ELSEVIER

Surface-mediated reductive carbonylation of SiO$_2$-supported RuCl$_3$ and Ru(NO)(NO$_3$)$_3$ studied by IR spectroscopy

Lin Huang*, Yide Xu

State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
457 Zhongshan Road, P.O. Box 110, 116023 Dalian, China

Abstract

The surface-mediated reductive carbonylation of SiO$_2$-supported RuCl$_3$ and Ru(NO)(NO$_3$)$_3$ has been studied by IR spectroscopy. Hydrated RuCl$_3$/SiO$_2$ reacts readily with CO (100–700 Torr) to form a mixture of Ru(CO)Cl$_2$(HOSi)$_3$ and Ru(CO)$_2$Cl$_2$(HOSi)$_2$ at 25°C, and a mixture of Ru(CO)Cl$_2$(HOSi)$_3$, Ru(CO)$_2$Cl$_2$(HOSi)$_2$, Ru(CO)$_3$Cl$_2$(HOSi) (major product) and [Ru(CO)$_3$Cl$_2$]$_2$ at 100°C. Hydrated Ru(NO)(NO$_3$)$_3$/SiO$_2$ reacts readily with CO to give a mixture of Ru(CO)$_2$(OSi)$_2$ and Ru(CO)$_3$(OSi)$_2$ at 25°C. At 100°C, hydrated Ru(NO)(NO$_3$)$_3$/SiO$_2$ is converted to a mixture of Ru(CO)$_2$(OSi)$_2$ and Ru(CO)$_3$(OSi)$_2$ under 100 Torr of CO, and a mixture of Ru$_3$(CO)$_{12}$ (good yield) and Ru(CO)$_3$(OSi)$_2$ under 700 Torr of CO. All these results are demonstrated by surface IR spectra and extraction experiments with organic solvents. While the carbonylation of hydrated Ru(NO)(NO$_3$)$_3$/SiO$_2$ proceeds, the stoichiometric reductions of NO$_3^-$ and NO: $2NO_3^- + 3CO + 2HOSi \rightarrow 2NO + 3CO_2 + H_2O + 2OSi^-$ and $2NO + CO \rightarrow N_2O + CO_2$ are suggested to occur on the surface, according to gaseous IR observation. The proportion of ruthenium(II) tricarbonyl species is found to increase with the increases of carbonylation temperature and CO pressure. In addition, the detrimental effect of calcination of RuCl$_3$/SiO$_2$ and Ru(NO)(NO$_3$)$_3$/SiO$_2$ at 400°C on the reductive carbonylation is discussed. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: SiO$_2$; RuCl$_3$; Ru(NO)(NO$_3$)$_3$; N$_2$O; Reductive carbonylation; Reduction of NO

1. Introduction

Over the last 20 years, the investigation of metallic carbonyl complexes in the field of both homogeneous and heterogeneous catalysis has achieved quite a lot of progress. The benefits of the application of metallic carbonyl complexes in the preparation of supported catalysts are that they can not only result in highly dispersed metallic catalysts but also serve as efficient bimetallic catalyst precursors. It has proven that metallic carbonyl complexes are rather more valuable

than inorganic salts in the preparation of supported metallic catalysts [1–3]. Nowadays, research has increasingly been focused on the direct conversion of inorganic salts to metal carbonyls on inorganic supports such as SiO$_2$, Al$_2$O$_3$, MgO and zeolites by surface-mediated carbonylation [2,4–12], so as to meet the needs of a simple and efficient synthesis or preparation of supported catalysts. Quite a number of examples have appeared, which particularly relate to the study of nucleation processes of polynuclear metallic clusters by reductive carbonylation of supported simple metal chlorides under mild conditions. Of these examples, the surface-mediated reductive carbonylation of SiO$_2$-supported MCl$_3$·3H$_2$O

* Corresponding author. Tel.: +86-411-4671991;
fax: +86-411-4691570.

(M = Rh, Ir, Os, Ru) which is analogous to the title study has been reported by Ugo and coworkers [7–10,13]. In the study of the carbonylation of $RuCl_3 \cdot 3H_2O/SiO_2$, it was shown that this physisorbed salt reacts with 1 atm of CO at 25–50°C to form the surface-bound species $Ru(CO)_2Cl_2(HOSi)_2$, which is converted to the corresponding tricarbonyl species $Ru(CO)_3Cl_2(HOSi)$ under 1 atm of CO at 100°C in high yield [9]. Despite that chlorine-free ruthenium inorganic salts like $Ru(NO)(NO_3)_3$ have widely been used to prepare supported catalysts [14–18], their surface chemistry on inorganic supports has seldom been reported [19]. In the present paper, we report a detailed study of surface-mediated synthesis of ruthenium carbonyl complexes from $RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ by IR spectroscopy. We afford detailed spectroscopic information on the reaction of these ruthenium inorganic salts with CO on the SiO_2 surface.

2. Experimental

$RuCl_3 \cdot nH_2O$ and $Ru(NO)(NO_3)_3$ were purchased from Aldrich and Beijing Chemicals companies, respectively. The support SiO_2 was a silica 'Aerosil' supplied by Degussa with a surface area of $380 \, m^2/g$. The organic solvents CH_2Cl_2 and C_2H_5OH were dried before use. The gases CO and Ar had a purity of 99.99%.

$RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ were prepared by incipient wetness impregnation. SiO_2 in powder was incipient wetted with an aqueous solution of ruthenium salt. After stirring, the resulting slurry was gently heated under an infrared lamp till it turned into a dry solid sample. At this stage, the solid sample is called hydrated $RuCl_3/SiO_2$ or hydrated $Ru(NO)(NO_3)_3/SiO_2$. If the solid sample underwent calcination at 400°C followed by rehydration at 25°C, it is called calcined $RuCl_3/SiO_2$ or calcined $Ru(NO)(NO_3)_3/SiO_2$. The samples prepared from $RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ contained 1.0 and 0.9% Ru, respectively.

IR experiments were carried out using a KBr cell for liquid samples and a single beam cell with CaF_2 windows for solid and gaseous samples. For the monitoring of surface-mediated synthesis, the above mentioned hydrated $RuCl_3/SiO_2$ and hydrated

$Ru(NO)(NO_3)_3/SiO_2$ were pressed into wafers of 20.0 mg each and placed in the IR cell. All IR spectra were recorded on a Bio-Rad FTS-7 spectrometer at ambient temperature. Surface IR spectra were measured in the presence of gas phase by subtracting the contribution of solid and gas phases.

The metal contents of the samples were determined by atomic absorption (AA) spectroscopy.

3. Results

3.1. Reactivity of hydrated $RuCl_3/SiO_2$ with CO

Fig. 1 shows the surface IR spectra collected during the carbonylation of hydrated $RuCl_3/SiO_2$ under 100 Torr of CO at 25°C. Once a brown wafer of hydrated $RuCl_3/SiO_2$ after outgassed under vacuum (10^{-2} Torr) at 25°C for 1 h, was exposed to 100 Torr of CO, a small single band at 2081 cm^{-1} emerged first
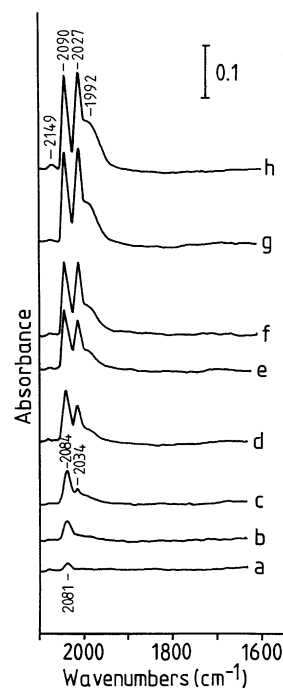

Fig. 1. Surface IR spectrum after carbonylation of hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) under 100 Torr of CO at 25°C for: (a) 2 min; (b) 10 min; (c) 0.5 h; (d) 3 h; (e) 8 h; (f) 21 h; (g) 51 h; (h) 99 h.

in the surface spectrum and shifted slowly upward as its intensity increased with time. Then another band at 2034 cm^{-1} appeared 10 min later. These two bands grew synchronously and progressively under CO, concomitant with the appearance of a shoulder band toward 1992 cm^{-1}. It was noted that the band intensities at 2090 and 2027 cm^{-1} increased no longer and the initial brown wafer turned yellow after over 50 h. This indicated the completion of carbonylation of RuCl$_3$ at 25°C. The observation of the doublet at 2090 and 2027 cm^{-1} in the spectra suggested the formation of surface ruthenium gem-dicarbonyl species like Ru(CO)$_2$Cl$_2$(HOSi)$_2$, [Ru(CO)$_2$Cl$_2$(HOSi)]$_2$ and physisorbed [Ru(CO)$_2$Cl$_2$] [8]. The doublet is attributed to the symmetric and asymmetric C–O stretching of the gem-dicarbonyl. The assignment of the single 1992 cm^{-1} band remains unknown in the range of ruthenium carbonyl species. It presumably corresponds to a mononuclear ruthenium carbonyl species on SiO$_2$. The initially observed single band at 2081 cm^{-1} may be assigned to physisorbed [Ru(CO)Cl$_3$] [8] which was further carbonylated into the surface ruthenium gem-dicarbonyl species.

Much the same surface spectral results were obtained during the carbonylation of hydrated RuCl$_3$/SiO$_2$ under 700 Torr of CO at 25°C, as shown in Fig. 2.

At this stage, an extraction experiment was conducted to identify the ruthenium carbonyl species formed from carbonylation of hydrated RuCl$_3$/SiO$_2$. In a Schlenk tube, 0.50 g of brown hydrated RuCl$_3$/SiO$_2$ was outgassed under vacuum (10^{-2} Torr) at 25°C for 1 h before admission of 700 Torr of CO. After 168 h of contact of hydrated RuCl$_3$/SiO$_2$ with CO at 25°C, the solid sample turned yellow. The solid sample was divided into two portions and transferred to two new Schlenk tubes under Ar. Onto the two portions were added CH$_2$Cl$_2$ and C$_2$H$_5$OH, respectively under Ar. The CH$_2$Cl$_2$ extract which was colorless, displayed no IR bands. This shows that the surface carbonyl species observed above are linked to the SiO$_2$ surface and cannot be extracted with a non-electron donor solvent. However, the C$_2$H$_5$OH extract whose color was black, displayed three IR bands at 2067, 1997 and 1928 cm^{-1} with almost the equal intensity, as shown in Fig. 3(a). The 2067 and 1997 cm^{-1} bands may be typical of Ru(CO)$_2$Cl$_2$ with C$_2$H$_5$OH as ligand [20]. The 1928 cm^{-1} band
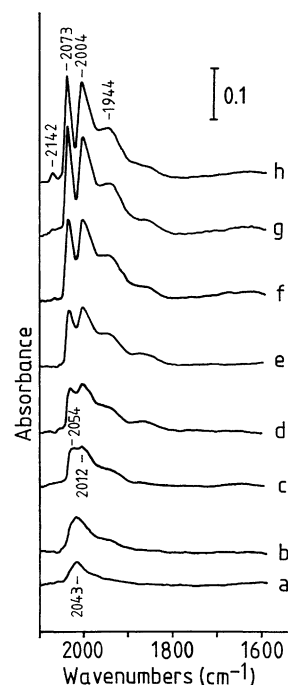

Fig. 2. Surface IR spectrum after carbonylation of hydrated RuCl$_3$/SiO$_2$ (1.0% Ru loading) under 700 Torr of CO at 25°C for: (a) 26 min; (b) 2 h; (c) 5.5 h; (d) 10 h; (e) 23.5 h; (f) 72 h; (g) 168 h; (h) after 1 min of evacuation following (g).

may match with the 1992 cm^{-1} band observed in the surface spectra, which may be due to a mononuclear ruthenium(II) monocarbonyl species not identified. It may be postulated as Ru(CO)Cl$_2$(HOSi)$_3$. This accounts for that the surface-linked carbonyl species can be removed with an electron donor solvent.

Based on the surface IR spectra and different reactivities of the surface ruthenium(II) carbonyl species with CH$_2$Cl$_2$ and C$_2$H$_5$OH, it is strongly suggested that Ru(CO)$_2$Cl$_2$ and Ru(CO)Cl$_3$ fragments bound to the silanol groups of SiO$_2$ surface, namely Ru(CO)$_2$Cl$_2$(HOSi)$_2$ and Ru(CO)Cl$_2$(HOSi)$_3$ are produced, by reductive carbonylation of hydrated RuCl$_3$/SiO$_2$ at 25°C. The production of Ru(CO)$_2$Cl$_2$(HOSi)$_2$ has been concluded by Roberto et al. who discussed in detail the possible surface ruthenium carbonyl species formed from carbonylation of RuCl$_3$·3H$_2$O/SiO$_2$ [8].

After the carbonylation temperature had been raised to 100°C, it was found that a new band at 2151 and 2090 cm^{-1} developed synchronously while
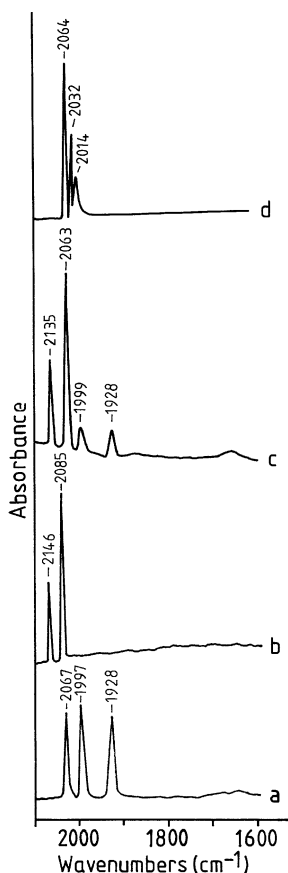
Fig. 3. IR spectra of ruthenium carbonyl extracts. (a) Extract in C_2H_5OH from hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) after 168 h of carbonylation under 700 Torr of CO at 25°C. After 40 h of carbonylation of hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) under 700 Torr of CO at 100°C; (b) extract in CH_2Cl_2; (c) extract in C_2H_5OH; (d) extract in CH_2Cl_2 from hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) after 70 h of carbonylation under 700 Torr of CO at 100°C.
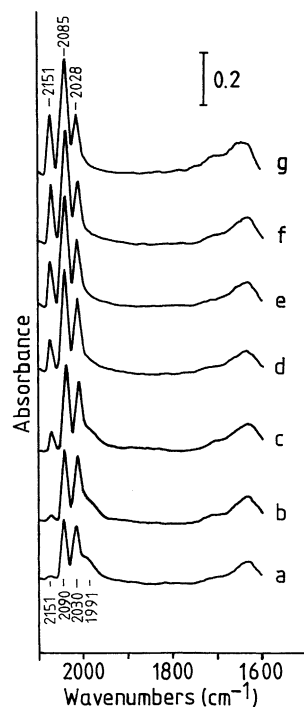

Fig. 4. Following Fig. 1(h), surface IR spectrum after carbonylation of hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) under 100 Torr of CO at 100°C for: (a) 15 min; (b) 1 h; (c) 3 h; (d) 7 h; (e) 13 h; (f) 25 h; (g) 31 h.

the band at $2030 \, cm^{-1}$ remained almost unchanged. The $2090 \, cm^{-1}$ band shifted slightly downward to $2085 \, cm^{-1}$ after 31 h. Meanwhile the $1992 \, cm^{-1}$ shoulder band vanished gradually with time. The spectral evolution is presented in Fig. 4. By 25 h, the carbonylation equilibrium was reached according to the spectral intensity, and the yellow wafer turned pale. Obviously, the intense band observed at $2085 \, cm^{-1}$ can be regarded as a superimposition of the $2090 \, cm^{-1}$ band due to $Ru(CO)_2Cl_2(HOSi)_2$ and a new band around $2080 \, cm^{-1}$. The appearance

of the latter band and the $2151 \, cm^{-1}$ band may be ascribed to the production of surface ruthenium(II) tricarbonyl species [8,21] by surface carbonylation of $Ru(CO)_2Cl_2(HOSi)_2$ at 100°C. The new species may be present in the forms of $[Ru(CO)_3Cl_2]_2$ and/or $Ru(CO)_3Cl_2(HOSi)$.

Similar surface spectra were achieved after hydrated $RuCl_3/SiO_2$ had been treated under 700 Torr of CO at 100°C, as presented in Fig. 5.

In order to identify the gaseous products and reveal the nature of the tricarbonyl species, analysis of the gas phase and extraction of the tricarbonyl species were carried out following 40 h of treatment of hydrated $RuCl_3/SiO_2$ (0.50 g) under 700 Torr of CO at 100°C. The gaseous products evolved from the carbonylation reaction in a Schlenk tube were admitted into an IR cell which had been previously evacuated. The gaseous IR spectrum exhibited only bands corresponding to CO and CO_2, as presented in Fig. 6(a). After carbonylation at 100°C, the brown
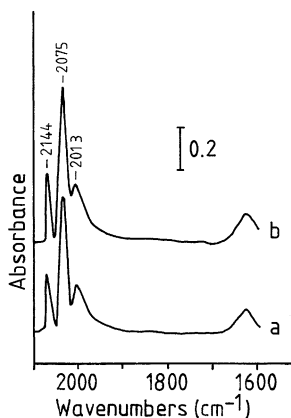
Fig. 5. Surface IR spectrum after carbonylation of hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) under 700 Torr of CO at 100°C for: (a) 24 h; (b) 48 h.

solid sample turned pale. Onto two portions of the solid sample were added CH_2Cl_2 and C_2H_5OH, respectively under Ar. As seen in Fig. 3(b and c), the CH_2Cl_2 extract which was colorless, showed two IR bands at 3146m and 2085s cm^{-1}; the C_2H_5OH extract which was colorless, gave two analogous IR bands at 2135m and 2063s cm^{-1}, and two weak ones at 1999 and 1828 cm^{-1}. Both the pair of bands at 2146m, 2085s cm^{-1} and the pair of bands at 2135m,
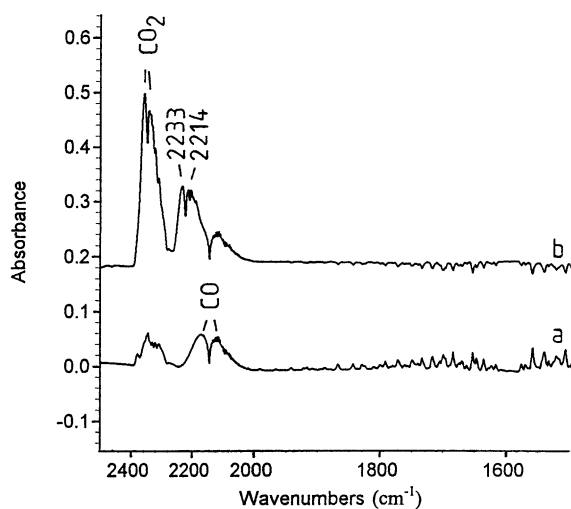

Fig. 6. Gaseous IR spectrum after carbonylation under 700 Torr of CO at 100°C of: (a) hydrated $RuCl_3/SiO_2$ (1.0% Ru loading) for 40 h; (b) hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) for 70 h.

2063s cm^{-1} in the extract spectra correspond to the bands at 2150m and 2090s cm^{-1} in the surface spectra, which are attributed to a ruthenium(II) tricarbonyl species. The extraction result with the non-electron donor solvent CH_2Cl_2 clearly demonstrates that this species is physisorbed in the form of $[Ru(CO)_3Cl_2]_2$ on SiO_2. However, according to ruthenium quantitative analysis of the solid samples, the percent of ruthenium in the CH_2Cl_2 extract was only 23 whereas that in the C_2H_5OH extract was 86, based on the initial amount of ruthenium on $RuCl_3/SiO_2$. The results indicate that after treatment of hydrated $RuCl_3/SiO_2$ under 700 Torr of CO at 100°C for 40 h, 86% of $RuCl_3$ are carbonylated among which the yield of $[Ru(CO)_3Cl_2]_2$ is only 23% and $Ru(CO)_3Cl_2(HOSi)$ remains as the major product. The co-presence of the weak bands at 1999 and 1828 cm^{-1} with the intense bands at 2135m and 2063s cm^{-1} in the C_2H_5OH extract spectrum indicates that some amounts of $Ru(CO)_2Cl_2(HOSi)_2$ and $Ru(CO)Cl_2(HOSi)_3$ coexist with $[Ru(CO)_3Cl_2]_2$ and $Ru(CO)_3Cl_2(HOSi)$ on the surface.

3.2. Reactivity of hydrated $Ru(NO)(NO_3)_3/SiO_2$ with CO

Figs. 7 and 8 show the surface IR spectra taken during the carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 100 Torr of CO. Fig. 7(a) represents N–O stretching vibrational bands of $Ru(NO)(NO_3)_3/SiO_2$. The bands at 1888 and 1512 cm^{-1} are attributed to the terminal NO and NO_3^-, respectively [22]. The following spectra of carbonylated samples are represented by subtracting that of the starting $Ru(NO)(NO_3)_3/SiO_2$.

As soon as a light brown wafer of hydrated $Ru(NO)(NO_3)_3/SiO_2$ which had been outgassed under vacuum (10^{-2} Torr) at 25°C for 1 h, was exposed to 100 Torr of CO at 25°C, a band at 2159 cm^{-1} appeared together with an inverse band at 1886 cm^{-1}. About 2.5 h later, two other bands at 2085 and 2028 cm^{-1} were discerned, with the concomitant appearance of the water band at 1629 cm^{-1} and another inverse band at 1533 cm^{-1}. As seen in Fig. 7, the bands at 2150, 2085 and 2028 cm^{-1} developed slowly as the carbonylation proceeded at 25°C. This set of bands closely resemble those superimposed of the carbonyl bands for $Ru(CO)_2Cl_2(HOSi)_2$ [8] and $Ru(CO)_3Cl_2(HOSi)$ [8,21] and thus are assignable
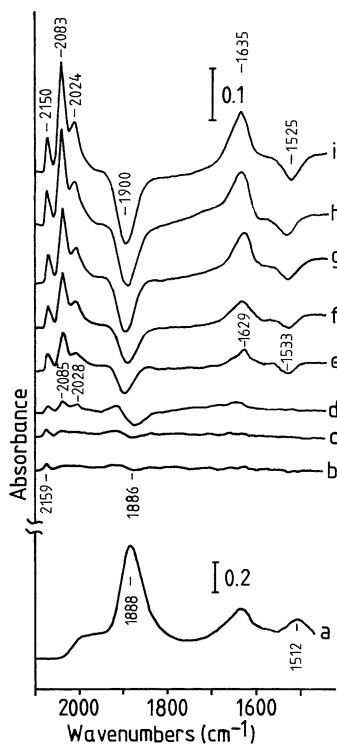
Fig. 7. (a) IR spectrum of $Ru(NO)(NO_3)_3/SiO_2$, surface IR spectrum after carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) under 100 Torr of CO at 25°C for: (b) 3 min; (c) 11 min; (d) 2.5 h; (e) 23 h; (1) 48.5 h; (g) 96.5 h; (h) 170.5 h; (i) 216 h.

Fig. 8. Surface IR spectrum after carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) under 100 Torr of CO at 100°C for: (a) 15 min; (b) 2.5 h; (c) 6 h; (d) 28 h; (e) 70.5 h.

to a surface mixture of ruthenium(II) dicarbonyl and tricarbonyl species on SiO_2. At the same time, the water band at $1629 \, cm^{-1}$ increased in intensity with time while the 1900 and $1525 \, cm^{-1}$ bands grew inversely with time, indicative of loss of NO and NO_3^- groups from the surface and concurrent increase of water amount on the surface during carbonylation. Increasing the temperature markedly enhanced the rates of carbonylation and conversion of NO and NO_3^- on SiO_2, as seen in Fig. 8. After 28 h of treatment under 100 Torr of CO at 100°C, the wafer had no apparent color change. But the carbonylation equilibrium of $Ru(NO)(NO_3)_3$ was reached because the carbonyl band intensities increased no more. It can be roughly estimated from the inverse NO band intensity at $1892 \, cm^{-1}$ (Fig. 8(d)) that 57% of $Ru(NO)(NO_3)_3$ is consumed. Furthermore, no other N–O stretching vibrational bands were present in the surface spectra.
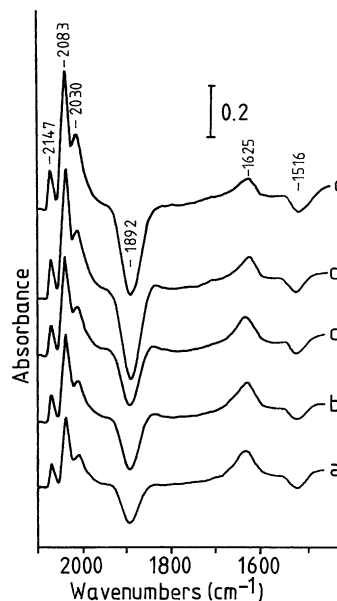
Due to the absence of other inorganic ligands except the silanol group of SiO_2 surface after carbonylation, the resulting surface ruthenium(II) dicarbonyl and tricarbonyl species are reasonably postulated to be $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$.

When hydrated $Ru(NO)(NO_3)_3/SiO_2$ was exposed to 700 Torr of CO, heating at 100°C led to the rapid growth of bands at 2144, 2081, 2036 and $1628 \, cm^{-1}$ and inverse bands at 1900 and $1525 \, cm^{-1}$ as shown in Fig. 9. The 2144 and $2081 \, cm^{-1}$ bands are reasonably assigned to the presumed $Ru(CO)_3(OSi)_2$. It was noticed that the position of the $2036 \, cm^{-1}$ band was significantly higher than that of the $2024 \, cm^{-1}$ band observed in Fig. 7. This band shifted slightly downward as its intensity increased. It as well as the 2144 and $2081 \, cm^{-1}$ bands increased in intensity with carbonylation time at 100°C. After 45 h of carbonylation at 100°C, the light brown wafer turned yellow. It can be roughly calculated from the inverse NO band intensity at $1900 \, cm^{-1}$ (Fig. 9(c)) that 64% of $Ru(NO)(NO_3)_3$ is converted. When the temperature was raised to 150°C, 20 h of carbonylation resulted in a marked increase of the $2034 \, cm^{-1}$ band and a marked decrease of the $2144 \, cm^{-1}$ band in intensity
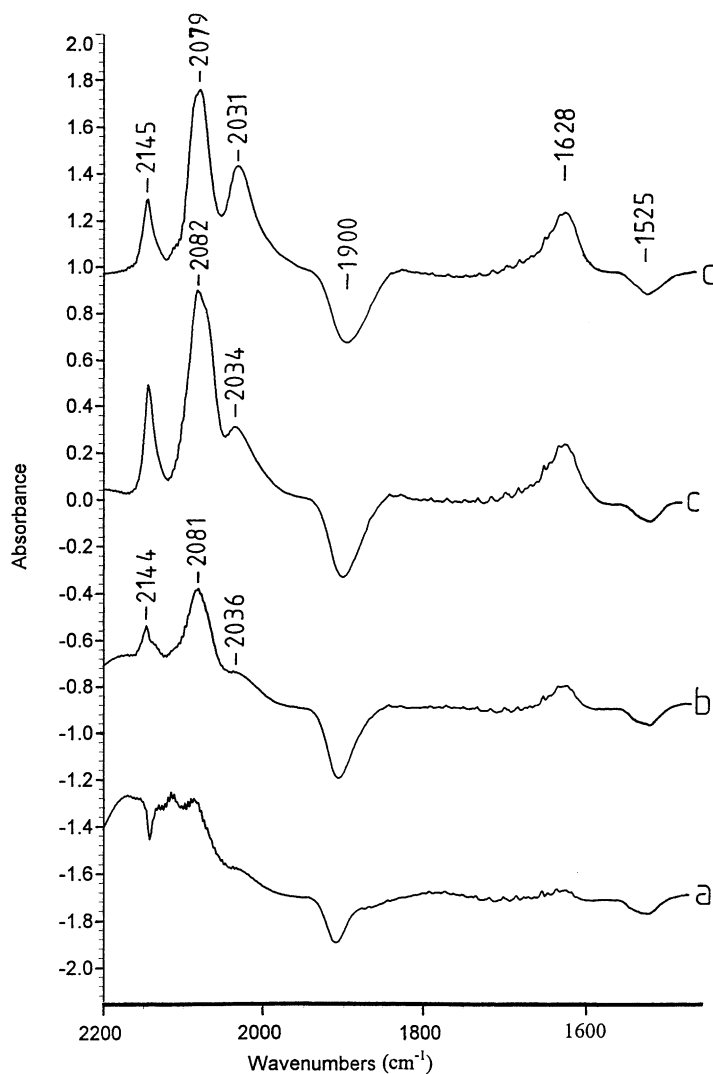
Fig. 9. Surface IR spectrum after carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) under 700 Torr of CO for: (a) 20 min at 100°C; (b) 2 h at 100°C; (c) 44.5 h at 100°C; (d) 22 h at 150°C.

simultaneously, with the 2082 cm^{-1} band being little changed. Meanwhile, the yellow wafer became deep yellow. It is highly likely that the 2082 cm^{-1} band results from the superimposition of two bands, one belonging to the $Ru^{2+}(CO)_3$ fragment and the other growing together with the 2034 cm^{-1} band. The former depletes while the latter develops when the temperature is varied from 100 to 150°C. Under the circumstances, the observed growth of the 2034 cm^{-1} band with the concomitant depletion of the 2144 cm^{-1}

band implies that the 2034 cm^{-1} band is not attributed to one of the features of the $Ru^{2+}(CO)_2$ fragment.

Similarly, extraction and gaseous product analysis were done after carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 700 Torr of CO. Following 7 days of carbonylation of a light brown hydrated $Ru(NO)(NO_3)_3/SiO_2$ sample (0.50 g) at 25°C, there was no color change on the solid sample. Onto two portions of the solid sample were added CH_2Cl_2 and C_2H_5OH, respectively under Ar. Both the CH_2Cl_2

and the C_2H_5OH extracts which were colorless, showed no IR bands. This indicates that the surface ruthenium carbonyl species cannot be removed by either an electron donor or a non-electron donor solvent. The results show accord with the surface IR observations, suggesting that the ruthenium(II) dicarbonyl and tricarbonyl fragments resulting from $Ru(NO)(NO_3)_3/SiO_2$ are strongly bonded to the SiO_2 surface. Following 70 h of carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.50 g) at 100°C, the color of the solid sample changed from light brown to yellow. The gaseous products in a Schlenk tube were admitted into an IR cell which had been previously evacuated. The gaseous IR spectrum exhibited not only the marked bands for CO and CO_2 but also two intense ones at 2233 and 2214 cm^{-1}, as shown in Fig. 6(b). These two bands are assigned to the symmetric and approximately asymmetric N–O stretching of N_2O. Onto two portions of the solid sample were added CH_2Cl_2 and C_2H_5OH, respectively under Ar. The C_2H_5OH extract was colorless and displayed no IR bands, whereas the CH_2Cl_2 extract was pale-yellow and displayed three IR bands at 2064s, 2032m and 2014w cm^{-1}, as shown in Fig. 3(d). The three bands are evidently characteristic of the ruthenium carbonyl cluster $Ru_3(CO)_{12}$. Moreover, this spectrum may match with the surface IR bands at 2034 and 2066 cm^{-1} which overlapped with the band at 2082 cm^{-1}. Note that $Ru_3(CO)_{12}$ is sparingly soluble in CH_2Cl_2 and insoluble in C_2H_5OH. The results suggest the formation of $Ru_3(CO)_{12}$ as well as SiO_2-bonded $Ru^{2+}(CO)_3$ from carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 700 Torr of CO at 100°C. Ruthenium quantitative analysis of the solid sample indicated that the yield of $Ru_3(CO)_{12}$ was 50% based on $Ru(NO)(NO_3)_3$. When hydrated $Ru(NO)(NO_3)_3/SiO_2$ (0.50 g) was subjected to 40 h of carbonylation at 150°C, the solid sample turned deep-yellow and $Ru_3(CO)_{12}$ was obtained with a 65% yield. After extraction with CH_2Cl_2, the solid sample turned light yellow.

3.3. Reactivities of calcined $RuCl_3/SiO_2$ and calcined $Ru(NO)(NO_3)_3/SiO_2$ with CO

The influence of calcination of $RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ on their carbonylation was investigated. Wafers of hydrated $RuCl_3/SiO_2$ and
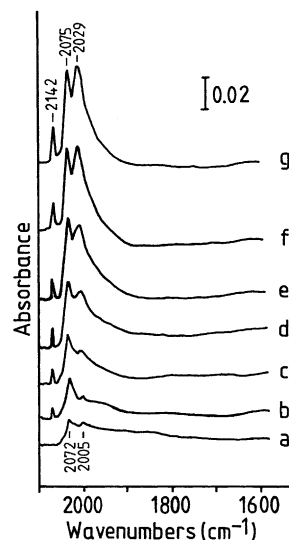

Fig. 10. Surface IR spectrum after carbonylation of calcined $RuCl_3/SiO_2$ (1.0% Ru loading) under 150 Torr of CO for: (a) 24 h at 25°C; (b) 10 min at 100°C; (c) 2.5 h at 100°C; (d) 9 h at 100°C; (e) 21.5 h at 100°C; (f) 57 h at 100°C; (g) 68 h at 100°C.

hydrated $Ru(NO)(NO_3)_3/SiO_2$ were first subjected to calcination under vacuum (10^{-2} Torr) or in air at 400°C for 4 h. Subsequently, the calcined wafers were rehydrated in air at 25°C for 12 h before carbonylation, since the water content is known to play an important role in the reductive carbonylation of MCl_3 (M = Rh, Ir, Os, Ru) on inorganic supports [7,9,23–25].

Fig. 10 gives the surface IR spectra obtained during the carbonylation under 150 Torr of CO of calcined $RuCl_3/SiO_2$. At 25°C, the calcined sample hardly reacted with CO to exhibit adsorbed CO signals, as seen in Fig. 10(a). After the temperature had been raised to 100°C, three bands appeared at 2147, 2070 and 2006 cm^{-1} and developed slowly with time. The carbonylation was completed after 57 h with the presence of three bands at 2142, 2075 and 2029 cm^{-1}, which are due to a surface mixture of ruthenium(II) dicarbonyl and tricarbonyl species. Apparently, the spectral intensities in this case were rather weak than those in the case of hydrated $RuCl_3/SiO_2$. This indicates that the conversion of Ru^{3+} to Ru^{2+} under CO is rather low after calcination of $RuCl_3/SiO_2$ under vacuum.

Fig. 11 gives the surface IR spectra observed during the carbonylation under 150 Torr of CO of calcined
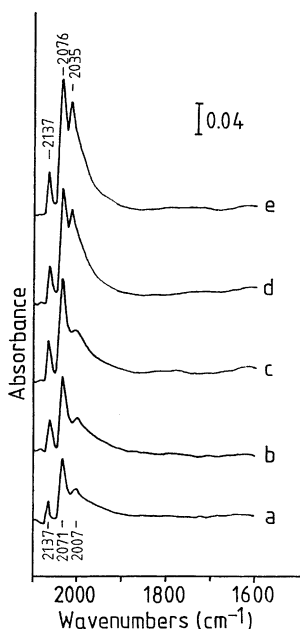
Fig. 11. Surface IR spectrum after carbonylation of calcined $Ru(NO)(NO_3)_3/SiO_2$ (0.9% Ru loading) under 150 Torr of CO at 100°C for: (a) 10 min; (b) 2.5 h; (c) 9 h; (d) 55 h; (e) 68 h.

$Ru(NO)(NO_3)_3/SiO_2$. When a calcined wafer was exposed to CO at 100°C, three bands emerged at 2137, 2071 and 2007 cm^{-1} and developed gradually with time. After 55 h of carbonylation, the spectrum consisting of bands at 2137, 2076 and 2035 cm^{-1} evolved no longer. The three bands are likewise attributed to a surface mixture of ruthenium(II) dicarbonyl and tricarbonyl species. Comparison of the spectral intensities in the case and those in the case of hydrated $Ru(NO)(NO_3)_3/SiO_2$ indicates that calcination under vacuum renders the $Ru^{3+} \rightarrow Ru^{2+}$ conversion decreased on SiO_2 under CO. It was noticed that the calcined wafer displayed no N–O vibrational band, showing full elimination of NO and NO_3^- groups from the surface by calcination.

Extraction experiments were carried out after 60 h of calcination under 700 Torr of CO at 100°C of calcined $RuCl_3/SiO_2$ and calcined $Ru(NO)(NO_3)_3/SiO_2$. In both cases, neither CH_2Cl_2 nor C_2H_5OH could extract any carbonyl species from the calcined samples. The results suggest that SiO_2-bonded ruthenium(II) dicarbonyl and tricarbonyl species such as $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ are

formed from carbonylation of both $RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ following calcination under vacuum.

When hydrated $RuCl_3/SiO_2$ and $Ru(NO)(NO_3)_3/SiO_2$ were subjected to calcination in air at 400°C, the surface IR spectra exhibited no carbonyl bands after treatment under CO at 100°C.

4. Discussion

In the light of achievements in the study of surface-mediated organometallic synthesis, the advantages that inorganic oxide surfaces present over liquid solvents lie in not only the simple manipulation of synthesis of organometallic complexes but also the easy control of desired synthetic conditions, e.g. acidic, basic or redox properties. Many examples have shown unusual and attractive synthetic results of organometallic complexes by surface-mediated approach [2,4,7–12]. Ruthenium carbonyl complexes such as $Ru(CO)_2Cl_2$, $[Ru(CO)_3Cl_2]_2$ and $Ru_3(CO)_{12}$ are of valuable utility in both the direct catalytic processes and the primary materials to synthesize polynuclear ruthenium organometallics and heteronuclear organometallics [26–30]. Starting from RuX_3, the synthesis of a mixture of $Ru(CO)_2X_2$ and $[Ru(CO)_3X_2]_2$ was first reported by Manchot and Konig [31]. Later on, the preparation of $[Ru(CO)_3Cl_2]_2$ by pressurizing methanolic $RuCl \cdot nH_2O$ solutions under CO was described by Bruce and Stone [32]. The synthesis of $[Ru(CO)_2Cl_2]_2$ and $[Ru(CO)_3Cl_2]_2$ from $RuCl_3$ requires more severe conditions. For example, $RuCl_3$ is refluxed in a mixture solution of HCOOH and HCl to give $[Ru(CO)_2Cl_2]_2$ in 77% yield after 5 h and $[Ru(CO)_3Cl_2]_2$ in 85% yield after 24 h [33]; $RuCl_3 \cdot 3H_2O$ reacts with CO at 10 atm and 60°C for 24 h to produce $[Ru(CO)_3Cl_2]_2$ in 71% yield [32]. Until the early 1990s, the surface-mediated synthetic route for mono- and di-nuclear ruthenium carbonyl complexes from $RuCl_3$ was opened up. Roberto et al. obtained successfully $[Ru(CO)_3Cl_2]_2$ from SiO_2-supported $RuCl_3 \cdot 3H_2O$ with 88–93% yields by reductive carbonylation at atmospheric CO and 100°C followed by extraction using acetone and recrystallization from CH_2Cl_2/pentane [7,8]. This convenient method brings about higher $[Ru(CO)_3Cl_2]_2$ yields than those obtained in the traditional solution syntheses.

Based on the IR spectroscopic observations in the present work, the carbonylation processes of $RuCl_3$ and $Ru(NO)(NO_3)_3$ on the hydrated SiO_2 surface are spontaneous and facile under CO. At 25°C, the mononuclear ruthenium(II) dicarbonyl fragments $Ru(CO)_2Cl_2$ and $Ru^{2+}(CO)_2$ are formed upon contact of hydrated $RuCl_3/SiO_2$ and hydrated $Ru(NO)(NO_3)_3/SiO_2$ with CO. Increasing the temperature to 100°C promotes the carbonylation which can be completed within 30 h in high conversions of $RuCl_3$ and $Ru(NO)(NO_3)_3$, in view of the evolution of IR spectral intensity and the elemental analysis. The easy carbonylation behaviors are similar to those of $RhCl_3/SiO_2$ and Rh_2O_3/SiO_2, although the carbonylation is relatively rapid to reach completion in the latter cases [34]. As far as the carbonylation products are concerned, the reactions of $RhCl_3$, Rh_2O_3 and $Rh(NO_3)_3$ with CO on SiO_2 give the pure rhodium gem-dicarbonyl complexes $[Rh(CO)_2]_2$ and $[Rh(CO)_2O_s]_2$ (O_s: surface oxygen) [13,25,34–37], whereas those of $RuCl_3$ and $Ru(NO)(NO_3)_3$ with CO on SiO_2 produce a complex mixture of ruthenium carbonyl species. Carbonylation of hydrated $RuCl_3/SiO_2$ forms a mixture of $Ru(CO)Cl_2(HOSi)_3$ and $Ru(CO)_2Cl_2(HOSi)_2$ at 25°C, and a mixture of $Ru(CO)Cl_2(HOSi)_3$, $Ru(CO)Cl_2(HOSi)_3$, $Ru(CO)_3Cl_2(HOSi)$ (major product) and $[Ru(CO)_3Cl_2]_2$ at 100°C. Carbonylation of $Ru(NO)(NO_3)_3/SiO_2$ yields a mixture of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ at 25°C. At 100°C, carbonylation of $Ru(NO)(NO_3)_3/SiO_2$ produces a mixture of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ under 100 Torr of CO, and a mixture of $Ru(CO)_3(OSi)_2$ and $Ru_3(CO)_{12}$ under 700 Torr of CO. The product complexity of carbonylation of $RuCl_3/SiO_2$ has also been stated in the paper of Roberto et al. [8]. As a whole, elevated carbonylation temperatures and elevated CO pressures favor the achievement of ruthenium(II) tricarbonyl species. Obviously, the carbonylation processes involve the reduction of Ru^{3+} to Ru^{2+} by CO in the presence of H_2O and OH on the SiO_2 surface. According to the analytical results of gas phases, CO_2 is the oxidation product of CO in the reductive carbonylation of Ru^{3+} on SiO_2 in analogy with the reductive carbonylation of Rh^{3+} on SiO_2 [23–25], while N_2O is the reduction product from NO and NO_3^- on SiO_2. Since the reductive carbonylation involving H_2O is known to

be significantly faster than that involving OH [25], the following equations are proposed to illustrate the reactivities of $RuCl_3$ and $Ru(NO)(NO_3)_3$ with CO on the hydrated SiO_2 surface:

$$2RuCl_3 + 4CO + H_2O + 5HOSi$$
$$\xrightarrow{25°C} Ru(CO)Cl_2(HOSi)_3 + Ru(CO)_2Cl_2(HOSi)_2$$
$$+CO_2 + HCl \quad\quad (1)$$

$$2RuCl_3 + 13CO + 2H_2O + 3HOSi$$
$$\xrightarrow{100°C} Ru(CO)_3Cl_2(HOSi) + Ru(CO)_2Cl_2(HOSi)_2$$
$$+[Ru(CO)_3Cl_2]_2 + 2CO_2 + 4HCl \quad\quad (2)$$

$$2Ru(NO)(NO_3)_3 + 19CO + 4HOSi$$
$$\xrightarrow[\text{or } 100°C, 100\,\text{Torr CO}]{25°C, 100-700\,\text{Torr CO}} Ru(CO)_2(OSi)_2$$
$$+Ru(CO)_3(OSi)_2 + 4N_2O$$
$$+14CO_2 + 2H_2O \quad\quad (3)$$

$$4Ru(NO)(NO_3)_3 + 46CO + 2HOSi$$
$$\xrightarrow[750\,\text{Torr CO}]{100-150°C} Ru_3(CO)_{12} + Ru(CO)_3(OSi)_2$$
$$+31CO_2 + 8N_2O + H_2O \quad\quad (4)$$
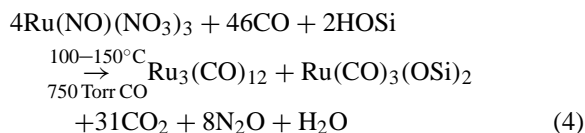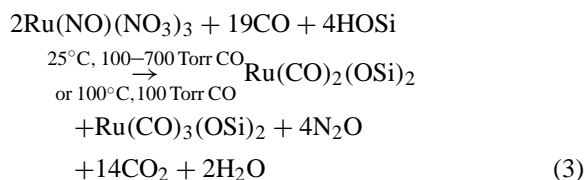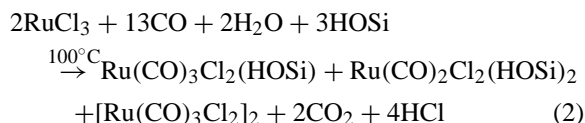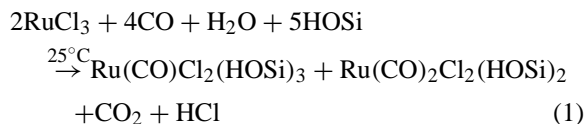
In the case of hydrated $RuCl_3/SiO_2$, carbonylation at 25°C leads to the formation of $Ru(CO)_2Cl_2(HOSi)_2$ and possible $Ru(CO)Cl_2(HOSi)_3$, as suggested by surface IR study and extraction extractions. The coexisting $Ru(CO)Cl_2(HOSi)_3$ having the 1992 cm^{-1} band was not observed in the work of Roberto et al. [8]. Raising the carbonylation temperature to 100°C results in the production of $Ru(CO)_3Cl_2(HOSi)$ and $[Ru(CO)_3Cl_2]_2$, as evidenced by surface IR study and extraction experiments. This demonstrates the conversions of $Ru(CO)Cl_2(HOSi)_3$ and $Ru(CO)_2Cl_2(HOSi)_2$ to $Ru(CO)_3Cl_2(HOSi)$ and the dimerization of $Ru(CO)_3Cl_2$ by ligand substitution under CO at elevated temperatures. The surface chemical equilibrium between $Ru^{2+}(CO)_2$ and $Ru^{2+}(CO)_3$ on SiO_2 has been reported by Zanderighi et al. [38]. Consistent with the shift of equilibrium toward the tricarbonyl species under CO, our surface IR spectra exhibit continuously increased band intensities of the ruthenium(II) tricarbonyl species with carbonylation time at 100°C. Above all, carbonylation

under 700 Torr of CO results in a dominating proportion of $Ru(CO)_3Cl_2(HOSi)$ and $[Ru(CO)_3Cl_2]_2$ to $Ru(CO)_2Cl_2(HOSi)_2$ and $Ru(CO)Cl_2(HOSi)_3$. Roberto et al. obtained merely $Ru(CO)_3Cl_2(HOSi)$ by heating a $Ru(CO)_2Cl_2(HOSi)_2$ sample under atmospheric CO at $100°C$ [8]. The finding of $Ru(CO)_3Cl_2(HOSi)$ as the major product arising from carbonylation of hydrated $RuCl_3/SiO_2$ under 700 Torr of CO at $100°C$ in our work shows substantial agreement with the result obtained by Roberto et al. The differences observed during the carbonylation processes may be due to the different silica materials used and different pretreatment of them.

The carbonylation of $Ru(NO)(NO_3)_3$ has not yet been reported. The reduction of Ru^{3+} to Ru^{2+} to release CO_2 takes place with the concurrent reduction of NO and NO_3^- groups to evolve N_2O. At $25°C$, the reaction of $Ru(NO)(NO_3)_3$ with CO on hydrated SiO_2 simultaneously gives rise to $Ru^{2+}(CO)_2$ and $Ru^{2+}(CO)_3$ bound to the surface, according to surface IR observations and extraction results. Under 100 Torr of CO, increasing the temperature to $100°C$ does not seem to influence the ratio of tricarbonyl fragment to dicarbonyl fragment. Under 700 Torr of CO at $100°C$, the dicarbonyl fragment is almost completely transformed to the tricarbonyl fragment. The fact that the band intensity of N–O stretching decreases continuously with increasing band intensities of the ruthenium(II) dicarbonyl and tricarbonyl fragments and water on the surface during carbonylation, suggests that the formation of the ruthenium(II) dicarbonyl and tricarbonyl fragments is accompanied by the occurrence of reduction of NO and NO_3^- groups and the increase of water amount on the surface, as indicated in Eqs. (3) and (4). Meanwhile, the surface IR results do indicate the presence of $Ru^{2+}(CO)_2$ and $Ru^{2+}(CO)_3$ fragments on the surface. The fact that these carbonyl fragments cannot be extracted from the surface by C_2H_5OH leads us to assume the formation of rigid Ru–O–Si bonds between $Ru^{2+}(CO)_n$ ($n = 2$, 3) and OSi^-. Taking into account the absence of other ligands in the system, we speculate that the surface ruthenium carbonyl species resulting from carbonylation of $Ru(NO)(NO_3)_3/SiO_2$ are present in the forms of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$. A similar surface-bonded species $[Rh(CO)_2O_s]_2$ has been proposed to form from carbonylation of $Rh(NO_3)_3/SiO_2$ [37].

It is worth pointing out that the reduction of NO and NO_3^- in $Ru(NO)(NO_3)_3/SiO_2$ by CO occurs at a temperature as low as $25°C$. NO_3^- is generally reduced to NO [39]. However, little is known about the reactivity of transition metal nitrates with CO [40]. Chernyaev et al. reported a solution reaction of $Ni(NO_3)_2(PEt_3)_2$ with CO to give $Ni(NO_3)(NO)(PEt_3)_2$ [40]. It may be presumed without evidence that NO_3^- groups in $Ru(NO)(NO_3)_3/SiO_2$ convert to NO ligands under mild CO reduction conditions following the equation below:

$$2NO_3^- + 3CO + 2HOSi$$
$$\rightarrow 2NO + 3CO_2 + H_2O + 2OSi^- \tag{5}$$
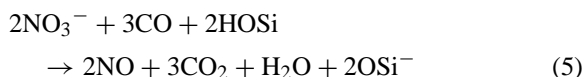
and that NO ligands thus formed continue to be reduced to N_2O by CO.

The reaction $2NO + CO \rightarrow N_2O + CO_2$ is a typical $DeNO_x$ process. A number of platinum metal complexes, as well as metals and metal oxides are found to catalyze this process under mild conditions [41]. However, few papers are devoted to dealing with this reaction with ruthenium catalysts [42,43]. By IR spectroscopic study of adsorption on reduced Ru/TiO_2 and Ru/ZrO_2, Guglielminotti et al. demonstrated that NO is dissociated on Ru^0 and gives rise to N_2O and CO_2 in the presence of preadsorbed CO at room temperature [43]. Reed and Eisenberg revealed earlier that ruthenium nitrosyl complexes are little active for the reaction in solution under pressure and on irradiation [42]. Surprisingly, SiO_2-supported $Ru(NO)(NO_3)_3$ can react stoichiometrically with CO to give $Ru(CO)_n(OSi)_2$ ($n = 2$, 3), N_2O and CO_2 at $25°C$. This result will encourage us to consider $Ru(NO)(NO_3)_3/SiO_2$ as a candidate of effective catalyst precursors for CO reduction of NO.

It is known that the reaction $2NO + CO \rightarrow N_2 + 2CO_2$ may proceed simultaneously as a result of complete decomposition of N_2O on the catalyst [43]. Although N_2 was not analyzed in our experiments, we assess that this reaction is unlikely to take place over $Ru(NO)(NO_3)_3/SiO_2$ or $Ru(CO)_n(OSi)_2$ ($n = 2$, 3) under working conditions. This is because N_2O decomposition to N_2 is proposed to be activated only on Ru^0 and Ru^{6+} surface sites in heterogeneous catalysis [43–45].

It is of interest to find that one-step carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 700 Torr

of CO at 100–150°C produces $Ru_3(CO)_{12}$ in good yields (50–65%). The AA analytical results after $Ru_3(CO)_{12}$ extraction experiments are in accord with the $Ru(NO)(NO_3)_3$ conversions under CO estimated by surface IR measurement. To synthesize $Ru_3(CO)_{12}$ in high yields (>50%), the traditional direct carbonylation of hydrated $RuCl_3$ in solution is known to require higher pressures of CO (>50 atm) [46–48]. At a pressure of 17 atm of CO, carbonylation of $RuCl_3 \cdot 3H_2O$ in refluxing methanol was reported earlier to give $[Ru(CO)_3Cl_2]_2$ in 71% yield and $Ru_3(CO)_{12}$ in only 18% yield [32]. Recently, Roberto et al. carried out the surface-mediated synthesis of $Ru_3(CO)_{12}$ from $RuCl_3/SiO_2$ in the presence of Na_2CO_3 aqueous solution [10]. They attained a 56% yield by one-step reduction at 1 atm of CO and 130°C, and enhanced the yield to 93% by two-step route: (i) preparation of $Ru(CO)_3Cl_2(HOSi)$ from $RuCl_3/SiO_2$ at 1 atm of CO and 110°C; (ii) treatment of $Ru(CO)_3Cl_2(HOSi)$ with a Na_2CO_3 aqueous solution at 1 atm of CO and 110°C. By surface IR study, Zanderighi et al. have demonstrated that $Ru(CO)_n(OSi)_2$ ($n = 2, 3$) are easily converted to physisorbed $Ru_3(CO)_{12}$ by treatment with CO and H_2O at 100°C [38]. Consistent with this result, the formation of $Ru_3(CO)_{12}$ in our case can likewise be explained in terms of the conversion under CO and H_2O of $Ru(CO)_3(OSi)_2$ which is issued from reductive carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$, since the hydrated SiO_2 surface contains a sufficient amount of H_2O. This is demonstrated by the increase of IR band intensities of $Ru_3(CO)_{12}/SiO_2$ at the expense of IR band intensities of $Ru(CO)_3(OSi)_2$ when the carbonylation

temperature is raised from 100 to 150°C. The determined enhancement of $Ru_3(CO)_{12}$ yield with increasing carbonylation temperature from 100 to 150°C is in accordance with the surface IR spectral evolution in Fig. 9. However, carbonylation of hydrated $RuCl_3/SiO_2$ cannot yield $Ru_3(CO)_{12}$ under equivalent conditions. This is probably due to the greater difficulty of removing chloride ligands from ruthenium [8]. Some syntheses of $Ru_3(CO)_{12}$ are summarized in Table 1 for comparison. The surface-mediated reductive carbonylation of hydrated $Ru_3(NO)(NO_3)_3/SiO_2$ not only facilitates the production of $Ru_3(CO)_{12}$ under mild conditions but also avoids the presence of contaminants such as sodium and chlorine.

Furthermore, the other advantage of surface-mediated synthesis of $Ru_3(CO)_{12}$ is that supported $Ru_3(CO)_{12}$ and $Ru_3(CO)_{12}$-derived supported catalysts can be prepared conveniently. Trouble is usually encountered during the impregnation manipulation starting from $Ru_3(CO)_{12}$ due to its poor solubility in solvents. But the surface-mediated synthesis can overcome this shortcoming. The reductive carbonylation of hydrated $Ru(NO)(NO_3)_3$ on SiO_2 is indeed able to produce uniform and clean supported $Ru_3(CO)_{12}$ that is utilized as a catalyst precursor. This beneficial approach deserves to be applied to the catalytic research.

The interactions of $RuCl_3$ and $Ru(NO)(NO_3)_3$ with the SiO_2 surface at 400°C seem to hinder the production of ruthenium(II) dicarbonyl and tricarbonyl species. Following treatments of hydrated $RuCl_3/SiO_2$ and hydrated $Ru(NO)(NO_3)_3/SiO_2$ under vacuum at 400°C, carbonylation gives rise to rather low amounts of ruthenium(II) dicarbonyl and

Table 1
Some syntheses of $Ru_3(CO)_{12}$

Starting material	Ru loading (%)	Conditions	Yield (%)	Reference
$RuCl_3$		125°C, 50 atm, CO	100	[48]
$Ru(AcAc)_3$		140–160°C, 200–300 atm, CO + H_2	>80	[49,50]
$RuCl_3$		65°C, 17 atm, CO, Zn	18	[32]
$RuCl_3$		75°C, 120 atm, CO + H_2, Ag	>50	[46]
$RuCl_3$		165°C, 160 atm, CO + H_2, Na(AcAc)	50–70	[47]
$[Ru_3O(OAc)_6(OH_2)_3]OAc$		75–80°C, 1 atm, CO	60	[51]
$RuCl_3/SiO_2$	2	130°C, 1 atm, CO, Na_2CO_3	56	[10]
$RuCl_3/SiO_2$	15	130°C, 5 atm, CO, Na_2CO_3	55	[10]
$Ru(CO)_3Cl_2(HOSi)$	2	110°C, 1 atm, CO, Na_2CO_3	93	[10]
$Ru(CO)_3Cl_2(HOSi)$	5	110°C, 1 atm, CO, Na_2CO_3	82	[10]
$Ru(NO)(NO_3)_3/SiO_2$	0.9	100°C, 1 atm, CO	50	This work

tricarbonyl species compared to the uncalcined cases, in view of the relative IR spectral intensity. The fact that the resulting ruthenium(II) dicarbonyl and tricarbonyl species cannot be extracted by either CH_2Cl_2 or C_2H_5OH suggests the formation of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ in the cases of both $RuCl_3$ and $Ru(NO)(NO_3)_3$.

The reactivities of $RuCl_3$ and $Ru(NO)(NO_3)_3$ with surface OH have not yet been elucidated. In the absence of O_2 or air, $RuCl_3$ may be converted to surface Ru_2O_3 to certain extent by interaction with the surface OH of SiO_2. Calcination of $RhCl_3/SiO_2$ and $[Rh(NH_3)_5Cl_2]Cl_2/SiO_2$ at 400°C has been shown to result in partial loss of chlorine and partial substitution of chlorine by surface OH [34,52]. In the case of $RuCl_3$, the extraction result with no ruthenium(II) carbonyl chloride species from carbonylation of calcined $RuCl_3/SiO_2$ implies that $RuCl_3$ is completely converted to surface Ru_2O_3 (all of chlorine are replaced by surface oxygen) after treatment of hydrated $RuCl_3/SiO_2$ under vacuum at 400°C. In the case of $Ru(NO)(NO_3)_3$, the surface IR spectra during carbonylation of calcined $Ru(NO)(NO_3)_3/SiO_2$ apparently do not exhibit a band of CO adsorbed on Ru^0/SiO_2. This accounts for that the thermal decomposition of $Ru(NO)(NO_3)_3$ on the SiO_2 surface does not simply give rise to Ru^0. Therefore, it is difficult to understand the decomposition behavior of $Ru(NO)(NO_3)_3$ on SiO_2 with the intervention of the surface OH of SiO_2 at 400°C. Solymosi and Rasko reported that Ru^0 can be easily oxidized by the surface OH of Al_2O_3 with the evolution of H_2 [53]. This may help us consider the possibility that the thermal decomposition of $Ru(NO)(NO_3)_3$ on SiO_2 at 400°C produces Ru^{2+}, or Ru^{3+} or a mixture of them. Both of them can be converted to surface $Ru^{2+}(CO)_n$ ($n = 2, 3$) species under CO [54–56]. Most likely, the observed lower production of surface $Ru^{2+}(CO)_n$ ($n = 2, 3$) species from calcined $RuCl_3/SiO_2$ and calcined $Ru(NO)(NO_3)_3/SiO_2$ is related to the difficult carbonylation of surface-bound Ru_2O_3 and RuO.

In the presence of air, calcination of hydrated $RuCl_3/SiO_2$ and hydrated $Ru(NO)(NO_3)_3/SiO_2$ at 400°C leads to the suppression of carbonylation. This may be interpreted by the oxidation of Ru^{3+} by O_2 with the formation of RuO_2 at 400°C that is promoted by the SiO_2 surface. Unsupported $RuCl_3$ is known to transform to RuO_2 under O_2 at 600°C [57].

5. Conclusions

In this paper, we have described the results of reductive carbonylation of SiO_2-supported $RuCl_3$ and $Ru(NO)(NO_3)_3$ treated under different conditions. The main conclusions are drawn as follows:

1. Hydrated $RuCl_3/SiO_2$ and hydrated $Ru(NO)(NO_3)_3/SiO_2$ react readily with CO (100–700 Torr) to form surface ruthenium carbonyl species. At 25°C, carbonylation of hydrated $RuCl_3/SiO_2$ produces a mixture of $Ru(CO)Cl_2(HOSi)_3$ and $Ru(CO)_2Cl_2(HOSi)_2$, carbonylation of hydrated $Ru(CO)(NO_3)_3/SiO_2$ yields a mixture of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$. At 100°C, a mixture of $Ru(CO)Cl_2(HOSi)_3$, $Ru(CO)_2Cl_2(HOSi)_2$, $Ru(CO)_3Cl_2(HOSi)$ (major product) and $[Ru(CO)_3Cl_2]_2$ are obtained from carbonylation of hydrated $RuCl_3/SiO_2$, a mixture of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ are achieved from carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 100 Torr of CO; a mixture of $Ru_3(CO)_{12}$ and $Ru(CO)_3(OSi)_2$ are gained from carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$ under 700 Torr of CO.
2. During the carbonylation of hydrated $Ru(NO)(NO_3)_3/SiO_2$, the stoichiometric reactions $2NO_3^- + 3CO + 2HOSi \rightarrow 2NO + 3CO_2 + H_2O + 2OSi^-$ and $2NO + CO \rightarrow N_2O + CO_2$ occur concurrently on the surface.
3. Increasing the carbonylation temperature to 100°C and increasing the CO pressure can lead to increased proportion of ruthenium(II) tricarbonyl species.
4. The calcination of hydrated $RuCl_3/SiO_2$ and hydrated $Ru(NO)(NO_3)_3/SiO_2$ has negative effect on the reductive carbonylation. After treatment under vacuum at 400°C, the carbonylation produces $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$ in low yields. After treatment in air at 400°C, the carbonylation gives no carbonyl species.

References

[1] J.M. Basset, B.C. Gates, J.P. Candy, A. Choplin, M. Leconte, F. Quignard, C.C. Santini, Surface Organometallic Chemistry: Molecular Approaches to Surface Catalysis, Kluwer Academic Publishers, Dordrecht, 1988.

[2] M. Ichikawa, Adv. Catal. 38 (1992) 283, and references therein.

[3] L. Huang, J. Mol. Catal. A 125 (1997) 47.

[4] Z. Xu, A.L. Rheingold, B.C. Gates, Inorg. Chem. 33 (1994) 4415.

[5] B.C. Gates, J. Mol. Catal. 87(1994)95, and references therein.

[6] G.C. Shen, A.M. Liu, T. Shido, M. Ichikawa, Topics Catal. 2 (1995) 141.

[7] D. Robert, R. Psaro, R. Ugo, Organometallics 12 (1993) 2292.

[8] D. Roberto, R. Psaro, R. Ugo, J. Organomet. Chem. 451 (1993) 123.

[9] D. Roberto, E. Cariati, R. Ugo, Organometallics 13 (1994) 734.

[10] D. Roberto, E. Cariati, E. Lucenti, M. Respini, R. Ugo, Organometallics 16 (1997) 4531.

[11] L. Huang, Y. Xu, Catal. Lett. 53 (1998) 177.

[12] L. Huang, Y. Xu, Bull. Chem. Soc. Jpn. 72 (1999) 199.

[13] D. Roberto, R. Psaro, R. Ugo, C. Dossi, A. Fusi, J. Mol. Catal. 74 (1992) 391.

[14] E. Iglesia, S.C. Reyes, R.J. Madon, Adv. Catal. 39 (1993) 221.

[15] E. Iglesia, S.L. Soled, R.A. Fiato, G.H. Via, J. Catal. 143 (1993) 345.

[16] D.O. Uner, M. Pruski, B.C. Gerstein, T.S. King, J. Catal. 146 (1994) 530.

[17] J. Steinwandel, T. Staneff, J. Weitkamp, S. Ernst, D. Schmid, Ger. Offen. DE 19537202 (1997).

[18] L. Huang, Y. Xu, Appl. Catal. A 205 (2001) 183.

[19] S. Sayan, S. Suzer, D.O. Uner, J. Mol. Struct. 410/411 (1997) 111.

[20] M.L. Berch, A. Davison, J. Inorg. Nucl. Chem. 35 (1973) 3763.

[21] J.J. Bergmeister III, B.E. Hanson, Inorg. Chem. 29 (1990) 4055.

[22] K. Nakamoto, IR and Raman Spectra of Inorganic and Coordination Compounds, 4th Edition, Wiley, New York, 1986.

[23] J.C. Conesa, M.T. Sainz, J. Soria, G. Munuera, V. Rives-Amau, A. Munoz, J. Mol. Catal. 17 (1982) 231.

[24] N. Takahashi, A. Mijin, H. Suematsu, S. Shinohara, H. Matsuoka, J. Catal. 117 (1989) 348.

[25] S.S.C. Chuang, S. Debnath, J. Mol. Catal. 79 (1993) 323.

[26] M.I. Bruce, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, p. 923.

[27] M.A. Bennett, T.W. Matheson, in: G. Wilkinson, F.G.A. Stone, B.W. Abel (Eds.), Cornprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, p. 889.

[28] M.A. Matheson, T.W. Matheson, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 4, Pergamon Press, Oxford, 1982, p. 931.

[29] W.I. Gladfelter, G.L. Geoffroy, Adv. Organomet. Chem. 18 (1980) 207.

[30] E.A. Seddon, K.R. Seddon, in: R.J.H. Clark (Ed.), The Chemistry of Ruthenium in Topics in Inorganic and General Chemistry, Monography 19, Elsevier, Amsterdam, 1984.

[31] W. Manchot, J. Konig, Chem. Ber. 57B (1924) 2130.

[32] M.I. Bruce, F.G.A. Stone, J. Chem. Soc. (A) (1967) 1238.

[33] M.J. Cleare, W.P. Griffith, J. Chem. Soc. (A) (1969) 372.

[34] L. Huang, Y. Xu, Catal. Lett. 55 (1998) 227.

[35] M.S. Scurrell, J. Mol. Catal. A 124 (1997) 57.

[36] M.P. Keyes, K.L. Watters, J. Catal. 100 (1986) 477.

[37] M.P. Keyes, K.L. Watters, J. Catal. 110 (1988) 96.

[38] G.M. Zanderighi, C. Dossi, R. Ugo, R. Psaro, A. Theolier, A. Choplin, L. D'ornelas, J.M. Basset, J. Organomet. Chem. 296 (1985) 127.

[39] K. Jones, in: J.C. Bailar Jr., H.J. Emeleus, R. Nyholm (Eds.), Comprehensive Inorganic Chemistry, Vol. 2, Pergamon Press, Oxford, 1973, p 147.

[40] I.I. Chernyaev, G.S. Muraveiskaya, K. Lorablina, Russ. J. Inorg. Chem. 10 (1965) 158.

[41] D. Michael, P. Mingos, D.J. Sherman, Adv. Inorg. Chem. 34 (1989) 293.

[42] J. Reed, R. Eisenberg, Science 184 (1974) 568.

[43] E. Guglielminotti, F. Boccuzzi, M. Manzoli, F. Pinna, M. Scarpa, J. Catal. 192 (2000) 149.

[44] E. Guglielminotti, F. Boccuzzi, J. Chem. Soc., Faraday Trans. 87 (1991) 337.

[45] F. Pinna, M. Scarpa, G. Strukul, E. Guglielminotti, F. Boccuzzi, M. Manzoli, J. Catal. 192 (2000) 158.

[46] J.M.S. Jamieson, J.V. Kingston, G. Wilkinson, Chem. Commun. (1966) 569.

[47] B.F.G. Johnson, J. Lewis, Inorg. Synth. 13 (1972) 92.

[48] C.R. Eady, P.F. Jackson, B.F.G. Johnson, J. Lewis, M.C. Malatesta, M. McPartlin, W.J.H. Nelson, J. Chem. Soc., Dalton Trans. (1980) 383.

[49] G. Braca, G. Sbrana, P. Pino, Chim. Ind. (Milan) 46 (1964) 206.

[50] G. Braca, G. Sbrana, P. Pino, Chim. Ind. (Milan) 50 (1968) 121.

[51] B.R. James, G.L. Rempel, W.K. Teo, Inorg. Synth. 16 (1976) 45.

[52] A.P. Gloor, R. Prins, J. Phys. Chem. 98 (1994) 9865.

[53] F. Solymosi, J. Rasko, J. Catal. 15 (1989) 107.

[54] G.H. Yokomiz, C. Louis, A.T. Bell, J. Catal. 120 (1989) 1.

[55] K. Hadjiivanov, J.-C. Lavalley, J. Lamotte, F. Mange, J. Saint-Just, M. Che, J. Catal. 176 (1998) 415.

[56] M. Kantcheva, S. Sayan, Catal. Lett. 60 (1999) 27.

[57] Wohler, Balz, Metz, Z. Amorg. Chem. 139 (1924) 205.