IR spectroscopic study on surface-mediated reductive carbonylation of hydrated SiO_2-supported $Ru(NO_3)_3$

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The surface-mediated reductive carbonylation of hydrated SiO_2-supported $Ru(NO_3)_3$ has been studied by IR spectroscopy. At 25 °C, hydrated $Ru(NO_3)_3/SiO_2$ reacts with CO to give a mixture of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$. At 100 °C, hydrated $Ru(NO_3)_3/SiO_2$ 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 $Ru_3(CO)_{12}$ and $Ru(CO)_3(OSi)_2$ under 700 Torr of CO.

KEY WORDS: silica; $Ru(NO_3)_3$; reductive carbonylation

1. Introduction

It is generally accepted that metallic carbonyl complexes are rather more valuable than inorganic salts in the preparation of 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_2O_3, MgO and zeolites by surface-mediated carbonylation [2,4–11], so as to meet the needs of a simple and efficient synthesis or preparation of supported catalysts. The surface-mediated reductive carbonylation of SiO_2-supported $MCl_3\cdot 3H_2O$ (M = Rh, Ir, Os, Ru) which is analogous to the title study has been reported by the laboratory of Professor Ugo [7–9,12]. In the study of the carbonylation of $MCl_3\cdot 3H_2O/SiO_2$, 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]. In the present letter, we report a study of surface-mediated synthesis of ruthenium carbonyl complexes from hydrated $Ru(NO_3)_3/SiO_2$ by IR spectroscopy.

2. Experimental

$Ru(NO_3)_3$ was purchased commercially. 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%.

Hydrated $Ru(NO_3)_3/SiO_2$ were prepared by incipient wetness impregnation. SiO_2 in powder was incipient wetted with an aqueous solution of $Ru(NO_3)_3$. After stirring, the resulting slurry was gently heated under an infrared lamp till it turned into a dry solid sample. All the samples prepared contained 1.0% Ru.

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 $Ru(NO_3)_3/SiO_2$ 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 spectroscopy.

3. Results and discussion

Figures 1 and 2 show the surface IR spectra taken during the carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ under 100 Torr of CO. Figure 1(a) represents a N–O stretching vibrational band of $Ru(NO_3)_3/SiO_2$ at 1888 cm^{-1}. The following spectra of carbonylated samples are represented by subtracting that of the starting $Ru(NO_3)_3/SiO_2$.

As soon as a light brown wafer of hydrated $Ru(NO_3)_3/SiO_2$ 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. As seen in figure 1, the bands at 2150, 2085 and 2028 cm^{-1} developed slowly as the carbonylation proceeded at 25 °C. This spectrum closely resembles that superimposed of the carbonyl bands for $Ru(CO)_2Cl_2(HOSi)_2$ [8] and $Ru(CO)_3Cl_2(HOSi)$ [8,13]. The 2150 and 2085 cm^{-1} bands may be attributed to surface ruthenium(II) tricarbonyl species; the 2085 and 2028 cm^{-1} bands may be ascribed to surface ruthenium(II)

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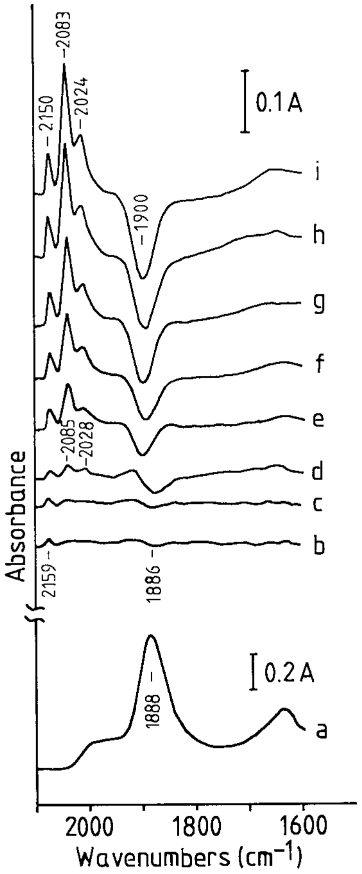

Figure 1. (a) IR spectrum of $Ru(NO_3)_3/SiO_2$. Surface IR spectrum after carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ (1.0% Ru loading) under 100 Torr of CO at 25 °C for: (b) 3 min, (c) 11 min, (d) 2.5 h, (e) 23 h, (f) 48.5 h, (g) 96.5 h, (h) 170.5 h and (i) 216 h.

dicarbonyl species. Thus the whole spectrum is assignable to a surface mixture of ruthenium(II) dicarbonyl and tricarbonyl species on SiO_2. At the same time, the 1900 cm^{-1} band grew inversely with time, indicative of loss of NO_3^- groups from the surface during carbonylation. Increasing the temperature markedly enhanced the rates of carbonylation and NO_3^- decomposition on SiO_2, as seen in figure 2. After 28 h of treatment under 100 Torr of CO at 100 °C, the wafer had no apparent color change. But carbonylation of $Ru(NO_3)_3$ was completed because the carbonyl band intensities increased no longer; NO_3^- was fully decomposed, judging from the 1892 cm^{-1} band intensity (figure 2(d)) that is equal to that of the starting $Ru(NO_3)_3/SiO_2$ (figure 1(a)).

When hydrated $Ru(NO_3)_3/SiO_2$ was exposed to 700 Torr of CO, heating at 100 °C led to the rapid growth of bands at 2144, 2081 and 2036 cm^{-1} and an inverse band at 1900 cm^{-1}, as shown in figure 3. 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 figure 1. 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. 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 2044 cm^{-1} band in intensity 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 concurrent 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.

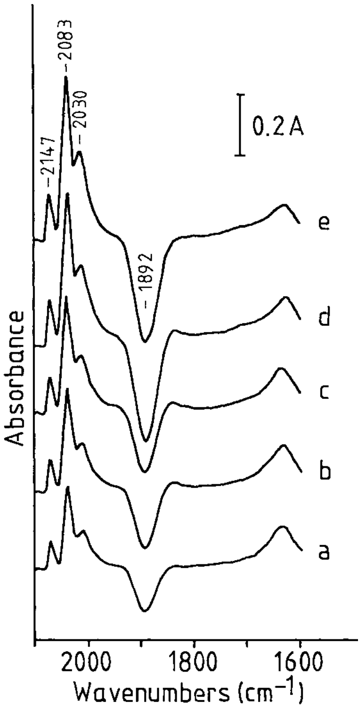

Figure 2. Surface IR spectrum after carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ (1.0% Ru loading) under 100 Torr of CO at 100 °C for: (a) 15 min, (b) 2.5 h, (c) 6 h, (d) 28 h and (e) 70.5 h.

In order to identify the gaseous products and reveal the nature of the tricarbonyl species, analysis of gas phase and extraction of the tricarbonyl species were carried out. In a Schlenk tube, 0.50 g of hydrated $Ru(NO_3)_3/SiO_2$ was outgassed under vacuum (10^{-2} Torr) at 25 °C for 1 h before admission of 700 Torr of CO. Following 7 days of carbonylation of a light brown hydrated $Ru(NO_3)_3/SiO_2$ 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 a donor or a non-donor solvent. The results show accord with the surface IR observations, suggesting that

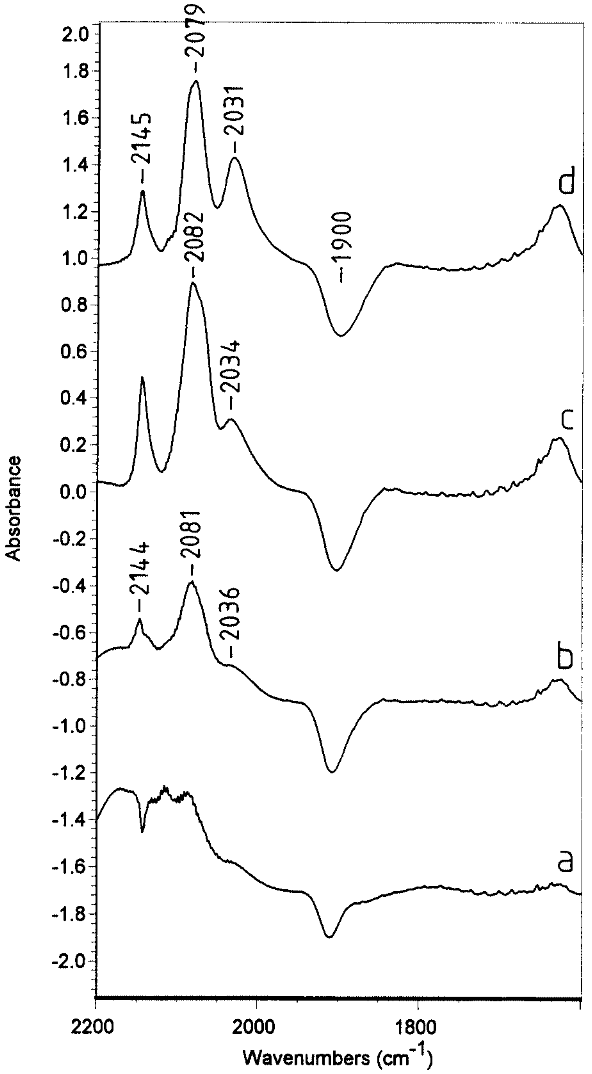

Figure 3. Surface IR spectrum after carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ (1.0% Ru loading) under 700 Torr of CO for: (a) 20 min at 100 °C, (b) 2 h at 100 °C, (c) 44.5 h at 100 °C and (d) 22 h at 150 °C.

the ruthenium(II) dicarbonyl and tricarbonyl fragments resulting from $Ru(NO_3)_3/SiO_2$ are strongly bonded to the SiO_2 surface. Following 70 h of carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ (0.50 g) at 100 °C, 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 figure 4. These two bands are due to the symmetric and asymmetric N–O stretching of N_2O. After carbonylation at 100 °C, the color of the solid sample changed from light brown to yellow. 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 figure 5. 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. Ruthenium quantitative analysis of the solid sample indicated that the yield of $Ru_3(CO)_{12}$ was 50% based on $Ru(NO_3)_3$. When $Ru(NO_3)_3/SiO_2$ (0.50 g) was subjected to 40 h of carbonylation at 150 °C, $Ru_3(CO)_{12}$ was obtained at a yield of 65%.

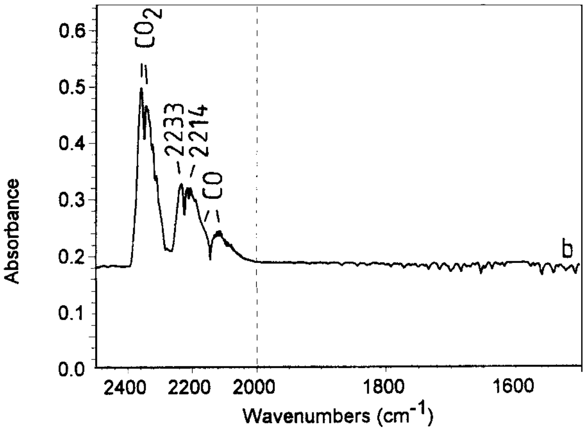

Figure 4. Gaseous IR spectrum after 70 h of carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ (1.0% Ru loading) under 700 Torr of CO at 100 °C.

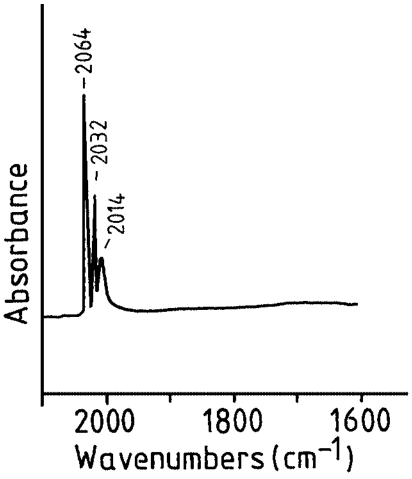

Figure 5. IR spectrum of extract in C_2H_5OH from hydrated $Ru(NO_3)_3/SiO_2$ (1.0% Ru loading) after 70 h of carbonylation under 700 Torr of CO at 100 °C.

The carbonylation of $Ru(NO_3)_3$ has not yet been reported. The reduction of Ru^{3+} to Ru^{2+} takes place with the formation of CO_2, concomitant with the reduction of NO_3^- groups to evolve N_2O. At 25 °C, the reaction of $Ru(NO_3)_3$ with CO on hydrated SiO_2 simultaneously gives rise to $Ru^{2+}(CO)_2$ and $Ru^{2+}(CO)_3$ bound to the surface. 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 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 $Ru(NO_3)_3/SiO_2$ are present in the forms of $Ru(CO)_2(OSi)_2$ and $Ru(CO)_3(OSi)_2$. A similar surface-bonded species $[Rh(CO)_2O_s]_2$ (O_s: surface oxygen) has been proposed to form from carbonylation of $Rh(NO_3)_3/SiO_2$ [14]. The formation mechanism remains unclear.

It is of interest to observe that carbonylation of hydrated $Ru(NO_3)_3/SiO_2$ under 700 Torr of CO at 100–150 °C produces $Ru_3(CO)_{12}$ in good yields (50–65%). 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) [15–17]. At a pressure of 17 atm of CO, carbonylation of $RuCl_3{\cdot}3H_2O$ in refluxing methanol was reported to give $[Ru(CO)_3Cl_2]_2$ at a yield of 71% and $Ru_3(CO)_{12}$ at a yield of 18% [18]. 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 [19]. 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 $Ru(NO_3)_3/SiO_2$, 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. In contrast, carbonylation of hydrated $RuCl_3/SiO_2$ cannot yield $Ru_3(CO)_{12}$ and can only yield $Ru(CO)_3Cl_2(HOSi)$ instead under equivalent conditions, according to the report of Roberto et al. [8]. This is probably due to the greater difficulty in removing chloride ligands from ruthenium [8].

Since the reductive carbonylation involving H_2O is known to be significantly faster than that involving OH^- [20], the following equations are proposed to illustrate the reactivity of $Ru(NO_3)_3$ with CO on the hydrated SiO_2 surface:

$$\begin{aligned}&2Ru(NO_3)_3 + 18CO + 4HOSi \xrightarrow[\text{or } 100\,^\circ\text{C, 100 Torr CO}]{25\,^\circ\text{C, 100–700 Torr CO}}\\&\quad Ru(CO)_2(OSi)_2 + Ru(CO)_3(OSi)_2 + 3N_2O\\&\qquad + 13CO_2 + 2H_2O \qquad (1)\end{aligned}$$

$$\begin{aligned}&4Ru(NO_3)_3 + 44CO + 2HOSi \xrightarrow[\text{700 Torr CO}]{100\text{–}150\,^\circ\text{C}}\\&\quad Ru_3(CO)_{12} + Ru(CO)_3(OSi)_2 + 29CO_2\\&\qquad + 6N_2O + H_2O \qquad (2)\end{aligned}$$

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