Mixed iron–rhodium carbidocarbonyl clusters on oxide supports: chemistry and catalysis of syn-gas reactions

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Abstract

Genesis of silica-supported $[Fe_5RhC(CO)_{16}]^-$ and $[Fe_4RhC(CO)_{14}]^-$ clusters with interstitial carbon atoms have been investigated in CO, syn-gas and Ar media. Complete conversion of the former cluster to the latter was obtained at 50°C in any medium, with $[Fe_4RhC(CO)_{14}]^-$ cluster yielding $Fe_4Rh_2C(CO)_{16}$ and $[Fe_3Rh_3C(CO)_{15}]^-$ mixtures at 100–150°C. Simultaneously, Fe^{2+} ions emerged on the SiO_2 surface. Mössbauer and electron microscopic studies on the silica-deposited clusters showed that at treatment in any medium in the range of 250–350°C highly dispersed FeRh particles are located on the silica surface, where Fe atoms exist mainly in the oxidized state even after H_2 reduction. Silica-supported catalysts derived from a family of FeRh carbidocarbonyl clusters were found to exhibit increased activity and selectivity toward oxygenates in CO hydrogenation and C_3H_6 hydroformylation compared to those of monometallic cluster-derived catalysts. Possible explanations are discussed.

Keywords: Carbonyl clusters; Surface chemistry; Organometallic chemistry; Carbon monoxide; Hydrogenation; Hydroformylation; Supported clusters; Propylene

1. Introduction

Considerable advances in the synthesis of carbonyl clusters, including the heteropolynuclear ones [1] made a wide use for preparation of supported catalysts possible. Profound interest of researchers to study the catalytic behaviour of carbonyl clusters is due to their close structural [2] and chemical [3] relationship with metal surfaces covered by adsorbed CO. Hence, metal carbonyl clusters or their close precursors could be considered as active sites for the reactions of syn-gas conversion. It is known [4,5], that solid supports can stabilize some metal carbonyl clusters, especially under CO or syn-gas. These materials show catalytic activity in CO hydrogenation giving non-Schulz–Flory distribution of hydrocarbon products [5]. Some of those catalyze gas-phase olefin hydroformylation [6].

In the present paper we report the transformation of a family of silica-supported FeRh carbidocarbonyl clusters in the conditions of supported catalysts activation and their catalytic performance in CO hydrogenation and C_3H_6 hydroformylation. These clusters were chosen as the catalyst precursors since supported carbonyl clusters with interstitial carbon atoms exhibited extreme stability in the conditions of CO hydrogenation and unique catalytic properties for oxygenate formation [7]. Furthermore, silica-supported catalysts derived from RhFe car-

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bonyl clusters with Rh atoms dominated in a cluster framework and free from interstitial carbon atoms showed high activity and selectivity for formation of ethanol and methanol in CO hydrogenation and improved activity in hydroformylation of olefins [8,9].

2. Experimental

Silica (surface area, 250 m^2 g^{-1}) dehydrated in vacuo at 500°C was used as support. [TEA][Fe$_5$RhC(CO)$_{16}$] ([TEA][1]) [10], [TEA][Fe$_4$RhC(CO)$_{14}$] ([TEA][2]) [10], Fe$_4$Rh$_2$C(CO)$_{16}$ [11], [TEA][Fe$_3$Rh$_3$C(CO)$_{15}$] [11], [TEA]$_2$[Fe$_6$C(CO)$_{16}$] [12] (TEA = N(C$_2$H$_5$)$_4$) and Rh$_4$(CO)$_{12}$ [13] prepared by procedures described in the literature were used as starting materials. The deposition of cluster compounds onto SiO$_2$ was performed under purified Ar as described previously [14]. The total metal loading for all catalysts was 2 wt.%.

The study of transformation of carbonyl clusters on the silica surface was carried out as follows. About 0.5 g of SiO$_2$, on which a Fe–Rh carbonyl cluster (~ 50 μmol per 1 g of support) had been deposited, was heated under CO, Ar or syn-gas (CO:H$_2$ = 1:1) for 2–10 h, followed by cooling to the room temperature in the medium in which the sample was treated. Then the solid was treated consecutively under Ar with 2.5 ml of dry hexane and CH$_3$CN or CH$_2$Cl$_2$ to extract carbonyl compounds. The solid was recovered by filtration and the supernatant solution examined by infrared spectroscopy. In any case the solution was evaporated to dryness under Ar and the IR spectrum of the residue was obtained on a KBr pellet. The Rh content in the silica after extraction of carbonyl compounds was examined by X-ray fluorescence spectroscopy.

Mössbauer spectra were obtained from the solids replaced without contact with air to a cell with beryllium or magnesium windows, as described

previously [14]. Isomer shifts are given relative to sodium nitroprusside.

An electron microscopic study (TEM) was done on a JEM-100 CX instrument with 4 A resolution as described elsewhere [15]. The size of the particles averaged for the area (d_s) was calculated from the curves of particle size distribution obtained by statistical treatment of the micrographs.

IR spectra of solids were recorded on a Bruker IFS-113 V Fourier spectrometer within 1300–4000 cm^{-1} with a resolution of 4 cm^{-1} as described elsewhere [16]. Powdered SiO$_2$ was pressed, forming self-supporting discs which were placed in a quartz IR cell with NaCl windows to enable an in situ deposition of FeRh clusters; the samples were treated in the cell under various gas media followed by extraction.

The CO hydrogenation reaction was performed at 300°C with a continuous flow copper reactor at 300°C, 5.0 MPa, CO:H$_2$ = 1:1. The space velocity was adjusted to maintain the CO conversion below 0.1%. Products were analyzed by gas chromatography.

C$_3$H$_6$ hydroformylation was conducted with a flow stainless steel reactor at 200°C, 1 atm, CO:H$_2$:C$_3$H$_6$:Ar = 1:1:1:7 with 5% propylene conversion, as described elsewhere [17]. Steady state activity and selectivity were determined. The reaction products were analyzed by means of gas chromatography.

3. Results and discussion

3.1. The study of the transformation of [Fe$_5$RhC(CO)$_{16}$]$^-$ and [Fe$_4$RhC(CO)$_{14}$]$^-$ on SiO$_2$ surface by IR spectroscopic measurements

On impregnation of FeRh carbidocarbonyl cluster from acetone solution onto the degassed pellet of silica, the resulting samples gave carbonyl bands at 2000(s,br) and 1850(w,br) which resemble those of an original cluster but were broader and ill-resolved. These bands were assigned to the CO terminally and bridging-

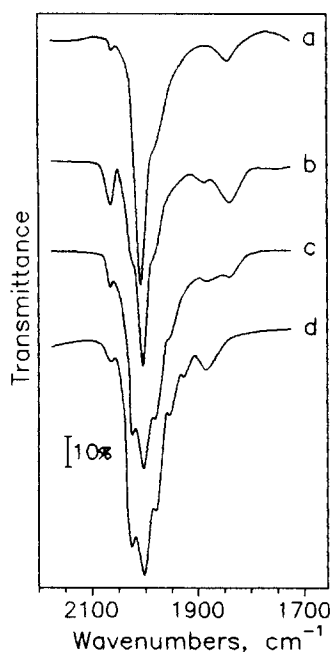Fig. 1. Infrared spectra of (a) [Fe$_5$RhC(CO)$_{16}$][TEA] in CH$_2$Cl$_2$, (b) compounds extracted with CH$_2$Cl$_2$ from [Fe$_5$RhC(CO)$_{16}$][TEA]/SiO$_2$ following 2 weeks exposure under Ar at room temperature and (c) compounds extracted with CH$_2$Cl$_2$ from [Fe$_5$RhC(CO)$_{16}$][TEA]/SiO$_2$ following its treatment by CO+H$_2$ flow for 1 h at 50°C, (d) [Fe$_4$RhC(CO)$_{14}$][TEA] in CH$_3$CN.

bonded with cluster framework. The treatment of supported clusters at 50–150°C under CO + H$_2$ or

CO did not result in significant changes in the IR spectrum of the pellet. An extraction of sample with acetone led to complete disappearance of absorption bands in the CO stretching region. It indicates the chemical frigidity of silica surface with respect to FeRh carbonyl clusters deposited thereon.

IR spectra of individual [TEA][1], [TEA][2] and compounds extracted from [TEA][1]/SiO$_2$ after treatment in Ar medium at 20°C and in CO + H$_2$ flow at 50°C are shown in Fig. 1. Band wave numbers are listed in Table 1. The spectrum of carbonyl compounds extracted from [TEA][1]/SiO$_2$ following 2 weeks exposure under Ar at 20°C consists of absorption bands at 2064(w), 2024(m sh), 2004(s), 1982(m sh), 1886(vw) and 1841(w) cm^{-1}. The bands at 2024 and 1886 cm^{-1} are unambiguously assigned to [Fe$_4$RhC(CO)$_{14}$]$^-$ (2) [11] and those at 2064, 2004, 1982 and 1841 cm^{-1} to [Fe$_5$RhC(CO)$_{16}$]$^-$ (1). It is worth noting that the bands at 2062, 2002 and 1982 cm^{-1} are also available in the IR spectrum of the former cluster. Thus, the partial conversion of 1 into 2 occurs under Ar at ambient temperature. Complete conversion of the former cluster to latter was obtained following treatment

Table 1

The ν(CO) vibrations of the carbonyl compounds extracted from SiO$_2$ after treatment of deposited FeRh carbonyl clusters with syn-gas (1:1) and individual clusters in solution

Solid	Treatment	ν(CO) vibrations [b], cm^{-1}
[Fe$_5$RhC(CO)$_{16}$][TEA] [a]/SiO$_2$	Ar, 20°C, 2 weeks	2064w, 2024m(sh), 2004s, 1982m(sh), 1886vw, 1841w (methylene chloride)
	CO + H$_2$ flow, 50°C, 1 h	2064vw, 2024s, 2003vs, 1984m, 1956w, 1886vw, 1841vw (methylene chloride)
	CO + H$_2$ flow, 150°C, 2 h	2072vw, 2055m, 2045m, 2026s, 2000vs, 1982m(sh), 1956w, 1880w (methylene chloride)
[Fe$_4$RhC(CO)$_{14}$][TEA]/SiO$_2$	CO + H$_2$ flow, 150°C, 10 h	2062vw, 2016s, 2002sh, 1980m, 1956w, 1877w, 1852vw (methylene chloride)
[Fe$_5$RhC(CO)$_{16}$][TEA]	–	2062vw, 2003vs, 1983m, 1843w (methylene chloride)
[Fe$_4$RhC(CO)$_{14}$][TEA]	–	2062vw, 2025s, 2002vs, 1982m, 1956w, 1930vw, 1880w (methyl cyanide)
Fe$_4$Rh$_2$C(CO)$_{16}$	–	2074vw, 2055s(sh), 2042vs, 2028m, 2018m, 1998w, 1982w, 1965vw (hexane)
[Fe$_3$Rh$_3$C(CO)$_{15}$][TEA]	–	2042vw, 2016vs, 1978s, 1934w,br, 1878w, 1852vw (methylene chloride)

[a] TEA = N(C$_2$H$_5$)$_4$.

[b] br = broad peak, s = strong intensity, vs = very strong, m = medium, w = weak, vw = very weak, sh = shoulder.

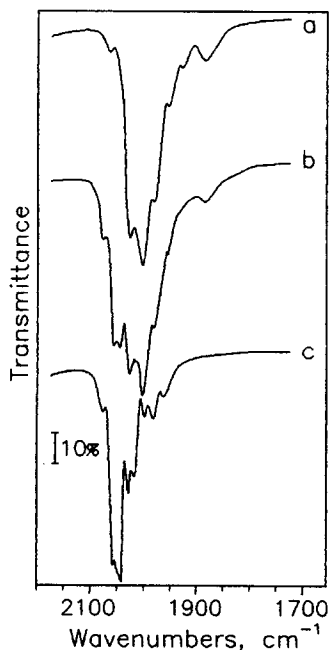Fig. 2. Infrared spectra of (a) [Fe$_4$RhC(CO)$_{14}$][TEA] in CH$_3$CN, (b) compounds extracted with CH$_2$Cl$_2$ from [Fe$_5$RhC(CO)$_{16}$][TEA]/SiO$_2$ following its treatment by CO+H$_2$ flow for 2 h at 150°C, (c) Fe$_4$Rh$_2$C(CO)$_{16}$ in CH$_2$Cl$_2$.

of the [TEA][1]/SiO$_2$ sample by syn-gas for 1 h at 50°C. In this case infrared bands of carbonyl compounds extracted from the solid coincide in fact with those of individual **2** (Table 1). Only a band at 1841 cm^{-1} indicates that small amounts of **1** are still present in the solution.

Rhodium was not detected by X-ray fluorescence analysis of the [TEA][1]/SiO$_2$ sample after its thermolysis both in syn-gas and Ar medium followed by extraction of carbonyl compounds. This shows that transformation of **1** to **2** occurs with very high selectivity. It is worth noting that conversion of **1** to **2** in solution is well known [11,18]. However, the selectivity of the process in these cases was equal to 70% when the reaction was carried out in diglyme media [11] and 92% towards the mixture of **2** and Fe$_4$Rh$_2$C(CO)$_{16}$ which was derived from **1** in the conditions of liquid-phase hydroformylation of pentene-1 (100°C, 60 atm, 1CO+1H$_2$) [18].

Infrared bands at 2072(vw), 2055(m), 2045(m), 2026(s), 2017(sh), 2000(vs), 1982(m sh), 1956(w) and 1880(w) cm^{-1} (Fig. 2, Table 1) were observed in IR spectra of

carbonyl compounds extracted from [TEA][1]/SiO$_2$ following treatment in CO+H$_2$ flow at 150°C for 2 h. The bands at 2026, 2000, 1982, 1956 and 1880 cm^{-1} are assigned to **2** [11] and those at 2072, 2055, 2045, 2026 and 1982 cm^{-1} to Fe$_4$Rh$_2$C(CO)$_{16}$. These measurements show the absence of initial cluster in the extract. Only trace amounts of rhodium on silica following extraction were found by means of X-ray fluorescence spectroscopy. Increasing the exposure of [TEA][1]/SiO$_2$ in syn-gas flow at 150°C up to 5 h resulted in the appearance in the extract of [Fe$_3$Rh$_3$C(CO)$_{15}$]$^-$. This cluster was identified by infrared spectroscopy of KBr pellets of the residue obtained by evaporation of the extract to dryness. The thermolysis of [TEA][1]/SiO$_2$ under Ar at 150°C led to similar changes as under syn-gas. However, in this case negligible amounts of Rh were detected on silica surface following extraction with CH$_2$Cl$_2$.

The treatment of [TEA][1]/SiO$_2$ sample at 250°C for 2 h resulted in complete decarbonylation of supported cluster under any gas medium.

Silica supported **2** was not markedly transformed in flowing CO+H$_2$ at temperatures below 150°C. The bands which do not relate to **2** were revealed by infrared spectroscopy of the solution obtained by extraction with CH$_2$Cl$_2$ from [TEA][**2**]/SiO$_2$ only following treatment in flowing syn-gas at 150°C for 3 h. At 10 h exposure of supported cluster infrared bands of the solution were observed at 2062(vw), 2016(s), 2002(sh), 1980(m), 1956(w), 1877(w) and 1852(vw) cm^{-1} (Fig. 3, Table 1). The band at 2016 and two bands at 1878 and 1850 assigned to bridging-bonded CO [11] indicate unambiguously that transformation of **2** into [Fe$_3$Rh$_3$C(CO)$_{15}$]$^-$ hexanuclear cluster occurs on the silica surface.

It is worth noting that none of the IR spectra of carbonyl compounds extracted had absorption bands which could be assigned to homonuclear clusters of Fe or Rh.

3.2. ^{57}Fe Mössbauer spectroscopy data

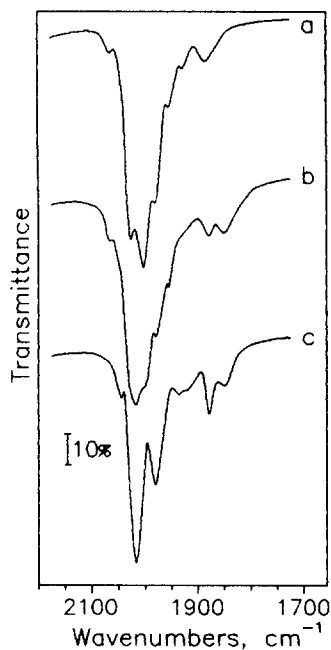The valence state of Fe in individual **1** and in **1** deposited on silica followed by exposure in

Fig. 3. Infrared spectra of (a) $[Fe_4RhC(CO)_{14}][TEA]$ in CH_3CN, (b) compounds extracted with CH_2Cl_2 from $[Fe_4RhC(CO)_{14}][TEA]/SiO_2$ following its treatment by $CO + H_2$ flow for 10 h at 150°C, (c) $[Fe_3Rh_3C(CO)_{15}][TEA]$ in CH_2Cl_2.

$CO + H_2$ flow at different temperatures was studied by Mössbauer spectroscopy. The Mössbauer spectrum of individual 1 was resolved into two pairs of quadrupole doublets (I.S., Q.S. = 0.33, 0.57 and 0.50, 0.94 mm/s, respectively) by computer fitting. It suggests that iron atoms occupy chemically unequivalent positions in the cluster framework. Most likely these are the *cis*- and *trans*-positions relative to rhodium atoms in octahedral 1, taking into account that the ratio of the peak areas of Fe_1^0/Fe^0 was 4.

Depositing [TEA][1] on silica surface led to the additional pair of quadrupole doublets assigned to Fe^{2+} (I.S. = 1.26, Q.S. = 2.28 mm/s). The relative contribution of this iron state into the integral spectrum increased following treatment of [TEA][1]/SiO_2 sample by flowing syn-gas at 50°C. At moderate temperature and in the absence of oxygen the appearance of Fe^{2+} ions on silica surface could be due to the oxidation of Fe atoms eliminated from 1 by surface OH-groups [19–21]. When the temperature of the treatment of [TEA][1]/SiO_2 sample by syn-gas increases from 50°C to 150°C, the Fe^{2+} peak area increases
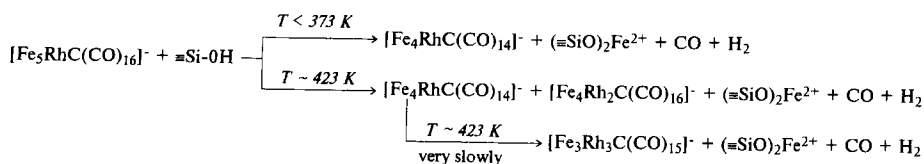
too. As evidenced by IR spectroscopy data, supported 1 transforms into mixtures of 2 and $Fe_4Rh_2C(CO)_{16}$ at 150°C. Formation of the last cluster could result in additional releases of Fe which could be oxidized by silica surface.

The treatment of silica supported 1 by syn-gas at 250°C resulted in complete decomposition of carbonyl compounds and hydrocarbon formation was observed at these conditions. Simultaneously Fe^{3+} (I.S. = 0.65, Q.S. = 0.90 mm/s) emerged on the support. Reduction of [TEA][1]/SiO_2 sample by H_2 led to an increase of the Fe^0 surface area in Mössbauer spectra and corresponding decrease in Fe^{2+} surface area. The Fe^{3+} fraction in this case remained almost the same compared to that for sample treated by syn-gas at 250°C.

From the preceding the transformation of silica supported 1 at the temperature ≤ 150°C can schematically be described in Scheme 1. Although in the present research there was no attempt to detect gaseous products during supported clusters transformation, they should be formed for mass balance and they were found in [19–21] where related transformations were studied. Since no homonuclear carbidocarbonyl iron clusters were revealed in the process of thermolysis of supported FeRh clusters, the fate of interstitial carbon atom remains unclear and needs further investigation. These atoms may form iron carbides in an inert atmosphere or hydrocarbons in the presence of hydrogen.

3.3. Electron microscopy study

The study of reduced at 350°C catalysts derived from FeRh carbonyl clusters with electron microscopy showed that all samples contained homogeneous metal particles with the size of ca. 0.5 nm. This value is close to the size of hexanuclear cluster framework [11]. Reduced at 350°C Rh_4/SiO_2 derived from $Rh_4(CO)_{12}$ contained Rh particles with a mean size of ca. 2.5 nm. Thus, small sizes and homogeneity of bimetallic particles in reduced catalysts along with the possibility of stabilization of small metal clusters on anchored ions, as reported elsewhere [22], suggests that reduced

$$[Fe_5RhC(CO)_{16}]^- + \equiv Si\text{-}OH \underset{}{\overset{T < 373\ K}{\longrightarrow}} [Fe_4RhC(CO)_{14}]^- + (\equiv SiO)_2Fe^{2+} + CO + H_2$$

$$\xrightarrow{T \sim 423\ K} [Fe_4RhC(CO)_{14}]^- + [Fe_4Rh_2C(CO)_{16}]^- + (\equiv SiO)_2Fe^{2+} + CO + H_2$$

$$\underset{\text{very slowly}}{\xrightarrow{T \sim 423\ K}} [Fe_3Rh_3C(CO)_{15}]^- + (\equiv SiO)_2Fe^{2+} + CO + H_2$$

Scheme 1.

catalysts involve dispersed FeRh particles which interact with Fe^{n+} ions bound chemically with the surface of silica.

3.4. CO hydrogenation on FeRh carbonyl cluster derived catalysts

The results of CO hydrogenation at 5.0 MPa are summarized in Table 2. All the catalysts had initially higher rates for hydrocarbons and lower rates for oxygenates, but changed gradually to oxygenate-producing catalysts. In each case, the catalytic activity slightly increased for the first 2–5 h on stream, then reached a steady state and remained constant for many subsequent hours.

Rh_4/SiO_2 catalysts prepared from $Rh_4(CO)_{12}$ produced hydrocarbons $C_1–C_5$ with 87% selectivity. The selectivity toward oxygenates in products was 13%; mainly methanol was obtained and some amounts of ethanol and propanol were produced. Fe_6C/SiO_2 prepared from an anion cluster

$[Fe_6C(CO)_{16}][TEA]_2$ demonstrated surprisingly high selectivity toward ethanol which reached 13% with 20% toward oxygenates in general. Among hydrocarbon products $C_3–C_4$ olefins prevailed. On all FeRh bimetallic catalysts with the exception of Fe_5RhC/SiO_2 prepared from $[Fe_5RhC(CO)_{16}][TEA]$ selectivities for oxygenates were substantially increased. Notably, the selectivity toward ethanol was strikingly increased on Fe_4RhC/SiO_2 and reached to 38%. Overall selectivity toward oxygenates on this catalyst was more than 70%. Increased selectivity toward methanol was observed for Fe_3Rh_3C/SiO_2 and Fe_4Rh_2C/SiO_2 catalysts. The feature of the latter catalyst is the marked formation of propanol. The FeRh catalysts promote methane formation as well, but relative enhancement of rates for oxygenates was much higher than for methane. Accordingly, the selectivities toward hydrocarbons C_{2+} were decreased from 66% for Rh_4/SiO_2 and 59% for Fe_6C/SiO_2 to less than 3% for

Table 2
CO Hydrogenation on SiO_2-supported Rh, RhFe and Fe carbonyl cluster-derived catalysts [a]

Precursor/SiO_2	At. ratio Fe/Rh	Total specific activity [b]	Selectivity (wt.%) [c,d]					
			CH_4	$C_2–C_3$	C_{3+}	CH_3OH	C_2H_5OH	$C_{3+}OH$
$RhCl_3 \cdot 3H_2O$	0	68	29	55	16	0	0	0
$FeCl_3$	∞	27	28	45	27	0	0	0
$RhCl_3 \cdot 3H_2O + FeCl_3$	4	22	87	9	4	0	0	0
$Rh_4(CO)_{12}$	0	235	21	22	44	8	2	3
$[Rh_3Fe_3C(CO)_{15}][TEA]$	1	8 [e]	40	8	1	28	16	6
$Rh_2Fe_4C(CO)_{16}$	2	11 [e]	55	7	1	15	5	17
$[RhFe_4C(CO)_{14}][TEA]$	4	267 [e]	24	2	<1	33	38	2
$[RhFe_5C(CO)_{16}][TEA]$	5	37	76	7	3	12	1	<1
$[Fe_6C(CO)_{16}][TEA]_2$	∞	17	21	33	26	5	13	2

[a] Reaction conditions: catalyst 0.3 g, total metal loading 2 wt.%, reaction temperature $300°C \pm 2°C$, $CO/H_2 = 1$, total pressure 5.0×10^6 Pa, space velocity 1000 h^{-1}, prior to catalytic run all the catalysts were reduced by H_2 at 325°C for 1 h.
[b] $mmol_{CO} \cdot (mol_{Rh+Fe})^{-1}$ h^{-1} in 2 h on stream.
[c] Selectivities were calculated in 2 h on stream as follows: $100 \times C_i/\Sigma C_i$, i = carbon number of the product molecule, C_i = weight concentration of the product molecule.
[d] C_{3+}, hydrocarbons with more than 3 carbon atoms in a molecule, $C_{3+}OH$, oxygenates with more than 3 carbon atoms in a molecule.
[e] In 5 h on stream.

Fe$_4$RhC/SiO$_2$. The latter catalyst had the highest catalytic activity, which exceeded that of Rh$_4$/SiO$_2$. The activities of other FeRh catalysts were similar to or even less than that of the Fe$_6$C/SiO$_2$ sample. The reason for this is unclear and needs further investigation. The salt-derived (Fe–Rh)/SiO$_2$ catalyst showed decreased activity and selectivity to oxygenates compared to that on Fe$_4$RhC/SiO$_2$ at the same Fe/Rh ratio of 4.0.

3.5. Hydroformylation of propylene on FeRh cluster-derived catalysts

There is some analogy between olefin hydroformylation and C$_{2+}$-oxygenate synthesis from CO + H$_2$ mixture. Oxygenates in the latter reaction appear to result from migratory insertion of CO adsorbed into the bond between surface metal atom and surface alkyl formed in turn from adsorbed CO and H$_2$ by the consequence of elementary steps [23–26]. The key step of olefin hydroformylation is also migratory CO insertion [27]. Hence, this reaction can be chosen to evaluate the ability of active sites for CO insertion.

The results of propylene hydroformylation on silica-supported FeRh cluster-derived catalysts are provided by Table 3. In all runs, the activity reached the steady state after 4–6 h on stream and remained constant for many subsequent hours.

Under the reaction conditions of 200°C and 0.1 MPa hydrogenation of propylene to propane dominates over hydroformylation on Rh$_4$/SiO$_2$. The selectivity toward oxygenates is only 17%. On Fe$_6$C/SiO$_2$ derived from [Fe$_6$C(CO)$_{16}$][TEA]$_2$, neither hydroformylation nor hydrogenation were observed under the reaction parameters used.

The activity for hydroformylation on the catalysts derived from FeRh carbidocarbonyl clusters was increased. For example, the rate for oxygenates for Fe$_4$RhC/SiO$_2$ was improved by factor 6 compared with Rh$_4$/SiO$_2$ sample. All the FeRh catalysts with the exception of Fe$_4$RhC/SiO$_2$ showed suppressed rates for hydrogenation of propylene. Thus, the selectivity toward oxygenates was substantially increased on the FeRh catalysts: 17% on the Rh$_4$/SiO$_2$, 40–47% on the FeRh/SiO$_2$. Mainly propanol-1 was obtained on the FeRh catalysts, although Rh$_4$/SiO$_2$ gave only aldehydes as oxygenates. The selectivity toward normal isomer of oxygenates was slightly affected by the Fe/Rh ratio in initial clusters: it was 77% on Rh$_4$/SiO$_2$ and 65–75% on FeRh cluster-derived catalysts. This implies that Fe does not produce steric hindrance around Rh to insert CO into metal–alkyl bond on the surface of a catalyst.

Thus, the propylene hydroformylation study suggests that supported FeRh carbidocarbonyl clusters could provide mixed FeRh sites which

Table 3
Hydroformylation of propylene on SiO$_2$-supported Rh, RhFe and Fe carbonyl cluster-derived catalysts [a]

Precursor/SiO$_2$	At. ratio Fe/Rh	Specific rate of formation [b], h^{-1}		Selectivity, mol%		
		C$_3$H$_8$	PrCHO + BuOH [c]	Oxygenates [d]	Alcohol [e]	n-Isomer [f]
Rh$_4$(CO)$_{12}$	0	3.27	0.66	17	0	77
[Rh$_3$Fe$_3$C(CO)$_{15}$][TEA]	1	1.26	0.84	40	74	75
Rh$_2$Fe$_4$C(CO)$_{16}$	2	2.99	2.72	47	66	72
[RhFe$_4$C(CO)$_{14}$][TEA]	4	4.47	3.82	46	78	68
[RhFe$_5$C(CO)$_{16}$][TEA]	5	1.43	0.96	40	70	65
[Fe$_6$C(CO)$_{16}$][TEA]$_2$	∞	0	0			

[a] Reaction conditions: catalyst 0.3 g, total metal loading 2 wt.%, reaction temperature 200°C ± 2°C, C$_3$H$_6$/CO/H$_2$/Ar = 1/1/1/7, total pressure 1 × 10^5 Pa, prior to catalytic run all the catalysts were reduced by H$_2$ at 300°C for 1 h.
[b] mol$_{CO}$·(mol$_{Rh+Fe}$)$^{-1}$ h^{-1}.
[c] n- and i-butanal + n- and i-butanol.
[d] (PrCHO + BuOH)/(C$_3$H$_8$ + PrCHO + BuOH) × 100.
[e] BuOH/(PrCHO + BuOH).
[f] (n-PrCHO + n-BuOH)/(PrCHO + BuOH) × 100.
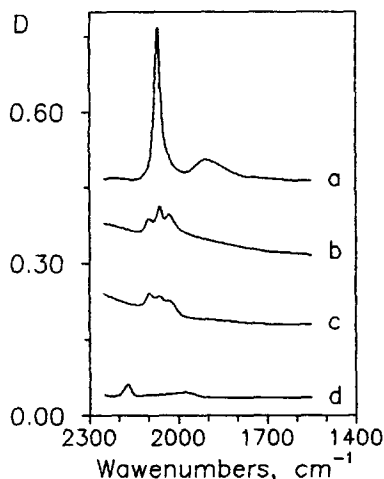
Fig. 4. FTIR spectra of CO adsorbed at 0.45 Torr pressure on (a) Rh_4/SiO_2, (b) Fe_4RhC/SiO_2, (c) Fe_5RhC/SiO_2 and (d) Fe_6C/SiO_2 following H_2 reduction at 350°C for 1 h.

have increased activity for hydroformylation. It is worth noting that similar results were obtained by M. Ichikawa et al. on silica-supported RhFe catalysts derived from RhFe clusters free from interstitial carbon atoms [8,9].

3.6. FTIR spectroscopy of adsorbed CO

FTIR studies of adsorbed CO were carried out for Rh_4/SiO_2, Fe_5RhC/SiO_2, Fe_4RhC/SiO_2 and Fe_6C/SiO_2 following H_2 reduction at 350°C. In the presence of CO, bands due to three CO species were observed (Fig. 4): a linear species at 2072 (Rh_4/SiO_2), 2062 $(FeRhC/SiO_2)$ and 1970 cm^{-1} (Fe_6C/SiO_2), a bridged species at 1920 cm^{-1} (Rh_4/SiO_2) and a geminal dicarbonyl species with twin bands at 2095 and 2035 cm^{-1} $(FeRhC/SiO_2)$. Besides, the relative intensities of the linear species to the geminal dicarbonyl ones in the spectrum of Fe_5RhC/SiO_2 are appreciably suppressed compared to Fe_4RhC/SiO_2. In addition, a band at 2170 cm^{-1} was observed for the Fe_6C/SiO_2 catalyst. The bridging CO band in $FeRhC/SiO_2$ catalysts was completely suppressed. It is worth noting that no low-frequency bands within 1600–1650 cm^{-1} were revealed in $FeRhC/SiO_2$ catalysts. A low-frequency band appeared at ca. 1630 cm^{-1} in $RhFe/SiO_2$ catalysts derived from RhFe carbonyl clusters free of inter-

stitial carbon atoms [8,9] was attributed to C- and O-bonded CO on mixed $Rh–Fe^{3+}$ sites. M. Ichikawa et al. [8,9] suggested that increased activity of such $RhFe/SiO_2$ catalysts toward oxygenates is due to the two-site activation of CO with $Rh–Fe^{3+}$ to enhance the migratory CO insertion into Rh–H and Rh–alkyl and enhance the hydrogenation of resulting formyl or acetyl complexes to methanol or ethanol. However, Fe_4RhC/SiO_2 catalysts derived from carbidocarbonyl $[Fe_4RhC(CO)_{16}]^-$ cluster exceeds Rh_4/SiO_2 in activity. Most of the $FeRhC/SiO_2$ and Fe_6C/SiO_2 catalysts exhibit higher selectivity toward oxygenates compared to that of Rh_4/SiO_2. This indicates that the availability of the two-site activated CO is necessary to provide enhanced activity of a supported metal catalyst. For example, terminal CO adsorbed on Rh^+ was demonstrated to be highly capable in migratory insertion [28]. Perhaps, as for $FeRhC/SiO_2$ catalysts, electron interaction between Rh, Fe and carbide C might have a dominant effect on the catalytic properties in the syn-gas reactions. The research to verify this assumption are in progress.

4. Conclusion

The transformation of silica-supported $[Fe_5RhC(CO)_{16}]^-$ and $[Fe_4RhC(CO)_{14}]^-$ clusters with interstitial carbon atoms have been investigated in CO, syn-gas and Ar media. Complete conversion of the former cluster to the latter was obtained at 50°C in any medium, with $[Fe_4RhC(CO)_{14}]^-$ cluster yielding $Fe_2Rh_4C(CO)_{16}$ and $[Fe_3Rh_3C(CO)_{15}]^-$ mixture at 100–150°C. Simultaneously Fe^{2+} ions emerged on the SiO_2 surface. Mössbauer and electron microscopic studies on the silica-deposited clusters showed that at treatment in any medium in the range of 250–350°C highly dispersed FeRh particles are located on the silica surface, where Fe atoms exist mainly in the oxidized state even after H_2 reduction. Silica-supported catalysts derived from FeRh carbidocarbonyl clusters were found to exhibit increased activity and selectivity

toward oxygenates in CO hydrogenation and C_3H_6 hydroformylation compared to those of mono-metallic cluster-derived catalysts. This activity and selectivity might be due to electron interaction between Rh, Fe and carbide C.

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