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Interaction Between FeRu Bimetallic Carbonyl Clusters and Oxide Supports. IV. $H_2FeRu_3(CO)_{13}$ on Hydrated Silica

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Abstract

Thermal behaviour of $H_2FeRu_3(CO)_{13}$ bimetallic cluster adsorbed on hydrated SiO_2 support was studied by FT-IR spectroscopy. At room temperature the molecules are bonded to the surface with very weak physisorption and partly to surface silanol groups with single and double hydrogen bonds of different strengths. In vacuum $H_2FeRu_3(CO)_{13}$ is much more stable than in hydrogen. $H_4FeRu_3(CO)_{12}$, $H_2Ru_4(CO)_{13}$, $Ru_3(CO)_{12}$, $HRu_3(CO)_{10}(OSi\leqslant)$, $H_4Ru_4(CO)_{12}$, $Ru^0(CO)_2$ and $Ru^{II}(CO)_2$ surface species were traced, and $H_4Ru_4(CO)_{11}L$ (where L is O^{2-} or OH^-) supposed at the different stages of thermal decomposition.

Introduction

In Part II and III of this series, it was shown that iron–ruthenium bimetallic carbonyl clusters, during an interaction with hydrated alumina, decomposed into the same ruthenium anchored surface species $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$, like a pure ruthenium cluster and no CO bonded to iron was found [1]. In the first steps of the interaction, metal–metal bonds split and bimetallic clusters form molecular $Fe(CO)_5$ and $Ru_3(CO)_{12}$. $Fe(CO)_5$ loses CO ligands producing Fe^{2+} and Fe^{3+} anchored ions, while $Ru_3(CO)_{12}$, through intermediate subcarbonyls, decomposes into the ruthenium dicarbonyls mentioned above [2]. This uniform behaviour of bimetallic clusters is due to the high reactivity of OH groups on hydrated alumina surfaces.

On dehydrated silica a milder interaction and, at room temperature, more or less distorted molecules of the starting clusters are expected, as shown for $Ru_3(CO)_{12}$ [3, 4].

On hydrated silica, however, it is questionable as to whether the metal frame of the cluster remains intact. Because, on the basis of qualitative similarity between infrared spectra of solutions and those of silica-supported clusters (which generally show frequency shifts of 10–20 cm^{-1} and some broadening of spectral bands [5]), it is not at all clear, to what extent the integrity of adsorbed molecules holds.

In order to spot original and secondary structures on the silica support, we attempted to use more sophisticated treatment of spectral data [1, 2]. In the series of bimetallic clusters ($Ru_3(CO)_{12}$), $H_2FeRu_3(CO)_{13}$, $FeRu_2(CO)_{12}$ and $Fe_2Ru(CO)_{12}$, on the basis of our preliminary study [5], $H_2FeRu_3(CO)_{13}$ seems to show the highest stability on hydrated silica. This is one of the reasons we have chosen it as the first example for a detailed spectroscopic study.

Experimental

The method given in ref. 6 was applied to produce $H_2FeRu_3(CO)_{13}$. The support was obtained from CABOT CORPORATION (Cab-O-Sil HS5) and heated in vacuum at 573 K for 12 h (by this treatment silica still remains hydrated: hydroxyl monolayer coverage is about 60%), then contacted with the pentane solution of the cluster compound. The supported cluster was dried under vacuum for 12 h and pressed into wafers (10 mg/cm^2), which were then placed in a heatable vacuum IR cell. Infrared spectra under vacuum or H_2 stream were recorded at temperatures ranging from 303 to 700 K. For each spectrum a 200 scan data accumulation was carried out at a resolution of 4 cm^{-1}, using a DIGILAB FTS-20C interferometer equipped with a DATA GENERAL NOVA 3 computer. As reference we used the single-beam spectrum of the sample totally decarbonylated at 700 K. All double-beam spectra were baseline corrected. Difference spectra were obtained using substraction between two spectra taken at different temperatures. First and second derivatives were computed by consecutive numerical derivation of baseline corrected spectra. For analysing the spectra, the sum of maximum 12 Gaussians was fitted to the data points.

Results and Discussion

Baseline corrected spectra recorded at different temperature of the systems $H_2FeRu_3(CO)_{13}/SiO_2/H_2$

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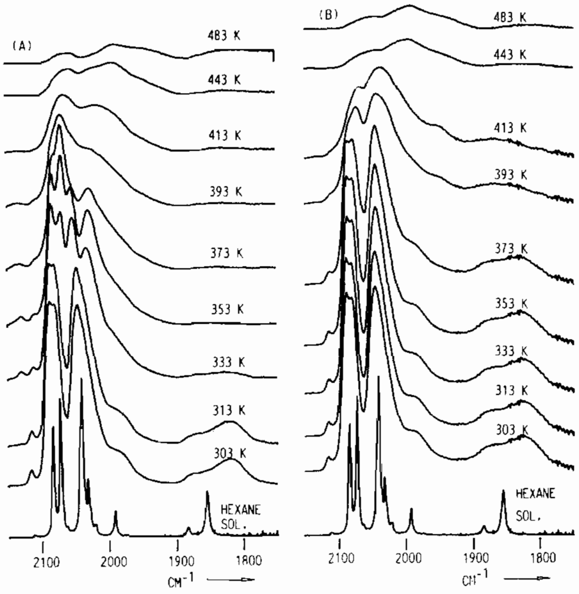

Fig. 1. Infrared spectra of the $H_2FeRu_3(CO)_{13}/SiO_2$ system, recorded during decomposition in hydrogen (A), and in vacuum (B) and the spectrum of $H_2FeRu_3(CO)_{13}$ in n-hexane solution.

and $H_2FeRu_3(CO)_{13}/SiO_2$/vacuum are shown in Fig. 1A and B, respectively. For easier comparison Fig. 1A and B are completed with the spectrum recorded in n-hexane solution. In order to fix accurate positions of the components of the overlapping band systems, we used the first and second derivatives. For the sake of brevity, we do not now present the first derivative spectra, but some representative second derivative spectra are shown in Fig. 2A and B. Using derivative representations of the spectra, a precision of ±1–2 cm^{-1} is possible for bands sharp enough, even if they appear in the original spectra as hardly visible shoulders. To locate broad components, however, derivatives are less valuable. An analysis of the experimental spectrum by fitting the sum of Gaussians to it, however, often helps us to trace broad bands, which are hidden by the overlapping bands.

Decomposition in Hydrogen

Comparing Fig. 1A and B, it is obvious that decomposition in vacuum (Fig. 1B) follows a relatively simple pathway, while in H_2 (Fig. 1A) a large variety of spectral events should take place, which indicates that decomposition produces a rather large number of surface species, all of them resulting in infrared bands in a very narrow spectral range of 1900–2150 cm^{-1}. Therefore the spectral band system to be analysed is the result of multiple overlapping. With the purpose of making the spectral features easier to survey, we have arranged the bands with their assignments into sets, as seen in Table I.

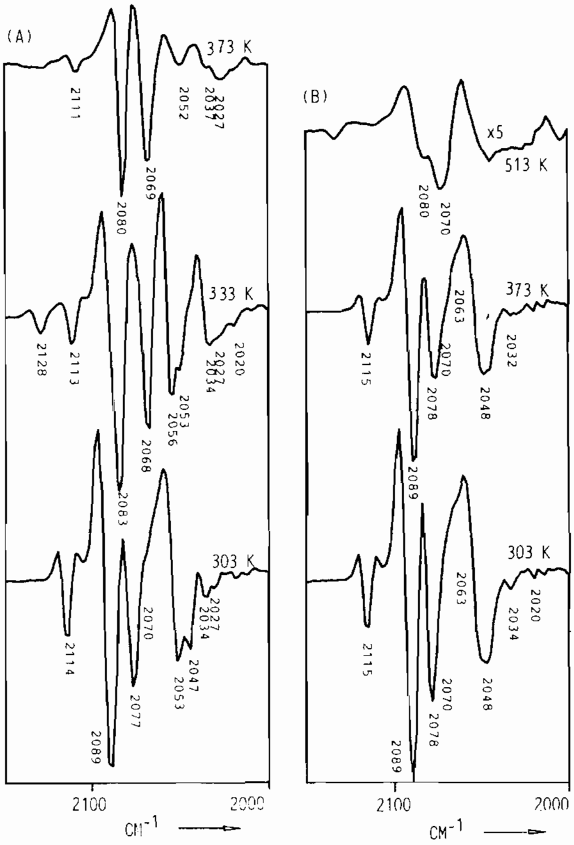

Fig. 2. Some characteristic second derivative spectra calculated from the spectra recorded during decomposition in hydrogen (A) and in vacuum (B).

Frequency set I

The general pattern of the spectra recorded at lower temperatures $T < 333$ K in H_2, (Fig. 1A) suggests that most of the $H_2FeRu_3(CO)_{13}$ molecules are practically intact, and only slightly distorted, because the frequencies and relative intensities of bands of set I (see Table I) assigned to adsorbed molecules (2114w, 2089s, 2077s, 2047vs,br, 2034sh, 1990(±8) cm^{-1}) are close to those in n-hexane solution (2113vw, 2085s, 2074s, 2041vs, 2033m, 1993m). It is apparent that the molecules are present on the surface in a physisorbed state and no sign of bands belonging to crystalline $H_2FeRu_3(CO)_{13}$ has been detected.

Frequency set II

In the system of $H_2FeRu_3(CO)_{13}/SiO_2/H_2$, near room temperature ($T < 313$ K) the spectra (set I) are similar to those recorded in vacuum (see later) indicating physisorbed $H_2FeRu_3(CO)_{13}$ on the surface. On heating the supported cluster in H_2, dramatic changes take place at rather low temperatures. At 333 K a new set of bands (set II) appears at the frequencies 2128w, 2083s, 2070s, 2053 and 2032s cm^{-1}.

TABLE I. Infrared Spectral Data

Grouping of exp. IR bands	Frequency (cm^{-1})	Assignment	Reference
In solution	2113vw, 2085s, 2074s, 2041vs, 2033m, 1993m	$H_2FeRu_3(CO)_{13}$	this work
Set I	2114w, 2089s, 2077s, 2047vs,br, 2034m, 1990m,br	$H_2FeRu_3(CO)_{13}$	this work
In solution	2085s, 2070s, 2054s, 2044vw, 2031m,br, 2012w, 1998w, 1990w	$H_4FeRu_3(CO)_{12}$	8
In solution	2083s, 2068s, 2056s, 2033m, 2026s, 2008w, 1880w	$H_2Ru_4(CO)_{13}$	9
Set II	2128w, 2083s, 2070s, 2053s, 2032s,br	$H_4FeRu_3(CO)_{12}$ $[H_2Ru_4(CO)_{13}]$	this work
In solution	2081s, 2067vs, 2030m, 2024s, 2009w	$H_4Ru_4(CO)_{12}$	8
In solution	2113vw, 2077s, 2068s, 2034sh, 2030vs, 1997w	$HRu_3(CO)_{10}Cl$	15
In solution	2112w, 2078s, 2068s, 2033vs, 1995m,sh	$HRu_3(CO)_{10}(OSi\leqslant)$	4
Set III	2134w, 2080s, 2069vs, 2027m	$H_4Ru_4(CO)_{12}$ $[HRu_3(CO)_{10}(OSi\leqslant)]$	this work
Set IV	2055m, 1986m	$Ru^0(CO)_2$	this work
Set V	2074w, 2008w	$Ru^{II}(CO)_2$	this work
	2097m, 2046s, 2030sh, 2023sh, 2014s, 1998w	$Ru_3(CO)_{11}(PPh_3)$	13
	2094m, 2086w, 2067s, 2055s, 2053sh, 2038w, 2027s, 2015m, 2008s	$H_4Ru_4(CO)_{11}(PPh_3)$	14
Set VI	2096w, 2069, 2055, 2046, 2034, 2024m, 2008w	$H_4Ru_4(CO)_{11}L$ $[Ru_3(CO)_{11}L]$	this work

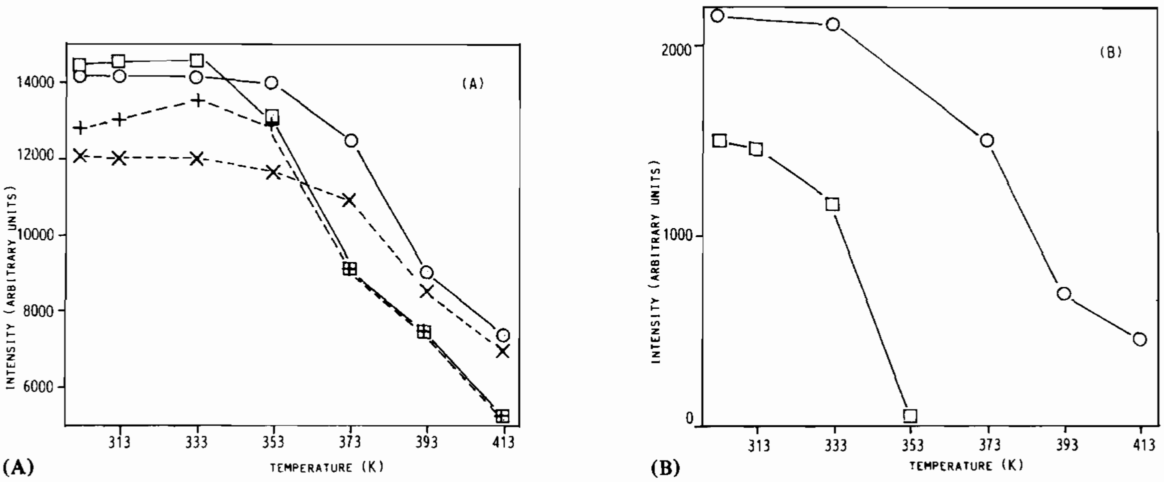

Fig. 3. Integrated intensities calculated (A) in the spectral range of +, terminal carbonyls (in hydrogen); □, terminal carbonyls + bridging carbonyls (in hydrogen); X, terminal carbonyls (in vacuum); ○, terminal carbonyls + bridging carbonyls (in vacuum); (B) □, bridging carbonyls (in hydrogen); ○, bridging carbonyls (in vacuum).

The frequencies of set II are very close to those of $H_2Ru_4(CO)_{13}$ and $H_4FeRu_3(CO)_{12}$.

Formation of $H_2Ru_4(CO)_{13}$ from $H_2FeRu_3(CO)_{13}$ is possible, if we suppose a reaction starting with decomposition into $Ru_3(CO)_{12}$ [7], which then reacts with H_2 producing $H_2Ru_4(CO_{13}$. This reaction, however, would be accompanied by a loss of 4 CO per one molecule of $H_2FeRu_3(CO)_{13}$. As seen in Fig. 3A, in the temperature range where set II starts developing, the total integrated intensity of the CO stretching band system is practically constant, which stands against the formation of $H_2Ru_4(CO)_{13}$ as a high percentage product.

On the other hand, $H_4FeRu_3(CO)_{12}$ can easily be formed in the facile reaction of H_2 with $H_2FeRu_3(CO)_{13}$ [8]. The frequencies of set II are also somewhat closer to those of $H_4FeRu_3(CO)_{12}$ than to $H_2Ru_4(CO)_{13}$. Furthermore, $H_2Ru_4(CO)_{13}$ contains two bridging carbonyls, which produce a band of very low intensity at 1880 cm^{-1} [9], while $H_4FeRu_3(CO)_{12}$ does not. In the frequency range of bridging carbonyl stretching modes in set II no band has been practically found [7], further reducing the probability of the presence of $H_2Ru_4(CO)_{13}$ as a main product. The reaction $H_2FeRu_3(CO)_{13} + H_2 = H_4FeRu_3(CO)_{12} + CO$ is also accompanied by a loss of carbonyl, but only one CO per molecule.

Figure 3B shows the temperature dependence of the integrated intensity of bridging carbonyl stretching modes. It is seen that at room temperature the intensity is already lower in H_2 than in vacuum, and that with increasing temperature the intensity drastically decreases. This decrease of bridging carbonyls and increase of terminal ones suggests the reaction converts bridging carbonyls into terminal groups. The sum of intensities of both terminal and bridging carbonyl stretching modes is constant (or slightly increasing) between $T = 303–333$ K indicating that the intensity of terminal carbonylic bands has increased in this temperature range at the expense of decreasing bridging ones. It is worth mentioning that the overall integrated intensity in this low temperature range is at the same level in both vacuum and H_2. All this behaviour of intensities seriously supports the assignment of set II to $H_4FeRu_3(CO)_{12}$ as the main product, and $H_2Ru_4(CO)_{13}$ should be considered as a byproduct of lower concentration.

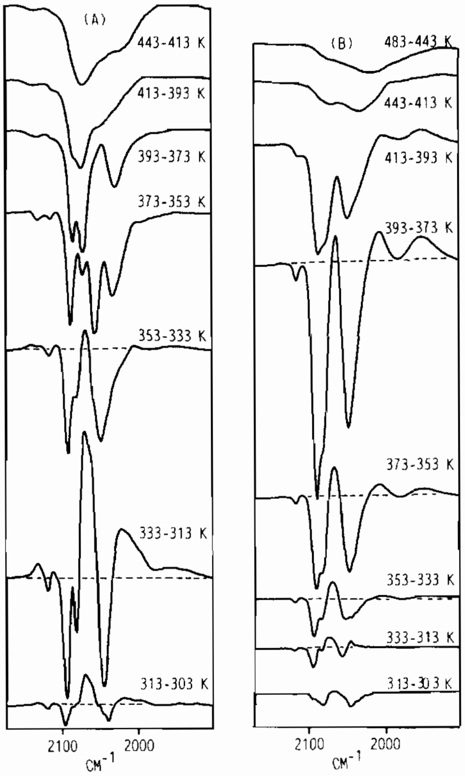

Fig. 4. Difference spectra calculated from the spectra of Fig. 1A (A) and Fig. 1B (B).

Frequency set III

At higher temperatures of $T > 353$ K, a third set of bands (set III) develops, with frequencies 2134w,br, 2080m, 2069s, and 2027m cm^{-1}.

The frequency set III also offers alternative assignments:

(a) The frequencies are rather close to those of $H_4Ru_4(CO)_{12}$ [10]. The formation of $H_4Ru_4(CO)_{12}$ is possible in a reaction, where as a first step Fe–Ru bonds in $H_4FeRu_3(CO)_{12}$ split by thermal activation.

(b) An assignment of set III to the surface grafted hypothetical $HRu_3(CO)_{10}(OSi\leqslant)$ is also possible which would also be in good agreement with recent literature data. Choplin *et al.* [11] investigating the reactivity of bimetallic cluster $H_2FeOs_3(CO)_{13}$ with silica support, concluded that by thermal activation of the physisorbed molecules, at *ca.* 400 K, in argon, Fe–Os bonds cleaved, and Os_3 fragments grafted to the surface, giving species $HOs_3(CO)_{10}(OSi\leqslant)$. The same surface species has also been supposed in the reaction of $Os_3(CO)_{12}$ with silica at 373–423 K [12], and the analogous ruthenium surface species $HRu_3(CO)_{10}(OSi\leqslant)$ in the reaction of $Ru_3(CO)_{12}$ with silica [4].

However, we have some doubts in assigning the frequency set III to $HRu_3(CO)_{10}(OSi\leqslant)$ rather than to $H_4Ru_4(CO)_{12}$, because

(i) Grafting of M_3 fragments to silica is supposed to occur by oxidative addition of one silanol group to an M–M bond [11]. In our case, however, the presence of H_2 is much more favourable to developing set III than in vacuum: in vacuum set III is only detectable in traces.

(ii) In the case of the cited papers, on hydrated silica IR bands of type set III develop in argon [4, 11, 12], or rather on silica dehydroxylated at 770 K [4].

In conclusion, we believe that at the moment no decisive spectroscopical evidence exists which could undoubtedly prove whether set III is to be assigned to $H_4Ru_4(CO)_{12}$ or to $HRu_3(CO)_{10}(OSi\leqslant)$, but the conditions are more favourable to $H_4Ru_4(CO)_{12}$ and, therefore, we consider it as the main component of the surface species existing at higher temperatures in H_2.

The difference spectra calculated from the spectra recorded in H_2 (Fig. 4A), at lower temperatures show both positive and negative peaks. Negative peaks indicate disappearing species, while positive peaks belong to new ones forming on the surface when heating the sample. Between $T = 303–353$ K the difference spectra are dominated by the decrease of the spectral bands of the original $H_2FeRu_3(CO)_{13}$ (set I) and by the development of new band systems, apparently by those of set II and set III. Above 353 K, there is no sign of positive peaks. Difference spectra of 373–353 K practically contain the peaks of set II, only, and consequently set III has not developed at the expense of set II. It seems that both set II and set III have simultaneously developed

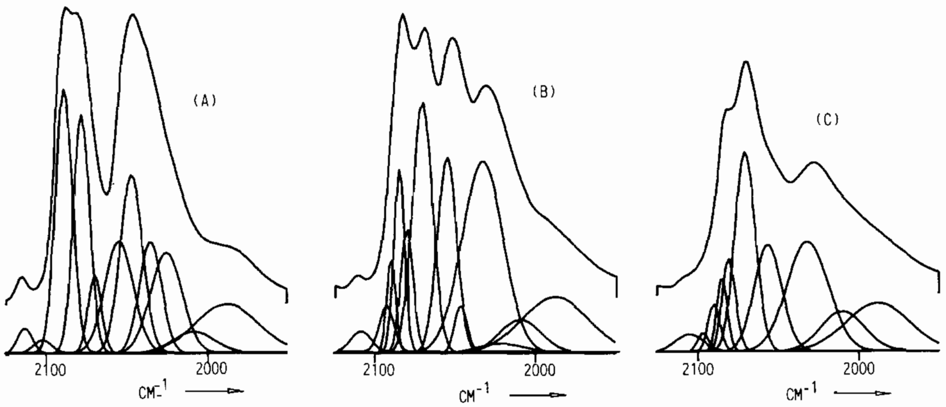

Fig. 5. Gaussian components calculated from the spectra recorded in the systems of $H_2FeRu_3(CO)_{13}/SiO_2/H_2$ at the temperatures (A) T = 303 K; (B) T = 333 K and (C) T = 373 K.

in the temperature range of 303–353 K, however, their thermal stability is different: surface species producing the bands of set II ($H_4FeRu_3(CO)_{12}$ and $H_2Ru_4(CO)_{13}$) mainly decompose in one step between 333–353 K, while those assigned to set III ($H_4Ru_4(CO)_{12}$ and $HRu_3(CO)_{10}(OSi\leqslant)$) start decomposing above 353 K, and their decomposition occurs in a very large temperature range of 373–443 K.

It should be mentioned that the broad positive band in the difference spectra occurring at about 2070–2060 cm^{-1} at lower temperatures might indicate, beside the increase of $H_4Ru_4(CO)_{12}$, developing $Ru_3(CO)_{12}$, too. Therefore, $Ru_3(CO)_{12}$ as an intermediate in the very complex surface reactions at lower temperatures is not excluded, supporting the possibility of forming $H_2Ru_4(CO)_{13}$, which was above supposed to be responsible for the bands of set II, as a product of lower concentration beside the main product of $H_4FeRu_3(CO)_{12}$.

Analysis of the Spectra by Fitting Gaussians

Frequency sets I–III have been traced using original spectra, derivatives and difference spectra. There must be, however, additional bands in the carbonylic band system, which cannot be traced by these means, because of being either very broad, or laying too close to another band to be resolved by the above treatments. In Figs. 5A–C are shown the results of the analysis of three characteristic spectra, namely those recorded in H_2 at 303, 333 and 373 K, respectively, performed by fitting Gaussians to the baseline corrected experimental spectra. In Table II are collected the numerical data of the analysis and the assignments of the Gaussian components.

Consulting Figs. 5A–C and Table II, first we can see that

(i) Traces of the original $H_2FeRu_3(CO)_{13}$ physisorbed molecules can be detected up to 373 K as indicated by the components at 2089 and 2046 cm^{-1} (the second band at 373 K was not resolvable), which belong to frequency set I.

(ii) Bands belonging to both set II and set III are already detectable at 303 K indicating the presence of surface molecules $H_4FeRu_3(CO)_{12}$ (+ $H_2Ru_4(CO)_{13}$) and $H_4Ru_4(CO)_{12}$ (+ $HRu_3(CO)_{10}(OSi\leqslant)$) at a very early stage of cluster support interaction.

(iii) In the same manner, surface molecule $H_4FeRu_3(CO)_{12}$ (+ $H_2FeRu_3(CO)_{13}$) does not totally collapse at 373 K (see the component at 2084 cm^{-1}).

(iv) New components indicate the presence of additional frequency sets and so further surface species.

Frequency set IV

The integrated intensity of the band at about 1986 cm^{-1} roughly changes parallel with that of 2055 cm^{-1}. The band at 2055 cm^{-1} is also a component of set II, but its very high intensity allows it to be assigned to two sets (II and IV) at the same time. The position of the bands of set IV, its shape (broadness) and the stability up to very high temperatures (483 K) suggests it belongs to the dicarbonylic anchored surface species of the type experienced in the case of alumina support ($Ru^0(CO)_2$, where carbonyls are bonded to non oxidised ruthenium atoms, or clusters of ruthenium atoms [1]).

Frequency set V

The relatively broad band at 2008 cm^{-1}, although the pair of this band expected at about 2074 cm^{-1} is not resolved, must indicate the presence of the anchored dicarbonyl of oxidized ruthenium $Ru^{II}(CO)_2$, analogous to that found on alumina [1, 2].

Frequency set VI

The weak band about 2096 cm^{-1}, as the only resolvable component of a hypothetical frequency set, may indicate the presence of a polynuclear ruthenium cluster derived from $Ru_3(CO)_{12}$ or H_4-

TABLE II. Numerical Data of Gaussian Components of Spectra in Figs. 5A–C

Wavenumber (cm^{-1})	Gaussian width (cm^{-1})	Amplitude (abs. ×100)	Intensity (arbitrary units)	Ampl/GW	Assignment
$H_2FeRu_3(CO)_{13}/SiO_2/H_2$ T = 303 K					
2115	4.5	16	180	3.6	set I
2102	5.5	8.6	118	1.6	set VI
2088.6	5.3	165	2192	31.1	set I
2077.6	5.1	149	1904	29.2	set I, III
2069.3	4.2	49	515	11.7	set II, III, VI
2053.8	9	70	1579	7.8	$Ru^0(CO)_2$, set II, IV, VI
2046	7	111.5	1956	16	set I, VI
2034	7	70	1228	10	set I, II, III, VI
2024	10	63	1579	6.3	set VI
2007	13	14	456	1.1	$Ru^{II}(CO)_2$
1986	20	31	1554	1.5	$Ru^0(CO)_2$
$H_2FeRu_3(CO)_{13}/SiO_2/H_2$ T = 333 K					
2111	6.2	13	202	2.1	set I
2094.8	4.6	29	334	6.3	set VI
2089.6	2.8	60	421	21.4	set I
2084.6	3.4	115	980	33.8	set II
2079.6	4	77	772	19.6	set I, III
2069.9	6.3	156	2463	24.8	set II, III, VI
2054.5	6	122	1834	20.3	$Ru^0(CO)_2$, set II, IV, VI
2045.6	4	30	300	7.5	set I, VI
2032	13	119	3877	9.2	set I, II, III, VI
2020	15	6	225	0.4	set VI
2008	13	21	684	1.6	$Ru^{II}(CO)_2$
1986	21	35	1842	1.7	$Ru^0(CO)_2$
$H_2FeRu_3(CO)_{13}/SiO_2/H_2$ T = 373 K					
2105	9	11	248	1.2	
2096	3.6	12	108	3.3	set VI
2089	3.8	30	285	7.9	set I
2084	3.3	47	388	14.2	set II
2079.6	4.2	58	610	13.8	set I, III
2069.3	6.4	124	1989	19.4	set II, III, VI
2055	8.7	66	1439	7.6	$Ru^0(CO)_2$, set II, IV, VI
2030	13	68	2215	5.2	set I, II, III, VI
2008	13.6	25	852	1.8	$Ru^{II}(CO)_2$
1986	20	30	1503	1.5	$Ru^0(CO)_2$

$Ru_4(CO)_{12}$, in which one of the carbonyls is substituted with some other ligand on the surface like O^{2-} or OH^- surface ions, both electron donors. On the basis of spectral data of analogous $Ru_3(CO)_{11}(PPh_3)$ [13] and $H_4Ru_4(CO)_{11}(PPh_3)$ [14] compounds, an assignment to $H_4Ru_4(CO)_{11}L$ ($L = O^{2-}$ or OH^-) surface molecule seems to be more reasonable (see Table I).

In Table II we have also given the ratios R = amplitude/halfwidth. In Part II and III of this series [1, 2] it was shown that this ratio was very characteristic of the nature of surface species, the band in question was assigned to. In the case of physisorbed molecules, or molecule-like species the ratio was rather large ($R > 1$–4). Beside molecules, for surface anchored species $Ru^{0-III}(CO)_2$ R was about 1–4, while the same dicarbonyls, if they were in an incipient stage, that is not anchored yet, produced a value of $R < 1$. In Table II the R = amplitude/halfwidth ratios for the bands of $Ru^0(CO)_2$ and $Ru^{II}(CO)_2$ suggest these dicarbonyls are anchored onto the silica surface, just as in the case of alumina. Furthermore, and in contrast to the case of hydrated alumina, all surface species on silica may be regarded as molecules bonded with weak forces, because *R* is practically always larger than 1, and no mobile fragments of non defined structures have been found.

Decomposition in Vacuum

In vacuum, up to 373 K, the spectra are governed by the bands of set I, that is the surface contains first of all slightly distorted adsorbed $H_2FeRu_3(CO)_{13}$ (Figs. 1B, 2B, 3A and B). However difference spectra (Fig. 4B), at lower temperatures also show positive peaks just as in H_2; first of all a rather broad one centered at about 2065 cm^{-1}, which indicates that, although in a smaller part only, when heated $H_2FeRu_3(CO)_{13}$ is transforming into similar surface species as found at decomposition in H_2. At temperatures higher than 413 K, in both vacuum and H_2, all surface species of polynuclear metal frames are supposed to decompose into monometallic subcarbonyls.

Bridging Carbonyls

We have also performed [7] a detailed spectroscopic study of bridging carbonyls of $H_2FeRu_3(CO)_{13}$ adsorbed on SiO_2 and Al_2O_3. We found that on SiO_2 surface three main bridging structures could be distinguished:

(1) The first one is a double bridging system characterized by the frequencies 1886 and 1845 cm^{-1} (see Table 2 in ref. 7), which is analogous to that of an unperturbed molecule and is stable in vacuum up to high temperatures (413 K). We think that molecules with this type of bridging carbonyl must be rather mobile in the surface layer.

(2) The second, also a double bridging system, is more perturbed and may be bonded to surface sites of weak acidity by weak hydrogen bonding, because the shift of the CO stretching bands to lower frequencies is small (15–20 cm^{-1}). On the other hand, the angle between the C–O bonds of both bridging carbonyls, which in the free molecule is very large (141°) significantly closes (63°) on the surface [7], suggesting that both bridging carbonyls of the molecule enter into hydrogen bonding with two adjacent silanol groups on the surface.

(3) The third type of bridging structure is a monobridging one with very low frequency (1820 cm^{-1}) that suggests a strong bonding to the surface. We think that molecules with this type of bridge should be in an activated state, and decomposition or transformation starts on these molecules.

Conclusions

(a) In contrast to interaction with hydrated alumina, where the carbonylic cluster rapidly decomposes into mononuclear dicarbonyls, $H_2FeRu_3(CO)_{13}$ at room temperature, from solution, is adsorbed on the surface of hydrated silica in the form of unperturbed or slightly perturbed molecules, which are characterized with the spectral bands named set I (2114w, 2089s, 2077s, 2047vs,br, 2034sh, 1990m,br cm^{-1}).

(b) The link to the surface is partly very weak physisorption, partly weak hydrogen bonding between two bridging carbonlys to two adjacent silanol groups, and partly strong hydrogen bonding between one bridging carbonyl of a distorted molecule and one surface silanol group.

(c) In H_2 the molecules rapidly decompose or transform into different surface cluster species at relatively low temperatures ($T < 333$ K).

(d) The first main group of new surface species is characterized with the bands named set II (2118w, 2083s, 2070s, 2053s, 2032s,br cm^{-1}), that may be assigned to $H_4FeRu_3(CO)_{12}$ as the main product, and to $H_2Ru_4(CO)_{13}$ as a product of lower concentration. This group of surface species is stable in the temperature range of 303–373 K. At this stage of surface reactions, decomposition into $Ru_3(CO)_{12}$ is also supposed.

(e) The second type of new surface species is characterized with the spectral band set III (2134w, 2080s, 2069vs, 2027m cm^{-1}), which is to be assigned to $H_4Ru_4(CO)_{12}$ and partly to $HRu_3(CO)_{10}(OSi\lessgtr)$. This group of surface species already exists at room temperature, its concentration increases with increasing temperature and it is stable up to 413–443 K.

(f) The next two surface species characterized with frequency set IV (2055m and 1986 m cm^{-1}) and set V (2074w and 2008 cm^{-1}) are the dicarbonyl of non oxidized ruthernium $Ru^0(CO)_2$, and that of double oxidized $Ru^{II}(CO)_2$, analogous to the anchored dicarbonyls found on alumina surfaces. They are already detectable at room temperature and the non oxidized species in hydrogen is stable up to very high temperatures (483 K).

(g) The presence of further surface species is also indicated with additional spectral bands, their assignment, however is uncertain. The presence of $Ru_3(CO)_{11}L$, or more probably $H_4Ru_4(CO)_{11}L$, is supposed, where L is O^{2-} or OH^- that substitutes one CO group of the dodecacarbonylic clusters.

(h) In vacuum the molecules preserve their entity up to rather high temperature of about 373 K.

(i) Transformation of $H_2FeRu_3(CO)_{13}$ on silica into new surface species in vacuum also occurs, but in traces only; except $Ru^0(CO)_2$ and $Ru^{II}(CO)_2$, which are present on the surface at concentrations comparable to those found in hydrogen.

(j) In contrast to hydrated alumina, on hydrated silica no mobile subcarbonyls of undefined structure have been detected. The lack of large amounts of mononuclear subcarbonyls and the fact that three- and four-nuclear molecules dominate on the surface, suggests that during transformations of the molecules the first step of the surface reaction is not necessarily the cleavage of all metal–metal bonds of the polynuclear frame, but this frame may be partly reserved. Of course, in a reaction, where an iron atom is replaced by ruthenium, the entity of some $H_2FeRu_3(CO)_{13}$ molecules should collapse, supplying ruthenium atoms to further reactions and, at the same time, forming dicarbonyl species, too, which once anchored to the surface, are excluded from further surface reactions.

(k) The tetranuclear frame of $H_2FeRu_3(CO)_{13}$ seems to be very stable on silica, also in contrast to those of bimetallic FeRu dodecacarbonyl clusters, as will be shown in the following parts of this series.

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