

## Quantitative FTIR Studies of the $\text{Ru}_3(\text{CO})_{12}$ Cluster Supported on Hydrated Alumina

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Recently there has been growing interest in the interaction of carbonyl clusters with oxidic surfaces. Because of its simple structure and well-known chemical behaviour,  $\text{Ru}_3(\text{CO})_{12}$  has been studied by several authors [1–4]. Qualitative examination of the IR spectra suggests that, depending on the circumstances,  $\text{Ru}_3(\text{CO})_{12}$  adsorbed on hydrated  $\text{Al}_2\text{O}_3$  decomposes into three structures, for which the band pairs at about 2140–2070, 2070–2000 and 2050–1970  $\text{cm}^{-1}$ , respectively, are characteristic. The interpretations of these band pairs are rather different [1–4]. In the present investigation FTIR spectroscopy and data analysis have been carried out on the  $\text{Ru}_3(\text{CO})_{12}/\text{Al}_2\text{O}_3$  system, in order to prove or disprove the existence of the above three structures.

### Experimental

The support was Degussa Alon C, SA = 100  $\text{m}^2/\text{g}$   $\text{Al}_2\text{O}_3$ , heated in vacuum at 573 K then contacted with the saturated pentane solution of commercial  $\text{Ru}_3(\text{CO})_{12}$ . Calculated metal loading was 0.7 wt% Ru. The supported cluster was dried under vacuum overnight and pressed into a wafer (10–20  $\text{mg}/\text{cm}^2$ ) which was placed in a heatable conventional vacuum IR cell. Infrared spectra, under vacuum or  $\text{H}_2$  stream were recorded at 303, 313, 353, 373, 393, 413, 483, 573 and 693 K, using a Digilab FTS 20C IR spectrometer operated with a resolution of 4  $\text{cm}^{-1}$  and 200 scans. As reference we used the spectrum of the catalyst completely decarbonylated.

### Results

Baseline corrected spectra are shown in Fig. 1. To analyse the spectra the sum of maximum 10 Gaussians was fitted to the data points. Since the Gaussians are not linear in their parameters, a method of non-linear least squares was used. The algorithm combined a gradient search and an analytical solution – far from and near to the minimum of the hypersurface of the sum of weighted squares of

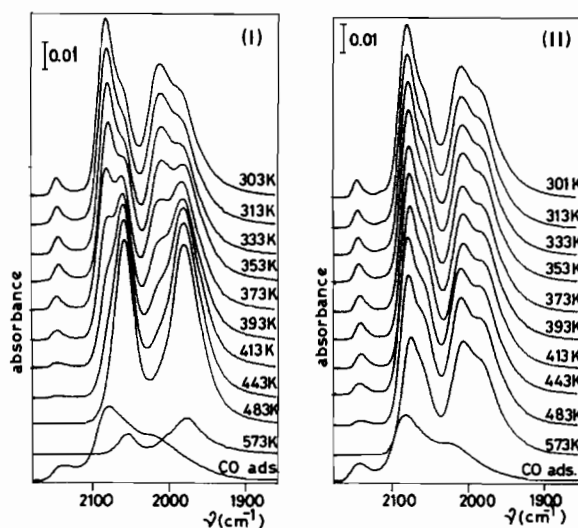


Fig. 1. Baseline corrected spectra of  $\text{Ru}_3(\text{CO})_{12}$  adsorbed on hydrated  $\text{Al}_2\text{O}_3$  recorded at different temperatures in  $\text{H}_2$  stream (I) and in vacuum (II).

deviations, respectively [5]. Weighting was done by assuming constant relative errors. The computations were performed on the NOVA-3 of the Digilab FTS-20C. The computation times were very long: 30–50  $\times$  15 minutes. As a result of this data analysis performed on some of the spectra in Fig. 1 we have developed two sets of Gaussians for the experiments in vacuum and in  $\text{H}_2$  stream, as shown in Table I, where the arrow refers to the direction of the change of the parameter with increasing temperature. These sets of Gaussians were then applied as ‘pure components’ to the program CURVEFIT supplied by Digilab [6]. The program expresses a composite spectrum in terms of a linear combination of its pure spectra by using multiple linear regression and requires less than three minutes for a computation. The contributions of the ‘pure components’ A–I and A’–I’ are shown in Fig. 2, except the very small values for the peak H which are neglected. The contributions of the peaks A and A’ were determined by direct integration of the peak area in the spectral region 2150–2115  $\text{cm}^{-1}$ . The Gaussians and integrated intensities of the spectra of the CO adsorbed on the catalyst at the end of the experiment are shown in Table II.

### Discussion

According to the papers [1–4], a maximum of 6 bands (3 pairs of bands), or, because of the overlapping of two bands between 2080–2060  $\text{cm}^{-1}$ , five

TABLE I. Gaussians Applied to Analyse the Spectra Recorded in H<sub>2</sub> Stream (I) and in Vacuum (II).

(I)									
Gaussians*	A	B	C	D	F	G	H	I	
Wavenumber of maximum	2138	2075 → 2072	2058 → 2050	2050 → 2046	2015	2005 → 2006	1995	1983 → 1971	
Width/cm <sup>-1</sup>	6 → 8	8	30	9 → 18 → 5	8	7 → 6	5	25 → 19	
Amplitude 100 × abs.	4 → 1	28 → 6	18	19 → 3	6	10 → 5	5	30 → 44	
(II)									
Gaussians*	A'	B'	C'	D'	E'	G'	H'	I'	
Wavenumber of maximum	2138	2080 → 2078	2069	2048	2032	2006	1994	1983 → 1982	
Width/cm <sup>-1</sup>	6 → 10	6	11	8	13	8	27	23 → 22	
Amplitude 100 × abs.	5 → 1	14	44	19	11	18	34	33 → 32	

\*The symbols A...I' refer to the symbols used in the text and to those in Fig. 2. → Increasing temperature.

TABLE II. The Composition of the Spectra of CO Adsorbed on the Decarbonylated Catalysts, Characterized by Gaussians and by Integrated Intensities.

Wavenumber of maximum	in H <sub>2</sub> stream	2138	2120	2079	2070	2027	1993
	in vacuum	2143	2129	2083	2073	2022	1984
Width cm <sup>-1</sup>	in H <sub>2</sub> stream	9.5	13.0	8.2	19.2	35.8	46.0
	in vacuum	8.2	10.6	8.8	20.8	24.9	32.9
Amplitude 100 × abs.	in H <sub>2</sub> stream	3.0	2.3	4.1	12.1	8.6	4.0
	in vacuum	4.2	3.0	5.0	16.7	9.4	3.5
Integrated intensity cm <sup>-1</sup> × abs.	in H <sub>2</sub> stream	72	76	84	583	772	468
	in vacuum	87	78	111	872	588	293

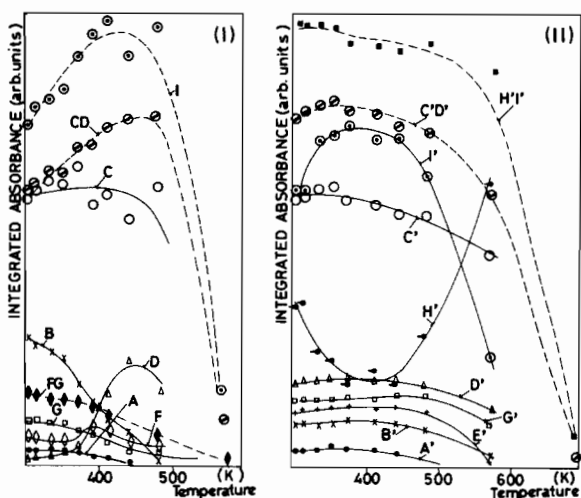


Fig. 2. The changes of the integrated intensities of the Gaussians A...I' used for expressing the compositions of the spectra recorded in H<sub>2</sub> stream (I) and in vacuum (II). Symbols A...I' refer to Gaussians collected in Table I; CD, FG, C'D' and H'I' are the sums of the respective integrated intensities.

bands are expected. The close-lying components C-D, F-G-H, C'-D' and H'-I' may belong to broad bands of non-Gaussian shapes. Hence, in Fig. 2 we also show their sums CD, FG (H neglected), C'D and H'I'.

In Fig. 2 CD (C'D') run parallel with I (H'I'), with a constant intensity ratio of  $0.7 \pm 0.1$ , meaning that the bands form a pair of bands which must be characteristic for a real structure named by Zecchina *et al.* as structure Ru<sub>c</sub> [1]. If the bands A, B, FG (A', B', G') represented only two well defined structures, Ru<sub>a</sub> and Ru<sub>b</sub> [1], and the band B (B') contained two overlapping components [1, 3, 7], the intensity ratios A/FG (A'/G') plotted against B/FG (B'/G') should be linear with the same slope and intersection for both experiments. However, the slope for the H<sub>2</sub> experiment is 0.3 and that for the vacuum one is 0.5 (the respective intersections are 6.2 and 0.5). This means that the above bands cannot be described as a linear combination of two pairs of bands, that is these bands cannot be characterized by the same structures Ru<sub>a</sub> and Ru<sub>b</sub> in both experi-

ments, or the experimental bands represent more than two pairs of bands, consequently more than two structures.

In Table II we show the parameters and the integrated intensities of the Gaussians calculated by the fit procedure from the spectra of CO adsorbed on the catalysts completely decarbonylated in H<sub>2</sub> stream and in vacuum. The two doublets at about 2138/2120 and 2079/2070 cm<sup>-1</sup> (2143/2129 and 2038/2073 cm<sup>-1</sup> in vacuum) may express the non-symmetric features of two singlets with intensity ratios of 4.5 and 6.0, respectively. For this band pair, Zecchina *et al.* estimated an intensity ratio of about 2.5 [1]. Table II shows that there are two further bands at 2027 and 1993 cm<sup>-1</sup> (2022 and 1984 cm<sup>-1</sup> in vacuum) with rather large integrated intensities.

### Conclusions

Quantitative analysis of the spectra of the decomposition products of Ru<sub>3</sub>(CO)<sub>12</sub> adsorbed on hydrat-

ed Al<sub>2</sub>O<sub>3</sub> has given evidence for the existence of a well defined structure characterized by a band pair at about 2050–1980 cm<sup>-1</sup>. Three further bands at about 2138, 2070 and 2000, which are also characteristic for the partially decarbonylated cluster, seem to belong to more than two structures.

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