

# Hydrogenation and isomerization of 1-hexene with $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$ immobilized in silica matrices via the sol–gel method

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## Abstract

$\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  have been heterogenized in silica matrices by the sol–gel method. Gels prepared with  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  were tested in the hydrogenation and isomerization of 1-hexene. At  $\text{H}_2$ -pressures of 16 psi in repeated runs (15 h, 90 °C) turnover numbers for 1-hexene hydrogenation were between 380 and 460. Isomerization products were *trans*-2-hexene, *cis*-2-hexene and *trans*-3-hexene. No *cis*-3-hexene, 2-methyl-1-pentene and 2-methylpentane were found. Leaching of ruthenium in each run was around 0.05% of ruthenium present in the original gel. UV–VIS and FT-IR spectra of the pure cluster compounds and the gels before and after the catalytic reactions showed that during the gel preparation some  $\text{Ru}_3$  units remain intact, but are cleaved when the gel is heated under vacuum or used in catalytic hydrogenation reactions. © 2002 Elsevier Science B.V. All rights reserved.

**Keywords:** Sol–gel process; Ruthenium clusters; Hydrogenation

## 1. Introduction

Ruthenium carbonyl clusters, especially  $\text{Ru}_3(\text{CO})_{12}$ , have been supported on the surface of silica through direct reaction [1–7], or via anchoring using hydrolysable ligands such as  $\text{HS}(\text{CH}_2)_3\text{Si}(\text{OMe})_3$ ,  $\text{H}_2\text{N}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  or  $\text{Ph}_2\text{P}(\text{CH}_2)_3\text{Si}(\text{OEt})_3$  [4,8,9]. Few reports deal with the preparation of heterogeneous ruthenium catalysts by the sol–gel method and most are related to mononuclear ruthenium complexes, mainly  $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$  [10–14]. Recently, the preparation of Ru–Si catalysts via encapsulation of  $\text{Ru}_3(\text{CO})_{12}$  in a silica matrix followed by thermal treatment under nitrogen was reported [15]. Although the main goal of all these works is the Fischer–Tropsch reaction,

ruthenium compounds are active in many reactions involving alkenes and we recently reported on the hydrogenation/isomerization of 1-hexene with  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  in solution [16]. In order to verify whether the cluster would remain intact inside the porous system of a silica matrix, and also to compare the behaviour of  $\text{Ru}_3$  clusters in homogeneous and heterogeneous phase, we prepared gels containing  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  for hydrogenation of 1-hexene. Gels containing  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  were also prepared for characterization purposes (UV–VIS and FT-IR spectra, surface area).

## 2. Experimental

### 2.1. General

$\text{Ru}_3(\text{CO})_{12}$  (Strem Chemicals) and  $\text{PPh}_3$  (Merck) were used as received.  $\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3$  [17]

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and 1,4-bis(triethoxysilyl)benzene [18] were prepared as described in the literature. Toluene was dried over sodium before used and 1-hexene (Aldrich, 97%) was stored over 4 Å molecular sieves. NMR spectra were recorded with a Bruker AC 300P in CDCl<sub>3</sub> (TMS 0.03%, v/v), with H<sub>3</sub>PO<sub>4</sub> as external standard for <sup>31</sup>P. Infrared spectra were recorded on a Bomem FT-IR spectrometer model MB-100 (16 scans) with a resolution of 4.0 cm<sup>-1</sup>; solution UV–VIS spectra were recorded with an HP 8452A diode array spectrophotometer; diffuse reflectance UV–VIS spectra of gels were obtained with a Gary 5G spectrophotometer. BET surface areas for Gels 1–3 were determined using a Micromeritics Flow Sorb 2300 equipment and nitrogen as the adsorbate at –196 °C. Nitrogen adsorption/desorption isotherms of Gels 1 and 2 were obtained at –196 °C with a Micromeritics ASAP 2010 automated porosimeter. All calculations were performed using the associated Micromeritics software. Samples were degassed at 50 °C for a minimum of 8 h prior to measurements.

## 2.2. Preparation of

### *Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub>*

The preparation of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> was similar to that described for Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> [19], employing 100 mg (0.156 mmol) Ru<sub>3</sub>(CO)<sub>12</sub> and 167 mg (0.5 mmol) PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub> in 40 ml of boiling hexane (2 h). Owing to the high solubility of the red product, it was washed with ice-cold hexane (4 × 10 ml). The compound was then dried under vacuum. Formation of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> was confirmed by the elemental analysis and comparison of its spectra with those of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub>.

#### 2.2.1. *Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub>*

<sup>1</sup>H NMR: δ 7.51–7.36 (Ph). <sup>13</sup>C NMR: δ 136.33–128.03 (Ph). <sup>31</sup>P NMR: δ 37.93 (s). IR (KBr): ν(CO): 2042 (w), 1981 (s), 1969 (s), 1934 (m) cm<sup>-1</sup> (Fig. 5a). The UV spectra is shown in Fig. 2a.

#### 2.2.2. *Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub>*

<sup>1</sup>H NMR: δ 7.4–7.36: 10H (Ph); δ 3.50 (s): 9H (OCH<sub>3</sub>); δ 2.58–2.50 (q): 1H (CH<sub>2</sub>P); δ 0.59–0.50 (t): 1H (CH<sub>2</sub>Si). <sup>13</sup>C NMR: δ 136.78–128.1 (Ph); δ 50.6 (s, OCH<sub>3</sub>); δ 26.73, 26.42 (d, CH<sub>2</sub>); δ 2.85, 2.82

(d, CH<sub>2</sub>). <sup>31</sup>P NMR: δ 35.13 (s). IR (KBr): ν(CO): 2039 (w), 1969 (s), 1961 (s), 1940 (m) cm<sup>-1</sup> (Fig. 5b). The UV spectra is shown in Fig. 2b. Elemental analyses: C: found 47.78%, calculated 46.26%; H: found 4.82%, calculated 4.46%.

## 2.3. Gel preparation

Gels 1–3 were prepared in the same manner in order to compare their chemical and physical properties. Gels 4 and 5 were prepared for IR and UV–VIS analyses.

Gel 1: 3.45 g (8.56 mmol) of 1,4-bis(triethoxysilyl)benzene, 7.65 ml (34.3 mmol) of TEOS ([1,4-bis(triethoxysilyl)benzene]/[TEOS] = 1/4), 2 ml of water and 10 ml of ethanol were added to a 200 ml Schlenk flask. The pH of the clear solution was lowered to 1.79 by the addition of 1 ml of diluted HCl (1.2 M). After 45 min of stirring, the pH was adjusted to ca. 6 with a 0.17 mol l<sup>-1</sup> aqueous solution of Na<sub>2</sub>CO<sub>3</sub>. At this stage, 4 ml of a saturated solution of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> in 4 ml toluene were added to the mixture. Upon the addition of another small amount of the Na<sub>2</sub>CO<sub>3</sub> solution a dark red gel was formed within 5 min. The gel was allowed to stand for 1 h and then dried under vacuum for 4 days, washed first with water, and then with toluene in a soxhlet for 1 day, followed by drying 24 h under vacuum. Some leaching was observed during the soxhlet treatment, but the gel maintained its red colour through all the steps of the preparation.

Gel 2: This red coloured gel was prepared without 1,4-bis(triethoxysilyl)benzene as a pure inorganic matrix from 10.9 g (52.3 mmol) TEOS.

Gel 3: This gel was prepared as described for Gel 2, but using a saturated toluene solution (4 ml) of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub>. After soxhlet washing with toluene (with leaching of red-purple Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub>) a yellowish gel was obtained.

Gel 4: 2.4 ml HCl (pH = 2.1), 10 ml of ethanol and 7.6 ml (34 mmol) of TEOS were added to a 200 ml Schlenk flask and stirred for 15 min. Then 268 mg (0.172 mmol) of Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> (dissolved in 8 ml THF) and 1 ml of NH<sub>4</sub>OH (pH = 11.2) were added to the solution. The gel was allowed to stand for 2 days and then dried under vacuum. A portion of this gel was washed in a soxhlet with toluene (1 day) and maintained its red colour. Another

portion was heated at 70 °C under vacuum for 20 h and its colour turned to yellow. After soxhlet washing (toluene, 1 day) the yellow gel was analysed by UV–VIS and FT-IR spectroscopy.

Gel 5: 1.2 ml HCl (pH = 2), 5 ml of ethanol and 3.8 ml (17 mmol) of TEOS were added to a 200 ml Schlenk flask and the solution was stirred at room temperature for 15 min. Then, 60 mg (0.045 mmol) of  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  (dissolved in 20 ml  $\text{CH}_2\text{Cl}_2$ ) followed by 0.5 ml of  $\text{NH}_4\text{OH}$  (pH = 11.50) were added to the solution. The gel was allowed to stand for 2 days and then dried under vacuum. By washing the red gel five times with  $\text{CH}_2\text{Cl}_2$  some red cluster was washed out, giving a yellowish gel at the end of the washing process. The gel was then dried under vacuum and analysed by UV–VIS and FT-IR spectroscopy.

#### 2.4. Catalytic experiments

Gel 1 (503.5 mg) and Gel 2 (533.6 mg), both containing 0.0208 mmol of ruthenium, were tested in the catalytic hydrogenation of 1-hexene. In a typical experiment, the gel, 1.35 ml (10.47 mmol) of 1-hexene and 5 ml of toluene were added to a 65 ml Fisher–Porter bottle. The mixture was purged three times with  $\text{H}_2$ . Reactions were performed over 15 h under stirring and with exclusion of light. After the reaction the solution was removed with a syringe and the gel washed thoroughly with toluene ( $2 \times 5$  ml) and then dried under vacuum. The combined reaction and washing solutions were used for ICP-EAS analyses on ruthenium. In a blank experiment (90 °C, 15 h, 16 psi  $\text{H}_2$ , 10.47 mmol 1-hexene, 5 ml toluene), the reaction vessel was inactive either in hydrogenation or in isomerization. Reaction products were analysed using an HP-5890 II gas chromatograph equipped with a flame ionization detector and an  $\text{Al}_2\text{O}_3/\text{KCl}$

on fused silica-capillary column (50 m  $\times$  0.32 mm). More details can be found in [16].

### 3. Results and discussion

The gels discussed in this work were prepared in the same manner as described for rhenium and molybdenum epoxidation catalysts [20,21] in which cases the complexes were entrapped inside the porous systems of inorganic or hybrid matrices. Although no experiment was carried out in order to determine the precise location of the active ruthenium species, the fact that the solids kept their red colour even after washing in a soxhlet strongly suggests that also in this case such sites are located inside the porous system.

#### 3.1. Gel preparation

The nitrogen adsorption–desorption isotherm of Gel 1 is of type I, characteristic of a microporous solid. The volume adsorbed at the lowest relative pressure represents about 60% of the total pore volume, indicating a large volume of extremely small pores. The lack of hysteresis in the desorption branch is generally interpreted to mean that the pores are smooth and cylindrical [22]. The pore volume and average pore size determined from the isotherms are presented in Table 1.

In the case of Gel 2, two types of isotherms are found: type I, well defined at lower pressures (up to  $p/p_0 = 0.1$ ) and type IV (above  $p/p_0 = 0.1$ , Fig. 1). Around 33% of the total pore volume is adsorbed in micropores. A large range of mesopores seems to be present as suggested by the inclination of the isotherms. Some relevant data are presented in Table 1.

Table 1  
Properties of Gels 1–3 (after soxhlet washing with toluene)

Gel	Ru loading (wt.%) <sup>a</sup>	BET surface area ( $\text{m}^2 \text{g}^{-1}$ )	Porous volume ( $\text{cm}^3 \text{g}^{-1}$ )	Average pore diameter (nm)
1	0.42	364	0.27 <sup>b,c</sup>	1.99 <sup>d</sup> (0.85) <sup>b</sup>
2	0.39	302	0.24 <sup>c</sup>	2.89 <sup>d</sup>
3	0.03	153	–	–

<sup>a</sup> Determined through ICP-EAS analyses.

<sup>b</sup> Horvath–Kawazoe method.

<sup>c</sup> Single point.

<sup>d</sup> Gurvitsch method.

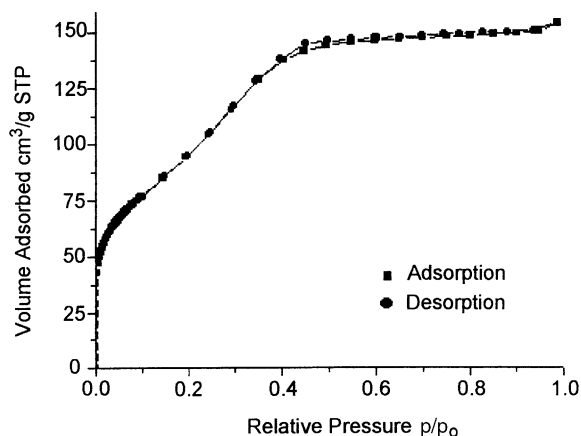


Fig. 1. Nitrogen adsorption/desorption isotherms for Gel 2.

A comparison of data obtained for Gels 1 and 2 shows the importance of the co-condensation agent: it not only allows the formation of a typical microporous solid but also leads to a higher surface area. Data in Table 1 also show that the presence of an hydrolyzable ligand in  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  allows the entrapment of a far higher amount of Ru. Comparing the surface areas of Gels 2 and 3, it is clear that the hydrolyzable ligand has also a positive effect on the surface area of the resulting solid.

### 3.2. Catalytic experiments

Table 2 shows the results of several hydrogenation–isomerization runs with the Gels 1 and 2. Because of

Table 2  
Hydrogenation of 1-hexene with Gels 1 and 2<sup>a</sup>

Run	$P_{\text{H}_2}$ (psi)	$n$ (%)	TON <sup>b</sup>	t3 (%)	t2 (%)	h1 (%)	c2 (%)	t2/t3	t2/c2	Ru leaching $10^{-5}$ mmol (%) <sup>b</sup>
Gel 1										
1	16	37.2	188	6.4	38.0	6.9	11.5	5.9	3.3	0.792 (0.038)
2	16	78.9	398	2.7	13.7	2.3	2.5	5.1	5.5	0.376 (0.018)
3	16	46.4	234	3.2	30.7	11.7	8.0	9.5	3.8	1.38 (0.066)
4	16	59.2	298	3.5	22.4	9.9	4.9	6.4	4.6	2.45 (0.118)
5	16	50.1	253	3.4	33.8	4.3	8.4	10.0	4.0	3.77 (0.182)
6	16	48.2	243	3.9	35.9	1.8	9.4	9.1	3.8	1.56 (0.075)
7	16	40.5	204	3.6	37.2	8.4	10.4	10.3	3.6	0.680 (0.033)
8	16	55.1	278	3.4	24.6	11.3	5.6	7.3	4.4	1.87 (0.090)
9	32	44.3	223	2.8	34.4	8.6	9.8	12.3	3.5	3.28 (0.158)
10	48	44.7	225	2.2	31.4	12.1	9.6	14.0	3.3	1.39 (0.670)
11	16	25.7	130	2.5	42.3	14.8	14.7	16.6	2.9	0.523 (0.025)
12	16	18.5	93.2	2.2	39.4	24.9	15.0	18.1	2.6	0.980 (0.047)
13	16	19.2	96.8	2.3	38.1	26.6	13.8	16.8	2.8	0.946 (0.046)
Gel 2										
1	16	87.2	439	0.4	2.0	8.7	0.5	4.5	3.7	2.35 (0.113)
2	16	91.4	461	0.2	1.6	4.9	0.5	7.1	3.5	1.14 (0.055)
3	16	77.4	390	0.7	6.5	11.2	3.1	9.5	2.1	1.37 (0.066)
4	16	80.5	406	0.3	3.2	14.0	1.1	11.1	2.9	1.11 (0.053)
5	16	76.5	386	0.2	2.8	18.3	1.0	2.7	2.8	0.996 (0.048)
6	16	83.4	420	0.1	0.9	13.6	0.3	12.7	2.6	1.68 (0.081)
7	16	75.2	379	0.2	1.5	20.5	0.5	9.3	2.7	0.413 (0.020)
8	16	74.8	377	0.1	0.9	20.1	1.6	8.2	0.5	0.329 (0.016)
9	16	75.5	381	0.1	0.7	19.2	0.3	6.4	2.2	0.925 (0.045)
10	16	80.2	404	0.1	0.5	14.9	0.2	8.2	2.2	0.564 (0.027)
11	0	1.4	7	1.5	18.3	75.2	3.5	12.4	5.2	0.781 (0.038)
12	0	0.2	1	0.6	8.4	88.8	2.1	14.2	4.1	0.816 (0.040)
13	16	84.6	426	0.0	0.2	12.2	0.1	–	4.3	0.495 (0.024)

<sup>a</sup> Reaction conditions: 503.5 mg of Gel 1 and 533.6 mg of Gel 2 (each 0.02076 mmol Ru); temperature: 90 °C; solvent: 5 ml of toluene; time: 15 h; 1.35 ml of 1-hexene (10.47 mmol);  $n$ :  $n$ -hexane; h1: 1-hexene; t2: *trans*-2-hexene; t3: *trans*-3-hexene; c2: *cis*-2-hexene.

<sup>b</sup> Calculated on the basis of 0.02076 mmol ruthenium.

its low ruthenium concentration Gel 3 has not been tested. Although the results obtained with Gel 1 may suggest a lack of reproducibility, it is clear that Gel 2 was more active than Gel 1, giving turnover numbers (moles of *n*-hexane/moles of ruthenium) of 380–460 for the hydrogenation reaction. Changes either in hydrogenation or isomerization activity of the gels in the first runs may be attributed to modifications of the Ru environment from run to run as indicated by their colour change. Thus, in the first reaction the gels changed from red to yellow or yellow-brown. In the following runs, the colour changed over brown to olive-brown or olive-green. These gels are more active in the hydrogenation of 1-hexene than solutions of  $\text{Ru}_3(\text{CO})_{12}$  or  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  under identical conditions [16]. Isomerization is less pronounced. When two reactions without hydrogen were performed (gel 2), most 1-hexene was not isomerized, whereas in reactions in homogeneous phase a complete isomerization was observed [16]. Also, in reactions under hydrogen the concentration of formed *trans*-3-hexene is considerably lower compared to the homogeneous reaction and no by-products of skeletal rearrangement, 2-methyl-1-pentene and 2-methylpentane, were found. In agreement with the thermodynamic stability of the five linear hexenes ( $t_2 > t_3 > c_2 > c_3 > h_1$  [23,24]), no *cis*-3-hexene was formed. All results taken together suggest that the active species in these gels are different from those observed in the homogeneous experiments. The higher activity of Gel 2 over Gel 1 may be attributed to its mesoporous system. Assuming that also at low pressure (16 psi) there is sufficient hydrogen in the pores, the hydrogenation kinetics would depend only on the diffusion of 1-hexene inside the pores, which might be easier when the pores are larger. This is in agreement with the fact that also at higher  $\text{H}_2$ -pressures (32 and 48 psi, Gel 1) the concentration of *n*-hexane was in the same range observed for reactions carried out at 16 psi. In 13 runs, the total ruthenium leaching reached only 0.96 and 0.62% of the initial ruthenium loading for Gels 1 and 2, respectively.

### 3.3. Spectroscopical characterization

#### 3.3.1. UV–VIS spectroscopy

Fig. 2 shows the UV–VIS spectra of  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$ .

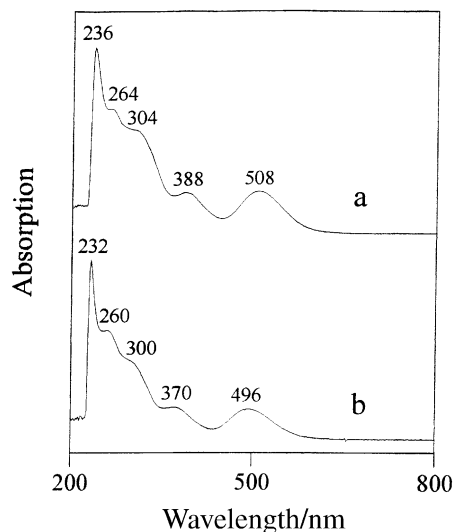


Fig. 2. UV–VIS spectra ( $\text{CH}_2\text{Cl}_2$  solution) of (a)  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  and (b)  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$ .

The pure clusters show strong absorptions at 508 or 496 nm, which have been assigned to  $\sigma^* \rightarrow \sigma^*$  electronic transitions [25]. This absorption is also present in the spectra of gels prepared with  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  before and after the washing procedures (Fig. 3a–d). In agreement with its red colour, the presence of this absorption shows that at least some intact  $\text{Ru}_3$  framework is present in the fresh gels. In the case of  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  changes are observed both in the absorption spectra and in the colours during the gelation process. Before the washing procedures these gels were red, too, but when they were washed and the red-violet  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  leached out their colour turned to yellow. The UV–VIS spectra (Fig. 3e and f) of the yellow gels no longer show the absorptions around 500 nm, which were present in the unwashed samples. These results suggest that the  $\text{Ru}_3$  triangle is affected by the silica matrix: by reacting with silanol groups of the newly formed silica matrix in its neighbourhood, the  $-\text{Si}(\text{OMe})_3$  hydrolysable end in  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  would prevent or reduce attacks of those groups on the  $\text{Ru}_3$  unit. The change observed for the  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$ -containing gels was not an effect of elevated temperatures during soxhlet washing with toluene since the same changes in colour and UV–VIS absorption were observed

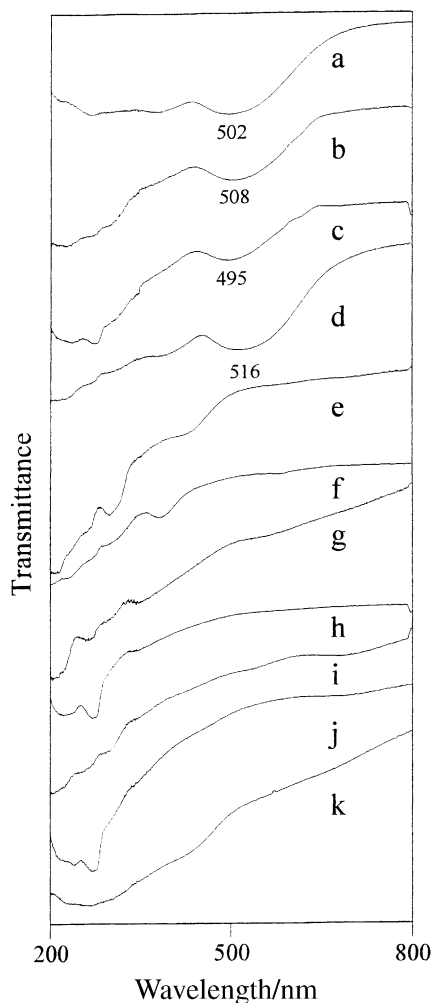


Fig. 3. UV–VIS spectra of (a) Gel 2 before the soxhlet washing; (b) Gel 2 after soxhlet washing with toluene; (c) Gel 1 after soxhlet washing with toluene; (d) Gel 3 before washing with toluene; (e) Gel 3 after soxhlet washing with toluene; (f) Gel 5 after washing with small portions of  $\text{CH}_2\text{Cl}_2$ ; (g) Gel 2 after repeated catalytic reactions; (h) Gel 1 after repeated catalytic reactions; (i) Gel 2 after soxhlet washing with toluene and 2.5 h at  $135^\circ\text{C}$  under vacuum; (j) Gel 1 after soxhlet washing with toluene and 2.5 h at  $135^\circ\text{C}$  under vacuum; (k) Gel 4 after 20 h at  $70^\circ\text{C}$  under vacuum and soxhlet washing with toluene.

when the gels were washed with small portions of  $\text{CH}_2\text{Cl}_2$  at room temperature.

Although gels from  $\text{Ru}_3(\text{CO})_9(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OMe})_3)_3$  maintained their colour and the UV–VIS spectra over at least 9 months when stored at room

temperature, the  $\text{Ru}_3$  triangle seems to be broken in catalytic reactions or at higher temperatures: in the hydrogenation of 1-hexene the colour of the red gels turned to yellow or yellow-brown in the first run and the UV–VIS spectra of the gels after various hydrogenation runs no longer show the absorption at

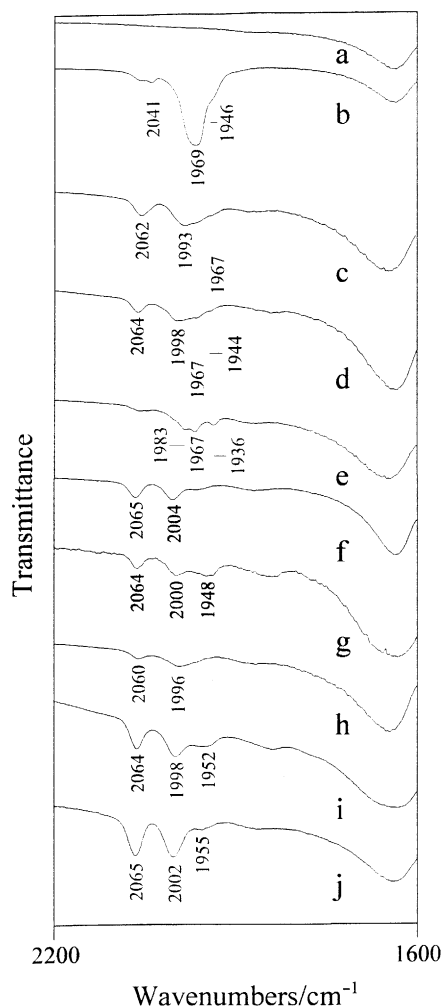


Fig. 4. FT-IR spectra (KBr) of (a) a pure TEOS gel; (b) Gel 2 before the soxhlet washing; (c) Gel 2 after soxhlet washing with toluene; (d) Gel 1 after soxhlet washing with toluene; (e) Gel 3 before washing; (f) Gel 5 after washing with small portions of  $\text{CH}_2\text{Cl}_2$ ; (g) Gel 1 after repeated catalytic reactions; (h) Gel 2 after soxhlet washing with toluene and 2.5 h at  $135^\circ\text{C}$  under vacuum; (i) Gel 1 after soxhlet washing with toluene and 2.5 h at  $135^\circ\text{C}$  under vacuum; (j) Gel 4 after 20 h at  $70^\circ\text{C}$  under vacuum and soxhlet washing with toluene.

nearly 500 nm (Fig. 3g and h). The same behaviour was observed when the gels were heated for 2.5 h at 135 °C or 20 h at 70 °C under vacuum (Fig. 3i–k), their colour turning from red to yellow.

### 3.3.2. FT-IR spectroscopy

The FT-IR spectra confirm that some of the Ru<sub>3</sub> units remain intact during the gelation process when Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> was used. The FT-IR spectra of Gels 1 and 2 after soxhlet washing (Fig. 4c and d) show an absorption at 1967 cm<sup>-1</sup>, close to the strong absorptions in the spectra of the pure cluster (1969 cm<sup>-1</sup>, Fig. 5b) and the unwashed gel (Fig. 4b). The IR absorptions of the pure cluster compound are also found in a sample of unwashed Gel 3 (Fig. 4e). On the other hand, all the gel samples which do not show such IR absorptions also do not have absorptions around 500 nm in their UV–VIS spectra. Besides this absorption at 1967 cm<sup>-1</sup>, Fig. 4c and d show two IR absorptions around 2065 and 1995 cm<sup>-1</sup>, which are not present in the pure cluster compound. IR absorptions at these positions are often found for Ru<sub>3</sub>(CO)<sub>12</sub> impregnated on silica [5,6] or applied in the sol–gel process [15], and assigned to surface oxidised [Ru(II)(CO)<sub>2</sub>]<sub>n</sub> species bonded to the oxygen atoms of the support. Thus, IR spectra are in good agreement with UV–VIS spectra and

reveal that in gels formed with Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> the Ru<sub>3</sub> unit is broken by reaction with the silica matrix. The same occurs to the intact Ru<sub>3</sub> unit when Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> is used and the gel is heated under vacuum or used in repeated catalytic reactions (Fig. 3g–j).

## 4. Conclusions

Ruthenium containing gels prepared from TEOS and Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> are active in the hydrogenation of 1-hexene. UV–VIS and FT-IR spectroscopic investigations of the pure cluster Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> and Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> and the gels show that in the gel formed with Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> the Ru<sub>3</sub> triangle is broken and [Ru(II)(CO)<sub>2</sub>]<sub>n</sub> species are formed. In gels prepared with Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub> some Ru<sub>3</sub> units remain intact since the cluster-containing –Si(OMe)<sub>3</sub> groups react with silanol sites of the silica matrix, preventing their attack on the cluster centre. When exposed to elevated temperatures under vacuum or in catalytic hydrogenation reactions the remaining Ru<sub>3</sub> groups react with the silica surface to give the IR spectra similar to those reported for gels with Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> and Ru<sub>3</sub>(CO)<sub>12</sub>. The higher activity in the hydrogenation of 1-hexene presented by these gels when compared to the solutions of Ru<sub>3</sub>(CO)<sub>12</sub> or Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> may be assigned to the formation of [Ru(II)(CO)<sub>2</sub>]<sub>n</sub> species, expected to be located inside the porous system of the matrices.

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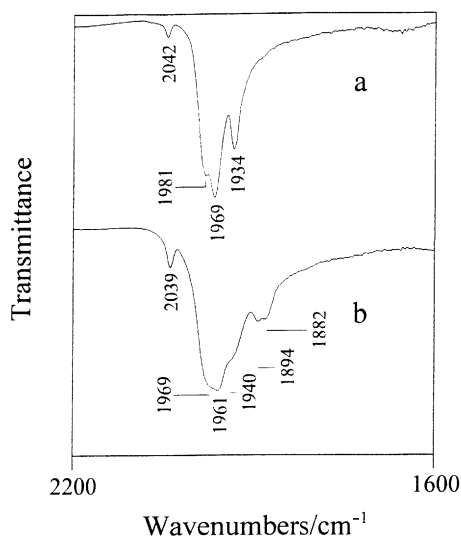


Fig. 5. FT-IR spectra (KBr) of (a) Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>3</sub>)<sub>3</sub> and (b) Ru<sub>3</sub>(CO)<sub>9</sub>(PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Si(OMe)<sub>3</sub>)<sub>3</sub>.

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