

Immobilization of a Homogeneous Ru Catalyst for Hexene and Canola Oil Hydrogenation: Synthesis and Activity

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Abstract: Dichlorodicarbonylbis (triphenylphosphine) ruthenium (II), a *cis*-selective and homogeneous catalyst, was immobilized on two types of inert solid supports: phosphinated polystyrenes and phosphinated silica gel. In both cases, spacer chains of different length were inserted between the phosphine attachment of the Ru complex and the support surface. Ru attachment efficiencies were determined by neutron activation analysis (NAA). The ability of the heterogenized catalysts to hydrogenate both 1-hexene and canola oil was also tested and the influence of linkage structure on activity was evaluated. In the case of the silica-supported catalysts, Ru dissociated from the support during hydrogenation. In contrast, the polymer-bound Ru remained immobilized during the catalytic reactions. Those polymer catalysts with the shortest linkage chains demonstrated the highest activity in the hydrogenation of 1-hexene. Despite this demonstrated activity, none of the polymer-bound Ru catalysts were active for canola oil hydrogenation.

Keywords: canola oil; hydrogenation; ruthenium; immobilization; 1-hexene; attachment efficiency.

1. Introduction

Hydrogenation of vegetable oils using typical Ni catalysts results in the formation of *trans* fatty acids. Because *trans* fats are harmful to human health (Asherio *et al.*, 1999; Hu *et al.*, 1997; Mensik and Katan, 1990), alternative catalysts that demonstrate minimal or no *cis* to *trans* isomerization during hydrogenation have been sought. We previously identified a homogeneous Ru complex (dichlorodicarbonylbis (triphenylphosphine) ruthenium (II), $\text{Cl}_2(\text{CO})_2(\text{PPh}_3)_2\text{Ru}(\text{II})$) which is *cis*-selective for canola oil hydrogenation (Bello *et al.*, 1985). Because industrial edible oil hydrogenation processes were designed to

use heterogeneous catalysts, the homogeneous $\text{Cl}_2(\text{CO})_2(\text{PPh}_3)_2\text{Ru}(\text{II})$ catalyst will have to be immobilized to allow its recovery and reuse prior to commercial application. Previous studies have shown that the catalytic properties of transitional metal complexes can be retained when the catalysts are supported on silica gel (Czakova and Capka, 1981; Michalska *et al.*, 1981; Skupinski and Malinowsky, 1975 and 1976). Other researchers have supported homogeneous catalysts on polymeric supports and demonstrated hydrogenation activity (Azran *et al.*, 1984; Strukul *et al.*, 1975). Pittman *et al.* (1975) supported Wilkinson's catalyst ($\text{Rh}(\text{PPh}_3)\text{Cl}$) on cross-linked phosphinated polystyrenes and $\text{Cl}_2(\text{CO})_2$

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$\text{PPh}_3)_2\text{Ru(II)}$) on styrene-divinylbenzene resins.

In this paper, the attachment of $\text{Cl}_2(\text{CO})_2(\text{PPh}_3)_2\text{Ru(II)}$ on silica gel using phosphinated alkoxy siloxanes as linkages and on polystyrene through phosphinated carbonyl chain linkages is reported. The attachment efficiencies for various linkage lengths were determined and the activities of the immobilized catalysts in hexene and canola oil hydrogenation are reported. In addition, loss of the Ru metal from the support during hydrogenation was quantified.

2. Materials and methods

Chlorodiphenylphosphine (>95% pure), 3-chloropropyltrimethoxysilane (>97% pure), chloromethyltriethoxysilane (>95% pure), silica gel (grade 62, 60-100 mesh, 140A), tetrahydrofuran (>99.5% pure), and xylene (isomeric mixture, >98.5% pure) were purchased from the Aldrich Chemical Company (Milwaukee, Wisconsin, U.S.A.).

The reagents purchased from Fluka Chemicals (Buchs, Switzerland) included 1-hexene (99.8% pure), 45% Na in paraffin, triphenylphosphine (>99% pure), 6-chloro-1-hexanol (>97% pure), dichloromethane (>98% pure), magnesium metal for Grignard reactions (>99.8% pure), polystyrene (Merifield Polymer Fluka, Buchs, Switzerland, 1.7 mmol Cl/g, 200-400 mesh, 1% DVB (chloromethylated styrene-divinylbenzene resin)), pyridinium chlorochromate (PCC, >98% pure), diphenylphosphino-polystyrene (copolymer of 98% styrene crosslinked with 2% divinylbenzene, diphenylphosphinated).

Lithium metal (1/2" diameter rod and shot 98.5% in liquid paraffin), hexanol (>98% pure) potassium hydroxide (>85% pure), and benzophenone (99% pure) were purchased from BDH Chemicals Inc. (Toronto, Ontario, Canada). 2-(Diphenylphosphino) ethyltriethoxysilane was purchased from Huls America Inc. (Bristol, Pennsylvania, U.S.A.) and dichlorodicarbonylbis (triphenylphosphine) ru-

thenium(II) (>98% pure) was purchased from Strem Chemicals (Newburyport, Massachusetts U.S.A.). Chloromethylated polystyrene was purchased from Polysciences, Inc. (Warrington, PA). Refined, bleached, and deodorized canola oil was supplied by CanAmera Foods (Toronto, Ontario, Canada) and Proctor and Gamble Inc. (North York, Ontario, Canada). Lastly, nitrogen and hydrogen (Ultra-High Purity) gases were purchased from Canox Ltd. (Mississauga, Ontario, Canada) and Canadian Liquid Air Ltd. (Toronto, Ontario, Canada) respectively.

2.1. Immobilization of the Ru complex

All reactions involving the tertiary phosphine compounds and the Ru complex were conducted under dry nitrogen using glassware which was placed in an oven at 110°C for at least 30 minutes prior to use to ensure dryness.

Immobilization of Ru on silica

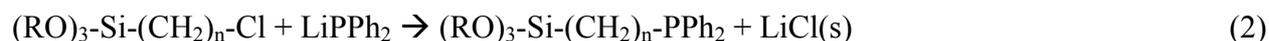
Alkoxy silyl-substituted phosphines

Alkoxy silyl-substituted phosphines were prepared by the reaction of alkoxy silyl-substituted alkyl halogenides with diphenylphosphinolithium, in tetrahydrofuran (THF). THF was dried by placing potassium hydroxide in the reagent bottle for 24 hr. The solvent was then poured into a three-neck flask and mixed with powdered sodium metal dispersed in solid paraffin (13 g Na metal for 2 L THF) and benzophenone (20 g for 2 L of THF) at room temperature. The mixture was refluxed for a few hours. In the first reaction step, diphenylphosphinolithium (LiPPh_2) was prepared according to the technique of Capka (1977):



After carefully cleaning a lithium rod (1.7 g) with hexane, the rod was suspended in THF (50 mL) under nitrogen. The chlorodi-

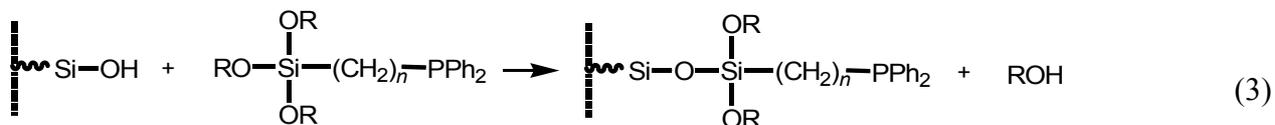
phenylphosphine (ClPPh₂, 30 g), dissolved in THF (30 mL), was added drop-wise with vigorous stirring. Cool temperatures were initially maintained with a water bath. The mixture was then heated, refluxed for 5 hr, cooled to room temperature, and filtered to remove the excess lithium. In the second reaction step,



Silane was suspended in 150 mL of THF and the LiPPh₂ solution was added drop-wise. The solution was stirred for 2 hr, refluxed for 4 hr, and then set aside overnight. LiCl and other inorganic salts were filtered out the next day and the silane was washed with THF. The solvent was then removed by vacuum distillation.

Phosphinated silicas

The silica gel support was initially dried in a vacuum oven for 5 hr in order to remove



10 g of silica gel and 50 mL of xylene were placed in a three-neck flask. A mixture of silane (about 2 mL) and xylene (50 mL) was added drop-wise. The solution was stirred for 30 min before the first 100 mL of xylene plus alcohol were distilled off. More xylene was added and the solution was refluxed for 4 more hr under nitrogen. This procedure ensured azeotropic distillation of the alcohol formed by the interaction of the alkoxy silane and the surface hydroxyl groups of the support. The silica-silane product was then vacuum filtered through a Buchner funnel and washed with dry xylene until the eluent was clear (two or three times). The compound obtained was then dried in a vacuum oven at room temperature for 5 hr and subsequently stored in a desiccator under nitrogen.

the diphenylphosphinolithium was reacted with a substituted silane according to Eq. (2), where R is methyl or ethyl and n represents the number of carbons in the linkage (n = 1, 2, or 3).

water and to promote access to all the hydroxyl groups on its surface (Czakova and Capka, 1981). Xylene was dried by adding calcium chloride (21 g/500 mL xylene), boiling the mixture, and removing the first 10% of the distillate (an azeotropic mixture of xylene and water). The remaining mixture was then refluxed for 4 hr. The general procedure for silica functionalisation follows Eq. (3), where R is methyl or ethyl and n represents the number of carbons in the linkage (n = 1, 2, or 3).

Attachment of the Ruthenium complex

The procedure described by Czakova and Capka (1981) was followed. The Ru catalyst was attached to the modified silica surface through the removal of one phenyl phosphine group. In this way, the catalyst was attached to the support as depicted in Figure 1. In a typical reaction, 10 g of functionalized silica was placed in a three-neck flask under nitrogen. The Ru catalyst, previously dissolved in toluene, was added drop-wise with stirring. The solution was refluxed for 4 hr, filtered, and washed twice with toluene. The heterogenized catalyst was then dried under vacuum at room temperature and stored in a desiccator for up to 3 days or in glass under vacuum for later use.

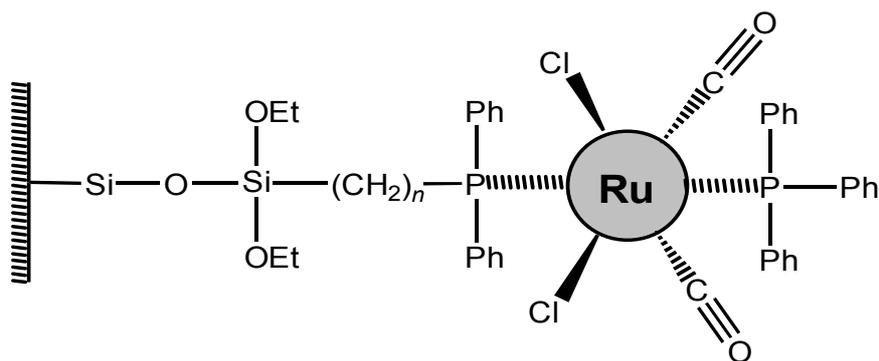


Figure 1. Attachment of the Ru complex to the modified silica surface

Immobilization of Ru on polystyrene

Functionalization of the carbon anchor chain

The attachment of Ru to the polystyrene (PS) support requires a diphenylphosphine (PPh₂) group. Therefore, PPh₂-substituted polystyrenes were prepared by the reaction of chloromethylated PS (PS-(CH₂)_n-Cl) with diphenylphosphinolithium (LiPPh₂). Dry THF

was mixed with powdered sodium metal (45% Na dispersed in solid paraffin, 6.5 g Na metal/L THF) and benzophenone (10 g/L THF) at room temperature. The mixture was refluxed under nitrogen for a few hr. The PS resin was suspended in anhydrous THF (150 mL) and the LiPPh₂ solution (prepared as described above) was added drop-wise according to Eq. (4), where n=1 or 7.



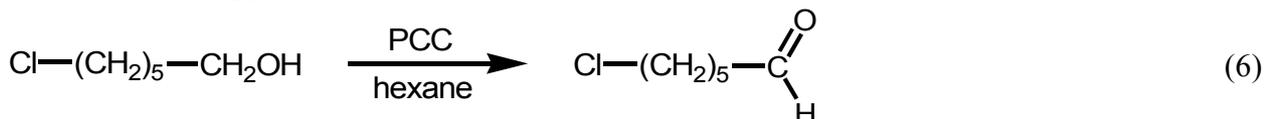
The solution was stirred for 2 hr, refluxed for 4 hr and left to sit overnight. The LiCl and other inorganic salts were then removed by filtration and the resin was washed with 100 mL acetone, two portions of 200 mL THF and lastly petroleum ether. The resin was then dried under vacuum at room temperature for 2 days.

A seven carbon anchor chain was synthesized starting with a single carbon chain. The first step involved the formation of the Grignard reagent (Williamson, 2003a) according to Eq. (5).



The six carbon chain linkage was also prepared according to Williamson (2003b). 6-Chloro-1-hexanol (Cl-(CH₂)₅-CH₂-OH) was oxidized with pyridinium chlorochromate

(PCC) to obtain 6-chlorohexanal (Cl-(CH₂)₅-CHO) as shown in Eq. (6).



The 6-chloro-1-hexanol (2.32 g, 17 mmol) was added to 40 g of PCC suspended in 50 mL of hexane and stirred for 15 hr. The solids

were then removed by filtration and washed three times with 10 mL of ether. The solvents were evaporated from the filtrate under a gen-

the stream of air and the residue was then vacuum dried.

Lastly, the Grignard reagent and the 6-chlorohexanal were reacted to form the activated polymer support (Williamson, 2003a). In this reaction, 5 g of the prepared polymer was swollen in xylene and then mixed with 20 mL of dry THF. 15 mL of dry THF mixed with the prepared 6-chlorohexanal was added slowly with cooling. The flask containing the mixture was swirled and allowed to reach room temperature before the contents were refluxed for two hr. The reaction mixture was then mixed with 100 mL of 10% sulphuric acid to hydrolyze the magnesium complex. The magnesium complex forms water-soluble neutral salts in the acid medium. A separatory flask was used to separate the polar phase from the non-polar phase which contained the polymer. To dry the compound, 100 mL of sulphuric acid and 100 mL of xylene were added to the polymer phase. The mixture was warmed slowly to between 60 and 80°C and then refluxed for 2 hr. The xylenes and azeotropic mixture with water were removed

by three distillations. The polymer was dried under vacuum at room temperature overnight.

Attachment of the Ru complex

Finally, the Ru complex was bound to the prepared phosphinated polystyrene resin. Typically, 10 g of the functionalized polymer resin was placed in a three neck flask and the Ru catalyst, dissolved in toluene, was added dropwise with stirring. Following the technique of Pittman and Evans (1973a) and Bailar (1974), a 10:1 molar ratio of polystyrene phosphine (P) to Ru complex (Ru) was used. The solution was refluxed for 4 hr, then filtered and washed twice with 70 mL of toluene. The heterogenized catalyst was dried under vacuum at room temperature and stored in a desiccator at atmospheric pressure for use within 3 days or stored in glass vials under vacuum for later use. Figure 2 depicts how the Ru complex is bound to the polymer's functional group.

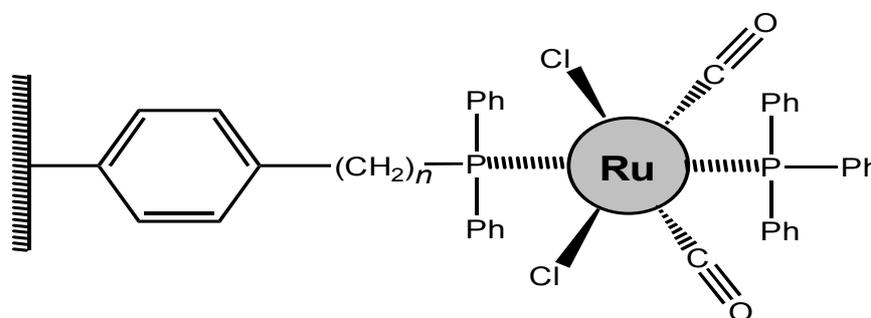


Figure 2. Attachment of the Ru complex to the polystyrene functional group

2.2. Hydrogenation reactions and subsequent analysis

Hydrogenations were carried out in a 300 mL stainless steel pressure reactor (Parr Instrument Co., Moline, Illinois, U.S.A.). The hydrogenation procedures were described previously (Wright *et al.*, 2003). In the case of 1-hexene, the alkene was first mixed with 1-hexanol which served as an inert solvent. The ratio of hexene/hexanol was fixed at 20/80

mol%. 1-Hexene was hydrogenated to hexane at a hydrogen pressure of 5.1 MPa at 130°C. After 3 hr, the bomb was cooled to avoid volatilization of the products as the samples were withdrawn.

The reaction products were subsequently analyzed by nuclear magnetic resonance (¹H NMR) using a Varian Gemini (200 MHz) Spectrometer. Spectra were determined in CDCl₃ and reported in parts per million (ppm) shift from tetramethylsilane (TMS) as an in-

ternal standard. Turnover frequencies (TOF) were calculated for each catalyst and reported as (moles of hexene reacted)/(Ru atom • s).

150 g of canola oil was hydrogenated at 110°C and 5.1 MPa. Samples were withdrawn from the bomb during the reaction and immediately vacuum filtered and analyzed at 60°C by refractive index (Bausch and Lomb refractometer) to approximate the iodine value (IV). The isolated *trans* isomer contents of the oils were determined according to the American Oil Chemists' Society (AOCS) Official Method (CD 14-16 (1988) using a Perkin Elmer model 1600 FTIR spectrophotometer.

In some cases the solid catalyst was recovered after hydrogenation for analysis or reuse, by vacuum filtration using a water-jacket heated Buchner funnel. The retentate was washed with hexane and dried under vacuum at room temperature. For the NAA, samples were irradiated in the SLOWPOKE nuclear reactor at the University of Toronto. A gamma spectrometer consisting of an Aptec (Aptec Engineering Ltd., Downsview, Ontario) intrinsic Ge semiconductor detector, coupled with a 4096-channel Series 8180 Multichannel Analyzer (Canberra Inc., Meriden, Connecticut) was used to count and integrate the radiation emission in the region of the Ru peak. For solid samples, an appropriate weight of catalyst was irradiated in polyethyl-

ene vials for 5 min at 10 kW. The gamma-ray emissions were counted for 300 s after 4 hr, a period during which the radioactive chlorine decayed.

3. Results and discussion

3.1. Ru immobilization on silica

Ru attachment efficiency

The efficiency of Ru attachment was determined by measuring the metal concentration on the silica surface by NAA. Table 1 shows that when a high linkage concentration (2.660 mmol/g silica), and hence a high ratio of P/Ru (40/1 mol/mol), was used, a low attachment efficiency (37%) was obtained. This result supports the assumption that, at high concentrations, the spacer chains react with silica sites that are very close to each other. This would position the terminal phosphine groups sterically too close to each other and prevent the bulky Ru complex from reaching every phosphine group on the support. The phosphine groups may also react with each other, creating looped inter-linkage bonds which would make attachment of the Ru complex impossible.

Table 1. Ru attachment efficiency to silica using different P/Ru molar ratios (2, 8, 40) and different amounts of Ru-linkage (0.125, 0.532, 2.660 mmol/g silica)

P/Ru ratio	Ru complex (g)	Linkage (in mmol/g of silica)	% Ru complex on silica (g/100g)	Reaction efficiency (%)
40/1	0.4747	2.660	1.75	37
8/1	0.4747	0.532	2.01	42
2/1	0.4747	0.125	2.70	57
2/1	1.8988	0.532	6.83	36

Table 2 shows that with a lower linkage concentration (0.125 mmol/g silica, at P/Ru of 2), 57% of the Ru was attached to the support.

To determine the optimal attachment parameters, the concentration of linkage was varied slightly from 0.125 mmol/g silica at a con-

stant P/Ru molar ratio of 2. The highest reaction efficiency (65%) was observed at 0.117 mmol/g silica. This linkage concentration was used in the subsequent Ru immobilizations.

Table 2. Effect of varying linkage concentration (0.125 – 0.100 mmol/g silica) on attachment efficiency at constant P/Ru= 2

Linkage (in mmol/g silica)	Ru complex (g)	Linkage (g)	% Ru complex on silica	Reaction efficiency (%)
0.125	0.4747	0.4495	2.7 ± 0.01	57
0.117	0.4468	0.4270	2.9 ± 0.20	65
0.113	0.4233	0.4045	1.6 ± 0.08	38
0.100	0.3760	0.3590	1.0 ± 0.01	27

Hexene hydrogenation

Ru immobilized on silica using methylene, ethylene, and propylene spacer chains were used as catalysts in the hydrogenation of 1-hexene. Table 3 compares the catalysts' turnover frequencies (TOF) at 130°C and 5.1 MPa. The catalyst prepared with the propylene spacer chains demonstrated a lower TOF (0.0786 s^{-1}) than those with the methylene and ethylene spacer chains for which the same catalytic activity (0.0995 s^{-1}) was observed. The decreased catalytic activity with the longer spacer chain could be related to length and flexibility which were sufficient to enable

the ethoxysilyl groups to be located in the vicinity of the Ru atom. These groups could inhibit the catalyst through steric hindrance or by weak interactions with the Ru atom. It is also possible that the three-carbon chain enables the formation of a multinuclear complex with reduced catalytic activity (Czakova and Capka, 1981; Michalska *et al.*, 1981). The formation of multinuclear complexes could result in a situation where the ligands of the Ru bond to each other. If the Ru ligands were prevented from dissociating and adsorbing hydrogen and substrate atoms, the rate of hexene hydrogenation would be decreased.

Table 3. Turnover frequencies for hexene hydrogenation (130°C and 5.1 MPa) with Ru complex immobilized on silica with methylene, ethylene, and propylene spacer chains

Catalyst support	Turnover frequency (s^{-1})
Ethylene	0.0995
Methylene	0.0995
Propylene	0.0786

Canola oil hydrogenation

The silica-immobilized catalysts were tested for canola oil hydrogenation under optimum conditions for *cis*-selective canola oil hydrogenation with the free Ru complex

(110°C and 5.1 MPa). Pseudo-first order reaction rate constants (*k*) were calculated from IV's for Ru concentrations between 11.2 and 32.6 ppm. The results are presented in Table 4. The effect of recycling the catalysts is also shown in Table 4 and will be discussed later.

Table 4. Hydrogenation activity ($k \times 10^5$) (s^{-1}) of homogeneous Ru complex and immobilized Ru complex catalysts (fresh and recycled catalysts) possessing methylene, ethylene, and propylene spacer chains

Catalyst support	11.2 ppm	13 ppm	19 ppm	23.7 ppm	32.6 ppm
Homogeneous Ru		11.0	18.8		
Methylene spacer chain	-	Inactive	Inactive	2.8	-
Methylene spacer chain recycled 1x	-			2.0	-
Ethylene spacer chain	-	-	11.0	13.8	25.3
Ethylene spacer chain recycled once	-	-	-	-	10.8
Ethylene spacer chain recycled 2x	-	-	-	-	7.7
Propylene spacer chain	49.8	-	-	86.3	-
Propylene spacer chain recycled 1x	Inactive	-	-	-	-

At 13 and 19 ppm the homogeneous Ru demonstrated activities ($k \times 10^5$) of 10.5 and 18.8 s^{-1} , respectively. The catalyst immobilized with the methylene spacer chain demonstrated the lowest activity and was inactive below 13 ppm Ru. The highest activity was observed for the catalyst prepared with the propylene spacer chain. At 23.7 ppm Ru, the activity was 2.8, 13.8, and 86.3 s^{-1} for the methylene, ethylene, and propylene linkages, respectively.

The fact that activity was increased for the ethylene and propylene type linkages, implies that the Ru complex requires spatial freedom to be active. Interestingly, the activity of the Ru immobilized with the propylene chain was greater than that of the homogeneous complex. Fixing the catalyst may favour the spatial positioning of the Ru near double bonds on fatty

acids. This suggests that the silica-supported complex reacts with hydrogen and the fatty acids predominantly via a surface adsorption mechanism rather than by a ligand exchange mechanism of the type generally accepted for homogeneous catalysis. These results agree with the conclusions of Sanchez-Delgado *et al.* (1981).

Table 5 compares the maximum *trans* content for the oils hydrogenated with the homogeneous and silica-immobilized Ru catalysts. At similar IV's, the active immobilized catalysts (*i.e.* those with ethylene and propylene spacer chains) produced approximately the same level of *trans* fatty acids. In the case of the methylene-linked catalyst, the activity was very low and very little changes in IV or *trans* were observed.

Table 5. Maximum level of *trans* isomers (%) formed during canola oil hydrogenation at 110°C and 750 psig for active Ru concentrations (homogenous, 19 ppm; methylene chain, 23.7 ppm; ethylene chain, 19 ppm; propylene chain, 29.9 ppm)

Catalyst	Maximum <i>trans</i> isomers (%)	Iodine value
Homogeneous complex	10.4 ± 0.2	45
Methylene spacer chain	2.5 ± 0.2	100
Ethylene spacer chain	12.1 ± 0.8	50
Propylene spacer chain	12.3 ± 0.5	50

The retention of Ru on the silica supports during hydrogenation was investigated using NAA. The amount of Ru lost from the support during canola oil hydrogenation was 15, 56, and 96% for the catalysts prepared with the methylene, ethylene, and propylene linkages, respectively. These results indicate that, regardless of the linkage length, some Ru dissociated from the support, although more Ru was lost when the longer spacer chains were used. Ru loss accounts for the decreased catalytic activity with catalyst recycling (see Table 4).

Both the highest catalytic activity and highest level of dissociation from the support were observed for the catalysts attached to the support via the propylene spacer chain. This finding can be explained by a reaction scheme in which the fatty acids associate with the Ru complex and disrupt the bonds linking the Ru complex to the support. During hydrogenation the double bonds of the fatty acids may substitute the triphenylphosphine ligands in the Ru complex. This would free the Ru complex from the silica support. If the Ru-support bond does not reform, the catalyst would remain soluble. The longer the spacer chain, the easier the contact should be between the dou-

ble bond and the phosphine group. Hence, more dissociation of Ru from the support is expected with the propylene chain.

3.2. Ru immobilization on polystyrene

Ru attachment efficiency

Table 6 shows that the attachment efficiency of the Ru complex to the polystyrene matrix was very high with a high P/Ru molar ratio >2 . For subsequent studies, a P/Ru molar ratio of 10 was used to avoid the possibility of inter-linkage reactions which would prevent the Ru complex from reaching all the phosphine groups. The polymers studied in this case were either 1 or 2% cross-linked. Compared with the 1% cross-linked matrix, the 2% cross-linked matrix demonstrated slightly higher (5%) attachment efficiency. The more cross-linked structure, because of its rigidity, should provide better access to the phosphine groups inside the matrix structure. Still, with the relatively low levels of cross-linking studied, the matrix will have a flexible structure and some interlinkage reactions may occur.

Table 6. Attachment efficiency of Ru complex on polystyrene (PS) support with different reaction conditions

Type of polymer	Polymer weight (g)	Ru complex weight (g)	Ru attached on polymer (g/g \pm 0.02)	Attachment efficiency (%)
PS-PPh ₂ (3 mmol PPh ₂ /g)	3	0.68	0.23	100
PS-CH ₂ -PPh ₂ (3.5 mmol PPh ₂ /g 1% DVB)	10	2.63	0.24	93
PS-CH ₂ -PPh ₂ (0.43 mmol PPh ₂ /g 2% DVB)	25	0.80	0.03	98
PS-CH=CH-(CH ₂) ₂ -PPh ₂ (1.7 mmol PPh ₂ /g 2% DVB)	10	1.28	0.11	85

Table 6 shows that the nature of the polymeric support and the linkage length had very little effect on the attachment efficiency. Compared to the silica-immobilized catalysts,

the polymer-supported catalysts demonstrated higher levels of attachment (27 to 57% vs. up to 100%). Various spacer chain structures (direct phosphine linkage to polymer, one carbon

atom spacer, and seven carbon chain spacer) were investigated. In all cases, the Ru complex reached the phosphine groups and was bound to the support (minimum 93% attachment). The attachment was slightly more efficient when the phosphine group was bound directly to the polymer or through short linkages. With the longer linkage, the number of phosphine groups to which the Ru can bind is decreased by inter-linkage reactions. In addition, the longer the linkage, the more mobile the chain inside the matrix will be. This could make it more difficult for the Ru complex to reach the phosphine group.

Hexene hydrogenation

The catalysts were kept in xylene for 1 hr before use in order to allow the polymer matrix to swell (3.5x) and hence provide better

access to the active sites. Table 7 shows that all of the polymer-supported catalysts were active in 1-hexene hydrogenation. TOFs were compared between the homogeneous Ru complex and those immobilized on the polymeric supports. The TOFs for the Ru complex linked directly to the support and via one methyl group were the same. With the longer (propylene) linkage, however, a lower TOF was observed. As with the silica-supported catalysts, the longer the linkage, the lower was the observed catalytic activity. Overall, immobilizing the Ru complex on polystyrene reduced its catalytic activity. This could be related to differences in the reactant concentration at active sites for the polymer-bound and dissolved catalysts (Evans *et al.*, 1974; Grubbs *et al.*, 1973). The diffusion of reactant molecules to the active sites may be inhibited by the matrix.

Table 7. Turnover frequencies ((moles of hexene reacted)/(Ru atom • s)) for 1-hexene hydrogenation (130°C and 5.1 MPa) with 135 ppm Ru immobilized on polystyrene (PS)

Catalyst	Turnover frequency (s ⁻¹)
Homogeneous complex	0.1133
PS-PPh ₂	0.0856
PS-CH ₂ -PPh ₂	0.0856
PS-CH=CH-(CH ₂) ₅ -PPh ₂	0.0716

Canola oil hydrogenation

Although the polymer-supported catalysts were active in 1-hexene hydrogenation, none of them hydrogenated canola oil. Triacylglycerols (TAGs) which make up the oil are large compared to hexene molecules and steric factors may prevent the bulky TAGs from diffusing into the polymeric matrix and reaching the catalysts' active sites. Even the seven-carbon spacer chain did not provide enough flexibility to allow the fatty acid double bonds to make contact with the active sites. The fact that no catalytic activity was observed indicates that the Ru complex did not dissociate

into the oil. While this is encouraging, it may indicate that chain-lengths of up to 18 carbon units may be needed for useful activity.

4. Conclusions

Attachment efficiencies of up to 57% were obtained for the silica-bound catalysts. Unfortunately, the Ru complex dissociated from the silica during hydrogenation of 1-hexene and canola oil. In contrast, higher attachment efficiencies were achieved for the polystyrene-bound Ru complex and the catalyst remained attached during 1-hexene hydrogenation. Despite the ability of the polymer-supported Ru

to hydrogenate 1-hexene, these catalysts were inactive for canola oil hydrogenation. Still, the activity for 1-hexene hydrogenation is encouraging. The next challenge is to immobilize the complex on a more macroporous resin or using a longer chain that will enable TAG molecules to reach the Ru complex. This would confirm that the inactivity for TAG hydrogenation is related to steric factors and allow us to take advantage of the Ru complex's *cis* selective character.

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