

Cr bound catalytically active sol–gel siloxane polymers

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Received 11 December 1997; accepted 20 July 1998

Abstract

Several types of Cr bound siloxane polymers were prepared by various modes of polymerization. The co-polymerization of $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ and $\text{Si}(\text{OMe})_4$ by the sol–gel process, and its subsequent curing, led to a hydrogenation reactive polymer catalyst. Its catalytic reactivity was retained throughout several cycles, contrary to siloxane polymers prepared by different methods. The hydrogenation reaction was studied with methyl sorbate, 3-nonen-2-one, and 1-octyne. Regio- and stereoselectivities were studied. Cyclohexane as solvent was found to be superior to THF in retaining the catalytic activity upon recycling of the polymeric catalyst in the hydrogenation reactions. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Siloxane polymers; Heterogeneous catalysts; Sol–gel process; Chromium

1. Introduction

The designing of transition metal complexes incorporated in siloxane polymers prepared by the sol–gel process, may give rise to new heterogeneous catalysts. The mode of action of such catalysts depends on the mode of incorporation of the complexes into the polymer, which may vary from physical encapsulation of the complex via a sol–gel process [1–3], to chemical binding of the complex to the polymer atoms [4,5]. With transition metal complexes, the siloxane polymers may function as a polymeric ligand capable of coordinating transition metals and also transition metal complexes. This may be achieved by one of two ways: (1) Contacting in solution a ligand type siloxane polymer with the desired transition metal complex, i.e., direct

complexation of the polymer. (2) Preparing in advance a metal bound siloxane monomer, followed by its polymerization.

The latter method ensures a better homogeneity of the complexed metal throughout the polymer, and also facilitates co-polymerization of the metal bound and metal free siloxane monomers of choice. Evidently the catalytic reactivity and the recycling feasibility of the latter type siloxane polymers are superior (vide infra).

It is difficult to predict the activity of such polymers vis-a-vis the catalytic activity of the discrete transition metal complex monomer in homogeneous solution. Factors such as surface area, porosity, and degree of polymerization may affect the catalytic activity of the metal complexes incorporated in the siloxane polymer. Once a catalytic activity has been established, the long term activity must still be exper-

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imentally assessed. Two principal factors may affect this property: (a) Changes in the internal structure of the polymer during the catalytic reaction as a result of solute–polymer or solvent–polymer interactions. (b) The leaching of the catalyst from the ligand bound polymer to the reaction solution, thus depleting the polymer of its catalytic activity.

In general the above two problems may be minimized by working in non-polar and non-ligand solvents.

Of course, the main practical objective in preparing and using transition metals bound to polymers is to solve the recycling problem of the catalyst, which ideally could be filtered at the end of the reaction (or during the reaction in a continuous process) and recycled without loss of activity. Furthermore, the backbone of a siloxane polymer is chemically more robust than that of an organic polymer, particularly when extreme reaction conditions are considered.

We were interested in testing catalysts bound to siloxane polymers with respect to regio and stereoselective hydrogenation of various unsaturated systems. $\text{Cr}(\text{CO})_6$ is known as a regio and stereospecific catalyst precursor in the 1,4 hydrogenation of a 1,3-diene to a *cis*-monoene under irradiation conditions [6]. However, various $[\text{Arene} \cdot \text{Cr}(\text{CO})_3]$ complexes were found to be more reactive than $\text{Cr}(\text{CO})_6$, giving rise to 92–100% yield and 95–98% selectivity, in the hydrogenation of methyl sorbate to (*Z*)-methyl-3-hexenoate [6–9]. The above complexes are also known to selectively catalyze the hydrogenation of α,β -unsaturated ketones and alkynes, to produce saturated ketones and *cis*-alkenes, respectively [10]. The arene group in the above Cr complexes functions as an η^6 -ligand.

Thus, an arene bound polymer may serve as a polymer ligand for chromium carbonyl. In fact this idea has already been advanced by Pittman et al. [11] with cross linked polystyrene, which showed a high regio and stereo selectivity (96–97%) in the hydrogenation of methyl sorbate to (*Z*)-methyl-3-hexenoate in several reaction cy-

cles. Pittman et al. [12] also reported the preparation of $\text{Cr}(\text{CO})_3$ bound poly-tetramethyl-*p*-silphenylsiloxane and poly-methylphenylsiloxane. These chromium bound Si polymers were well defined, but were not examined for their catalytic activity.

Recently, Moran et al. [13] have prepared and characterized a series of η^6 -(organo silyl)arene-chromiumtricarbonyl complexes. The paper reports the heterogenation of the above silyl-arenechromium complexes on silica gel. The catalytic activity of these polymers has been examined only for the polymerization of phenylacetylene.

Awal et al. [14] prepared $\text{Cr}(\text{CO})_3$ bound polyphenylsilsesquioxane and polyphenyl siloxane polymers and studied their catalytic hydrogenation activity. In cyclohexane as solvent, the authors report loss of catalytic activity and mechanical problems in recycling. Improved results were obtained in THF where the polymer was soluble and recovered after concentration and precipitation. Loss of Cr was noted.

In light of the above mentioned reports, we examined the catalytic hydrogenation activity, and the recycling options, of a co-polymer prepared by polymerization of $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ in the presence of $\text{Si}(\text{OMe})_4$. The polymer was prepared by the simple sol–gel process [15].

2. Experimental

All the catalysts tested were found to be extremely sensitive toward oxygen, therefore all the preparative manipulations were carried out under nitrogen atmosphere, using Schlenck techniques.

2.1. Preparation of the monomer $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$

$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ was prepared and characterized according to a modified procedure [13]. $\text{Cr}(\text{CO})_6$ (10.0 g; 0.045 mole) and $(\text{EtO})_3$ -

SiPh (10.9 g; 0.045 mole) were refluxed for 72 h in dimethoxyethane (220 ml) in a Srtohmeier apparatus [16]. After cooling, the reaction mixture was filtered to remove a small amount of insoluble green decomposition products and unreacted $\text{Cr}(\text{CO})_6$. The solvent was distilled out at atmospheric pressure, followed by vacuum distillation. Crystallization of the residue from pet. ether (60–80°) by cooling to -70°C for 72 h gave yellow crystals, infrared: ν (nujol): 1980, 1908, 1119, 1100, 1103 and 1085 cm^{-1} .

2.2. Preparation of the xerogels from $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3/\text{Si}(\text{OMe})_4$

$\text{Si}(\text{OMe})_4$ (1.64 g; 10.8 mmole), methanol (3.8 ml), and $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ (1.017 g; 2.7 mmole) were stirred under nitrogen, then 0.25 M ammonium hydroxide solution (0.46 ml) was added to initiate polymerization. The gel was

kept in a closed vessel overnight, then dried in vacuum at room temperature (6 h at 15 mm and 12 h at 0.5 mm Hg) to give a xerogel. In order to obtain a cured xerogel, the following drying conditions were used: 6 h at 15 mm Hg at room temperature, followed by 22 h at 0.5 mm Hg at 60°C , infrared: ν (nujol): 1977, 1898, $1097\text{ (br)}\text{ cm}^{-1}$.

The surface area of the cured xerogel according to BET analysis, which was determined with an automatic surface area analyzer, was found to be $321.5\text{ m}^2/\text{g}$.

2.3. Preparation of SiO_2 -supported $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$

The silica supported catalyst was prepared and characterized according to a published procedure [13]. On the basis of the amount of unreacted $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ which was left in

Table 1
Hydrogenation data for methyl sorbate^a

No.	Catalyst	Substrate [M] solvent	Ratio (catalyst/ substrate)	Cycle (no.)	Time (h)	Conversion (%)	Z-isomer (%)	E-isomer (%)
1	$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$	0.2 cyclohexane	1:20	1	2	96	100	
2	$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3/\text{Si}(\text{OMe})_4$ -xerogel	0.16 cyclohexane	1:20	1	6	74	96	4
				2	5	74	97	3
				3	5	75	97	3
				4	5	47	95	4
3	$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3/\text{Silica gel}$	0.1 cyclohexane	1:20	1	8	97.5	96	4
				2	8	74	91	9
				3	8	35	71	29
				4	8	38	64	36
4	$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3/\text{Si}(\text{OMe})_4$ -cured xerogel	0.2 cyclohexane	1:20	1	5	95	97 ^b	3
				2	5	90	97 ^b	3
				3	5	91	97	3
				4	5.5	96	98	2
5	$(\text{EtO})_3\text{SiPhCr}(\text{CO})_3/\text{Si}(\text{OMe})_4$ -cured xerogel	0.2 THF	1:20	1	3	100	95	1
				2	3	100	92	1
				3	3	55	91	2
				4	3	21	90	–
6	$\text{Cr}(\text{CO})_6$	0.2 cyclohexane	1:10	1	3	92	100	

^aHydrogen pressure: 430 psi.

^bQuantitative GC analysis using 1-phenylethanol as an internal standard gave 95% yield.

Table 2
Hydrogenation data for 3-nonen-2-one in cyclohexane^a

No.	Catalyst	Substrate [M]	Ratio (catalyst/substrate)	Temperature (°C)	Cycles (no.)	Time (h)	Conversion (%)
1	(EtO) ₃ SiPhCr(CO) ₃	0.11	1:10	125	1	24	92
2	(EtO) ₃ SiPhCr(CO) ₃ / Si(OMe) ₄ -cured xerogel	0.11	1:10	140	1	16	95 ^b
					2	17	100
					3	20	100
					4	15	85
					5	17	80

^aHydrogen pressure: 430 psi.

^bQuantitative GC analysis using 1-methyl naphthalene as an internal standard gave 93% yield.

the filtrate of the reaction mixture, it was determined that the gel contains 1.06 mmole of reacted (EtO)₃SiPhCr(CO)₃ per 2 g gel.

2.4. Recycling of the catalyst

In order to refrain from filtering the solid polymer catalyst after each hydrogenation cycle, the reaction was carried out in a 450-ml agitated Parr reactor fitted with a dip pipe with a sintered (2 μm) metal piece at its dipping end. Upon termination of the reaction, the hydrogen was replaced by nitrogen (ca. 3 atm), and the reaction solution was forced out through the sintered dip pipe, thus retaining the catalyst in the reactor. Carried over catalyst could be detected by the development of a green color (oxidized Cr species) upon exposure of the fil-

tered solution to air. A fresh batch of reactants was then loaded by generating a low pressure inside the reactor, followed by suction of a fresh solution of the substrate to be hydrogenated through a thin Teflon pipe connected to the reactor.

In a typical reaction run, the siloxane polymer catalyst (in the first batch only), the substrate (0.1–0.2 M) and the solvent (200–250 ml) were charged into the reactor. The reactor was flushed 3–4 times with nitrogen (ca. 50 psi), followed by the introduction of hydrogen (430 psi), and the content was heated for the specified time and temperature (see Tables).

The filtered reaction solution (see recycling procedure above) was passed through a short alumina (basic) column. The solvent was distilled out, and the product was purified (if necessary) by vacuum distillation. The identity of

Table 3
Hydrogenation data for 1-octyne in cyclohexane^a

No.	Catalyst	Substrate [M]	Ratio (catalyst/substrate)	Temperature (°C)	Cycle (no.)	Time (h)	Conversion (%)	1-Octene (%)	<i>n</i> -Octane (%)
1	(EtO) ₃ SiPhCr(CO) ₃	0.11	1:10	125	1	38	94	100	
2	(EtO) ₃ SiPhCr(CO) ₃ / Si(OMe) ₄ -cured xerogel	0.11	1:10	140	1	41	63	82	18
					2	44	80	84 ^b	16
					3	46	97	82	18
					4	46	97	82	18
					5	44	96	82	18

^aHydrogen pressure: 430 psi.

^bQuantitative GC analysis using 1-methylnaphthalene as an internal standard gave 100% yield.

the products was determined by comparison with authentic samples.

The percent conversions were determined from GC measurements, which agreed reasonably well with the results obtained from one quantitative analysis performed for each table (see footnote b in Tables 1–3).

3. Results

The hydrogenation data of methyl sorbate is presented in Table 1. Examination of the selectivity values reveals that aside from the silica gel polymer (Exp. 3) which lost selectivity upon recycling, all other systems exhibited stereoselectivity in excess of 95% towards (*Z*)-methyl-3-hexenoate. This implies that the hydrogenation process occurred by the same mechanism using $\text{Cr}(\text{CO})_6$, monomer (1), and the rest of the polymers tested.

The monomer (Exp. 1) exhibited a slightly enhanced reactivity relative to $\text{Cr}(\text{CO})_6$, (Exp. 6). The xerogel (Exp. 2) was found to be sluggish, and resulted in a low conversion with a substantial loss of reactivity in the fourth cycle. The loss of reactivity was accompanied by the appearance of Cr compounds in the filtered reaction solution (green color). The silica gel anchored polymer (Exp. 3) tended to lose both reactivity and selectivity upon consecutive recycling.

The cured xerogel (Exp. 4) is a promising catalyst to the degree that it retained both its reactivity and selectivity in the hydrogenation of methyl sorbate throughout the four tested cycles, using cyclohexane as a solvent. Using the same cured xerogel, but performing the reaction in THF (Exp. 5), resulted in good reactivity and selectivity in the first two cycles, followed a by substantial loss of reactivity, but retention of selectivity, with subsequent recycling. Obviously, no recycling could be achieved with $\text{Cr}(\text{CO})_6$.

The hydrogenation data for 3-nonen-2-one is presented in Table 2. The reactions were com-

pletely regioselective in as much as only one product, 2-nonanone, was obtained. Loss of neither selectivity nor reactivity was observed throughout three consecutive cycles, which were followed by two cycles with diminished conversions.

The hydrogenation data of 1-octyne, using the cured xerogel (Exp. 2), is summarized in Table 3. The major product, 1-octene, was accompanied by *n*-octane, identified by MS, NMR, and GC comparison with an authentic sample. This loss of selectivity prevailed throughout all five tested cycles. It is noteworthy that the monomer exhibited 100% selectivity towards 1-octene (Exp. 1). Furthermore, the reactivity of the polymer catalyst was comparatively low in the first two cycles and improved throughout the subsequent three cycles (Exp. 2).

4. Discussion

Preliminary experiments were conducted to elucidate the relative catalytic activity of the Cr bound polymers which were not studied previously. Methyl sorbate, a 1,3-diene substrate, served as a model for testing the chemical as well as the stereochemical reactivity of the polymer catalysts in hydrogenation reactions (Table 1). The reactivity of the various polymers was compared to that of the monomer (Exp. 1), and hexacarbonylchromium(0) (Exp. 6). The results in Table 1 indicate that optimal hydrogenation and recycling performances were achieved by: (a) using the *cured* xerogel as the siloxane polymer catalyst. (b) using cyclohexane as the solvent with the above catalyst.

The xerogel that results from the curing process is known to possess a higher degree of polymerization, and is chemically more robust. It is also reasonable to assume that consequently, the pores' size decrease upon curing. The active catalytic species which is formed during the hydrogenation reaction must be better stabilized by this unique structure of the

cured xerogel, thus diminishing the leaching of the catalyst from the ligand bound polymer.

XPS analysis of the polymer sample yielded the following atomic concentration ratios: C:Cr = 9:1; Si:Cr = 5:1. These ratios satisfactorily conform to the proposed structure of the polymer. The high resolution XPS for Cr(2p1) and Cr(2p3) exhibited peaks at 575.75 and 585.4 eV, respectively. The value for Cr(2p1) is in accordance with known values for $C_6H_6 \cdot Cr(CO)_3$, 575.5 and 576.3 eV [17]. The corresponding value for Cr(2p3) and the differential value of the two peaks are not known.

The XPS for Si(2p) shows a broad binding energy peak, which after an analyzer calculation was found to be composed of three peaks at 103.59, 102.34 and 101.18 eV. These energy values fit well the known values for SiO_2 -gel, Si–O and Si–C, respectively [17].

It should be recalled that the Cr atoms are bound to the siloxane polymer via η^6 -arene interactions with the polymer's phenyl groups [12–14]. This type of bonding has now been supported by the XPS study. Mechanistically, at least three metal coordination sites are required in order to achieve the hydrogenation of a 1,3-diene system [6,8,18]. This must imply the dissociation of the metal from the polymer during the hydrogenation, and its transformation into reactants bound $Cr(CO)_3$ species. The survival of the Cr bound CO ligands was verified by measuring the infra red spectrum of the catalyst before and after the hydrogenation reaction. In the cured xerogel the reaction probably occurs wholly in the polymer pores, which provide arene and oxygen ligands for metal stabilization in the non-ligand cyclohexane solvent. Such interactions minimize the diffusion of metal species into the solution bulk. The probability of such a diffusion increases when using the non-cured gel which possesses larger pore size and therefore reduced ligand–metal interaction. This description may account for the higher efficiency of the cured xerogel, and it is also supported by the pronounced diminished activity of the recycled catalyst in THF as shown by

Exp. 5, Table 1. In the presence of excess THF, a coordinating solvent, the following equilibrium must be shifted to the right [6],

$$(\text{P})\text{-Si-arene-Cr(CO)}_3 + 3\text{THF} \rightleftharpoons (\text{P})\text{-Si-arene} + (\text{THF})_3\text{Cr(CO)}_3$$
 with the solvated Cr species being now the active catalyst in the hydrogenation reaction, while at the same time soluble in the reaction medium. The final outcome being the leaching of the metal from the siloxane polymer.

In contrast to our results, little hydrogenation activity was observed with the $Cr(CO)_3$ bound polyphenylsilsesquioxane polymer, in *cyclohexane*, in the second cycle [14]. The above metal bound polymer was prepared by impregnation of the polymer with the metal, rather than by polymerization of a pre-metal complexed monomer by a sol–gel process. The loss of activity of the above polymer in the hydrogenation of methyl sorbate, supports our hypothesis that with polymers prepared by the sol–gel process, the reaction is taking place within the polymer pores. Impregnation is principally a surface phenomenon which provides a little opportunity for ligand stabilization.

In conclusion, the preferred hydrogenation catalyst is the one prepared by the sol–gel polymerization process of a metal bound monomer, which is then cured at higher temperature, and the solvent must be a non-ligating one.

Upon finding the optimal conditions for recycling the catalyst, we examined additional substrates. Satisfactory results (Table 2) were obtained using 3-nonen-2-one as a substrate, as the hydrogenation proceeded with loss of neither reactivity nor selectivity throughout 3 consecutive cycles. Some loss of reactivity in the later cycles might be due to interaction between the ketone and the catalyst, the former acting as a Cr ligand via its oxygen atom, partially solubilizing and thereby leaching some of the catalyst from the polymer.

The reaction with 1-octyne as a substrate showed a moderate selectivity. The major product, 1-octene, was accompanied by *n*-octane. It

is assumed that 1-octene was further hydrogenated to *n*-octane under the reaction conditions. However, it is noteworthy that no *n*-octane was produced in the hydrogenation of 1-octene using the monomer $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ in Exp. 1, Table 3. This again may be attributed to the fact that with the polymeric xerogel, the reaction takes place in the polymer's pores, in which a local high concentration of the reduced 1-octene is being generated, thus effectively increasing the rate of its further hydrogenation to *n*-octane.

5. Conclusions

Attempts to bind a reactive catalyst to a siloxane polymer by co-polymerization of $(\text{EtO})_3\text{SiPhCr}(\text{CO})_3$ with $\text{Si}(\text{OMe})_4$ led to a catalytically reactive polymer. A sol–gel type of polymerization with subsequent curing was found to be superior to other types of polymerization processes. The polymer thus obtained was characterized by XPS, BET analysis and infrared spectrum. Its hydrogenation reactivity persisted throughout several cycles, and its significance lies in the recycling feasibility of the catalyst. A non-ligating solvent in the hydrogenation reaction was found to be essential for retaining the catalytic activity upon recycling of the polymeric catalyst. Experimental

evidences attest that the reaction is taking place within the polymer pores.

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