APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. **14**, 164–169 (2000)

Pentamethylcyclopentadienylrhodium(I) Complexes Incorporated into Porous Polysiloxanes Prepared by a Sol–gel Process: Catalysts for Hydrogenation of Crotonic Acid in Water

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Pentamethylcyclopentadiene-functionalized polysiloxanes were prepared by a sol–gel process from tetraethoxysilane and (pentamethylcyclopentadienylmethyl)methyldiethoxysilane without a catalyst. The polysiloxanes are microporous–mesoporous solids, of which the BET surface areas and micropore volumes are inversely proportional to the concentration of the functionalizing agent (5–21 mol%) in the starting mixture of alkoxysilanes. The polysiloxanes were also characterized by CP MAS ^{13}C NMR spectroscopy, revealing essentially the same structure of organofunctional ligand as that in particulate materials with low surface areas prepared earlier in a sol–gel process catalyzed by dibutyltin diacetate. Novel alkoxysilyl-substituted pentamethylcyclopentadienyl (1,5-cyclo-octadiene)rhodium(I) complexes were synthesized from the corresponding cyclopentadienes by deprotonation followed by reaction with $[(cod)RhCl]_2$ (cod = cyclo-octadiene). Polysiloxane-bound rhodium complexes were prepared by a sol–gel reaction analogous to the one mentioned above and were found to catalyze the hydrogenation of crotonic acid in water; to the best of our knowledge, this constitutes the first example of catalysis by a well-defined polysiloxane-bound transition metal complex in an aqueous system. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: catalysis; water; cyclopentadienyl; rhodium; polysiloxane-bound metal complex; heterogenization

Received 27 February 1999; accepted 1 November 1999

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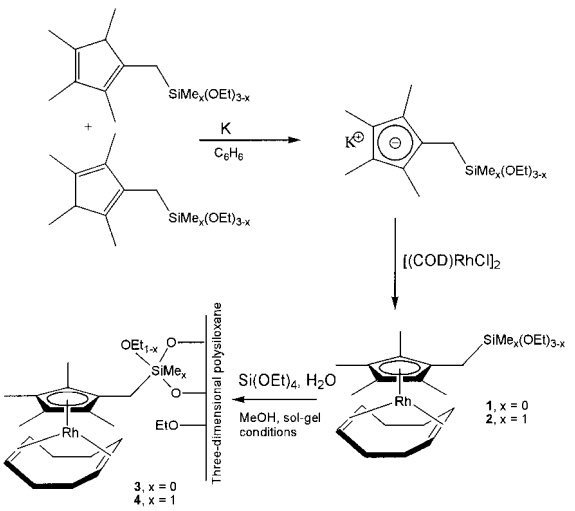
Contract/grant sponsor: Academy of Sciences of the Czech Republic; Contract/grant number: A4072610.

INTRODUCTION

Organofunctional ligands and transition-metal complexes heterogenized by formation of a covalent bond to polysiloxanes prepared by a sol–gel method, and the use of such materials in catalysis, have attracted considerable interest recently.[1,2] The usefulness of this approach to heterogenization of molecularly well-defined transition-metal catalysts was demonstrated in syntheses of polysiloxane-bound phosphines,[3,4] ether phosphines[5–8] and an aminophosphine.[9] Hydrogenation[3,6,8] and *N*,*N*-dimethylformamide synthesis[4,10] were carried out under catalysis by these materials, in the latter case with turnover numbers exceeding 100 000. Polysiloxane-bound cyclopentadienylmetal complexes made by the sol–gel method were reported only in one case of a polysiloxane-bound ferrocene,[11] despite the great importance of cyclopentadienyl metal complexes in organometallic chemistry.[12] At the same time polysiloxane-bound cyclopentadienyls[13] and their utilization for surface-supported titanium hydrogenation catalysts[14] have been reported.

Sol–gel-entrapped hydrophilic ruthenium-, rhodium-, and iridium-phosphine complexes were prepared recently[15] and used as isomerization catalysts, but their activity in aqueous systems was not tested. Homogeneous transition-metal catalysis in aqueous (usually biphasic) systems is



Scheme 1 Synthesis of the complexes **1–4**.

currently a fast-developing branch of catalytic research;[16–19] therefore it seemed of interest to us to study the sol–gel preparation and catalytic properties of a polysiloxane-bound cyclopentadienylmetal complex in water. The rhodium(I) complex was chosen because of the simplicity of its preparation and known catalytic activity in hydrogenation. Hydrogenation of water-soluble compounds in an aqueous system can be used as a model reaction for biological systems.[20,21]

EXPERIMENTAL

Materials and methods

All the manipulations were carried out in an atmosphere of dry argon or nitrogen, except when stated. The benzene, hexane and THF used in synthesis of rhodium complexes were dried by standard procedures. Tetraethoxysilane (Aldrich) and methanol (Lachema) were used as received. $[(cod)RhCl]_2$[22] and tetramethylcyclopentadienylmethylalkoxysilanes (mixtures of two isomers)[14] were prepared according to reported procedures.

Solution NMR spectra were taken on a Varian Unity 200 spectrometer at 200.1, 50.3 and 39.7 MHz for ^1H, ^{13}C and ^{29}Si, respectively.

The CP MAS solid-state ^{13}C NMR spectra were recorded on a Bruker DSX 200 spectrometer using double-bearing 7 mm bore ZrO_2 rotors with a Teflon cap. Spinning speed in all experiments was 4500 Hz, contact time 4 ms and recycle delay 6 s. ^{13}C NMR spectra were externally referenced to glycine (176.03 ppm). Specific surface areas (S_{BET}) and volumes of micropores (V_{micro}) were determined from nitrogen physisorption at 77 K using a Micromeritics ASAP 2010M instrument. Before measurements were made, the samples were degassed to 0.1 Pa at 378 K.

Chromatographic analyses of hydrogenation products were carried out using an HP 1090M instrument on a 250 mm × 8 mm stainless steel column (Nucleosil C18, 7 μm particles) with methanol (0.6 ml min^{-1}) as the mobile phase and crotonic acid, butyric acid, butyraldehyde and crotyl alcohol (all Aldrich) as standards.

Sol–gel preparation of pentamethylcyclopentadiene-functionalized polysiloxanes

The preparation was carried out in air. Distilled water (1.6 ml), methanol (2.3 ml) and $Si(OEt)_4$ (2.5 ml) were stirred for 4 h, then left to stand overnight at ambient temperature. The calculated amount of [(tetramethylcyclopentadienyl)methyl]-methyldiethoxysilane) was added with stirring, which was continued until the mixture reached gelation point. The gel was left to stand overnight, then dried at 40 °C to constant weight. The resulting material was crushed and dried at 80 °C for 5 h, then the specific surface area was measured.

Synthesis of functionalized rhodium complexes 1 and 2 (Scheme 1)

[(Tetramethylcyclopentadienyl)methyl]triethoxysilane (1.5 g, 5 mmol) was dissolved in 15 ml benzene in a Schlenk tube and 0.4 g (0.1 mol) potassium metal was added. The mixture was stirred for 5 h at 55 °C. The very viscous solution was filtered, and on standing overnight a white precipitate separated from the solution. The precipitate was filtered and dried *in vacuo*, giving 1.3 g (76%) of an air-sensitive white powder.

The compound was dissolved in 20 ml THF and the solution was added dropwise (over the course of about 20 min) to a suspension of $[(cod)RhCl]_2$ (0.95 g, 1.9 mmol) in 10 ml THF. The mixture was stirred for 5 h, during which time it turned red–brown and a fine precipitate separated. After three days of standing, the precipitate was filtered off, the solvent evaporated and the product dried *in vacuo*, yielding 1.7 g (87%) of a red–brown oil **1**. ^{29}Si

NMR ($CDCl_3$): $\delta = -51.9$ppm ($^3J_{Rh-Si} = 1.1$ Hz); 1H NMR ($CDCl_3$): $\delta = 1.17$ (t, $J = 7.0$ Hz, 9H), 1.65 (s, 2H), 1.75 (s, 6H), 1.8 (s, 6H), 1.89 (m, 4H), 2.12 (b, 4H), 2.85 (b, 4H), 3.75 ppm (q, $J = 7.0$ Hz, 6H); 13C{^{1}H} NMR ($CDCl_3$): $\delta = 8.49$ (s, $SiCH_2$), 9.50 (s, CH_3), 9.82 (s, CH_3), 18.16 (s, OCH_2CH_3), 32.72 (s, CH_2), 58.40 (s, OCH_2), 70.27 (d, $^1J_{Rh-C} = 14.2$ Hz, CH═), 95.43 (d, $>$C═, $^1J_{Rh-C} = 4.4$ Hz), 95.73 (d, $>$C═, $^1J_{Rh-C} = 4.4$ Hz), 96.64 ppm (d, $>$C═, $^1J_{Rh-C} = 3.9$ Hz).

The same procedure was used for the synthesis of rhodium complex **2** (yield 69%). The starting potassium salt was prepared in hexane in 57% yield, since filtration of the supersaturated benzene solution was not possible in this case. For **2**, ^{29}Si NMR: $\delta = -9.50$ ppm ($^3J_{Rh-Si} = 0.9$ Hz); ^{1}H NMR ($CDCl_3$): $\delta = 0.14$ (s, 3H), 1.19 (t, $J = 7.0$ Hz, 6H), 1.65 (s, 2H), 1.76 (s, 6H), 1.78 (s, 6H), 1.82–1.95 (m, 4H), 2.05–2.2 (m, 4H), 2.85 (b, 4H), 3.72 ppm (q, $J = 7.0$ Hz, 4*H*); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -4.81$ (s, $SiCH_3$), 9.45 (s, CH_3), 9.91 (s, CH_3), 11.82 (s, $SiCH_2$), 18.25 (s, OCH_2CH_3), 32.65 (s, CH_2), 58.03 (s, OCH_2), 70.30 (d, $^1J_{Rh-C} = 14.2$ Hz, CH═), 95.04 (d, $>$C═, $^1J_{Rh-C} = 3.9$ Hz), 95.71 (d, $>$C═, $^1J_{Rh-C} = 4.4$ Hz), 97.34 ppm (d, $>$C═, $^1J_{Rh-C} = 3.9$ Hz).

Sol–gel preparation of polysiloxane-bound complexes

The mixture of distilled water (7.3 ml), methanol (10.5 ml) and $Si(OEt)_4$ (11.5 ml) was stirred for 4 h and then left to stand overnight at ambient temperature. A solution of the functionalized rhodium complex **1** (1.4 g) in 1.9 ml of THF was added with stirring from a Schlenk tube which was subsequently rinsed with another 0.6 ml portion of THF and the rinsing added to the mixture. The mixture was stirred until it reached gelation point and then left to stand overnight. The gel was dried under a moderate stream of nitrogen at 45–55 °C to constant weight. The resulting polysiloxane-bound complex **3** (Scheme 1) was quickly ground to a fine powder in air and stored under nitrogen (yield 3.7 g). Complex **4** (Scheme 1) was prepared by the same procedure from 18.3 ml of $Si(OEt)_4$ and 2.1 g of **2** (yield 5.2 g).

Before the hydrogenation of crotonic acid, both polysiloxane-bound complexes were repeatedly extracted with an aqueous solution of crotonic acid of the same concentration as that to be used in the hydrogenation experiments (0.25 M) at 60 °C until leaching of rhodium in any one run was lower than 3% of the original content. During this procedure the rhodium content of the polysiloxane-bound complexes decreased considerably. The materials were then washed thoroughly with water and dried in vacuum. (The leachates were not catalytically active.)

Hydrogenation experiments

The polysiloxane-bound rhodium catalyst was placed in the flask of a hydrogenation apparatus[23] kept at 60 °C, and the argon atmosphere was replaced by hydrogen. Then 12 ml of water containing 3 mmol of crotonic acid was added slowly and the mixture was stirred vigorously. Consumption of hydrogen gas started immediately. Complete conversion was reached in every case, as indicated by hydrogen consumption. The solutions obtained by filtration of the reaction mixtures were analyzed by reverse-phase HPLC. Turnover number (TON) and frequency data (TOF) were calculated from the values of hydrogen consumption and time on reaching 100% conversion.

RESULTS AND DISCUSSION

Preparation of pentamethylcyclopentadiene-functionalized polysiloxanes

Acid or base catalysis is usually employed in the sol–gel preparation of silica-like materials to speed up the process of alkoxysilane hydrolysis and condensation.[24] However, in order to adapt the conditions of a sol–gel process to the planned incorporation of an acid-and air-sensitive rhodium complex, new protocol had to be devised. It consisted of a simple prehydrolysis of tetraethoxysilane in methanol (without any catalyst) in an inert atmosphere, followed by the addition of an organofunctional alkoxysilane. For comparison, the protocol was first tested on the synthesis of pentamethylcyclopentadiene-functionalized polysiloxanes, since those materials were previously prepared by a sol–gel reaction catalyzed by dibutyltin diacetate.[14] Polymeric gels obtained without a catalyst gave (after drying) functionalized polysiloxanes. The CP MAS ^{13}C NMR spectra of these polysiloxanes (Fig. 1) confirmed the presence of the pentamethylcyclopentadiene rings. In contrast to polysiloxanes prepared by the sol–gel method with catalysis by dibutyltin diacetate,[14] the new materials were porous with surface areas

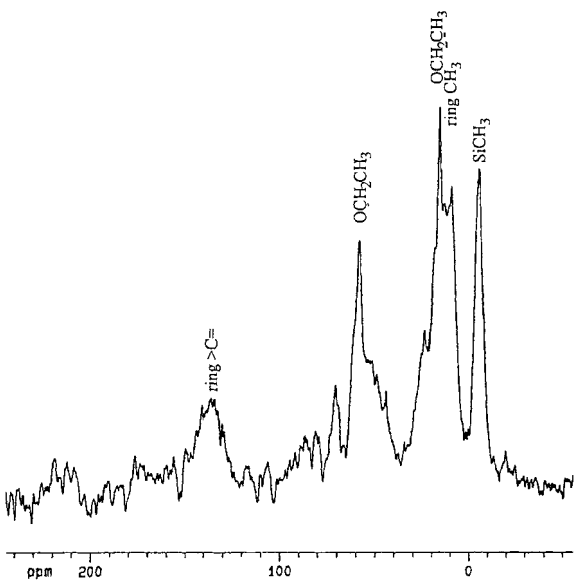


Figure 1 CP MAS ^{13}C NMR spectrum of a Cp*-containing polysiloxane (S_{BET} = 402 m^2 g^{-1}, 8 mol% of [(tetramethylcyclopentadienyl)methyl]methyldiethoxysilane).

depending on the amount of alkoxysilyl-substituted pentamethylcyclopentadiene.

Control of the surface area

It was found (Fig. 2) that the surface areas S_{BET} of the–pentamethylcyclopentadiene-functionalized polysiloxanes were in the range 135–465 m^2 g^{-1}, and were inversely proportional to the amount of functionalizing agent (5–21 mol%) in the starting mixture of alkoxysilanes. Our results are in agreement with the earlier results of Schubert *et al.*[1] obtained with sol–gel systems with catalysis by phosphoric acid, and show that the inverse dependence of the specific surface area of functionalized gels on the amount of organofunctional alkoxysilane is a general feature independent of the presence of the catalyst of a sol–gel process. The polysiloxanes are microporous–mesoporous solids with the adsorption isotherm (e.g. Fig. 3) between types I and IV according to the IUPAC nomenclature. The pore-size distribution was determined by the Barret, Joyner and Halenda (BJH) method (Fig. 4). Since it is known that measurement of S_{BET} of such materials by the standard procedure is influenced by condensation of liquid in micropores,[25] we have also determined the volume of micropores from a *t*-plot.[26] It was found

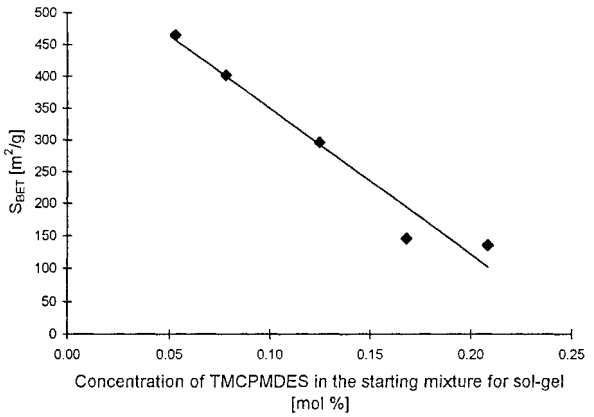


Figure 2 Dependence of specific surface area (S_{BET}) of pentamethylcyclopentadiene-functionalized polysiloxanes on the amount of [(tetramethylcyclopentadienyl)methyl]methyldiethoxysilane) (TMCPDES) in the sol–gel mixture.

that the volume of micropores was inversely proportional to the amount of the functionalizing agent (Fig. 5). Therefore low amounts of functionalizing agent lead to also a higher volume of micropores, besides a higher S_{BET}.

Synthesis and characterization of alkoxysilyl-substituted rhodium complexes

Alkoxysilyl-substituted rhodium(I) complexes were prepared by the reaction of the potassium salt of the corresponding alkoxysilyl-substituted pentamethylcyclopentadiene with chloro(1,5-cyclo-octadiene)rhodium dimer in THF at ambient temperature (Scheme 1). The products, in the form of red–brown moderately air-sensitive oils, were characterized by ^{1}H, ^{13}C and ^{29}Si NMR spectroscopy. Although the complexes could be prepared in higher yield in a one-pot reaction from the alkoxysilyl-substituted pentamethylcyclopentadienes without the isolation of the potassium salt, preparation of analytically pure products required use of the intermediate in a strictly stoichiometric ratio.

Incorporation of alkoxysilyl-substituted rhodium complexes into polysiloxanes

The complexes were then included as components in the sol–gel preparations of polysiloxanes under the same conditions as those used for the synthesis

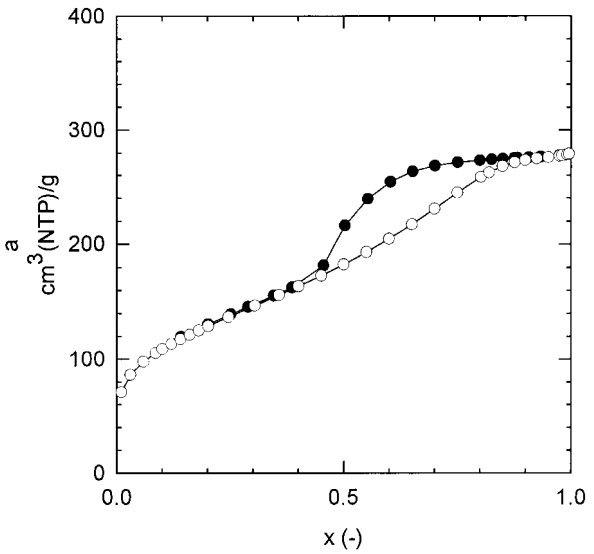


Figure 3 Adsorption isotherm of pentamethylcyclopentadiene-functionalized polysiloxane with $S_{BET} = 465\ m^2\ g^{-1}$ ○, adsorption; ●, desorption; $x = p/p_0$.

of pentamethylcyclopentadiene-functionalized polysiloxanes. The amount of alkoxysilyl-substituted rhodium complex used is a compromise between high surface area and low metal loading. Since the solubility of the complexes in small amounts of methanol was low, THF was added to dissolve the complexes before mixing with the pre-hydrolyzed sol–gel mixture. After drying, the products were brown, easily pulverizable materials

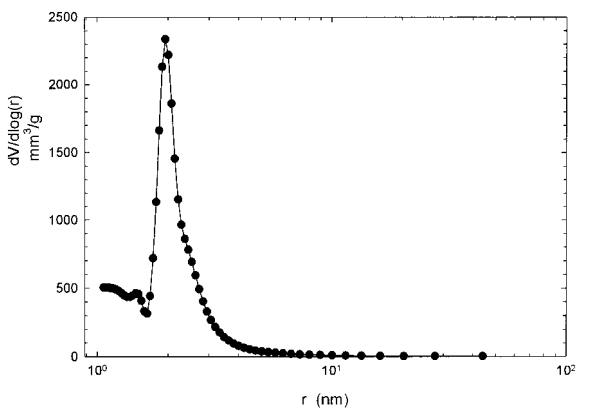


Figure 4 BJH desorption pore distribution of pentamethylcyclopentadiene-functionalized polysiloxane with $S_{BET} = 465\ m^2\ g^{-1}$; r = pore radius.

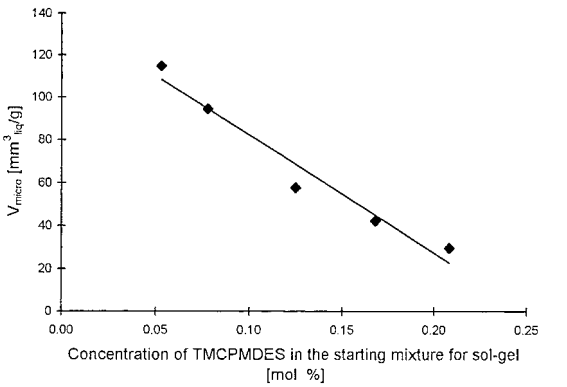


Figure 5 Dependence of the volume of micropores (V_{micro}) on the amount of [(tetramethylcyclopentadienyl)methyl]-methyldiethoxysilane) (TMCPDES) in the sol–gel mixture.

with specific surface areas (BET) of 360 and $305\ m^2\ g^{-1}$. CP MAS ^{13}C NMR measurement of the polysiloxane-bound rhodium complex 4(Fig. 6) confirmed the presence of intact Cp*–Rh bonds (signal at 98.7 ppm) as well as the presence of coordinated 1,5-cyclo-octadiene (signals at 31.6 and 70.1 ppm).

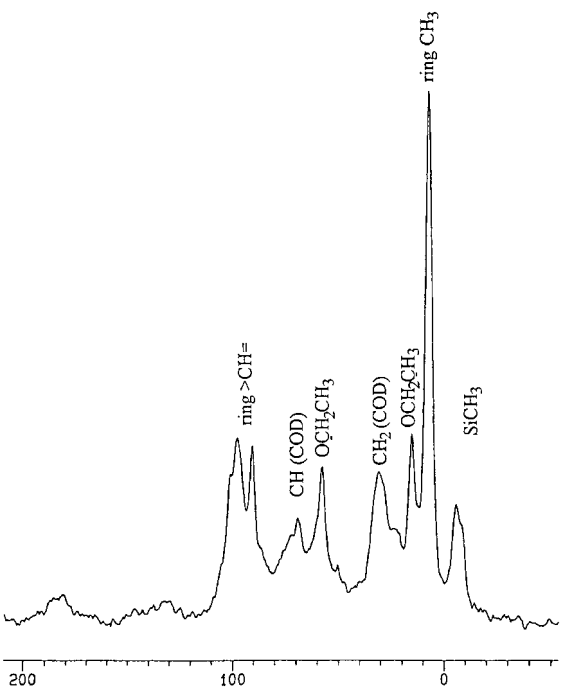


Figure 6 CP MAS ^{13}C NMR spectrum of a polysiloxane-bound rhodium complex **4**.

Table 1 Hydrogenation of crotonic acid in water catalyzed by polysiloxane-bound rhodium complexes[a]

Catalyst/ substrate ratio	TOF [mol H_2 (mol Rh)$^{-1}$ min^{-1}]	TON [mol H_2 (mol Rh)$^{-1}$]
0.017[b]	1.61	65
0.014[b]	1.55	62
0.025[c]	0.23	13
0.050[c]	0.14	14
0.075[c]	0.14	10
0.098[c]	0.14	9

[a] Reaction conditions: substrate concentration 0.25 M, 60 °C, p_{H2} = 127.7 kPa.
[b] Polysiloxane **3** (1.0% Rh).
[c] Polysiloxane **4** (1.8% Rh).

Hydrogenation of crotonic acid

Crotonic acid (*trans*-2-butenoic acid) was chosen as a substrate for hydrogenation in aqueous medium owing to its good solubility in water and use in previous model studies.[20] To avoid catalysis of hydrogenation by a soluble rhodium coumpound leached into the aqueous solution of crotonic acid, the polysiloxane-bound complexes were first subjected to thorough washing with the crotonic acid solution (0.25 M) at the hydrogenation temperature until less than 3% of the original rhodium was leaching. This condition also applied to hydrogenation experiments, the supernatants being inactive as hydrogenation catalysts.

The results of the hydrogenation experiments (Table 1) show that both polysiloxane-bound rhodium complexes catalyze hydrogenation with moderate activity up to TOF 1.6 mol (molRh)$^{-1}$ min^{-1}. The TOFs do not change dramatically with the substrate/catalyst ratio, indicating the first-order dependence on the catalyst concentration. Turnover numbers increase with increasing the substrate/catalyst ratio, since the experiments were carried out at constant substrate concentration. The maximum TON of 65 was achieved with polysiloxane **3** prepared from the triethoxysilyl-substituted pentamethylcyclopentadienyl complex, which was more active than polysiloxane **4**. Reaction mixtures from hydrogenation were analyzed by reverse-phase HPLC to detect possible hydrogenation of acid functionality. However, butyric acid was found as the sole product of the hydrogenation.

Acknowledgements The authors thank Dr O. Šolcová for carrying out texture analysis and Ms M. Bártlová for HPLC analysis. This research was supported by the Grant Agency of the Academy of Sciences of the Czech Republic (grant no. A4072610).

REFERENCES

1. Schubert U, Rose K, Schmidt H. *J. Non-Cryst. Solids* 1988; **105**: 165.
2. Schubert U. *New J. Chem.* 1994; **18**: 1049.
3. Parish RV, Habibi D, Mohammadi V. *J. Organomet. Chem.* 1989; **369**: 17.
4. Kröcher O, Köppel RA, Baiker A. *Chem. Commun.* 1996; 1497.
5. Lindner E, Bader A, Mayer HA. *Inorg. Chem.* 1991; **30**: 3783.
6. Lindner E, Kemmler M, Mayer HA, Wegner P. *J. Am. Chem. Soc.* 1994; **116**: 348.
7. Lindner E, Kemmler M, Mayer HA. *Z. Anorg. Allg. Chem.* 1994; **620**: 1142.
8. Lindner E, Schneller T, Auer TF, Wegner P, Mayer HA. *Chem. Eur. J.* 1997; **3**: 1833.
9. Bachert I, Braunstein P, Hasselbring R. *New. J. Chem.* 1996; **20**: 993.
10. Kröcher O, Köppel RA, Fröba M, Baiker A. *J. Catal.* 1998; **178**: 284.
11. Cerveau G, Corriu RJP and Costa N. *J. Non-Cryst. Solids* 1993; **163**: 226.
12. Janiak C Schumann H. *Adv. Organomet. Chem.* 1991; **33**: 291.
13. Jutzi P, Heidemann T, Neumann B, Stammler HG. *J. Organomet. Chem.* 1994; **472**: 27.
14. Čermák J, Kvíčalová M, Blechta V, Čapka M, Bastl Z. *J. Organomet. Chem.* 1996; **509**: 77.
15. Sertchook H, Avnir D, Blum J, Joó F, Kathó Á, Schumann H, Weimann R, Wernik S. *J. Mol. Catal. A— Chem.* 1996; **108**: 153.
16. Herrmann WA, Kohlpaintner CW. *Angew. Chem, Int. Ed. Engl.* 1993; **32**: 1524.
17. Horváth IT, Joó F, (eds). *Aqueous Organometallic Chemistry and Catalysis*, *NATO ASI Series* 3/5. Kluwer: Dordrecht, 1995.
18. Cornils B, Herrmann WA, (eds). *Aqueous-Phase Organometallic Catalysis*. VCH: Weinheim, 1998.
19. Roundhill DM. *Adv. Organomet. Chem.* 1995; **38**: 155.
20. Joo F, Balogh N, Horvath LI, Filep G, Horvath I. and Vigh L. *Anal. Biochem.* 1991; **194**: 34.
21. Maresca B and Cossins AR. *Nature (London)* 1993; **365**: 606.
22. Giordano G and Crabtree RH. *Inorg. Synth.* 1979; **19**: 218.
23. Vilím J. and Hetflejš, J. *Chem. Listy* 1976; **70**: 188.
24. Brinker CJ. and Scherer G. *Sol–Gel Science, the Physics and Chemistry of Sol–Gel Processing*. Academic Press: New York, 1990.
25. Schneider P. *Appl. Catal. A: Gen.* 1995; **129**: 157.
26. Gregg SJ, Sing KSW. *Adsorption, Surface Area and Porosity*, 2nd edn. Academic Press New York, 1982.

