashira coupling using phosphines bound to MeOPEG [19], Sharpless asymmetric olefin dihydroxylation [20], and PEG-functionalized phosphines as ligands for rhodium-catalyzed olefin hydroformylation [21].

Considering our results for hex-1-ene hydrogenation and the ability of PEO to segregate the transition metal catalyst phase, we decided to study the rhodium-catalyzed hydrogenation of dienes. The hydrogenation of dienes is relevant to the fuel refining industry because the burning of a diene-containing fuel inside the engine can lead to undesirable heavy products that can damage the engine. We tested a phosphine-free

---

[*] Corresponding author. Fax: +55 51 3308 7304.
E-mail address: ricardo.gomes@ufrgs.br (R.G. da Rosa).

[1] Present address: Departamento de Química, Fundação Universidade Federal do Rio Grande, Rio Grande, RS, Brazil.

doi:10.1016/j.jcat.2008.01.015

cationic rhodium complex, $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$, where $Cp^* =$ pentamethylcyclopentadienyl, as a precatalyst to help overcome the phosphine leaching process. This complex contains a Cp* ligand that could be an excellent substitute for the phosphine ligands, helping to stabilize the catalyst and allowing easy product separation and catalyst phase recycling. In this paper, we report our findings on the hydrogenation of 1,7-octadiene, 1,9-decadiene, and 1,5-cyclooctadiene catalyzed by $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ in PEO 3350/MeOH polar phase.

2. Experimental

2.1. Materials

Dienes (Aldrich, 98%) were passed through a column of activated neutral alumina to eliminate peroxides and stocked over 3A activated molecular sieves under argon atmosphere. Heptane was distilled over Na/benzophenone, and MeOH was distilled over CaH_2. PEO (Alfa) 3350 was evacuated for 12 h under dynamic vacuum at room temperature and stocked under argon. Hydrogen (White Martins, 99.999%) was used as received. Argon (White Martins, 99.998%) was passed through two traps filled with 3A activated molecular sieves and one trap containing BASF catalyst R3-11 to remove traces of water and oxygen.

2.2. Characterizations

All NMR spectra were obtained using a Varian VXR Multinuclear spectrometer. ^1H NMR spectra were obtained at 200 MHz using C_3D_6O (d_6-acetone) or $CDCl_3$ as solvents and calibrated by the TMS signal. $^{31}P\{^1H\}$ NMR analysis were carried out at 121 MHz using a capillary tube filled with H_3PO_4 as reference and C_3D_6O as solvent. Elemental analyses were run in a Perkin–Elmer 2400 CHN Elemental Analyzer. UV spectra were performed between 300 and 800 nm in a Shimadzu (UV–1601 PC) spectrometer, using a quartz cell with an optical path length of 1 cm. IR spectra were collected in solid phase by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), 32 scans, in a Bomen MB102 spectrometer. GC/MS analyses were done using a Shimadzu 17A gas chromatograph equipped with a capillary column DB-5 (30.0 m × 0.25 mm), using He as carrier gas, coupled to a Shimadzu GCMS-QP5050 mass spectrometer operating at 70 eV (EI).

2.3. Catalyst precursor preparation

$[(\eta^5\text{-Cp}^*)Rh(\mu_2\text{-Cl})Cl]_2$ was prepared from $RhCl_3{\cdot}3H_2O$ and pentamethyl–cyclopentadiene (Aldrich, 99%) as stated in the literature, in almost quantitative yield [22]. The monocationic complex $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ was prepared from $[(\eta^5\text{-Cp}^*)Rh(\mu_2\text{-Cl})Cl]_2$ as described previously, replacing NH_4PF_6 with KPF_6 [23]. The yield of the recrystallized product (orange-red crystals) was 60%. Its ^1H NMR spectrum demonstrating one singlet at 1.73 ppm related to the methyl groups of Cp*. The spectrum of phosphorus resonance presented a heptuplet at −144 ppm related to the phosphorus atom coupled to six fluorine nuclei, confirming the presence of PF_6^- anion in the complex. The presence of chlorine was detected, with formation of a white precipitate of AgCl observed on the addition of an excess of aqueous $AgNO_3$ to a solution of the complex in MeCN. The weight of the AgCl obtained corresponded to 14.00% chlorine in the complex, very close to the expected value of 14.62%. The results of its elemental analysis (Perkin–Elmer 2400 CHN Elemental Analyzer) were $C = 30.09\%$, $H = 3.86\%$, $N = 6.53\%$ (Anal. calcd: $C = 29.51\%$, $H = 3.71\%$, $N = 6.45\%$). These results lead us to conclude that the replacement of the cation NH_4^+ by K^+ on the hexafluorophosphate salt led to the same rhodium complex, as could be predicted.

2.4. Characterization of the complex $[(\eta^5\text{-Cp}^*)Rh(MeOH)_3](PF_6)_2$

IV (DRIFTS): $\nu_{O\text{–}H} = 3427\ cm^{-1}$, $\nu_{C\text{–}H_{aliphatic}} = 2960\ cm^{-1}$ and $2929\ cm^{-1}$, $\nu_{C=C} = 1469\ cm^{-1}$, $\nu_{C\text{–}C} = 1020\ cm^{-1}$, $\nu_{P\text{–}F} = 873\ cm^{-1}$, $862\ cm^{-1}$ and $559\ cm^{-1}$;

^1H *NMR* (CD_2Cl_2, 200 MHz, δ in ppm referred by TMS): δ 3.49 (CH_3–CH_3OH), δ 1.68 (CH_3–Cp*);

C, H, N: observed: $C = 25.24\%$, $H = 4.20\%$. Anal. calcd: $C = 25.01\%$, $H = 4.36\%$; UV/vis (CH_3OH): 351 nm (sh), 394 nm and 505 nm.

2.5. Catalytic experiments

All catalytic systems were prepared under argon atmosphere. Reactions were performed under 40 bar hydrogen pressure in the MeOH/PEO polar phase, and the products were extracted at the end of the reaction using *n*-heptane. Samples for GC or GC/MS were withdrawn directly from the *n*-heptane phase. In a typical experiment, 1.4×10^{-2} mmol (10.2 mg) of $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ was added to an argon-purged Schlenk tube, followed by 1.8 g of PEO 3350 (Sigma). These solids were dissolved by adding 7 ml of MeOH and 3.1 mmol (∼0.4 ml) of diene under magnetic stirring. This solution was then transferred by cannula to a stainless steel reactor that had been purged by vacuum/argon cycles. The reactor was closed, purged 3 times with H_2, and then pressurized to 40 bar. The products were analyzed by GC and GC/MS.

2.6. Filtration test for an active heterogeneous component in the catalysis

Maitlis and coworkers have developed a simple and very convenient test to verify whether small metal aggregates are involved in the catalytic activity of a homogeneously catalyzed reaction conducted under reducing conditions [24]. This method involves adding an inert filter aid, such as cellulose, to the reaction solution to adsorb small metal particles that could be very active catalysts in many processes. Then the mixture is filtered, and the catalytic activity of the filter aid and the filtered solution are evaluated. The catalytic experiments were done as described above using 1,7-octadiene (0.4 ml, 3 mmol) as a substrate and $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ (1.4×10^{-2} mmol, 10.2 mg) as a catalyst precursor. The catalytic system was recycled until it reached peak performance (7 recyclings, pale-yellow color for the catalyst phase). Hydrogen consumption was monitored by a pressure transducer device attached to the reactor, and the data were analyzed using appropriate software (FieldChart, NOVUS). After the plot $p(\text{bar}) \times t(\text{min})$ for the active catalyst was registered, about 2 g of cellulose powder (Whatman, standard grade) was added to the pale-yellow catalyst solution under stirring. The suspension was filtered through a sintered glass filter under argon, and both the filtrate and the remaining cellulose were evaluated for diene hydrogenation under the same reaction conditions. The cellulose was washed with methanol (3 × 5 ml) and transferred to the reactor along with more methanol (7 ml) and 1,7-octadiene. In the case of the filtrate, more diene was added, and a small amount (about 1.5 ml) of methanol was required to complete the initial reaction volume (7 ml). All the catalytic tests were run using a clean reactor glass liner.

3. Results and discussion

Compared with olefins, harsh conditions are required for the hydrogenation of dienes [25,26]. Therefore, the activity of $[(\eta^5\text{-Cp}^*)_2\text{Rh}_2(\mu_2\text{-Cl})_3]\text{PF}_6$ was initially evaluated at 50 °C and 40 bar H_2 for 24 h (entry 1, Table 1). Note that all of the reactions presented in Table 1 were performed using the same catalytic phase.

Considering the hydrogenation of 1,7-octadiene, a consistent decrease in alkane selectivity was observed until entry 5 (fourth recycling). This effect can be explained by the fact that methanol evaporated during reactor depressurization, inducing precipitation of the poly(ethylene oxide), which led to encapsulation of the rhodium complex. Because dienes are almost insoluble in the PEO phase, the substrate/catalyst contact thus would be diminished. This hypothesis was confirmed by our observation that adding MeOH before each recycle restored the selectivity (entries 6–10). Considering the drop in pressure observed during the reaction, we decided to reduce the reaction time to 4 h (entry 8), and found that the reaction had indeed already finished. Lowering the temperature to 25 °C and maintaining a 4-h reaction time resulted in complete conversion of the diene (entry 9). In fact, an even shorter reaction time (30 min; entry 10) gave complete conversion at room temperature, with TOF reaching 720 h^{-1}. It is also interesting to note the catalyst phase color changes at each recycling, ranging from orange to colorless.

Maintaining the same catalyst phase to hydrogenate 1,9-decadiene (at 25 °C for 1 h) also resulted in high conversion and alkane selectivity (entries 11–13). The reactivity of this catalytic system can be clearly seen in entry 14, which was stopped at 10 min yet still afforded a remarkable TOF (2247 h^{-1}). Entries 15–19 refer to the hydrogenation of 1,5-cyclooctadiene. This cyclic diene was harder to hydrogenate than the open-chained ones, with only 75% conversion obtained in 20 min of reaction at the same hydrogen pressure (entry 16). This could be related to the chelating property of 1,5-COD, which hinders hydrogen coordination. Reducing the H_2 pressure (entries 16–18), it was possible to observe the same behavior presented by the other dienes; the lower the conversion, the lower the selectivity to alkanes. Moura et al. [27] reported that cyclooctadiene can

Table 1
Hydrogenation of dienes using the same catalytic phase

Entry	Recycle	Diene	t (h)	p (bar)	Conversion (%)	Alkane (%)	Olefins[c] (%)	TOF (h^{-1})	TON	Color[d]
1	–	1,7-Octadiene[a]	24	40	100	93	7	16	376	Orange
2	1		24	40	100	93	7	16	376	Brown
3	2		24	40	100	86	14	15	362	Brown
4	3		24	40	100	78	22	14	346	Brown
5	4		24	40	93	52	48	11	275	Beige
6	5		24	40	100	86	14	15	362	Pale beige
7	6		24	40	100	99	1	16	387	Colorless
8	7		4	40	100	93	7	94	376	Colorless
9[b]	8		4	40	100	93	7	94	376	Colorless
10[b]	9		0.5	40	100	85	15	720	360	Colorless
11	10	1,9-Decadiene[b]	1	40	100	97	3	383	383	Colorless
12	11		1	40	100	96	4	381	381	Colorless
13	12		1	40	100	98	2	385	385	Colorless
14	13		0.17	40	100	95	5	2247	382	Colorless
15	14	1,5-COD[b]	2	40	100	95	5	190	379	Colorless
16	15		0.3	40	75	64	36	798	239	Colorless
17	16		0.3	30	70	58	42	716	215	Colorless
18	17		0.3	20	57	48	52	547	164	Colorless
19	18		4	10	35	46	54	25	99	Colorless

Note. $[\text{Rh}^{3+}] = 2.8 \times 10^{-2}$ mmol, 10.9 mmol of double bonds.

[a] 50 °C.

[b] 25 °C.

[c] Isomer mixtures.

[d] Catalytic phase color observed at the end of the reaction time.

be hydrogenated by iridium clusters to cyclooctene with high selectivity, even at complete substrate conversion. Comparing our results to theirs [27] demonstrates one basic difference: Our system led to the reduction of the dienes in two steps, which means that it can be coordinated effectively to either a diene or an olefin; in contrast, the iridium cluster appears to require substrates with hapticity >2 to form stable adducts. This difference demonstrates the monometallic nature of the catalytic species in the case of our rhodium-based system.

3.1. Studying the catalyst activation phenomena

The results in Table 1 suggest that catalyst activation during recycling was accompanied by color changes. To investigate this more thoroughly, we prepared and tested a fresh catalytic system to hydrogenate 1,7-octadiene. The findings for this system, given in Table 2, show a color evolution during recycling very similar to that shown in Table 1; however, the color change seems to be more related to the recycling workup than to the reaction time. In addition, considering the initial rate (calculated by sampling the H_2 pressure drop by a pressure transducer until about 10% of conversion was attained) and TOF results, it is possible to conclude that six recycling are required to reach the highest catalytic activity.

Fig. 1 presents UV spectra taken from the catalytic phase solutions after each reaction detailed in Table 2. Despite these results, whether the catalyst was formed by molecular colorless species (e.g., poly-hydrides [28]) or PEO-stabilized rhodium nanoparticle dispersion [29] remains unclear.

3.2. Hydrogenation of 1,9-decadiene under optimized conditions and kinetic studies

To verify the catalytic performance along a large number of recycles and to establish the kinetic effects of H_2 pressure and substrate concentration, we used 1,9-decadiene as a model substrate. The results, given in Table 3 (mainly at 40 and 50 bar) as well as in the literature, lead us to conclude that this is one of the most active catalytic systems for diene hydrogenation yet described [25,26,30,31]. The efficiency of this system in terms of recycling is clearly demonstrated by the very high TON value calculated over the 25 reactions (≈9000). As was observed with the other dienes studied, a remarkable activation profile was obtained during the course of recycling. Fig. 2 compares the catalytic activity attained at the first reaction with that at the 22nd recycling.

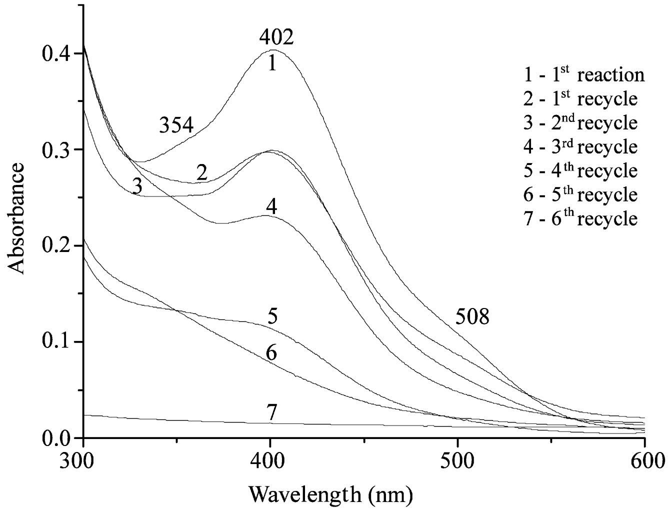


Fig. 1. UV spectra of the catalytic phase after each hydrogenation of the 1,7-octadiene presented in Table 2.

3.3. Kinetic studies

3.3.1. Effect of diene concentration

The kinetic effects of the diene concentration were evaluated by the integral method. Fig. 3 presents a ln([diene]/[diene]$_o$) versus time plot with a perfect linear correlation. The reaction rate was first-order dependent on the substrate concentration, as expected.

3.3.2. Effect of hydrogen pressure

The effect of hydrogen pressure was calculated using initial rate values (conv. <15%) for each pressure. The reactions chosen for this study were entries 22–25 in Table 3, covering a 50- to 20-bar range for hydrogen consumption. Considering that hydrogen solubility is directly related to its pressure in methanol at 25 °C [32], it is possible that $r_i = k(\mathrm{pH}_2)^x$ and its linear expression is $\ln r_i = \ln k + x \ln(\mathrm{pH}_2)$. Thus, the order

Table 2
Hydrogenation of 1,7-octadiene: effect of the recycle in the activity and color evolution

Entry	Recycle	Conversion (%)	Octane (%)	Olefins[a] (%)	TOF (h^{-1})	v_i[b] ($\mathrm{mol\,l^{-1}\,h^{-1}}$)	TON	Color[c]
1	–	68	71	29	113	0.42	226	Orange
2	1	67	72	28	112	0.48	224	Orange
3	2	64	73	27	108	0.66	216	Pale orange
4	3	82	83	17	146	0.72	292	Yellow
5	4	87	82	18	154	0.78	308	Yellow
6	5	89	84	16	159	0.84	319	Pale yellow
7	6	98	87	13	179	0.90	357	Colorless

Note. $[\mathrm{Rh}^{3+}] = 2.8 \times 10^{-2}$ mmol, 2 h, $\mathrm{pH}_2 = 40$ bar, 25 °C, 10.9 mmol of double bonds.

[a] Isomer mixtures.

[b] Initial rate calculated at conv. <10%.

[c] Catalytic phase color observed at the end of the reaction time.

Table 3
Hydrogenation of 1,9-decadiene: effect of the recycle and hydrogen pressure in the activity and color evolution

Entry	Recycle	*t* (h)	*p* (bar)	Conversion (%)	Decane (%)	Olefins[a] (%)	TOF (h^{-1})	TON	Color[b]
1	–	2	40	62	39	61	83	166	Orange
2	1	2	40	72	38	62	96	192	Orange
3	2	2	40	87	63	37	137	273	Yellow
4	3	2	40	95	82	18	167	333	Yellow
5	4	2	40	95	89	11	173	346	Beige
6	5	2	40	95	90	10	174	348	Pale beige
7	6	2	40	100	93	7	186	372	Pale beige
8	7	2	40	100	90	10	183	366	Colorless
9	8	2	40	100	90	10	183	366	Colorless
10	9	2	40	100	90	10	183	366	Colorless
11	10	2	40	100	94	6	187	374	Colorless
12	11	2	40	100	92	8	185	370	Colorless
13	12	0.16	40	100	95	5	2350	376	Colorless
14	13	0.16	40	100	90	10	2290	366	Colorless
15	14	0.16	40	100	94	6	2335	374	Colorless
16	15	0.16	40	100	96	4	2362	378	Colorless
17	16	0.16	40	100	97	3	2374	380	Colorless
18	17	0.16	40	100	96	4	2362	378	Colorless
19	18	0.16	40	100	97	3	2374	380	Colorless
20	19	0.16	40	100	93	7	2326	372	Colorless
21	20	0.16	40	100	98	2	2387	382	Colorless
22	21	0.08[c]	50	100	97	3	4749	380	Colorless
23	22	0.10[c]	40	100	98	2	3818	382	Colorless
24	23	0.20[c]	30	100	91	9	1842	368	Colorless
25	24	0.45[c]	20	100	90	10	814	366	Colorless

Note. $[Rh^{3+}] = 2.8 \times 10^{-2}$ mmol, 1,9-decadiene = 10.8 mmol; 25 °C.

[a] $\sum$% of decenes.

[b] Catalytic phase color observed at the end of the reaction time.

[c] Time required for a complete conversion.

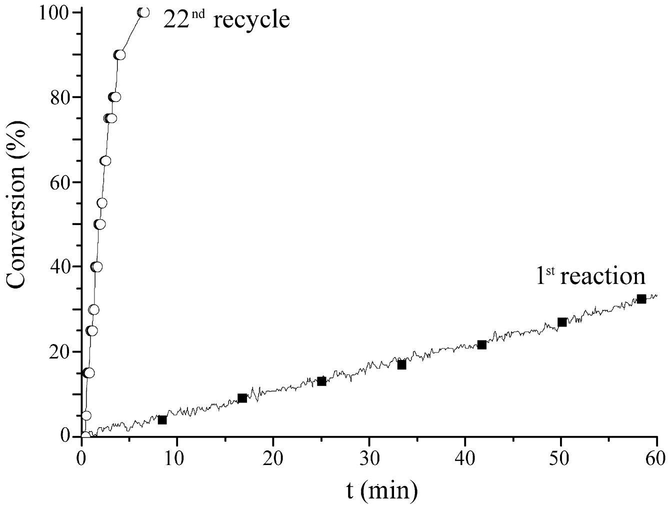


Fig. 2. Substrate consumption along the reaction time estimated by H_2 consumption for the first reaction and for the 22nd recycle.

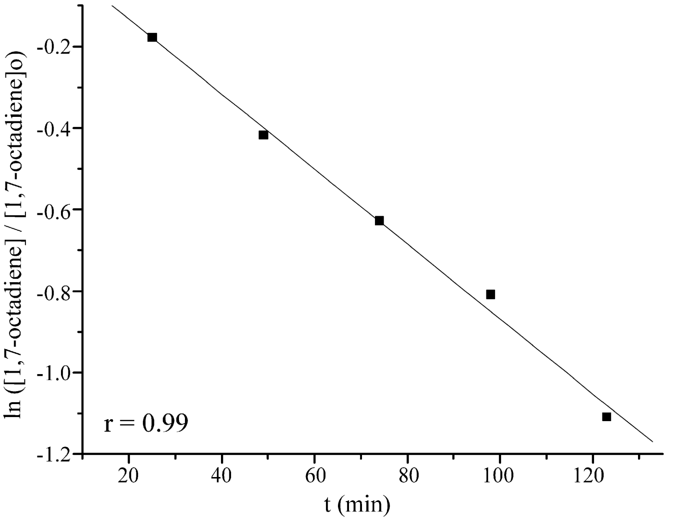


Fig. 3. Plot expressing the first-order dependence of the reaction rate on the 1,7-octadiene concentration. Data taken from entry 7, Table 2.

with respect to the hydrogen pressure (x) will be the angular coefficient.

From the plot of Fig. 4, it is possible to calculate an order value (x) of 2.2 for the hydrogen pressures in the range of 20–40 bar. For pressures >50 bar, the reaction rate appears to become independent of hydrogen pressure. The second-order dependence of hydrogen pressure is consistent with a slow, two-step process for hydrogenation of the dienes, as discussed above.

3.3.3. *Effect of rhodium complex concentration*

The effect of rhodium concentration on the reaction rate was evaluated considering initial rates while keeping the hydrogen pressure at 40 bar and the diene concentration at 0.77 mol/l.

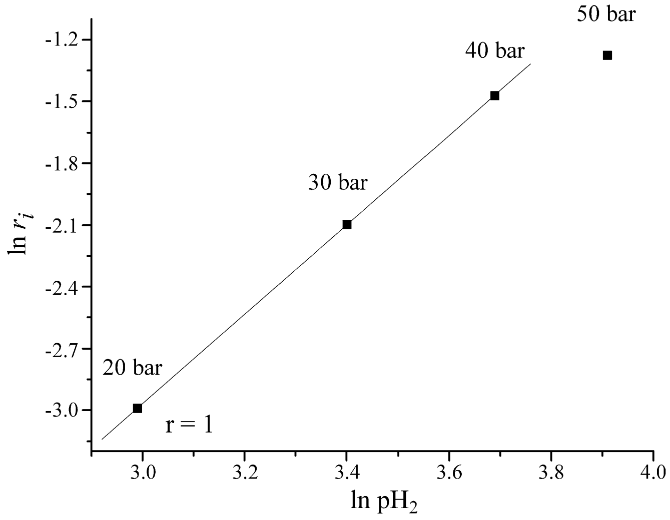


Fig. 4. Effect of the hydrogen pressure (pH_2) on the initial rate values (r_i) for 1,9-decadiene hydrogenation.

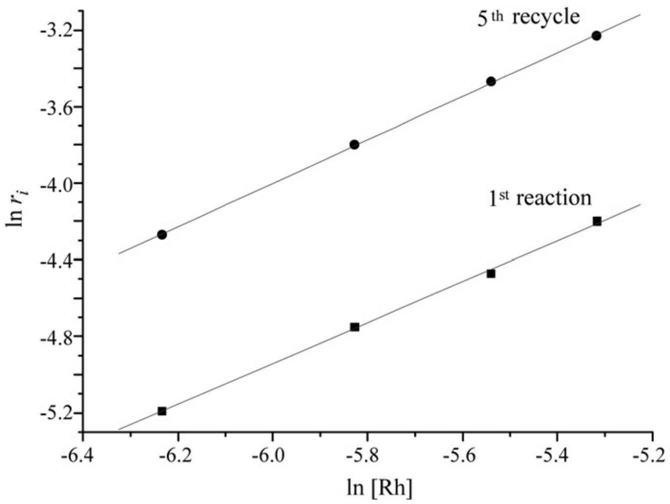


Fig. 5. Effect of rhodium concentration on the reaction rate at the first run and at the fifth recycle.

The rhodium concentration ranged from 2 to 5 mmol/l. From Fig. 5, we can calculate a first-order dependence of the reaction rate on the rhodium concentration at the first reaction (order = 1.07; orange-colored solution) and also at the fifth recycling (order = 1.13; pale-yellow solution). This is in agreement with our earlier assumption that the catalytic species is mononuclear. Thus, the activation profile observed along the recycles should be due to the slow increase in the concentration of the molecular catalytic active species.

3.4. *Isolating possible metal complex intermediates*

Considering the foregoing results, which point to a molecular colorless complex as the catalyst, we ran an experiment using just the precursor complex in methanol, under 40 bar of H_2 at 25 °C for 2 h. After the reaction, the reactor was depressurized and the solution transferred to a Schlenk tube under argon. The solution initially was dark-brown in color and became progressively more orange overnight. In an effort to obtain a colorless solution (which should correlate to the most active form of the catalyst), we submitted the orange solution to five additional hydrogenation procedures; the color remained the same, however. But after the seventh treatment, the solution assumed a stable brown color, and a significant amount of an orange precipitate formed at the bottom of the Schlenk tube, which was subsequently removed by centrifugation. At this time, the solution was *trap-to-trap* distilled and analyzed by GC. No peaks related to the Cp* ligand were detected. The brown solid remaining in the Schlenk tube was identified as $[(\eta^5\text{-Cp}^*)\text{Rh}(\text{MeOH})_3](\text{PF}_6)_2$. The reaction sequence in Scheme 1 represents our proposal to address the formation of this complex and of the orange precipitate.

In this proposition, the orange precipitate corresponds to the neutral complexes (2) and (4), which may have low solubility in methanol medium. The HCl lost due to recycling drives the equilibrium to the right, producing complexes (3) and (4).

Repeating this activating process in the presence of PEO, we found the same color evolution of the solution, as well as the formation of the orange precipitate. Thus, it is clear that the substrate plays a special role in formation of the colorless active catalyst.

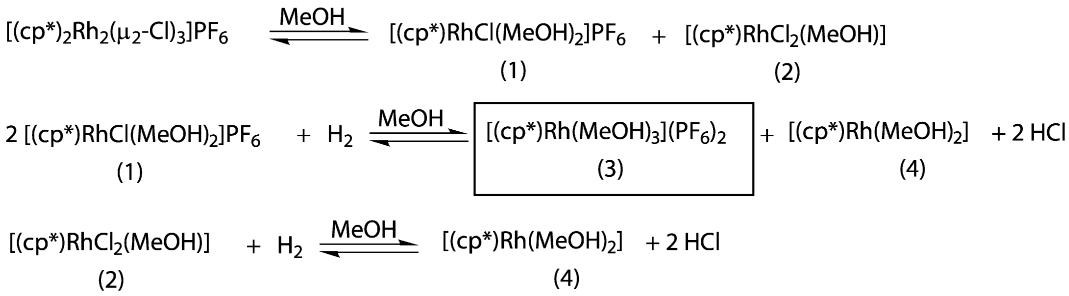
We evaluated the catalytic performance of the brown isolated complex (3) by using it in a 1,5-cyclooctadiene hydrogenation. The results, presented in Table 4, clearly indicate that complex (3) behaved similarly to its precursor [Scheme 1, complex (1)]—that is, catalytic activity increased as the color faded.

3.5. *The nature of the catalytic species*

Determining the actual nature of a catalytic species is a very complicated task. Here we describe our efforts in this area, which involved (i) a physical test, adding an inert filter aid to the reaction mixture to adsorb possible rhodium nanoparticles formed, which are filtered-off [24]; (ii) inhibition of catalytic activity by CS_2 [33]; and (iii) hydrogenation of an aromatic compound [34].

3.5.1. *Cellulose filtration test*

As described in Section 2, this test was developed to identify whether small metal particles could be participating in the catalytic process [24]. In this test, cellulose powder was used as a metal cluster adsorbent. Fig. 6 presents the reaction profile for a very active catalytic phase in a 1,7-octadiene hydrogenation. After addition of the cellulose and filtration, the filtrate solution exhibited the performance characterized in Fig. 7. Both plots exhibit very similar profiles, indicating almost the same hydrogen consumption as a function of time; indeed, in both systems, the reaction was finished after about 10 min of reaction. However, analyzing the first 2 min of reaction for each system allows us to calculate an initial rate for hydrogen consumption of 0.72 bar min^{-1} (Fig. 6) before and 0.54 bar min^{-1} (Fig. 7) after the addition of cellulose and filtration. This initial rate reduction may be due to the loss of some active nanoparticles adsorbed by the cellulose or simply may be an experimental er-



Scheme 1. Proposed reaction steps describing the products formation from hydrogenation of $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ in methanol, under 40 bar of H_2 at 25 °C, for 2 h.

Table 4
1,5-Cyclooctadiene hydrogenation by $[(\eta^5\text{-Cp}^*)Rh(MeOH)_3](PF_6)_2$

Entry	t (h)	Conversion (%)	Cyclooctane (%)	Cyclooctene (%)	TOF (h^{-1})	Colors initial/final
1st reaction[a]	2	100	98	2	49.5	Brown/deep red
1st recycle	0.3	84	52	47	211.4	Deep red/pale red
2nd recycle	0.3	87	49	50	214.6	Pale red/pale red
3rd recycle	0.3	93	75	25	271.3	Beige/pale beige

[a] $[Rh^{3+}] = 5.9 \times 10^{-2}$ mmol, 1,5-COD = 5.9 mmol, $H_2 = 40$ bar, 25 °C.

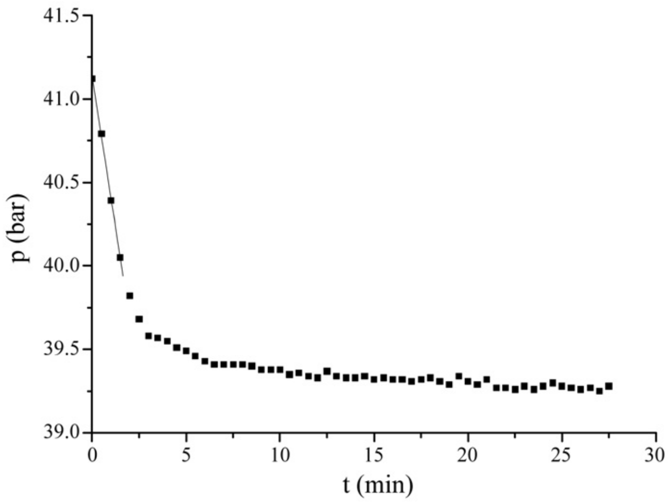


Fig. 6. Filtration test. Hydrogenation of 1,7-octadiene by a very active catalytic system before filtration. $pH_2 = 40$ bar, $T = 25\,°C$ [Rh] = 4 mmol/l. Linear regression data for the first 2 min of reaction: $r = 0.999$; angular parameter = −0.72 bar min^{-1}; linear parameter = 41.1 bar.

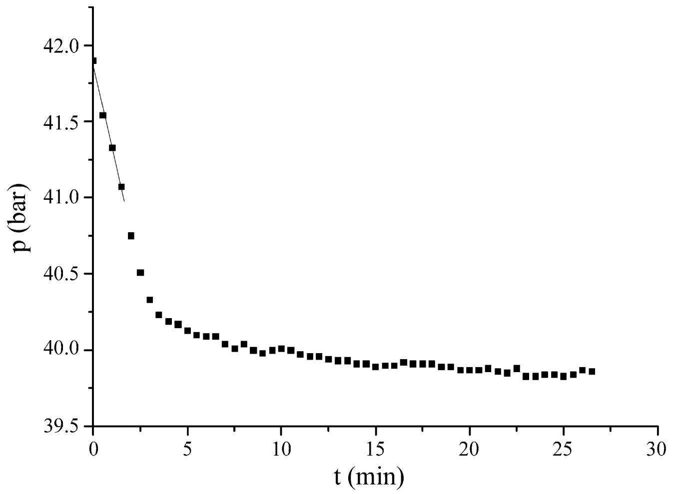


Fig. 7. Filtration test. Hydrogenation of 1,7-octadiene by the filtrate solution obtained using cellulose as an adsorbent for metal particles. $pH_2 = 40$ bar, $T = 25\,°C$. Linear regression data for the first 2 min of reaction: $r = 0.994$; angular parameter = −0.54 bar min^{-1}; linear parameter = 41.9 bar.

ror caused by, for example, a stirring problem leading to poor hydrogen diffusion.

To clarify these results, we performed hydrogenation of 1,7-octadiene using the cellulose used in the filtration as the catalyst. The plot of hydrogen consumption as a function of the time for this system indicates that it is almost inactive (Fig. 8). These results suggest that the catalysis was composed of soluble molecular species.

3.5.2. *Catalytic inhibition with CS_2*

We also evaluated the effect of CS_2 addition on catalytic performance. It is well known that CS_2 forms a stable complex with rhodium at room temperature and that molecular catalytic species present an inhibition profile directly proportional to the molar amount of CS_2 added. On the other hand, if the catalysis is effectuated by small metal aggregates, then the reaction may be significantly affected by even a very low molar ratio of CS_2/M. Fig. 9 shows the results of hydrogenation of 1,9-decadiene, in which CS_2 (2.8×10^{-3} mmol) was added to a catalytic system that had been submitted to four recyclings (2.8×10^{-2} mmol, rhodium based), about 8 min after the reaction started (36.5% conversion). As detailed in Table 3, this system should give about 95% conversion in 2 h (entry 5). The drop observed here was due to the abrupt pressure variation caused by the valve of the CS_2 reservoir. The picture shows

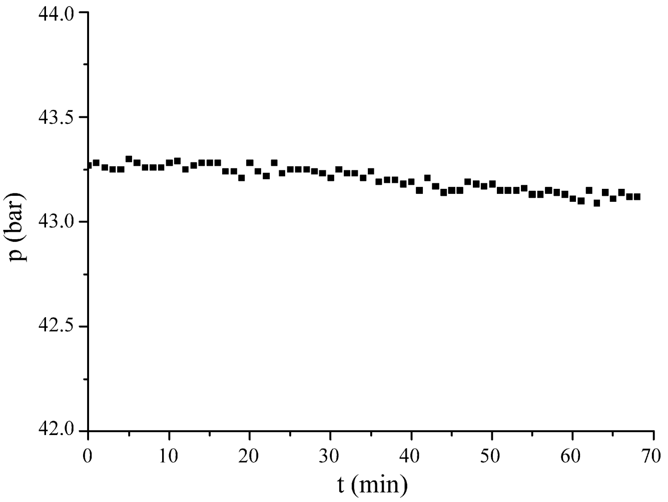


Fig. 8. Filtration test. Hydrogenation of 1,7-octadiene catalyzed by the cellulose used in the filtration. $pH_2 = 40$ bar, $T = 25\,^{\circ}C$.

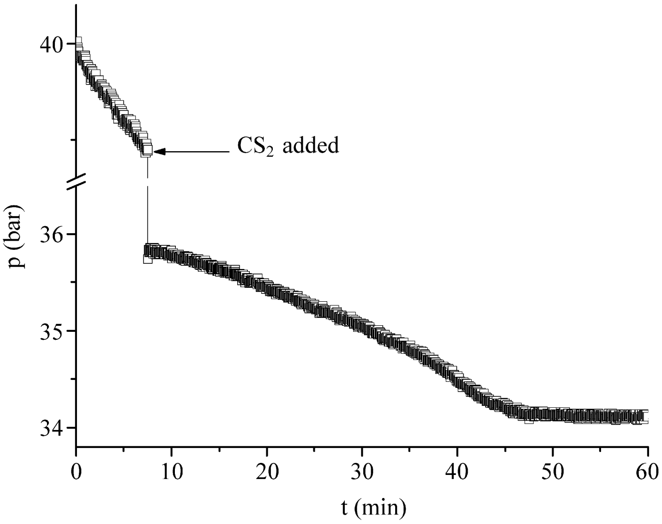


Fig. 9. CS_2 inhibition test. Hydrogenation of 1,9-decadiene, $pH_2 = 40$ bar, $T = 25\,^{\circ}C$. $[Rh] = 4$ mmol/l; $[CS_2] = 0.4$ mmol/l.

that even in the presence of CS_2, the reaction maintained almost the same hydrogen consumption profile as was observed in the regular reaction, affording 97% conversion after 2 h. This indicates that the catalyst is mainly molecular in nature.

3.5.3. Benzene hydrogenation test

It has been well demonstrated in the literature that hydrogenation of aromatic compounds is best performed by heterogeneous or colloidal metal catalysts [33,34]. Therefore, we chose benzene as the substrate in a hydrogenation experiment conducted under similar conditions as in the experiments with dienes. Fig. 10 shows that even for a long reaction period, conversions were very low, again indicating the molecular nature of the active species. Along with these findings, another remarkable observation was the absence of an induction period for all of the reactions (see Fig. 9, for instance), as would be expected for a colloidal catalyst [33,34].

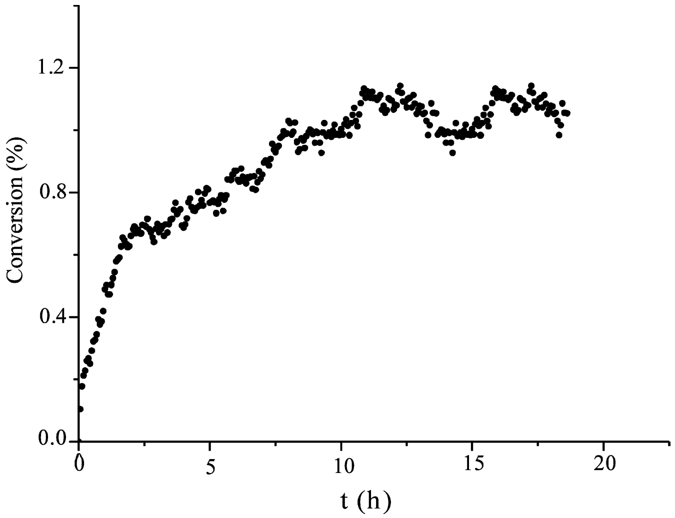


Fig. 10. Benzene hydrogenation test. $[Rh] = 4$ mmol/l, $[benzene] = 0.77$ mol/l, $T = 25\,^{\circ}C$, $pH_2 = 40$ bar.

4. Conclusion

A catalytic system using the phases n-heptane/PEO + MeOH and the complex $[(\eta^5\text{-Cp}^*)_2Rh_2(\mu_2\text{-Cl})_3]PF_6$ has proven to be effective and very robust in diene hydrogenation, allowing multiple recyclings with no noticeable loss of activity or selectivity. Moreover, the Cp* ligand can replace phosphines in the stabilization of rhodium species. The results of catalytic experiments indicate that the colorless catalytic species were slowly formed during recycling and that the diene hydrogenation occurred in two steps. Kinetic studies demonstrated first-order effects for rhodium and diene concentration but a second-order dependence of the reaction rate on the hydrogen pressure.

Experiments conducted to isolate some molecular complex near the catalytic cycle in the absence of the substrate led to a brown complex ($[(\eta^5\text{-Cp}^*)Rh(MeOH)_3](PF_6)_2$) and an orange precipitate. Despite the catalytic activity demonstrated by this brown complex, the best catalytic performance was achieved when the solution became colorless. All of the data and observations presented here suggest that under the conditions used in this work, diene hydrogenation was catalyzed by a mononuclear rhodium complex containing Cp* ring and diene molecule(s) with a hapticity that rendered it colorless. In addition, diene hydrogenation reaction likely occurred in two slow steps, explaining the reaction's second-order dependence on hydrogen pressure. Finally, the results of typical inhibition and filtration experiments suggest that the catalytic process was mainly molecular.

Acknowledgments

The authors thank FAPERGS (02/0351.8 and 04/1085.4) and PRONEX for financial support. A.T. thanks CAPES for a scholarship.

References

[1] G. Centi, S. Perathoner, Catal. Today 77 (2003) 287.
[2] O. Wachsen, K. Himmler, B. Cornils, Catal. Today 42 (1998) 373.

[3] I.T. Horvath, Acc. Chem. Res. 31 (1998) 641.
[4] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. DeSouza, J. Dupont, Polyhedron 15 (1996) 1217.
[5] P.A.Z. Suarez, J.E.L. Dullius, S. Einloft, R.F. DeSouza, J. Dupont, Inorg. Chim. Acta 255 (1997) 207.
[6] A.L. Monteiro, F.K. Zinn, R.F. DeSouza, J. Dupont, Tetrahedron: Asymmetry 8 (1997) 177.
[7] D.E. Bergbreiter, Catal. Today 42 (1998) 389.
[8] D.E. Bergbreiter, P.L. Osburn, T. Smith, C. Li, J.D. Frels, J. Am. Chem. Soc. 125 (2003) 6254.
[9] R.G. Da Rosa, L. Martinelli, L.H.M. Da Silva, W. Loh, Chem. Commun. (2000) 33.
[10] L.H.M. Da Silva, W. Loh, Chem. Commun. (1998) 787.
[11] M. Spitzer, L.H.M. Da Silva, W. Loh, J. Braz. Chem. Soc. 11 (2000) 375.
[12] M. Spitzer, E. Sabadini, W. Loh, J. Braz. Chem. Soc. 13 (2002) 7.
[13] D.J. Heldebrant, P.G. Jessop, J. Am. Chem. Soc. 125 (2003) 5600.
[14] K. Dallmann, R. Buffon, W. Loh, J. Mol. Catal. A Chem. 178 (2002) 43.
[15] S.M. Nobre, S.I. Wolke, R.G. Da Rosa, A.L. Monteiro, Tetrahedron Lett. 45 (2004) 6527.
[16] Q.L. Luo, S. Eibauer, O. Reiser, J. Mol. Catal. A Chem. 268 (2007) 65.
[17] S. Kotha, K. Mandal, Eur. J. Org. Chem. 23 (2006) 5387.
[18] S. Chandrasekhar, Ch. Narsihmulu, S.S. Sultana, N.R. Reddy, Org. Lett. 4 (2002) 4399.
[19] A. Kollhofer, H. Plenio, Chem. A Eur. J. 9 (2003) 1416.
[20] S. Chandrasekhar, Ch. Narsihmulu, S.S. Sultana, N.R. Reddy, Chem. Commun. (2003) 1716.
[21] C.L. Feng, Y.H. Wang, J.Y. Jiang, Y.C. Yang, F.L. Yu, Z.L. Jin, J. Mol. Catal. A Chem. 248 (2006) 159.
[22] J.W. Kang, K. Moseley, P.M. Maitlis, J. Am. Chem. Soc. 91 (1969) 5970.
[23] C. White, S.J. Thompson, P.M. Maitlis, J. Chem. Soc. Dalton Trans. (1977) 1654.
[24] J.E. Hamlin, K. Hirai, A. Millan, P.M. Maitlis, J. Mol. Catal. 7 (1980) 543.
[25] Y. Raoult, R. Choukroun, M. Basso-Bert, D. Gervais, J. Mol. Catal. 72 (1992) 47.
[26] J. Dupont, P.A.Z. Suarez, A.P. Umpierre, R.F. DeSouza, J. Braz. Chem. Soc. 11 (2000) 293.
[27] F.C.C. Moura, E.N. Dos Santos, R.M. Lago, M.D. Vargas, M.H. Araujo, J. Mol. Catal. A Chem. 226 (2005) 243.
[28] R.C. Schnabel, P.S. Carroll, D.M. Roddick, Organometallics 15 (1996) 655.
[29] L.M. Bronstein, D.M. Chernyshov, G.I. Timofeeva, L.V. Dubrovina, P.M. Valetsky, A.R. Khokhlov, J. Colloid Interface Sci. 230 (2000) 140.
[30] I.M. Angulo, E. Bouwman, J. Mol. Catal. A Chem. 175 (2001) 65.
[31] G.F. Pregaglia, G.F. Ferrari, A. Andreetta, G. Capparella, F. Genoni, J. Organomet. 70 (1974) 89.
[32] K. Radhakrishnan, P.A. Ramachandran, P.H. Brahme, R.V. Chaudhari, J. Chem. Eng. Data 28 (1983) 1.
[33] B.J. Hornstein, J.D. Aiken III, R.G. Finke, Inorg. Chem. 41 (2002) 1625.
[34] C.M. Hagen, J.A. Widegren, P.M. Maitlis, R.G. Finke, J. Am. Chem. Soc. 127 (2005) 4423.