Interaction between FeRu Bimetallic Carbonyl Clusters and Oxide Supports. III. Mechanism of Interaction and Decomposition on Hydrated Alumina

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Abstract

Initial steps of the interaction of $Ru_3(CO)_{12}$, $Fe_3(CO)_{12}$, $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ clusters with hydrated alumina surfaces have been studied by FT-IR spectroscopy combined with data handling procedures. The first stage of the interaction is a pure physisorption. At the second stage the metal–metal bonds split producing a large variety of mobile subcarbonyls. In the case of $Fe_3(CO)_{12}$ the subcarbonyls form molecular $Fe(CO)_5$, while at the bimetallic clusters they form molecular $Fe(CO)_5$ and $Ru_3(CO)_{12}$. $Fe(CO)_5$ loses CO ligands producing Fe^{2+} and Fe^{3+} anchored ions. $Ru_3(CO)_{12}$, through further intermediate subcarbonyls, slowly decomposes into incipient anchored species $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$.

Introduction

Several papers have dealt with the application of bimetallic carbonyl clusters for preparation of highly dispersed supported catalysts [1–4]. It has been shown that the catalysts prepared from a mixture of two monometallic clusters, $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$, had similar catalytic properties as those prepared from bimetallic clusters, $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$ [2].

In our previous paper it was shown that the bimetallic carbonyl clusters, $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$, adsorbed from solutions on hydrated alumina, decomposed into monometallic species like $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$ and iron is oxidized to Fe^{2+} and Fe^{3+} during a 12 h standard drying process in vacuum. The infrared spectra of the Fe_2Ru/Al_2O_3 and H_2FeRu_3/Al_2O_3 systems were practically identical with that of Ru_3/Al_2O_3 [5].

It was not absolutely clear how all these rather different precursors could be transferred into a system in which carbonyls are only bonded to ruthenium atoms forming in all cases the same $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$ species.

We emphasize that all these phenomena hold only for hydrated alumina (hydroxile monolayer coverage higher than 60%) because of its very high reactivity.

In the present paper we attempt to obtain some information about the very first steps of the adsorption–decomposition. Since decomposition of the bimetallic carbonyl clusters contacted with hydrated alumina is generally a rapid process [5], the mechanism could be elucidated only if this surface reaction is slowed down. This can possibly be achieved by the competitive adsorption of a large hydrocarbon molecule, e.g. nujol. By this treatment not only is part of the cluster molecules displaced from the alumina but bond strength between the cluster and alumina controlling the decomposition can be decreased due to the repulsive interaction between the two large molecules. As a net result the rate of decomposition can be brought into a measurable range.

Experimental

Materials

$Fe_3(CO)_{12}$ (STREM Chemicals) and $Ru_3(CO)_{12}$ (ICN Pharmaceuticals) were used without purification. The method given in ref. 6 was applied to produce $Fe_2Ru(CO)_{12}$ and $H_2FeRu_3(CO)_{13}$. Alumina was obtained from Degussa (Al_2O_3C).

The samples were prepared in the following way. The carbonyl clusters were adsorbed on the support evacuated at 570 K overnight from a n-hexane solution and the solvent was evaporated at room temperature. The metal loading was approximately 1%.

Infrared Spectroscopy

Immediately after the evaporation of the solvent the sample was wet with paraffin oil and put between two KBr windows and from time to time a one-scan infrared spectrum was recorded on a Digilab FTS 20 C spectrometer equipped with a Nova-3 computer with a resolution of 4 cm^{-1}. Difference spectra were

obtained by subtracting two spectra taken at two different times.

Results

The IR spectra of the CO stretching region of the carbonyl clusters solved in n-hexane are shown in Fig. 1.

The spectra for the Fe_3/Al_2O_3/nujol system are seen in Fig. 2. The spectrum taken at $t = 0$ essentially resembles that of dissolved $Fe_3(CO)_{12}$, but differs considerably from those taken without nujol. The bands are at the same frequencies but a little broadened, that is less resolved. This pattern suggests that the molecules are slightly perturbed which refers to pure physisorption. We should also notice that there is a very broad band overlapping the band system of the physisorbed molecules. After a while, two sharp bands at 2022 and 2000 cm^{-1} are being developed, whereas the intensity of the bands attributed to $Fe_3(CO)_{12}$ is decreasing. The two new bands can be assigned to $Fe(CO)_5$ because of their characteristic frequencies, relative intensities and shapes [7]. In the first hour of the process the decrease of $Fe_3(CO)_{12}$ dominates which means that there is no strict correlation between the two events. Taking into account the increase of the overlapping broad featureless band (see the first and second difference spectra in Fig. 2) we may suppose that $Fe_3(CO)_{12}$ first results into an undefined structure or series of structures as intermediates for $Fe(CO)_5$.
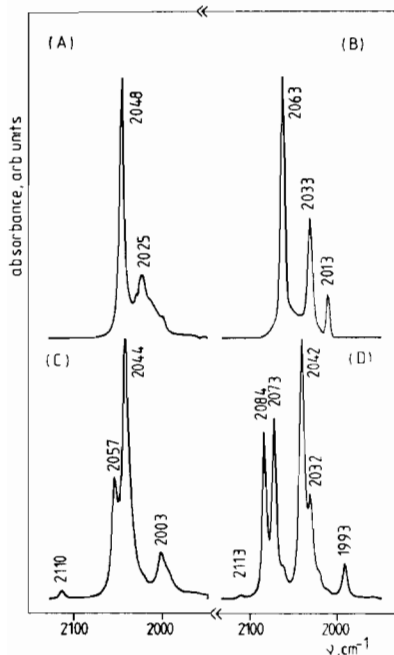

Fig. 1 Spectra of clusters $Fe_3(CO)_{12}$ (a), $Ru_3(CO)_{12}$ (b), $Fe_2Ru_3(CO)_{12}$ (c) and $H_2FeRu_3(CO)_{13}$ (d) in n-hexane solution.
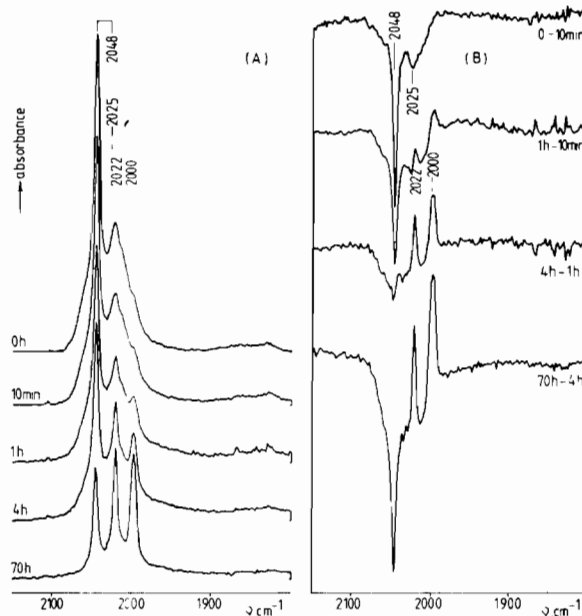

Fig. 2. (a) Spectra of the Fe_3/Al_2O_3/nujol system at different times; (b) difference spectra.
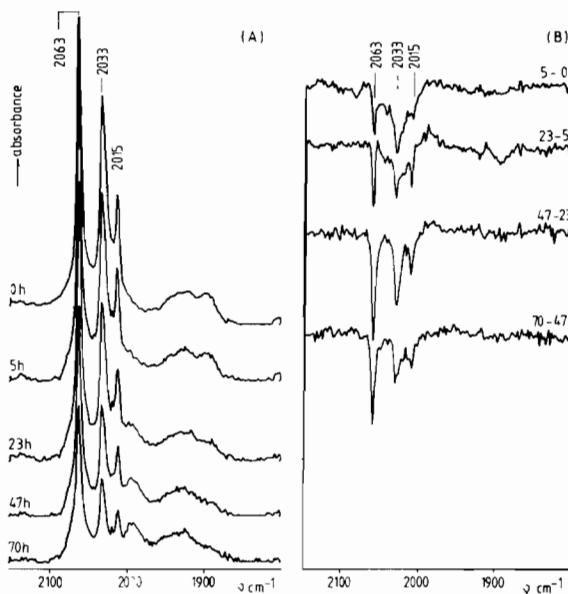

Fig. 3. (a) Spectra of the Ru_3/Al_2O_3/nujol system at different times; (b) difference spectra

Figure 3 shows the spectra of the Ru_3/Al_2O_3/nujol system. $Ru_3(CO)_{12}$ does not follow the mechanism of decomposition found for $Fe_3(CO)_{12}$, because there is no sign of $Ru(CO)_5$ [8]. The sharp band system, assigned as physisorbed $Ru_3(CO)_{12}$, dominates the spectra, overalpping a very broad band system. There is also a new band system of medium broadness containing two components at about 1900 cm^{-1}. The component at about 1890
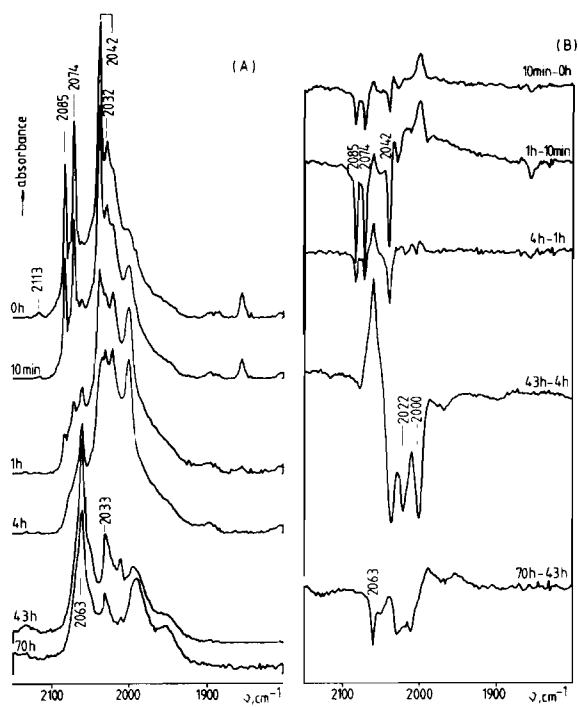
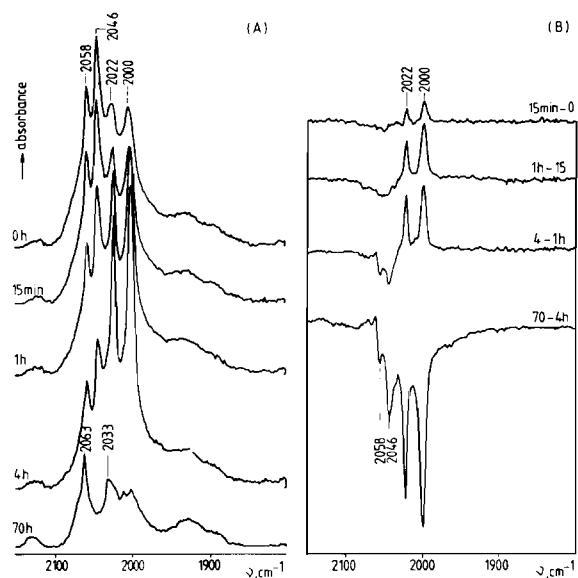Fig. 4. (a) Spectra of the H_2FeRu_3/Al_2O_3/nujol system at different times; (b) difference spectra.

Fig. 5. (a) Spectra of the Fe_2Ru/Al_2O_3/nujol system at different times; (b) difference spectra.

cm^{-1} and at higher frequencies may be assigned to incipient bridging carbonyls and to subcarbonyls with negative charge [9], respectively.

Apparently, at the very beginning of the process a broad band system of rather high intensity overlaps the spectrum of physisorbed $H_2FeRu_3(CO)_{13}$ in the system H_2FeRu_3/Al_2O_3/nujol (see Fig. 4). The

intensity of the latter spectrum rapidly decreases and after 4 h there is no $H_2FeRu_3(CO)_{13}$ left. Simultaneously, the pair of bands characteristic of Fe-$(CO)_5$ appear together with the characteristic band of $Ru_3(CO)_{12}$ at 2063 cm^{-1}, while the broad intensive band system remains. After 23 h the spectrum is dominated by three bands at 2063, 2033 and 2013 cm^{-1} overlapping a broader band system which, however, does not seem to be identical with that observed at the beginning of the process (see later).

A few moments after the impregnation ($t \sim 0$), the sample of Fe_2Ru/Al_2O_3/nujol (see Fig. 5) already contains a large amount of $Fe(CO)_5$ and a very small amount of $Fe_2Ru(CO)_{12}$. Furthermore, there is the usual broad overlapping band system present that refers to undefined subcarbonyl species. The lower frequency band of the doublet at about 1900 cm^{-1} may be assigned to very asymmetric, 'incipient' bridged carbonyls and that of the higher frequency one to subcarbonyls with a negative charge, similar to the Ru_3/Al_2O_3/nujol system. The amount of $Fe(CO)_5$ in the first moment increases then decreases, and after 70 h practically disappears. Simultaneously, to our surprise, the spectrum of Ru_3-$(CO)_{12}$ is developing, while the broad bands remain. There is one extra feature in the spectrum at about 2135 cm^{-1}, which is absent in the other systems.

Discussion

In order to understand the mechanism of the decomposition of the clusters in the presence of nujol we have to consider the role of nujol. The surface concentration of the hydrocarbons is by several orders of magnitude higher than that of the cluster. So the molecules of the hydrocarbons can efficiently compete in occupying the active sites of the support surface. This means that the probability of a stronger link between the cluster and the support (*i.e.* a simultaneous link with two or more active sites) is expected to be suppressed, therefore surface reactions leading to strongly bonded, 'anchored species' are slowed down. This is the reason why the cluster molecules, at the first stage of the process, are in the physisorbed state. Besides, the nujol prevents atmospheric oxygen from contacting the surface and CO from leaving the system.

The above considerations are in good agreement with the most prominent feature of the systems, *i.e.* the presence of physisorbed cluster molecules at the beginning. However, in all systems containing iron, there is $Fe(CO)_5$ rising, which must be considered as an 'endproduct' of the first stage of the process rather than an intermediate. On the other hand, $Ru_3(CO)_{12}$ seems to be also an 'endproduct' for the systems of Fe_2Ru/Al_2O_3/nujol and H_2FeRu_3/Al_2O_3/ nujol.
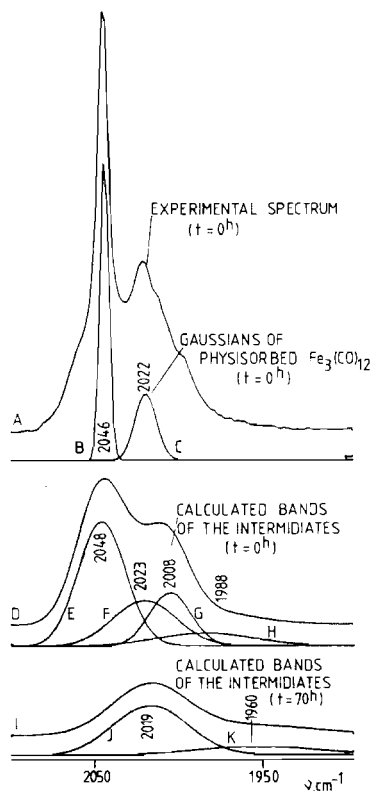
Fig. 6. (A) Experimental spectrum of Fe_3/Al_2O_3/nujol system at $t = 0$; (B)–(C) Gaussian components of physisorbed $Fe_3(CO)_{12}$ at $t = 0$; (D) computed spectrum of the intermediate subcarbonyls at $t = 0$; (E)–(H) Gaussian components of the intermediate subcarbonyls at $t = 0$; (I) computed spectrum of the intermediate subcarbonyls at $t = 70$ h; (J)–(K) Gaussian components of the intermediate subcarbonyls at $t = 70$ h.

Although it is quite obvious that the formation of intermediate species must be supposed between the starting clusters and the above mentioned 'end-products', no sign of new well defined molecular structures has been observed in the spectra. Instead, there have always been broad overlapping bands present in the stretching region of terminal carbonyls offering assignment to hypothetical intermediates. This assignment, however, would involve the consequence that 'intermediates' means a series of subcarbonyls having a different number of CO ligands and occupying very different sites. The broad band system belonging to these species is decreasing and changing its shape with time.

Besides all these general characteristics, the individual systems show up some peculiar features.

$Fe_3/Al_2O_3/Nujol$

The first step in this system, as already suggested, is the decomposition of the $Fe_3(CO)_{12}$ molecule into intermediate structures that must occur very quickly since the spectrum taken at $t = 0$ already

contains the broad band system of intermediates. In order to obtain more information about the shape of the spectrum we analysed it by fitting Gaussians to the data points. In Fig. 6 is shown the experimental spectrum taken at $t = 0$ (A) and the IR Gaussian components that can be divided into two series. The first series (B–C) contains the components of physisorbed molecular $Fe_3(CO)_{12}$. The second one contains the components assigned to the intermediates (E–H). The line D is the sum of the latter components, that is the 'broad overlapping band system' we were previously talking about. Lines I–K show the results for intermediates analogously derived from the spectrum recorded after 70 h. The separation of the components into two groups, molecular species and intermediates, has been done on the basis of 'sharpness', that is of the ratio of two parameters: amplitudes and half widths

$$R = \frac{A}{HW}$$ which will be discussed in more detail

for Fe_2Ru/Al_2O_3/nujol (for the sake of brevity we neglect to tabulate all the parameters of the other three systems). Comparing the spectra in Fig. 6 there is a significant change in the number, intensity and broadness of the components of the intermediates at $t = 0$ and $t = 70$ h which is in good agreement with our earlier supposition that the intermediates are quite mobile.

Taking into account the calculations of Haas and Sheline for the $Fe(CO)_{5-x}L_x$ molecules [10], in the spectrum recorded at $t = 0$, the bands centred at 2023 and 2008 cm^{-1} might be assigned to eq-$Fe(CO)_4L$ species; the bands centred at 2048 cm^{-1} and 1988 cm^{-1} to cis-$Fe(CO)L_4$, respectively, while for $t = 70$ h the bands centred at 2020 cm^{-1} to axial monocarbonyl species $Fe(CO)L_4$. (L means electron donor sites on the surface like O^{2-} and OH^-.) Such an assignment, however, would be rather misleading. For instance a pair of bands may be assigned to species containing two or three metal atoms, too. Further, the widths of the bands are as great as 20–70 cm^{-1} reflecting a very wide distribution of more or less analogous structures. Finally remember, that in vacuum, as we reported in our previous paper, the total amount of CO disappears [11].

$Ru_3/Al_2O_3/Nujol$

Figure 7 shows the spectrum of the Ru_3/Al_2O_3/nujol system recorded at $t = 0$ h, and its components and the spectrum of intermediates at $t = 70$ h. The spectrum of intermediates at $t = 0$ (E) contains three very broad component at 2031, 1931 and 1894 cm^{-1} and a band of medium broadness at 2059 cm^{-1}. The computed spectrum of intermediates at $t = 70$ h (I) contains one more broad component at 1966 cm^{-1}. It is worth mentioning that the frequencies of the components at 2059 and 1996 cm^{-1} are very

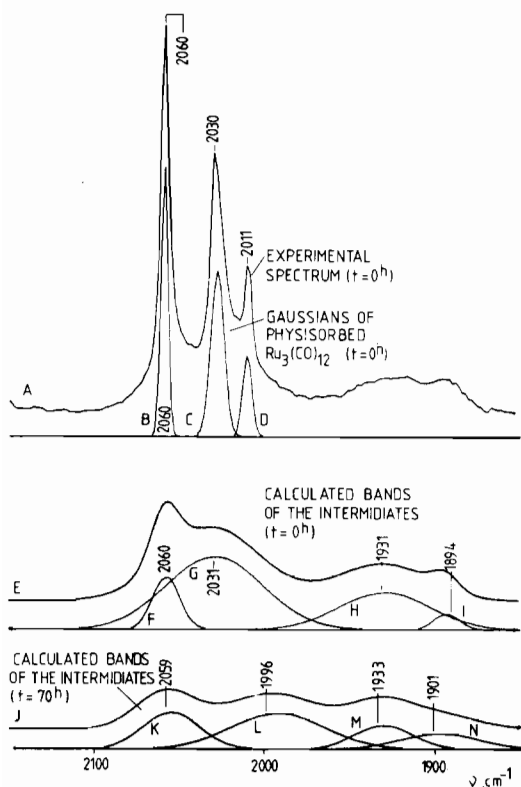Fig. 7. (A) Experimental spectrum of Ru$_3$/Al$_2$O$_3$/nujol system at $t = 0$; (B)–(D) Gaussian components of physisorbed Ru$_3$(CO)$_{12}$ at $t = 0$; (E) computed spectrum of the intermediate subcarbonyls at $t = 0$; (F)–(I) Gaussian components of the intermediate subcarbonyls at $t = 0$; (J) computed spectrum of the intermediate subcarbonyls at $t = 70$ h; (K)–(N) Gaussian components of the intermediate subcarbonyls at $t = 70$ h.

Fig. 8. (A) Experimental spectrum of H$_2$FeRu$_3$/Al$_2$O$_3$/nujol system at $t = 0$; (B)–(F) Gaussian components of physisorbed H$_2$FeRu$_3$(CO)$_{13}$ at $t = 0$; (G) computed spectrum of the intermediate subcarbonyls at $t = 0$; (H)–(L) Gaussian components of the intermediates subcarbonyls at $t = 0$; (M) computed spectrum of the intermediate subcarbonyls at $t = 70$ h; (N)–(R) Gaussian components of the intermediate subcarbonyls at $t = 70$ h.

close to those of Ru^{II}(CO)$_2$ anchored species [11]. The relative intensity of this pair of bands increases with time, showing that the system is slowly approaching the anchored species. At 70 h, however, these components are much broader than the bands of the well defined Ru^{II}(CO)$_2$ anchored species showing that the structures in this case are in a very early 'incipient' stage having not yet anchored at the final sites of the lowest energy.

H$_2$FeRu$_3$/Al$_2$O$_3$/Nujol

The computed spectrum of the intermediates at $t = 0$ (line in Fig. 8) may be described by five components at 2074, 2026, 1995, 1975 and 1960 cm^{-1}. After 70 h (M–R) the band at 2074 is replaced by a band at 2062 and that of 1995 cm^{-1} by a band at 1990 cm^{-1}. The band at 2026 cm^{-1} preserves its frequency but its intensity markedly decreases. It is very interesting that the two bands at 2062 and 1990 cm^{-1} ($t = 70$ h) are of medium broadness ($R = A/HW \sim 1$) just as the pair of bands of the anchored species Ru^{II}(CO)$_2$ [11]. It means this system is

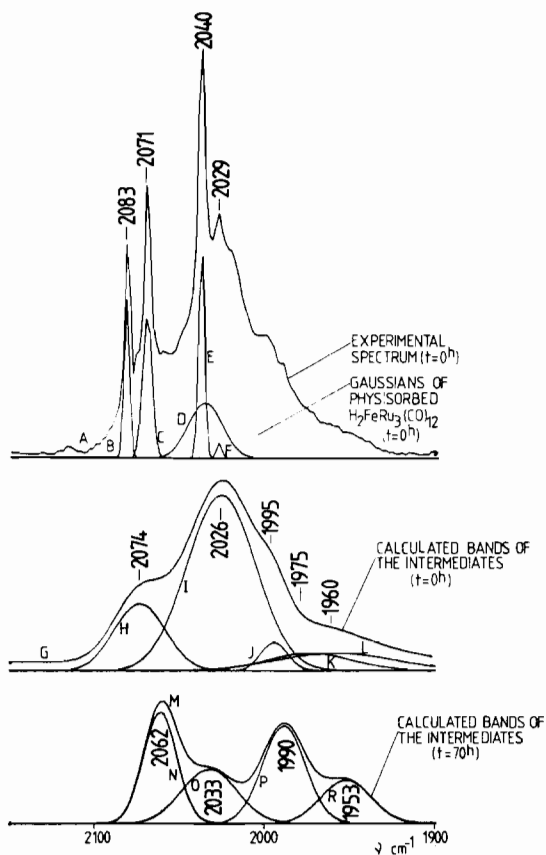surprisingly closer to the final stage experienced at samples kept under vacuum [11], than the Ru$_3$ and Fe$_2$Ru ones. Further, the bands at 2033 and 1953 cm^{-1} are also similar to those of the anchored species Ru^0(CO)$_2$ [11] with the difference that they are somewhat shifted to lower frequencies.

Fe$_2$Ru/Al$_2$O$_3$/Nujol

To give an example for the values of Gaussian parameters, we collected the numeric results of analysis for this system in Table I. In Fig. 9 are shown the respective spectra. The most significant difference in the spectrum of intermediates between the spectra recorded at $t = 0$ and $t = 70$ h is that the band at 2046 cm^{-1} ($t = 0$) splits into two components: 2063 and 2032 cm^{-1} ($t = 70$). The bands at 2128, 2063 and 2005 cm^{-1} clearly show the presence of 'incipient' anchored species of Ru^0(CO)$_2$ and Ru^{II}·(CO)$_2$.
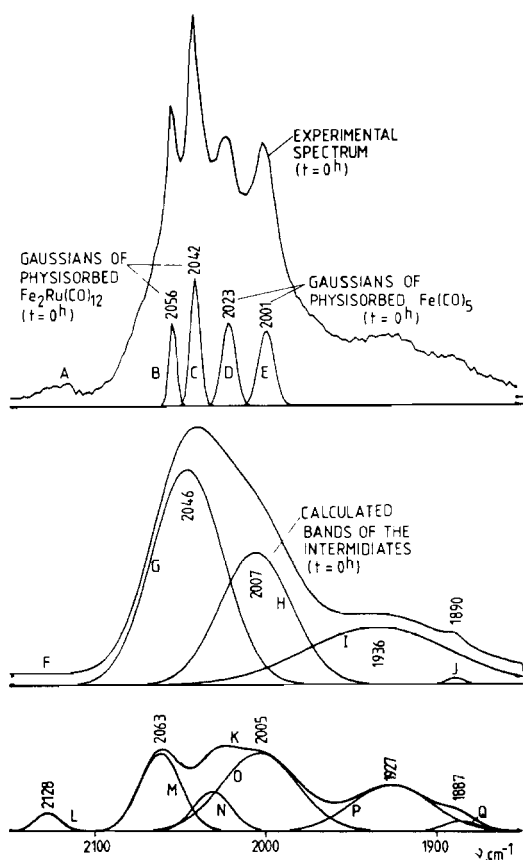
Fig. 9. (A) Experimental spectrum of $Fe_2Ru/Al_2O_3/nujol$ system at $t = 0$; (B)–(C) Gaussian components of physisorbed $Fe_2Ru(CO)_{12}$ at $t = 0$; (D)–(E) Gaussian components of physisorbed $Fe(CO)_5$ at $t = 0$; (F) computed spectrum of the intermediate subcarbonyls at $t = 0$; (G)–(J) Gaussian components of the intermediate subcarbonyls at $t = 0$; (K) computed spectrum of the intermediate subcarbonyls at $t = 70$ h; (L)–(Q) Gaussian components of the intermediate subcarbonyls at $t = 70$ h.

In Table I it is seen that the ratio $R = A/HW$ is $\leqslant 0.5$ for the components of intermediates and for those of 'incipient' anchored species. In our previous paper the ratios of anchored species were between 1 and 4, that is the latter bands were significantly sharper [11]. For physisorbed molecules these ratios are generally between 1 and 3 ($\sim$1 for $Fe(CO)_5$ and $>$2 for the cluster molecules). For solved Fe_2Ru-$(CO)_{12}$ $R \gg 3$, with some exceptions like the bands assigned to bridged CO groups.

Conclusion

The first stage of the interaction between the carbonyl clusters and the alumina surface is a pure physisorption where the molecules are slightly perturbed. The surface layer may be regarded as a two dimensional liquid with highly mobile molecules in it. When the cluster molecule comes to an active site of the alumina, e.g. a Lewis site of Al^+, the metal–metal bonds of the clusters must quickly split (*i.e.* neither highly distorted original nor intermediate polynuclear carbonyl cluster molecules have been detected!) producing a large variety of mobile and supposed monometallic subcarbonyls containing a different number of CO groups.

In the case of $Fe_3(CO)_{12}$ part of these subcarbonyls form $Fe(CO)_5$. Both $Fe(CO)_5$ and subcarbonyls lose CO ligands presumably due to the reaction with OH^- groups of the surface producing Fe^{2+} and Fe^{3+} anchored ions [13].

The bimetallic clusters $Fe_2Ru(CO)_{12}$ and H_2-$FeRu_3(CO)_{13}$ follow a similar pathway. The first step is a physisorption then, at the active sites, metal–metal bonds split producing a series of mobile subcarbonyls. These intermediates serve as precursors for molecular $Fe(CO)_5$ and $Ru_3(CO)_{12}$ and for

TABLE I. Gaussian Parameters and the 'Sharpness' of the Bands (R = Amplitude (A)/Half Width (HW)) for Molecular Fe_2Ru-$(CO)_{12}$ and for Different Physisorbed and Chemisorbed Surface Species

Sample	Wavenumber (cm^{-1})	A (abs $\times$ 100)	HW (cm^{-1})	$R = A/HW$
$Fe_2Ru(CO)_{12}$ hexane	2056.1	96.41	2.89	33.4
	2043.6	173.06	3.97	43.6
	2041.7	58.12	13.87	4.2
	2003.9	16.14	2.09	7.7
	2001.7	32.15	6.95	4.6
	1993.4	8.03	11.58	0.7
$Fe_2Ru(CO)_{12}$ physisorbed	2055.6	5.10	2.10	2.4
	2042.4	7.66	2.75	2.8
$Fe(CO)_5$ physisorbed	2023.0	4.63	3.26	1.4
	2000.7	5.16	5.05	1.0

(continued)

TABLE I *(continued)*

Sample	Wavenumber (cm⁻¹)	A (abs × 100)	HW (cm⁻¹)	R = A/HW
Intermediates $t = 0$	2046.4	12.77	20.72	0.6
	2006.5	7.83	21.10	0.4
	1935.7	3.40	42.03	0.1
	1889.7	0.40	4.82	0.1
Intermediates $t = 70$ h	2128.5	1.10	7.27	0.1
	2062.6	4.61	11.91	0.4
	2032.1	2.37	11.01	0.2
	2004.5	4.64	22.94	0.2
	1927.0	2.76	23.16	0.1
	1886.9	0.63	9.85	0.1
Anchored species $Ru^{0-III}(CO)_2$ (ref. 11)	2139.0	10.35	5.38	1.9
	2074.0	22.95	7.22	3.2
	2065.1	32.23	13.39	2.4
	2006.0	15.02	14.09	1.0
	1985.7	15.87	18.50	0.8
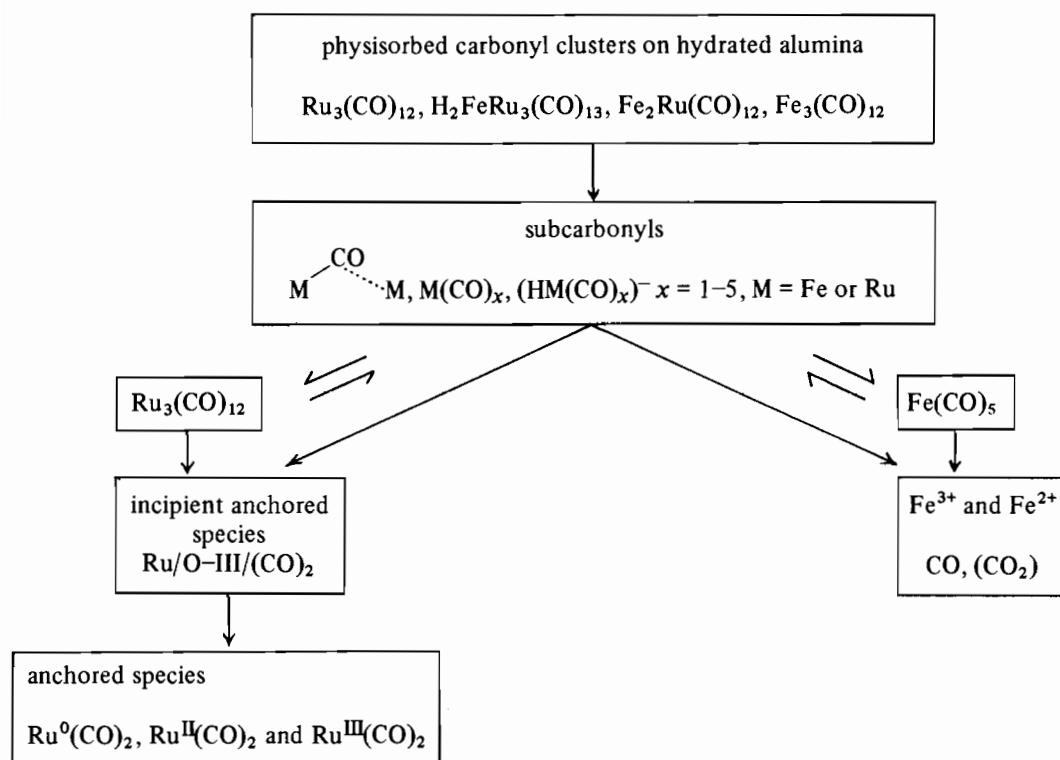
Scheme 1.

incipient anchored species $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$.

For $H_2FeRu_3(CO)_{13}$ the direct decomposition into $Fe(CO)_x$ ($x = 0–5$) and $Ru_3(CO)_{12}$ might also have been supposed, (as was shown for H_2RuOs_3-$(CO)_{13}/Al_2O_3$ in refs. 4 and 14), but we have ruled it out, first because of the presence of a very high amount of intermediate subcarbonyls, and second because the $Fe_2Ru(CO)_{12}$ concludes into identical molecular products though for the last molecule no direct path leading to $Ru_3(CO)_{12}$ was imaginable. The complete supposed mechanism of decomposition is seen in Scheme 1.

The subcarbonyl intermediates have been found in the $Ru_3/Al_2O_3/nujol$ system, too; that means Ru subcarbonyls or a part of them must be in equilibrium with molecular $Ru_3(CO)_{12}$, however, oxidation and anchoring of the ruthenium atoms proceeds slowly. At the very end of the decomposition process in the system of $Ru_3/Al_2O_3/nujol$ — consequently in both Ru containing systems Fe_2Ru and $H_2FeRu_3/Al_2O_3/nujol$ — only $Ru^0(CO)_2$, $Ru^{II}(CO)_2$ and $Ru^{III}(CO)_2$ have been found.

The infrared spectroscopy combined with quantitative treatment of the spectra proved to be a very sensitive tool in distinguishing between free and slighly perturbed physisorbed molecules and/or between differently distributed sets of analogous structures.

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