FT-IR studies on the catalyst $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 and related ruthenium–bipyridine surface complexes

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Abstract

The influence of the preparation method and conditions on the highly active, supported catalyst $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 was studied by diffuse reflectance FT-IR spectroscopy. Two liquid-phase methods, impregnation from organic solvent and pulse impregnation, and an atomic layer epitaxy (ALE)-derived gas-phase method were applied in the catalyst preparation. In all preparation methods the surface reaction proceeded via physisorbed $[Ru_3(CO)_{12}]$ and 2,2'-bipyridine. Irrespective of the method employed, the original cluster $[Ru_3(CO)_{12}]$ was lost during activation and new ruthenium monobipyridine surface species were formed. The solvent played a critical role in the liquid-phase methods. Use of chlorinated solvents such as dichloromethane favoured the formation of the less active chlorinated surface species $[\{Ru(bpy)(CO)_2Cl_m\}_n]/SiO_2$ ($m = 1$, 2 and $n \geqslant 1$), whereas use of non-chlorinated solvents or the gas-phase method gave rise to more active $[\{Ru(bpy)(CO)_2\}_n]/SiO_2$ ($n \geqslant 1$). Supported mononuclear $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ and $[Ru(bpy)(CO)_2ClH]$ complexes proved to be useful model compounds for the $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 catalyst yielding similar IR patterns to those of $[\{Ru(bpy)(CO)_2Cl_m\}_n]/SiO_2$.

Keywords: Ruthenium; Bipyridene; Catalysis

1. Introduction

Unsupported ruthenium bipyridine and ruthenium bipyridine carbonyl compounds are known to be active in several catalysis processes. The most widely studied of these processes are CO_2 reduction [1] and the water–gas shift (WGS) reaction [2]. The catalytic behaviour of the supported ruthenium bipyridines has been less frequently investigated. Among the most promising supported systems is a cluster-derived $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 which has been found to be highly active in the WGS reaction [3] and in 1-hexene hydroformylation [4]. In WGSR, $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 has showed 3–10-times higher activities [3b,5] than the corresponding homogeneous ruthenium bis(bipyridine) [2c] catalysts at relatively low temperatures (150°C). The activity, selectivity and catalytic reproducibility of $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 depends strongly on the method of preparation. For example, the highest hydroformylation activities have been obtained for catalysts prepared by conventional impreg-

nation from organic solvent with subsequent thermal activation [4], whereas the highest WGSR activities have been achieved for catalysts prepared by the ALE-derived (Atomic Layer Epitaxy) method [5]. Although several reports on the catalytic behaviour of $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 have been published [3–6], so far no extensive study on the structure of the catalyst has been reported.

In the present work we studied $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 catalyst prepared by conventional impregnation, pulse impregnation and an ALE-derived gas-phase method by diffuse reflectance FT-IR spectroscopy. In the impregnation methods, solvent effects were investigated by using chlorinated and non-chlorinated solvents or solvent mixtures. Solvent effects on the activated catalyst and air sensitivity were also investigated by monitoring the spectral changes during solvent/air exposure. Supported mononuclear $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ and $[Ru(bpy)(CO)_2ClH]$ compounds were studied as potential model compounds for the $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 catalyst. The possibility of using NaOH as a dechlorination agent for supported monomers was also studied.

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2. Experimental details

2.1. Materials and measurements

All solvents and reagents were p.a. grade and degassed before use. Dichloromethane was dried over molecular sieves. THF was distilled from benzophenone solution using metallic Na as the drying agent or dried over molecular sieves. $Ru_3(CO)_{12}$ was either obtained from Johnson & Matthey or prepared using a literature method [7]. 2,2'-Bipyridine was obtained from Aldrich. Silica gel SG-60 (Merck, surface area 500 m^2 g^{-1}, specific pore volume 0.8 ml g^{-1} ϕ 0.063–0.200 mm) and silica F-22 (Akzo Chemie, surface area 400 m^2 g^{-1} ϕ 0.074–0.179 mm), calcined at 600°C for 24 h, was used in the preparation of impregnated and pulse-impregnated catalysts. Most of the catalysts prepared via the gas-phase method were supported on silica F-22, which was dried overnight under vacuum at 300°C. FT-IR studies of the supported catalysts and solid compounds were carried out by the diffuse reflectance method in a glove-box under a nitrogen atmosphere. IR spectra were measured directly from the dried catalyst powder without any additional matrix by using a Mattson Instruments 6020 galaxy series FT-IR spectrometer. IR studies on the soluble compounds were carried out with a Nicolet Magna-IR 750 FT-IR instrument. Gas evolution during impregnations was also monitored by IR spectroscopy. The ruthenium and nitrogen contents of the pulse-impregnated catalysts were determined by atomic absorption spectroscopy and elemental analysis.

2.2. Preparation of the $Ru_3(CO)_{12}$ / 2,2'-bipyridine / SiO_2 catalyst

The $Ru_3(CO)_{12}$/2,2'-bipyridine/SiO_2 catalyst was prepared by impregnation (I), pulse impregnation (PI) [6] and an ALE-related gas-phase method (G) [5]. All preparations were carried out under nitrogen or CO atmospheres. In a typical impregnation process (I), $Ru_3(CO)_{12}$ and 2,2'-bipyridine precursors were deposited simultaneously on to the calcined silica from the organic solvent {dichloromethane (I1), THF (I2) and a

THF/dichloromethane mixture [1/1 (v/v)] (I3)} at room temperature. After impregnation for 17–24 h, the excess solvent was removed under vacuum. The dried catalyst was activated by heating under N_2 at 100°C for 17 h. During activation the active dark blue catalyst was formed. Calculated loadings of Ru and 2,2'-bipyridine were 1.2–1.9 wt.% and 2.3–3.0 wt.%, respectively (the ruthenium/2,2'-bipyridine ratio was 1).

Pulse impregnation (PI) was used to produce catalysts with a low Ru loading (< 1% of Ru). PI is a two-step method consisting of separate deposition and activation steps [6]. In deposition, the precursor solution is pulsed through the support bed and the precursors are distributed between the solvent and support according to their adsorption coefficients. With sufficiently long pulses, uniform coverage can be achieved throughout the support bed. Precursors can be deposited either simultaneously from the same solvent or successively from different solvents. The final immobile catalyst phase is formed during activation when the initially physisorbed precursors react with the support and/or each other. Catalyst loading can be increased by repeating the deposition–activation cycles. In this work, both successive and simultaneous deposition of $Ru_3(CO)_{12}$ and 2,2'-bipyridine were applied. In PI1, the 2,2'-bipyridine was pulsed from THF and $Ru_3(CO)_{12}$ from hexane, whereas in PI2 the two components were pulsed simultaneously from a mixture of THF/CH_2Cl_2 (20% v/v), or separately: $RU_3(CO)_{12}$ from hexane and 2,2'-bipy from THF/CH_2Cl_2 mixture. The PI catalysts were activated at 90–100°C for 10 to 20 min after each deposition cycle, and were washed with the more polar solvent (THF in PI1 and the THF/CH_2Cl_2 mixture in PI2).

In the gas-phase method (G), the catalyst was prepared by vapourizing $Ru_3(CO)_{12}$ at 135°C in a separate sublimation oven and transferring the cluster in a CO flow on to the silica bed in a fluidized bed reactor. In this method, sublimation can be achieved at a low pressure of CO, but better mixing is achieved with 200–300 ml min^{-1} flow of CO at normal pressure. 2,2'-Bipyridine was added by a similar technique at 100°C or was mixed with $Ru_3(CO)_{12}$/SiO_2 and activated separately at 100°C in a sealed glass cell under vacuum. In the former method, the thermal activation of

Table 1
Preparation methods for the $Ru_3(CO)_{12}$/2,2'-bipyridine/SiO_2 catalyst

Preparation method	Abbreviation	Solvent	Ru content (wt.%)	Impregnation time (h)	Activation/sublimation temp. (°C)	Activation time
Impregnation	I1	CH_2Cl_2	1.2–1.9	17–24	100	17 h
	I2	THF	1.2–1.9	17–24	100	17 h
	I3	CH_2Cl_2/THF	1.2–1.9	17–24	100	17 h
Pulse impregnation	PI1	THF/hexane	< 1		90–100	10–20 min
	PI2	CH_2Cl_2/THF(/hexane)	< 1		90–100	10–20 min
Gas-phase method	G	sublimed [a]	1–1.6	135 [b]/100 [c]		

All impregnations and pulse impregnations were carried out under a nitrogen atmosphere. [a] Sublimed under a CO atmosphere. [b] Sublimation temperature for $Ru_3(CO)_{12}$. [c] Sublimation temperature for 2,2'-bipyridine.
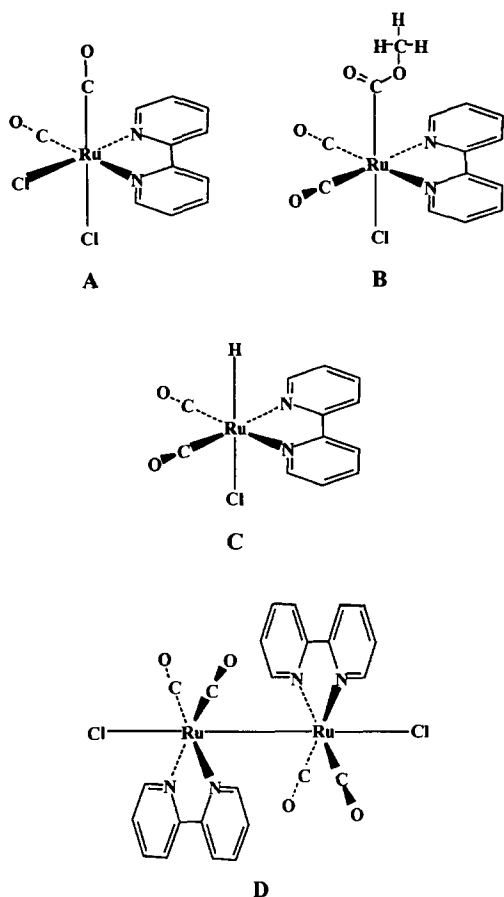
Fig. 1. Schematic structures of (A) cis-(CO),cis-(Cl)-[Ru(bpy)-(CO)$_2$Cl$_2$], (B) [Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)], (C) [Ru(bpy)(CO)$_2$-ClH] and (D) [{Ru(bpy)(CO)$_2$Cl}$_2$].

the catalyst and the formation of the dark blue catalyst take place simultaneously with the deposition of 2,2′-bi-pyridine. Preparation methods and conditions are summarized in Table 1.

2.3. Impregnation and NaOH treatment of [Ru(bpy)-(CO)$_2$Cl$_2$], [Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)], [Ru(bpy)-(CO)$_2$ClH] and [{Ru(bpy)(CO)$_2$Cl}$_2$]

The mononuclear model compounds [Ru(bpy)(CO)$_2$-Cl$_2$], [Ru(bpy)(CO)$_2$OlCl(C(O)OCH$_3$)] and [Ru(bpy)-(CO)$_2$ClH] (Fig. 1) were impregnated on to calcined SiO$_2$ under a nitrogen atmosphere using similar conditions to those applied in the impregnation of Ru$_3$-(CO)$_{12}$/2,2′-bipyridine/SiO$_2$ catalysts (impregnation times 17–20 h for monomeric complexes, theoretical Ru loading 0.5–1.9 wt.%). Synthesis of the model compounds has been described elsewhere [9].

Sodium hydroxide treatment of both unsupported and silica-supported ruthenium monobipyridine compounds was carried out under a nitrogen atmosphere by using excess of a 0.1 mol l^{-1} NaOH solution.

3. Results and discussion

3.1. Impregnated Ru$_3$(CO)$_{12}$ / 2,2′-bipyridine / SiO$_2$ catalysts

During a typical I1 impregnation, the colour of the support changed from yellow to brown. However, in the IR spectra the dominating carbonyl stretching bands were found at 2066 (vs) cm^{-1} and 2036 (m, sh) cm^{-1} [Fig. 2(a)] indicating physisorbed Ru$_3$(CO)$_{12}$ [10]. Similarly, IR signals due to 2,2′-bipyridine rings at the region 1300–1600 cm^{-1} were comparable with physisorbed 2,2′-bipyridine [11]. In addition to the main ν(CO) bands there were typically a broad adsorption band in the 2020–1950 cm^{-1} region, a shoulder band at 2077 cm^{-1} (s) and a sharp but weak band at 2118 cm^{-1}. The dark colour and the tailing adsorption band at 2020–1950 cm^{-1} indicated that the reaction between Ru$_3$(CO)$_{12}$ and 2,2′-bipyridine was already initiated during impregnation. Although the shoulder band at
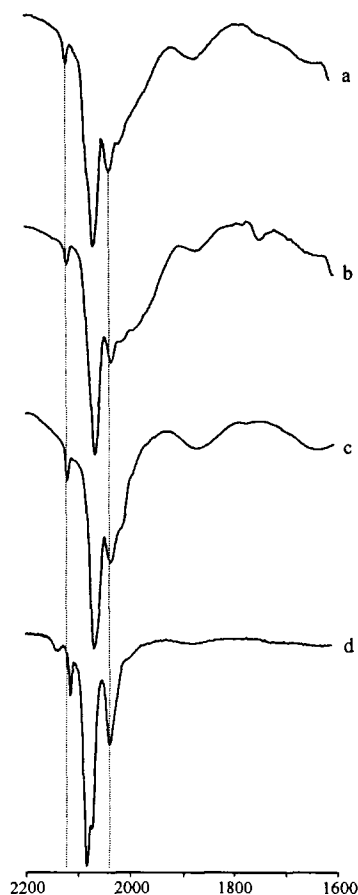

Fig. 2. (a) IR spectra of CH$_2$Cl$_2$-impregnated (I1) sample before thermal activation, (b) Ru$_3$(CO)$_{12}$/2,2′-bipyridine/SiO$_2$ impregnated on to SiO$_2$ from THF (I2), (c) physisorbed [Ru$_3$(CO)$_{12}$]/SiO$_2$ (impregnated from THF), (d) chemisorbed [HRu$_3$(CO)$_{10}$]/SiO$_2$ prepared by the ALE-derived gas-phase method under a nitrogen atmosphere. The broad and weak band at 1830–1900 cm^{-1} is due to the silica support.

2077 cm^{-1} and the sharp 'high frequency' band at 2118 cm^{-1} somewhat resembled the bands assigned to chemisorbed [HRu$_3$(CO)$_{10}$]/ SiO$_2$ [5,10b,12], the spectrum is much closer to physisorbed [Ru$_3$(CO)$_{12}$] [Fig. 2(c)] than a true chemisorbed cluster [Fig. 2(d)]. Thus the bands at 2118 cm^{-1} and 2077 cm^{-1} may arise from partially decarbonylated 'sub-carbonyl' species, which are typical especially for thermally treated [Ru$_3$-(CO)$_{12}$]/SiO$_2$ [10,12], rather than a true chemisorbed cluster.

The main IR patterns in the non-activated I2 and I3 samples were close to those in I1 samples [Fig. 2(b)]. The tailing band formation at < 2020 cm^{-1} was even more apparent than in I1, but the shoulder at 2078 cm^{-1} was either very weak or not present at all. The spectra of I2 samples also included a weak and broad band at 1743 cm^{-1}, which may be an indication of a bridging CO group. However, since this band was found only in THF-impregnated samples, it may also arise from the THF residues bound to the samples.

During activation, all samples turned dark blue or bluish black and became insoluble. In the I1 catalysts the spectrum of [Ru$_3$(CO)$_{12}$]$_{phys}$ disappeared and two broad, poorly resolved band pairs appeared [Fig. 3(a)]. The relative intensities of these band pairs varied from a nearly pure 2073/2013 cm^{-1} pair to a nearly pure 2050/1977 cm^{-1} pair indicating two ruthenium carbonyl surface species, a 'high pair' A species and a 'low pair' B species. In the THF impregnations (I2), only the B species appeared with ν(CO) bands at 2047 and 1973 cm^{-1} and an additional shoulder at 1997 cm^{-1} [Fig. 3(b)]. Furthermore, a weak band at ca. 1745 cm^{-1}, which was observed already after impregnation, was found in the spectrum. Impregnation from methanol also yielded pure species B, but in this case no clear band was found at 1745 cm^{-1} [Fig. 3(c)]. In the spectra
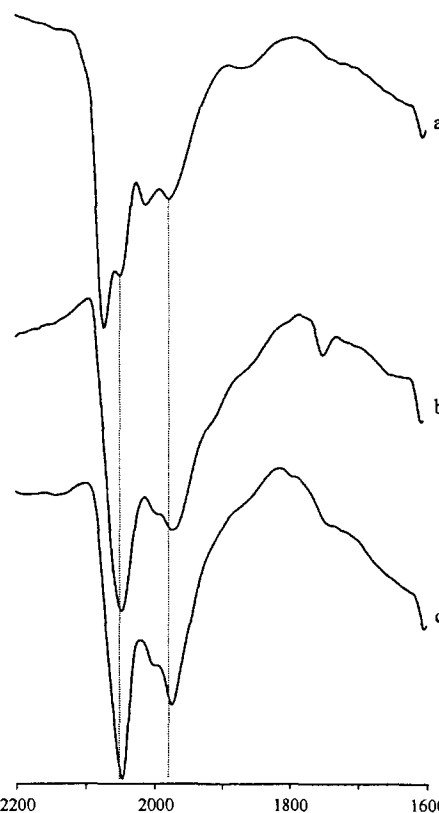

Fig. 3. IR spectra of impregnated Ru$_3$(CO)$_{12}$ /2,2'-bipyridine/SiO$_2$ catalysts after thermal activation: (a) impregnated from CH$_2$Cl$_2$ (I1), (b) impregnated from THF (I2) and (c) impregnated from methanol. [(······) species B.]

of the I3 catalysts (Table 2), variable mixtures of species A and B were again observed with species B typically dominant.

Although none of the activated Ru$_3$(CO)$_{12}$/2,2'-bi-pyridine/SiO$_2$ catalysts were extractable with organic

Table 2
IR spectra of supported ruthenium bipyridines

Compound	Solvent	Preparation method	Wavenumbers (cm^{-1})
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	CH$_2$Cl$_2$	impregnation (I1)	2073 [a]; 2050 [b]; 2013 [a], 1977 [b]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	CH$_2$Cl$_2$/THF	impregnation (I3)	2069 [a]; 2049 [b]; 2006 [a], 1974 [b]; 1745 [c]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	THF	impregnation (I2)	2047 [b]; 1997 [d]; 1973 [h]; 1746 [c]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	CH$_2$Cl$_2$/THF(/hexane)	pulse impregnation (PI2)	2073 [a]; 2043 [b]; 2009 [a]; 1976 [b]; 1744 [c]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	THF/hexane	pulse impregnation (PI1)	2045 [b]; 1994 [d]; 1972 [b]; 1745 [c]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	–	sublimed (G)	2043 [b]; 1991 [d]; 1968 [b]
[Ru$_3$(CO)$_{12}$]/2,2'-bipyridine	MeOH	impregnation	2045 [b]; 1998 [d]; 1974 [b]
[Ru(bpy)(CO)$_2$Cl$_2$]	CH$_2$Cl$_2$	impregnation	2080; 2021
[Ru(bpy)(CO)$_2$Cl$_2$]	THF	impregnation	2076; 2012
[Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)]	CH$_2$Cl$_2$	impregnation	2078; 2052 [d]; 2016; 1979 [d]
[Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)]	THF	impregnation	2074; 2039 [d]; 2010; 1970 [d]
[Ru(bpy)(CO)$_2$ClH]	CH$_2$Cl$_2$	impregnation	2078; 2049 [d]; 2015; 1978 [d]
[Ru(bpy)(CO)$_2$ClH]	THF	impregnation	2072 [d]; 2044; 1979; 1770 [c]
[Ru$_3$(bpy)(CO)$_{10}$]	CH$_2$Cl$_2$	impregnation [e,f]	2097; 2076; 2037; 2008; 1980; 1959; 1932; 1924; 1806; 1744
[Ru$_3$(bpy)(CO)$_{10}$]/2,2'-bipyridine	CH$_2$Cl$_2$	impregnation [f]	2039; 1994 [d]; 1968; 1743 [c]

Impregnation times varied between 15–20 h and R loadings from 0.5 to 1.5 wt.%. [a] Species A. [b] Species B. [c] Weak and broad band. [d] Poorly resolved shoulder. [e] No thermal activation. [f] Impregnation time, 1 h.
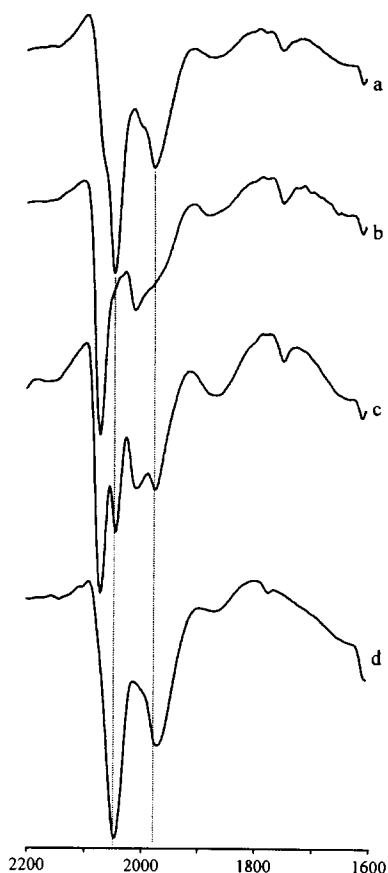
Fig. 4. IR spectra of $Ru_3(CO)_{12}$ /2,2'-bipyridine/SiO_2 catalyst prepared (a) by pulse impregnation with THF used for 2,2'-bipyridene and hexane for $Ru_3(CO)_{12}$, (b) by pulse impregnation from THF/CH_2Cl_2 bipyridene and hexane $Ru_3(CO)_{12}$, (c) summation spectrum of pure species A and B prepared by pulse impregnation and (d) $Ru_3(CO)_{12}$ /2,2'-bipyridine/SiO_2 prepared by the ALE-derived gas-phase method (G).

solvents, both I1 and I2 catalysts were 'extractable' with concentrated HCl (37%) (at 100°C for 3 h). After evaporation of the extract to dryness, the residue was dissolved in $CHCl_3$ and analyzed by IR and ^{1}H NMR spectroscopy. The dominating ν(CO) bands appeared at 2071 and 2008 cm^{-1}, which is in good agreement with the spectrum of [Ru(bpy)(CO)$_2$Cl$_2$] [13a]. The formation of [Ru(bpy)(CO)$_2$Cl$_2$] was confirmed by ^{1}H NMR analysis.

3.2. Pulse-impregnated $Ru_3(CO)_{12}$ / 2,2'-bipyridine / SiO_2

In the pulse-impregnation procedure, only the final activated catalyst could be studied by IR spectroscopy. The spectra of PI1 catalysts included two main bands at 2045 cm^{-1} (s) and 1972 cm^{-1} (m), which tended to broaden with increased Ru loading [Fig. 4(a), Table 2]. The spectrum of the PI1 catalyst is thus in agreement with the spectrum produced by the species B. When dichloromethane was present in the pulse-impregnation

solutions (PI2), two new bands appeared. Typical the PI2 spectrum showed a strong ν(CO) signal at 2072 cm^{-1} and a weaker signal at 2009 cm^{-1} [Fig. 4(b)], resembling the bands of the A species (Table 2). Again this 'high pair' spectrum of species A occurred only if the impregnation solution contained dichloromethane, which is in agreement with the results obtained for the conventionally impregnated catalyst. The average nitrogen/ruthenium ratio in the pulse-impregnated (PI1 and PI2) catalysts was 2.1, indicating the presence of ruthenium monobipyridine complexes in agreement with HCl extraction results of conventionally impregnated catalysts.

3.3. $Ru_3(CO)_{12}$ / 2,2'-bipyridine / SiO_2 prepared by the gas-phase method

The first step in the gas-phase deposition (G) of $Ru_3(CO)_{12}$ on to the silica support was physisorption of the cluster. The physisorbed cluster anchored rapidly on to the silica by losing carbonyl groups. This process was observed by IR spectroscopy, which revealed the presence of both physisorbed and chemisorbed [2112 (w); 2081 (vs); 2071 (vs); 2037 (m); 2001 (w) cm^{-1}] ruthenium clusters [5]. Under a CO atmosphere, chemisorption of $Ru_3(CO)_{12}$ was reversible and the physisorbed and chemisorbed clusters were in dynamic equilibrium. Although the wavenumbers of the physisorbed $Ru_3(CO)_{12}$ and chemisorbed [HRu$_3(CO)_{10}$]/ SiO_2 were in agreement with the results reported in the literature [10,12], the band intensities differ from the literature values, owing to the use of different IR techniques. Addition of 2,2'-bipyridine again led to a dark blue catalyst with two distinct ν(CO) bands at 2043 and 1968 cm^{-1} [Fig. 4(d)] and a shoulder at 1991 cm^{-1}. Similarly to the pulse-impregnated catalysts, the broadness of the bands increased with ruthenium loading. Yet again the spectrum of the activated G catalyst confirmed the formation of species B. As expected, species A was not observed in any catalyst prepared via the gas-phase technique.

3.4. Reactions between [$Ru_3(CO)_{12}$] and 2,2'-bipyridine

In hexane [14a] or cyclohexane [14b] solution, [$Ru_3(CO)_{12}$] and 2,2'-bipyridine react under reflux, yielding the 'mono-substituted' cluster [Ru$_3$(bpy)(μ_2-CO)$_2$(CO)$_8$] [Fig. 5(a), Scheme 1]. There is some evidence that the reaction may continue via consecutive replacement of CO ligands by 2,2'-bipyridine. The first step in the continued reaction between [Ru$_3$(bpy)(μ_2-CO)$_2$(CO)$_8$] and 2,2'-bipyridine in polar solvents such as CH_2Cl_2 or THF was the formation of a labile carbonyl-bridged 'soluble intermediate'. Downward shifted terminal ν(CO) bands and a sharpened ν(μ-CO) band [Fig. 5(b)] with increased relative intensity sug-

gested further addition of 2,2'-bipyridine and the formation of new or more symmetrical CO bridges. The soluble intermediate was easily converted to a bluish black, air-sensitive and insoluble precipitate, whose ν(CO) bands were shifted still further downwards. The final product also showed activity in the WGS reaction [3b] and 1-hexene hydroformylation [4a] similarly to the supported $Ru_3(CO)_{12}$/2,2'-bipyridine/SiO_2 catalyst. Although the final product was stable in a nitrogen atmosphere, the elemental composition varied considerably from lot to lot, perhaps due to the co-existence of several complexes. Possible reaction routes for $[Ru_3(bpy)(\mu_2-CO)_2(CO)_8]$ and 2,2'-bipyridine are collected in Scheme 1. This presentation is based solely on IR results and more investigation is needed to establish the reaction route.

Bridging carbonyl bands were also found for supported $[Ru_3(bpy)(CO)_{10}]$/SiO_2 (Table 2), but they were strongly reduced after the addition of excess 2,2'-bipyridine and thermal activation (100°C for 20 h). During thermal treatment the sample rapidly turned from reddish brown to dark blue, yielding an IR spectrum almost identical with that of species B, except for an additional broad and weak signal at 1743 cm^{-1}. The appearance of such additional signal may be due to a bridging CO group. As discussed earlier in CH_2Cl_2-impregnated $Ru_3(CO)_{12}$/2,2'-bipyridine/SiO_2 samples, no distinct ν(CO) bands that could be indisputably assigned to bridging CO were found, but in typical THF-impregnated or PI catalysts a broad and weak band appeared at about 1745 cm^{-1} (Table 2).

The strongest argument against the formation of a
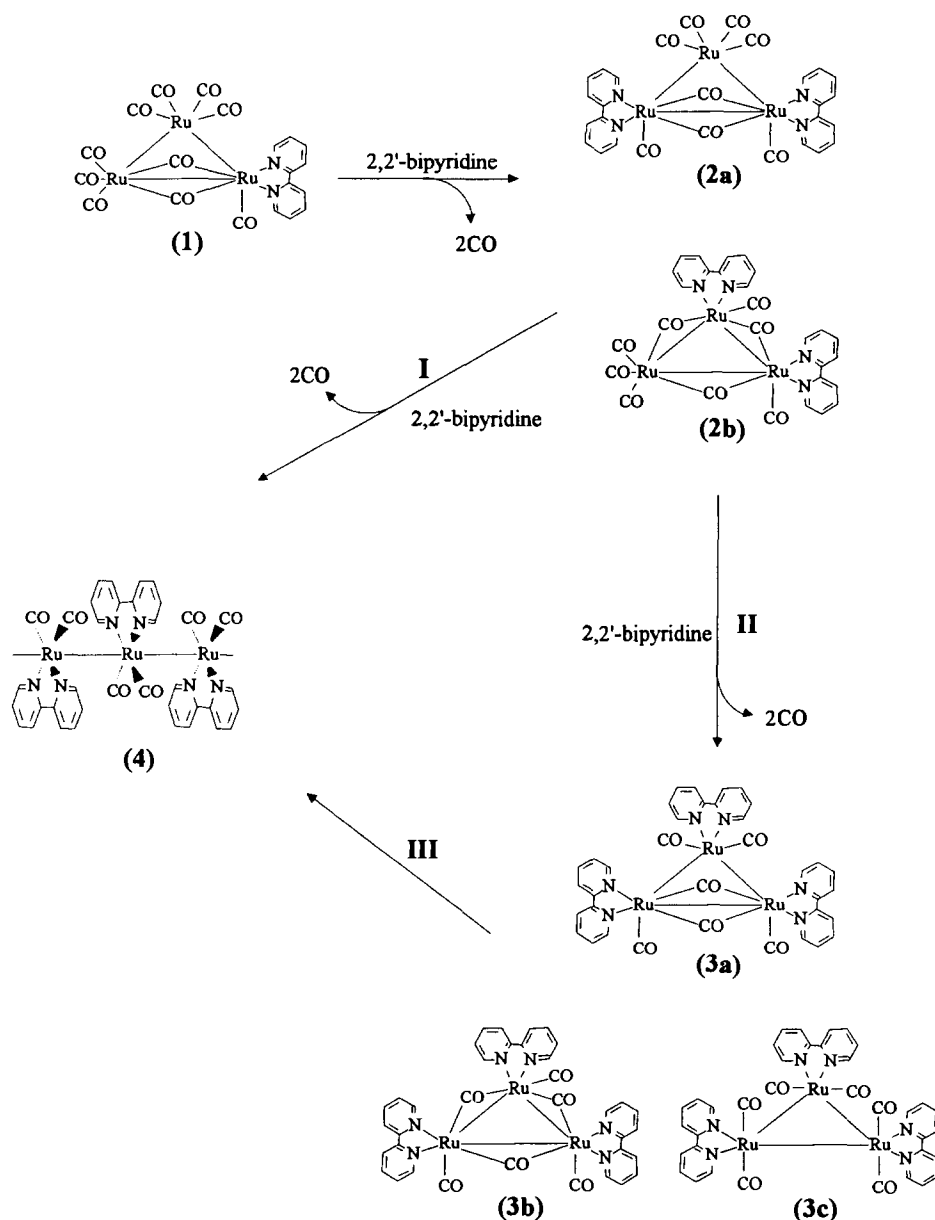
Scheme 1. Possibilities for the routes for $[Ru_3(bpy)(\mu_2-CO)_2(CO)_8]$ and 2,2'-bipyridine.

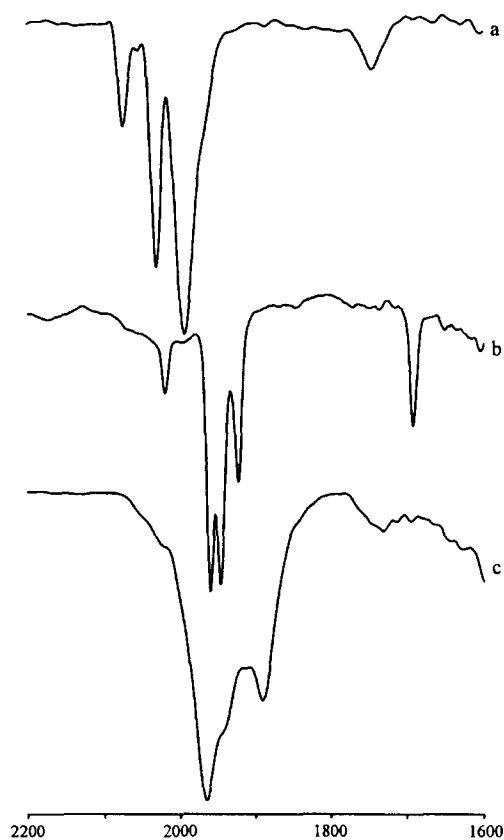Fig. 5. IR spectra of (a) [Ru$_3$(bpy)(μ-CO)$_2$(CO)$_8$] [2076 (m); 2033 (vs); 1993 (vs, br); 1970 (w, sh); 1740 (w, br) cm^{-1}, in CH$_2$Cl$_2$], (b) 'soluble intermediate' [2022 (w); 1961 (vs); 1946 (vs); 1924 (s); 1693 (m) cm^{-1}, in THF], (c) the final, catalytically active precipitate [1966; 1892 cm^{-1}, in KBr, measured by DRIFTS].

linear, polymeric [{Ru(bpy)(CO)$_2$}$_n$] (Scheme 1 (4)) in the reaction between Ru$_3$(CO)$_{12}$ and 2,2'-bipyridine is the mismatch between the reported IR spectrum of the polymer [1e,1f,1g] (two bands at 2017 and 1996 cm^{-1}) and the final product obtained by refluxing [Ru$_3$(CO)$_{12}$] and 2,2'-bipyridine. However, the spectral differences may be partially due to different IR techniques. There is also a possibility that the polymers may have different absolute structures (presence of bridging CO groups or rotamerism similar to [{Ru(bpy)(CO)$_2$Cl}$_2$]) [9]). Nevertheless the disparity in the IR spectra is discouraging. Therefore, instead of linear polymer, formation of a cyclic ruthenium bipyridine oligomer or polymer with 2,2'-bipyridine and two carbonyl ligands per ruthenium may also be possible.

It seems possible that the supported [Ru$_3$(bpy)(μ-CO)$_2$(CO)$_8$]/SiO$_2$ could react with 2,2'-bipyridine similarly to the unsupported cluster by the consecutive addition of 2,2'-bipyridine, yielding oligomeric or polymeric [{Ru(bpy)(CO)$_2$}$_n$]/SiO$_2$ (species B) as the main product. In such a case, the higher ν(CO) bands of [{Ru(bpy)(CO)$_2$}$_n$]/SiO$_2$ compared to unsupported [{Ru(bpy)(CO)$_2$}$_n$] are due to the support effect of the silica.

3.5. Solvent and air manipulation of the Ru$_3$(CO)$_{12}$/ 2,2'-bipyridine / SiO$_2$ catalyst

Solvent effects on the formation of the species A were studied by treating the activated catalysts with chlorinated solvent or THF. Samples were stored in the solvent overnight under a nitrogen atmosphere. Dichloromethane treatment of species B prepared by PI1 leads to a brownish product with a four-band spectrum [2076(vs); 2044(sh); 2016(m); 1979(sh) cm^{-1}] resembling the spectrum of the A + B mixture. Formation of the species A was also observed with catalysts prepared by impregnation (I2) or by the gas-phase method (G). Furthermore, the appearance of species A was recorded when species B was treated with chloroform. Exposure of species B to other chlorine sources such as CCl$_4$ or gaseous Cl$_2$ also caused a band shift to higher wavenumbers, indicating chlorination/oxidation. Unlike chlorinated solvents, non-chlorinated solvents such as THF did not cause any significant spectral changes. Neither dichloromethane nor THF treatment of species A caused any major spectral changes.

The colour of all impregnated, pulse-impregnated and gas-phase prepared catalysts changed drastically from dark blue to brown during exposure to air. In the IR spectrum of species B, exposure to air caused slight broadening of the 2040–2050 cm^{-1} band and formation of a shoulder at about 2060 cm^{-1}. Air treatment of the A species did not cause any considerable spectral changes. After several days exposure to air however, the band intensities of both species A and B weakened probably due to slow decomposition of the catalyst. Both the colour change and appearance of the new shoulder band in the case of species B may be due to oxidation of the catalysts.

3.6. IR spectra of related ruthenium monobipyridine compounds

3.6.1. [Ru(bpy)(CO)$_2$Cl$_2$] / SiO$_2$

The IR spectrum of an isomeric mixture (cis-(CO), cis-(Cl)- and cis-(CO), trans-(Cl) isomers) of [Ru(bpy)-(CO)$_2$Cl$_2$] in dichloromethane exhibited strong bands at 2067(vs) and 2003(vs) cm^{-1} [9]. In THF the bands were slightly shifted to lower wavenumbers, 2059 and 1991 cm^{-1}, due to the effect of solvent.

Pale yellow [Ru(bpy)(CO)$_2$Cl$_2$] adsorbed readily on to SiO$_2$ from dichloromethane. In a typical dichloromethane impregnation, a yellow product was formed giving two strong and broad ν(CO) bands at 2080 and 2021 cm^{-1}. During impregnation only trace amounts of CO and CO$_2$ were evolved, indicating that no severe decarbonylation occurred. Washing the dichloromethane-impregnated product with THF gave an orange solution with two bands at 2058 and 1993 cm^{-1}, identical to the original [Ru(bpy)(CO)$_2$Cl$_2$].

Washing with dichloromethane was less effective, yielding only a light yellow solution. However, even in this case the original $\nu(CO)$ signals of $[Ru(bpy)(CO)_2Cl_2]$ were found at 2066 and 2005 cm^{-1} showing, in agreement with Hanson et al. [15], that the adsorption is mainly physisorption. Impregnation from THF gave slightly lower wavenumbers at 2076 and 2012 cm^{-1} for $[Ru(bpy)(CO)_2Cl_2]/SiO_2$. A weak solvent effect was thus observable even on supported $[Ru(bpy)(CO)_2Cl_2]/SiO_2$.

After thermal treatment (100°C, for 15–20 h) of the dichloromethane-impregnated $[Ru(bpy)(CO)_2Cl_2]$, the yellowish colour was somewhat darkened but no change in the IR spectrum was observed [Fig. 6(a)]. Only slight evolution of CO or CO_2 was observed during the treatment and the main surface species was physisorbed $[Ru(bpy)(CO)_2Cl_2]/SiO_2$. A slight band shift to lower wavenumbers, due to solvent effect, was again observed in the THF-impregnated samples. Evidently some THF residues remain on the silica even after thermal treatment [8]. The breadth of the bands of $[Ru(bpy)(CO)_2$-$Cl_2]/SiO_2$ may arise from a mixture of supported cis-(CO), cis-(Cl) and cis-(CO), trans-(Cl) isomers or it
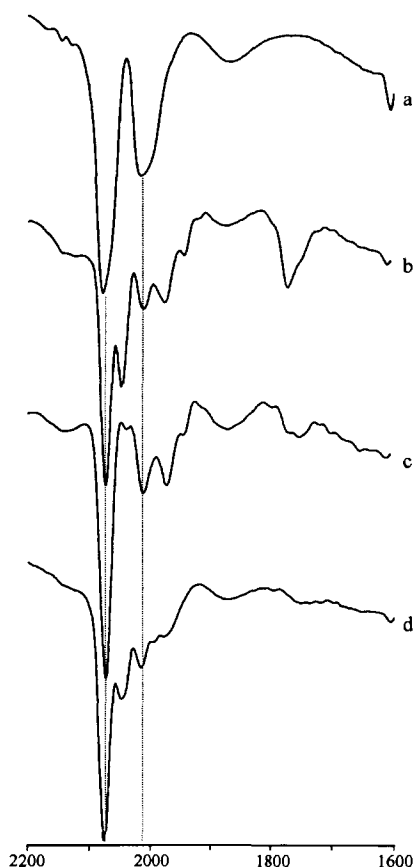
Fig. 6. IR spectra of (a) silica-supported $[Ru(bpy)(CO)_2Cl_2]$ after thermal treatment (at 100°C for 15 h), (b) silica-supported $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ impregnated from THF, (c) sample (b) washed with THF, (d) sample (b) washed with CH_2Cl_2.
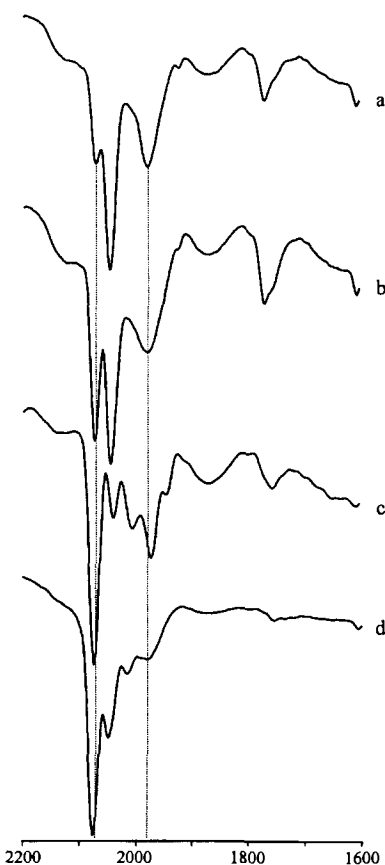

Fig. 7. IR spectra of (a) $[Ru(bpy)(CO)_2ClH]/SiO_2$ impregnated from THF, (b) sample (a) heated at 100°C for 15 h, (c) sample (b) washed with THF, (d) sample (b) washed with CH_2Cl_2.

may due to topological effects of the silica surface. Topological effects have been proposed for physisorbed $[Ru(CO)_2Cl_2(HOSi)_2]$ [16].

3.6.2. [Ru(bpy)(CO)₂ClH] impregnated on to SiO₂

Reddish brown $[Ru(bpy)(CO)_2ClH]$ gave two sharp peaks at 2035 (vs), 1966 (vs) cm^{-1} in CH_2Cl_2 and at 2028 and 1958 cm^{-1} in THF. Impregnation of $[Ru(bpy)(CO)_2ClH]$ on to silica from THF shifted the $\nu(CO)$ bands upwards to 2046 and 1977 cm^{-1}, which resembles the surface species B (Table 2). However, a distinct additional band was also found at about 2070 cm^{-1} [Fig. 7(a)]. Some evolution of CO_2 was observed during impregnation, possibly due to minor decarbonylation of $[Ru(bpy)(CO)_2ClH]$. Washing the support with THF yielded a light yellow solution with $\nu(CO)$ bands at 2059 (vw); 2028 (s); 1992 (vw); 1957 (sh, m); 1950 (s) cm^{-1}. The weak bands at 2059 and 1992 cm^{-1} are very close to those produced by $[Ru(bpy)(CO)_2Cl_2]$ and are probably due to $[Ru(bpy)(CO)_2Cl_2]$ impurities in $[Ru(bpy)(CO)_2ClH]$ [9]. Alternatively, an additional chlorine ligand may be obtained from decomposed $[Ru(bpy)(CO)_2ClH]$ molecules. The band at 2028 cm^{-1} and the shoulder at 1957 cm^{-1} are identical with those

of free [Ru(bpy)(CO)₂ClH] indicating the presence of physisorbed [Ru(bpy)(CO)₂ClH]. However, since the colour of [Ru(bpy)(CO)₂ClH] in THF changed rapidly from reddish brown to red, it may be possible that in THF solution the hydride ligand is replaced with the THF molecule yielding labile [Ru(bpy)(CO)₂Cl(THF)]. THF is known to be able to coordinate in several transition metals, for example Cr, Mn and Ru complexes [13a, 17], including both monomeric ruthenium compounds and ruthenium clusters [13a, 17a]. Removal of the hydride ligand is further supported by the tendency of [Ru(bpy)(CO)₂ClH] to convert into dimeric [{Ru(bpy)(CO)₂Cl}₂] during longer exposure to THF.

Despite the physisorbed species, the supported [Ru(bpy)(CO)₂ClH]/SiO₂ was not completely removable with THF. Washing the support with THF caused the colour of the support to change from grey to brown. The IR spectrum of the washed support revealed the presence of four ν(CO) bands [2073 (s); 2046 (m); 2005 (w); 1974 (m); 1946 (w)] resembling the mixture of species A + B. The bands at 2073 and 2005 cm⁻¹ possibly arise from surface species similar to species A. Although these bands are also close to [Ru(bpy)(CO)₂-Cl₂]_phys, they are probably due to more strongly adsorbed species. The bands at 2046 and 1974 cm⁻¹ are close to those found in species B, but since the relative intensities of these bands were changed and reduced during the THF wash they more probably arise from the residues of physisorbed [Ru(bpy)(CO)₂ClH] and physisorbed [{Ru(bpy)(CO)₂Cl}₂], which is easily formed from [Ru(bpy)(CO)₂ClH] giving multiple ν(CO) bands at 2019–1910 cm⁻¹ [9].

Washing the THF-impregnated [Ru(bpy)(CO)₂ClH]/SiO₂ with dichloromethane yielded an almost colourless solution with no signals in the carbonyl region. However, exposure to dichloromethane changed the spectrum of the support. The relative intensity of the highest band increased and the band shifted slightly upwards from 2073 to 2076 cm⁻¹. In addition, another signal arose at 2015 cm⁻¹. The bands at 2076 and 2015 cm⁻¹ are again close to those of species A. Similarly, impregnation of [Ru(bpy)(CO)₂ClH] directly from dichloromethane favoured the formation of the same species.

Thermal treatment (at 100°C for 15 h) of THF-impregnated [Ru(bpy)(CO)₂ClH]/SiO₂ also increased somewhat the relative intensity of the highest band above 2070 cm⁻¹ [Fig. 7(b)] and the grey-coloured sample turned dark brown. Some evolution of CO₂ was observed during heating which may be a sign of minor decarbonylation. Washing the heated sample with THF again revealed the presence of physisorbed [Ru(bpy)-(CO)₂ClH] and yielded an identical surface spectrum with the impregnated samples above [Fig. 7(c)]. Even though the ν(CO) band positions in the washed samples still resembled a mixture of species A and B [Fig. 4(c)],
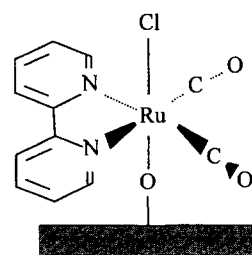

Fig. 8. Possible structure for species A.

the relative intensities of the bands were changed and no longer supported the presence of species B, but more likely a mixture of species A, physisorbed [Ru(bpy)-(CO)₂ClH], [{Ru(bpy)(CO)₂Cl}₂] and possibly minor amounts of physisorbed [Ru(bpy)(CO)₂Cl₂]. Exposure of thermally treated [Ru(bpy)(CO)₂ClH]/SiO₂ to dichloromethane again favoured the formation of species A [Fig. 7(d)].

Since [Ru(bpy)(CO)₂ClH] reacts easily via hydride ligand, the reaction of [Ru(bpy)(CO)₂ClH] with SiO₂ most probably leads to formation of the chlorinated species [{Ru(bpy)(CO)₂Cl_m}_n] (m = 1 or 2, n ⩾ 1). Similar conversions to [Ru(bpy)(CO)₂Cl₂] or to [{Ru(bpy)-(CO)₂Cl}₂] are typical for [Ru(bpy)(CO)₂ClH] in solution [9]. Such reactions would explain the appearance of physisorbed [Ru(bpy)(CO)₂Cl₂], [{Ru(bpy)(CO)₂Cl}₂] and the poorly removable strongly adsorbed A-like complex, which is most probably chemisorbed on the silica via an Si–O–Ru bond (Fig. 8). Although the reaction of [Ru(bpy)(CO)₂ClH] with silica occurs most probably via replacement of the hydride ligand, alternative chemisorption cannot be completely excluded. The hydride ligand has a strong *trans* effect on the axial chlorine, which may labilize the Ru–Cl bond. It is then possible that chlorine too may be replaced either by a surface bond or by another ruthenium unit giving a monomeric or polymeric product [{Ru(bpy)(CO)₂L₂}] (L = SiO or [Ru(bpy)(CO)₂]). However, such a reaction is not very probable and it is more likely that the overall spectrum of [Ru(bpy)(CO)₂ClH]/SiO₂ arises from a mixture of species A and the physisorbed species [Ru(bpy)(CO)₂ClH] and [{Ru(bpy)(CO)₂Cl}₂].

3.6.3. [Ru(bpy)(CO)₂Cl(C(O)OCH₃)] on SiO₂

The infrared spectrum of pale yellow [Ru(bpy)(CO)₂-Cl(C(O)OCH₃)] in CH₂Cl₂ consisted of ν(CO) bands at 2058 (vs) and 1994 (vs) cm⁻¹ and of a low frequency carbonyl stretching band of (C(O)OCH₃) at 1640 (br, w) cm⁻¹ [9]. THF lowered the ν(CO) bands to 2050 and 1986 cm⁻¹. The colour of the dichloromethane-impregnated product varied from yellow brown to orange brown, whereas THF-impregnated supports were typically dark brown. Unlike [Ru(bpy)(CO)₂ClH]/SiO₂, impregnation of the [Ru(bpy)(CO)₂Cl(C(O)OCH₃)] even from non-chlorinated solvents favoured the forma-

tion of an A-type surface complex [Fig. 6(b)]. Direct impregnation from dichloromethane or exposure of the THF-impregnated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ to dichloromethane further facilitated the formation of species A [Fig. 6(d)]. Generally, the spectrum of $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ resembled the summation spectrum of species A + B [Fig. 4(c)]. The $\nu(CO)$ signal of the $(C(O)OCH_3)$ group reduced or disappeared completely during the impregnation, indicating decomposition of the methoxycarbonyl group. Furthermore, considerable amounts of CO_2 and minor amounts of CO were evolved during impregnation due to decomposition of the methoxycarbonyl group and/or the possibly partial decarbonylation of $[Ru(bpy)(CO)_2$-$Cl(C(O)OCH_3)]$. Washing low loading samples (0.5 wt.% Ru) with THF yielded a light yellow solution with four weak carbonyl stretching bands at 2061; 2029; 1993; 1950 (br) cm^{-1} and a similar surface spectrum [Fig. 6(c)] to the corresponding $[Ru(bpy)(CO)_2ClH]/SiO_2$ [Fig. 7(c)]. The bands at 2061 and 1993 cm^{-1} are again very close to those in the spectrum of $[Ru(bpy)$-$(CO)_2Cl_2]$ whereas the lower signals at 2029 and 1950 cm^{-1} are close to those found in $[Ru(bpy)(CO)_2ClH]$ (or $[Ru(bpy)(CO)_2Cl(THF)]$). The formation of $[Ru(bpy)(CO)_2Cl_2]$ requires the presence of a suitable chlorine source. Since the only possible chlorine source in THF-impregnated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ is the precursor itself, additional chlorine may be obtained only via partial decomposition of the complex. In samples with a higher Ru loading (1.5 wt.%) considerable amounts of physisorbed $[Ru(bpy)(CO)_2Cl(C(O)$-$OCH_3)]$ were also observed even after thermal treatment (100°C, 15–16 h). Although the thermal treatment of the supported $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ caused some further evolution of CO_2, only small changes appeared in the IR spectrum.

The behaviour of $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ during impregnation was thus very similar to that of $[Ru(bpy)(CO)_2ClH]$. It was either physisorbed or it lost its methoxycarbonyl group yielding the chlorinated species $[\{Ru(bpy)(CO)_2Cl_m\}_n]$ ($m = 1, 2, n \geqslant 1$). Formation of $[\{Ru(bpy)(CO)_2Cl_m\}_n]$ is even more emphasized with $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ than with $[Ru(bpy)(CO)_2ClH]$. Although replacement of the methoxycarbonyl group is obviously the most probable reaction route, the $(C(O)OCH_3)$ group also has a *trans* effect on the Ru–Cl bond, which may facilitate alternative substitution of the chlorine ligand to also yield $[\{Ru(bpy)(CO)_2L_2\}]$ similarly to $[Ru(bpy)(CO)_2ClH]$.

Despite the spectral similarities of $[Ru(bpy)(CO)_2$-$ClH]/SiO_2$ and $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$, there were some differences in the catalytic behaviour of the supported monomers in 1-hexene hydroformylation [8]. $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ was clearly more active than $[Ru(bpy)(CO)_2ClH]/SiO_2$. Unlike $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 catalysts, dichlo-

romethane-impregnated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$-$/SiO_2$ was not able to produce C_7 alcohols but gave the C_7 aldehydes as the main products. However, impregnation from THF improved the alcohol selectivity [8]. $[Ru(bpy)(CO)_2ClH]/SiO_2$ was poorly active in hydroformylation, favouring direct formation of alcohols, whereas $[Ru(bpy)(CO)_2Cl_2]/SiO_2$ was practically inactive. $[Ru(bpy)(CO)_2ClH]/SiO_2$ was highly active in hydrogen-transfer processes such as the isomerization of 1-hexene and the hydrogenation of aldehydes, but $[Ru(bpy)(CO)_2Cl_2]/SiO_2$ showed only poor activity in these reactions. The catalytic activity of the supported $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ (impregnated from CH_2Cl_2) and $[Ru(bpy)(CO)_2Cl_2]/SiO_2$ was comparable with that of the unsupported complexes and arises thus mainly from physisorbed species. In the case of THF-impregnated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ and $[Ru(bpy)(CO)_2ClH]/SiO_2$, the improvement in the alcohol selectivity is a clear indication of the active role of the new surface species discussed above. Furthermore, the similarities in catalytic behaviour of THF-impregnated $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ and $[Ru(bpy)$-$(CO)_2ClH]$ are in agreement with the similarities of the IR spectra.

3.7. Treatment of the monobipyridine model compounds with NaOH

Although the IR spectra of $[Ru(bpy)(CO)_2Cl_2]/SiO_2$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ and $[Ru(bpy)$-$(CO)_2ClH]/SiO_2$ showed similarities with the Ru_3-$(CO)_{12}/2,2'$-bipyridine/SiO_2 catalyst, the dark blue colour of $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 was not achieved by supporting monomeric reactants. Furthermore, the catalytic activity of the supported monomers was different from the cluster-derived catalyst. Ziessel et al. [1e,1f] have reported that $[Ru(bpy)(CO)_2Cl_2]$ can be dechlorinated to polymeric $[\{Ru(bpy)(CO)_2\}_n]$ through electrochemical reduction. The physical properties of the polymer are close to those of $Ru_3(CO)_{12}/$ $2,2'$-bipyridine/SiO_2, the dark blue polymer being poorly soluble and highly air-sensitive. Furthermore, it is active in the electrochemical reduction of CO_2 [1e,1f] whereas $Ru_3(CO)_{12}/2,2'$-bipyridine/SiO_2 is highly active in the related WGS reaction [3,5]. Since electrochemical methods are not very convenient for supported complexes, we tested NaOH as a possible dechlorination/reduction agent for $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$, $[Ru(bpy)(CO)_2ClH]$ and $[\{Ru(bpy)(CO)_2Cl\}_2]$.

Treatment of unsupported $[Ru(bpy)(CO)_2Cl_2]$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$, $[Ru(bpy)(CO)_2ClH]$ or $[\{Ru(bpy)(CO)_2Cl\}_2]$ with an excess of 0.1 mol l^{-1} NaOH solution under a nitrogen atmosphere gave a dark blue or bluish black product. The reaction was instanta-

neous with $[Ru(bpy)(CO)_2ClH]$ and very fast with $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ at room temperature. Also $[\{Ru(bpy)(CO)_2Cl\}_2]$ reacted with NaOH at room temperature but the reaction was much slower than with monomers. In contrast, $[Ru(bpy)(CO)_2Cl_2]$ reacted only poorly at room temperature and the reaction was not completed even after heating at 100°C for 15 h. No evolution of CO or CO_2 was observed during the reaction of NaOH with $[Ru(bpy)(CO)_2ClH]$, $[\{Ru(bpy)-(CO)_2Cl\}_2]$ or $[Ru(bpy)(CO)_2Cl_2]$ at room temperature. However, when the reaction of $[Ru(bpy)(CO)_2Cl_2]$ was continued at 100°C for 1 h, trace amounts of CO_2 were found, indicating decarbonylation and possibly immediate oxidation of CO, as in the WGSR reaction. Carbon dioxide was also evolved in the reaction of NaOH with $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$, but in this case it is probably due to the decarboxylation of the methoxycarbonyl group. A clear indication of chlorine was observed in all the NaOH residues, suggesting dechlorination of the complexes during NaOH treatment. Regardless of the reactant, the IR spectra of the unsupported dark blue solid product were very similar in all experiments, showing three broad $\nu(CO)$ bands at 1977, 1912 (sh) and 1888 cm^{-1}.

The elemental analyses of the NaOH-treated products were not very reproducible, but analysis of the NaOH-treated $[Ru(bpy)(CO)_2ClH]$ gave a reasonable fit with $[Ru_2(bpy)_2(CO)_4OH_2]$ indicating incomplete reduction and oligomerization.

The dark blue product was also obtained when silica-supported $[Ru(bpy)(CO)_2ClH]$ or $[Ru(bpy)(CO)_2-Cl(C(O)OCH_3)]$ was treated with 0.1 mol l^{-1} NaOH. The reactions were instantaneous as for the unsupported complexes. Signals for $\nu(CO)$ were found at 2046, 1993 (sh) and 1970 cm^{-1}, resembling very closely component B (Table 2). In contrast to component B, the colour

the NaOH-treated $[Ru(bpy)(CO)_2ClH]/SiO_2$ was not air-sensitive and remained almost unchanged even after 24 h exposure to air. However, dichloromethane treatment led to the appearance of 2077 and 2012 cm^{-1} bands similar to species B.

From the catalytic point of view, NaOH treatment was an effective activation method for $[Ru(bpy)(CO)_2-ClH]/SiO_2$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$, $[\{Ru(bpy)(CO)_2Cl\}_2]/SiO_2$ and $[Ru(bpy)(CO)_2Cl_2]/SiO_2$. Although the activities of the NaOH-treated complexes remained at most moderate in 1-hexene hydroformylation, NaOH treatment clearly activates the complexes and, even more importantly, all catalysts showed very high alcohol selectivity, similar to $Ru_3(CO)_{12}/$ 2,2'-bipyridine/SiO_2 [8].

3.8. Summary of reactions and possible surface species in the preparation of $Ru_3(CO)_{12}$ / 2,2'-bipyridine / SiO_2 catalyst

The proposed reactions and surface species are summarized in Scheme 2. The initial step in all methods is physisorption of $[Ru_3(CO)_{12}]$ and 2,2'-bipyridine on to the support. However, in the gas-phase method elevated temperature also permits immediate chemisorption and formation of $[HRu_3(CO)_{10}]/SiO_2$. Typically, deposition in the G method was carried out under carbon monoxide where an equilibrium was established between the chemisorbed $[HRu_3(CO)_{10}]/SiO_2$ and the physisorbed $[Ru_3(CO)_{12}]_{phys}$. In conventional impregnations, physisorption was clearly dominant. Regardless of the method of preparation, thermal activation turned the catalyst dark blue or bluish black. If no excess of 2,2'-bipyridine was used, the IR bands of the physisorbed $[Ru_3(CO)_{12}]$ and 2,2'-bipyridine diminished considerably or disappeared completely during activa-
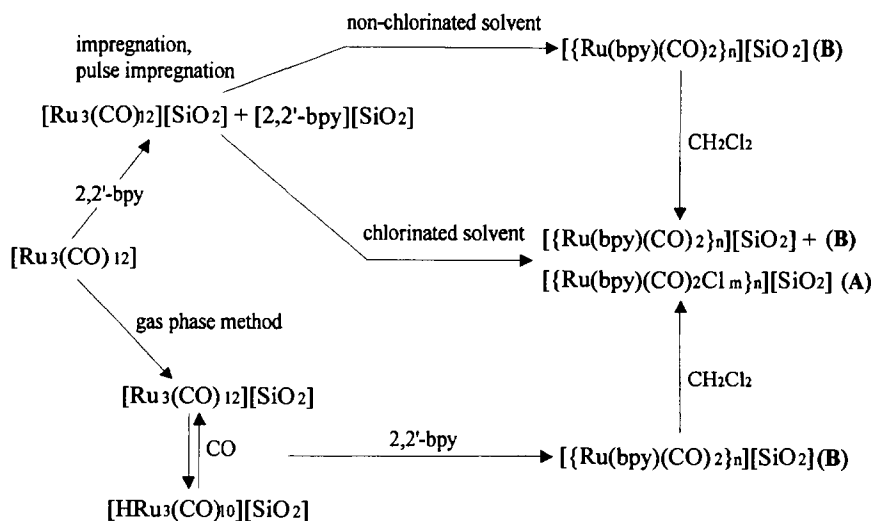
Scheme 2. Proposed reaction routes in the preparation of $[Ru_3(CO)_{12}]$/2,2'-bipyridine/SiO_2. In the various reactions, $n \geqslant 1$, $m = 1$ or 2.

tion. In conventional impregnations, however, some physisorbed bipyridine was usually observed even in activated catalysts, which would also allow the presence of ruthenium carbonyl species without the 2,2'-bipyridine ligand. The IR spectra of several ruthenium subcarbonyls prepared from $[Ru_3(CO)_{12}]$ via thermal treatment are closely related to species A or B [10,12] found in $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ and therefore coexistence of such species cannot be completely excluded.

In contrast to conventional impregnation, no physisorbed bpy was observed in pulse-impregnated catalysts although an excess of 2,2'-bipyridine was used during deposition. Similarly, an excess of 2,2'-bipyridine was used in the gas-phase method to ensure complete complexation of the ruthenium carbonyls and hence the formation of non-bipyridine complexes is highly unlikely.

All activated catalysts prepared by methods G, I2 and PI1 gave similar main carbonyl stretching bands around 2045 and 1970 cm^{-1}(species B). This indicates that the chemisorbed intermediate $[HRu_3(CO)_{10}]/SiO_2$ formed in the G method has no significant role in the formation of the final catalyst, but the reaction proceeds via $[Ru_3(CO)_{12}]_{phys}$. If this is the case, the reaction between $[Ru_3(CO)_{12}]$ and 2,2'-bipyridine proceeds most probably by consecutive replacements of CO ligands with 2,2'-bipyridine yielding low-valent oligomeric or polymeric $[\{Ru(bpy)(CO)_2\}_n]$ (linear or cyclic) as the main product.

All activated PI2 catalysts and most of the I1 and I3 catalysts gave two new bands in the IR spectrum around 2070 and 2012 cm^{-1} (species A). The appearance of species A, evidently a chlorinated surface species with two carbonyl ligands, depended on the presence of a suitable chlorine source. Chlorination of species B most probably leads to a surface structure(s) $[\{Ru(bpy)(CO)_2Cl_m\}_n]/SiO_2$ ($m = 1$ or 2, $n \geqslant 1$) including the strongly adsorbed species A and possibly a physisorbed species to a minor extent. Similar species can also be obtained by the impregnation of monomeric $[Ru(bpy)(CO)_2ClH]$ or $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]$ on SiO_2.

The catalytic behaviour of $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ is in agreement with Scheme 2. Although the highest activities in 1-hexene hydroformylation have been obtained with conventionally impregnated $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ catalysts [4,8], the reproducibility of the catalytic activity is poor, especially with catalysts impregnated from dichloromethane (I1) [8]. The reproducibility can be somewhat improved by using non-chlorinated impregnation solvents such as THF (I2), but considerable improvement of the reproducibility can been obtained only by using more controlled preparation methods such as pulse impregnation from THF (PI1) [6] or the ALE-derived method (G) [5]. The uncontrolled formation of several surface species in

conventional impregnation is thus the main reason for variations in the catalytic activity of $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$.

Conventional impregnation from non-chlorinated solvents yields no chlorinated species, which are typically less active species [8], leading to improved reproducibility. However, since conventional impregnation method allows the formation of ruthenium sub-carbonyl species as side-products, and after thermal activation even the formation of metallic ruthenium or ruthenium bipyridines without carbonyl ligands, the reproducibility remains at most moderate [8]. The considerable improvement in the catalytic reproducibility of pulse-impregnated (PI1) [6] or gas-phase prepared (G) [5] catalysts is then most probably due to the formation of a more uniform catalyst surface with $[\{Ru(bpy)(CO)_2\}_n]$ as a dominating species.

The use of the more controlled gas-phase method also improves the activity of the $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ catalyst in the WGS reaction compared to the dichloromethane-impregnated catalyst, which is again due to the more selective formation of species B.

4. Conclusions

The choice of preparation method and the conditions are of considerable importance in the preparation of the $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ catalyst. In liquid-phase methods such as impregnation and pulse impregnation, the choice of the solvent is critical. The preparation of $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ by the gas-phase method or impregnation from non-chlorinated solvent leads to the formation of a catalytically active non-chlorinated surface species $[\{Ru(bpy)(CO)_2\}_n]/SiO_2$ ($n \geqslant 1$). The structure of this species is most probably that of a low-valent cyclic or linear oligomer or polymer. The use of chlorinated impregnation solvents such as dichloromethane favours the conversion of $[\{Ru(bpy)(CO)_2\}_n]/SiO_2$ to chlorinated surface species of the type $[\{Ru(bpy)(CO)_2Cl_m\}_n]/SiO_2$ ($m = 1$ or 2, $n \geqslant 1$). The formation of chlorinated species seems to lower the activity of the $Ru_3(CO)_{12}/2,2'$-bypyridine$/SiO_2$ catalyst. The poor reproducibility in the activity of the conventionally impregnated $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ catalyst in 1-hexene hydroformylation is most probably due to the uncontrolled formation of several surface species.

Mononuclear $[Ru(bpy)(CO)_2Cl_2]/SiO_2$, $[Ru(bpy)(CO)_2Cl(C(O)OCH_3)]/SiO_2$ and $[Ru(bpy)(CO)_2ClH]/SiO_2$ produce comparable IR patterns to $[\{Ru(bpy)(CO)_2Cl_m\}_n]/SiO_2$. However, impregnation of these monomers on to SiO_2 also yielded considerable amounts of physisorbed complexes, which are mainly responsible for their catalytic behaviour. The dark blue colour of the $Ru_3(CO)_{12}/2,2'$-bipyridine$/SiO_2$ catalyst was not

obtained with any of the supported mononuclear complexes. Dark blue products could be produced from [Ru(bpy)(CO)$_2$ClH]/ SiO$_2$ and [Ru(bpy)(CO)$_2$Cl(C(O)OCH$_3$)]/ SiO$_2$ by NaOH treatment. Although these NaOH-treated products resemble [{Ru(bpy)(CO)$_2$}$_n$]/ SiO$_2$, the polymerization may be incomplete yielding a mixture of oligomeric and polymeric species.

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