

# Deposition of tungsten hexacarbonyl on alumina: a diffuse reflectance infrared Fourier transform spectroscopy study

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## Abstract

Alumina-supported tungsten hexacarbonyl with catalytically relevant metal content was prepared by controlled gas phase adsorption and studied by IR spectroscopy. New assignments for adsorbed surface species are proposed. Interactions of tungsten penta- and tricarbonyl species with three kinds of surface cationic sites are suggested. The formation of carbonaceous surface species was observed during thermal decomposition; CO, CO<sub>2</sub>, bicarbonate and formate were detected. Formation of surface tungsten oxides was observed to depend on the gas atmosphere and temperature. Higher metal loading changes the spectrum of the hydroxyl region; the most significant changes are associated with the most basic OH groups. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Gas phase adsorption; IR spectroscopy; Carbonaceous surface species

## 1. Introduction

Catalysts prepared from alumina-supported W(CO)<sub>6</sub> are reported to be active in olefin metathesis and Fischer–Tropsch synthesis [1,2]. Tungsten oxide-based catalysts have also been widely studied in hydrotreating processes. Due to the strong interaction between oxide-form complex and the surface [3–8], however, oxide catalysts are difficult to reduce or sulfurize at moderate temperature. Thus, zerovalent tungsten hexacarbonyl may be a more promising

precursor for these reactions. The method of preparation greatly affects the quality of a catalyst. Strict control of the preparation process is an essential requirement, therefore, in a recent study, we introduced a controlled gradual preparation process for alumina-supported W(CO)<sub>6</sub> in gas phase [9]. The controllability of the process is achieved through successive deposition and decarbonylation treatments made by fluidized bed technique.

A full understanding of the preparation process also requires a tool for following the surface changes. A number of studies have demonstrated the suitability of IR spectroscopy for the analysis of adsorbed tungsten carbonyl [1,10–15], especially where the findings can be combined with information obtained by another

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method such as temperature-programmed decomposition (TPDE) [16–18].

Kazusaka and Howe have reported IR studies of  $W(CO)_6$  adsorbed on variously pre-treated  $\gamma$ -alumina. On hydroxylated alumina, Howe [11] observed only adsorbed tungsten hexacarbonyl, whereas on partially dehydroxylated support, Kazusaka and Howe [12] concluded, on the basis of IR and TPDE results, that  $W(CO)_5$ ,  $W(CO)_3$  and dimeric surface subspecies were present. Bilhou et al. [1] have investigated adsorption on partially hydroxylated  $\eta$ -alumina, and presented IR spectroscopical evidence at least for  $W(CO)_5$  structure.

Zecchina et al. [13] have shown that on highly dehydroxylated alumina,  $W(CO)_6$  interacts with three kinds of Lewis acid site, differing in geometry and acid strength. For molybdenum and chromium carbonyls, it has been shown that also subspecies can interact with these different acidic sites [13]. However, for corresponding tungsten structures, no such interactions has been reported.

The aim of this work was to study the preparation process of tungsten catalyst by IR spectroscopy. In a work reported in the literature, both liquid and gas phase methods have been used to deposit  $W(CO)_6$  on alumina. However, neither of these methods is easily controlled and, moreover, the tungsten loading has typically been low [1,11–13]. Our method provides for gradual and controlled deposition from the gas phase. It also allows deposition over a wide concentration range, so that loading of tungsten can be studied at levels meaningful for real catalyst systems. Furthermore, decarbonylation can be adjusted to a level that allows accurate information to be obtained about the bonding of adsorbed subspecies. The used method and IR spectroscopy provide also a tool for studying the oxidation process and the formation of carbonaceous species during decomposition. The information obtained can be used to control the preparation process, and further, to prepare better catalyst precursors. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy

has been utilized because of its suitability for powdered porous samples [19].

## 2. Experimental

$W(CO)_6$  (99%) was supplied by Aldrich Chemical and used without further purification. The aluminium oxide (Brockmann I, standard grade ca. 150 mesh, 58 Å, surface area = 55 m<sup>2</sup>/g, supplied and reported by Aldrich Chemical) provided the support. Nitrogen (99.999%) and hydrogen (99.999%), both purchased from AGA, were used as carrier and fluidization gas.

For the partial dehydroxylation, the alumina support was preheated at 500°C in vacuum for 10 h. After cooling to room temperature, the alumina powder was removed and stored in a nitrogen glove box. All handling of the support was done without exposure to air or moisture.

The samples were prepared in a fluidized bed reactor by gas phase adsorption. Tungsten hexacarbonyl vapour was transferred from the vaporization section to the fluidized bed reactor in nitrogen flow (30 ml/min). Two sublimation temperatures, 80 and 90°C, were applied. The temperature of the fluidized bed reactor and alumina support was 100°C in all experiments. Depending on the method of preparation, a temperature of 200 or 350°C was applied for partial or almost total removal of the CO ligands. A more detailed description of our reactor arrangement and preparation methods has already been published [9].

The IR measurements of powdered samples were carried out with a Nicolet Impact 400 D FTIR spectrometer. The system was equipped with an MCT (mercury–cadmium–tellurium) detector and a DR (diffuse reflectance) apparatus, placed in a glove box. A more detailed description of the FTIR system designed for air-sensitive samples has been reported elsewhere [20]. All DRIFT measurements were made under nitrogen atmosphere. Resolutions of the measurements were 2 cm<sup>-1</sup> and spectra were obtained after 50 scans. The background spec-

trum of pure alumina was subtracted from all spectra except in the hydroxyl region. The interpretation of intensities is only a relative one, since band intensities can be accurately compared only within the same spectrum.

Determination of the tungsten content of the samples was carried out with an energy dispersive X-ray fluorescence spectrometer (ACAX 300 EDXRF). Measurement time was 100 s and resolution of the device was 0.15 keV. The powdered sample was placed between two mylar sheets in a specially designed sample cell. Non-homogeneity was eliminated by measuring each sample twice, with the sample cell turned 90° between each measurement.

### 3. Results and discussion

#### 3.1. Deposition decarbonylation studies

##### 3.1.1. Tungsten hexacarbonyl on alumina

Earlier IR studies of tungsten hexacarbonyl adsorbed on alumina have typically been made in a special vacuum cell, and only a few experiments have been made at a higher temperature [1,11–13,15]. The metal loading in these studies has been low; for instance, 0.3 wt.% maximum loading has been reported by Kazusaka and Howe [12]. Our IR results are for samples that could represent a real catalyst preparation route. The concentration of  $W(CO)_6$  was increased gradually over a wide range. Metal loadings studied were from 0 to 6 wt.%.

The spectrum in Fig. 1a shows a typical IR spectrum after deposition treatment (Table 1). The tungsten content of this particular sample was ~1.2 wt.%, but the shape of the spectrum remained almost unchanged when the metal loading was increased through higher vaporization temperature or longer deposition time. The dominating structure of the spectrum is a broad band at around  $2000\text{ cm}^{-1}$  which, however, is not very informative because many structures begin to be superimposed.

Zecchina et al. [13] have argued that the adsorption of the hexacarbonyls on highly dehy-

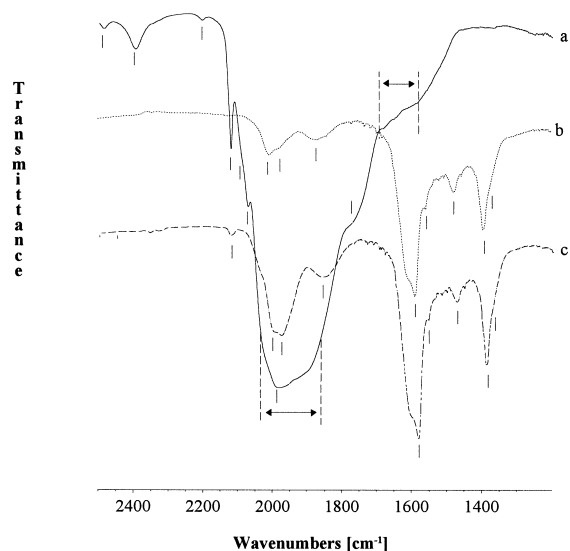


Fig. 1. Carbonyl region of  $W(CO)_6$  supported on  $\gamma$ -alumina pre-treated at  $500^\circ\text{C}$  (a) after deposition at  $80^\circ\text{C}$  for 5 h under  $N_2$ , (b) after decarbonylation at  $350^\circ\text{C}$  for 6 h under  $N_2$  and (c) after decarbonylation at  $350^\circ\text{C}$  for 6 h under  $N_2$  with slight air exposure. The wave numbers of the bands marked with vertical lines are presented in Table 1.

droxylated alumina occurs via O-bonding between CO ligand and  $Al^{3+}$  ion at octa- or tetrahedral sites. There are also some defective cation sites on the surface, but their proportion is small. As the result of this interaction, one would expect to see at least two sets of quartets in the IR spectra. Five terminal CO ligands have normal modes  $2A_1$ ,  $B_2$  and E [14], which give four vibrations in higher carbonyl region at  $2140\text{--}1995\text{ cm}^{-1}$  [ $(A_1)_2$  can be seen only as a shoulder of strong E]. The O-bonded CO group should give one vibration at  $1900\text{--}1600\text{ cm}^{-1}$  [13,21].

In our case, deposition was made near  $100^\circ\text{C}$ . When the  $W(CO)_6$  interacts with the surface, it can be assumed to form intermediate subcarbonyl structures quickly, so that the portion of chemisorbed hexacarbonyl on the surface will be small. The absence of band for the highest  $(A_1)_1$  mode of  $W(CO)_6$  (ads), at around  $2140\text{ cm}^{-1}$  reported by Zecchina et al. [13], is in accord with this suggestion. It should be added that the pre-treatment of the support may also affect the shift of bands.

Table 1  
Wavenumbers of spectra in Fig. 1

Spectra a	Spectra b	Spectra c
2487 (w)	2008 (w)	2127 (w)
2398 (w)	1982 (w)	2005 (m)
2201 (w)	1866 (w)	1984 (m)
2119 (m)	1620 (sh,s)	1860 (w)
2086 (sh,m)	1591 (s)	1620 (sh,s)
2070 (m)	1558 (sh,w)	1591 (s)
1993 (s)	1478 (w)	1558 (sh,w)
2032–1870 (s)	1394 (m)	1478 (w)
1770 (sh,m)	1375 (sh,w)	1394 (s)
1690–1580 (sh,m)		1375 (sh,w)

Intensities of bands: weak (w), medium (m), strong (s) and shoulder (sh).

The presence of physisorbed hexacarbonyl on the surface is probable, given the relatively fast rate of substrate addition. Three bands, at 2126, 2021 and 1997  $\text{cm}^{-1}$ , have been reported for the  $A_{1g}$ ,  $E_g$  and  $T_{1u}$  modes of gaseous  $\text{W}(\text{CO})_6$  [14]. Thus, the intense and sharp band at 2119  $\text{cm}^{-1}$  and strong band at 1993  $\text{cm}^{-1}$  can be attributed to the  $A_{1g}$  and  $T_{1u}$  modes of physisorbed complex, respectively. The  $E_g$  vibration mode is covered by the broad band at 2000  $\text{cm}^{-1}$ .

### 3.1.2. Tungsten pentacarbonyl on alumina

The spectrum in Fig. 1a does not allow the determination of the exact number of CO groups lost during deposition. It is clear, nevertheless, that the temperatures we used do not lead to a very low subcarbonyl level. The TPDE results reported by Brenner and Hucul [16] indicate that the temperature region, where the loss of the first three CO occurs, fluctuates and loss does not usually terminate until 200°C. Thus, the existence at least of pentacarbonyl complex on the surface during deposition treatment can be proposed.

During chemisorption on  $\eta$ -alumina at room temperature, Bilhou et al. [1] observed several bands (2085, 2065, 2023 and 1745  $\text{cm}^{-1}$ ) which they assigned to pentacarbonyl species. After outgassing at 100°C on  $\gamma$ -alumina, Kazusaka and Howe [12] suggested the band at 1750 to be

due to tungsten pentacarbonyl. During outgassing at room temperature on highly dehydroxylated  $\gamma$ -alumina, Zecchina et al. [13] did not observe any bands for tungsten subcarbonyl structures.

The band at 2070 and shoulder at 2086  $\text{cm}^{-1}$  are the highest carbonyl vibrations in spectrum a. They are too low for  $A_1$  modes of hexacarbonyl species, but correlation is good with wave numbers reported in the literature for tungsten pentacarbonyl [1]. The corresponding molybdenum compound likewise exhibit the highest pentacarbonyl band in this region [22]. Zecchina et al. [13] report subcarbonyl species of chromium and molybdenum in this region, though these were not identified specifically as pentacarbonyl.

The wave numbers of the band and shoulder at 2070 and 2086  $\text{cm}^{-1}$  observed here differ by less than 20  $\text{cm}^{-1}$ , which according to the literature is too small for two successive  $A_1$  modes of  $C_{3v}$  symmetry [10,13]. We therefore suggested that the vibrations at 2070 and 2086  $\text{cm}^{-1}$  are rather due to the highest  $A_1$  mode of the pentacarbonyl species interacting with different cation sites. Adsorption to a Lewis acid site causes an increase in the stretching frequency of terminal ligands, and the upward shift is greater for a tetrahedral than for an octahedral site [13,21]. Thus, the band at 2070  $\text{cm}^{-1}$  could be due to a terminal CO ligand of tungsten complex on an octahedral site, and the shoulder at 2086  $\text{cm}^{-1}$  to a similar group on a tetrahedral site. The other two bands ( $A_1$  and E), due to terminal ligands of adsorbed pentacarbonyl structures, are presumably hidden by the broad band at around 2000  $\text{cm}^{-1}$ .

The lower carbonyl region includes a shoulder at 1770  $\text{cm}^{-1}$ , which may be due to a CO group O-bonded to an octahedral Lewis site. For the molybdenum analogue, the corresponding structure has been suggested to give a band at 1760  $\text{cm}^{-1}$  [22]. The region 1690–1580  $\text{cm}^{-1}$  would be expected to include at least a vibration for CO on tetrahedral site, but this has not been accurately resolved.

### 3.1.3. Carbonaceous surface species

Decarbonylation begins during deposition and is seen first in the presence of three bands in the high frequency region (2487, 2398 and 2201  $\text{cm}^{-1}$ ). The bands at 2487 and 2398  $\text{cm}^{-1}$  can be assigned to adsorbed  $\text{CO}_2$ . One possible mechanism for the formation of  $\text{CO}_2$  is the reaction of liberated CO with an oxo-group on the surface [23]. A second possible mechanism involves the nucleophilic attack of OH to the CO ligands [24], but in this system,  $\text{H}_2$  should also form, and according to TPDE results in the literature [16–18], this is unlikely under reaction conditions we used. The Boudouard mechanism has also been discussed in this context [16,17].

A linear form of  $\text{CO}_2$  on the most acidic site has been reported to give bands around 2400  $\text{cm}^{-1}$  [25–29]. The band at 2398  $\text{cm}^{-1}$  might therefore be due to linear  $\text{CO}_2$  on a tetrahedral or defective site. Bands due to adsorption on less acidic cation sites are not observed. The vibration at 2487  $\text{cm}^{-1}$  is not resolved, but may be due to  $\text{CO}_2$  at a site where it can interact with adsorbed tungsten species.

Morterra and Magnacca [25], Morterra et al. [31] and Zecchina et al. [29,30] have reported that the weak acid base type  $\text{CO} \cdots \text{Al}_{\text{tet}}^{3+}$  interaction gives a band at  $\sim 2190\text{--}2210$   $\text{cm}^{-1}$ . Although this band has been observed most clearly at the temperature of liquid nitrogen, it also appears in adsorption at ambient temperature. In our study, the cooling of the sample from 100°C to room temperature occurred slowly and the reaction chamber was not evacuated, so there was possibly enough free CO in the gas circulation for adsorption. The third band at higher frequency, at 2201  $\text{cm}^{-1}$ , can therefore be assigned to liberated CO adsorbed on tetrahedral cationic site. The absence of a further band due to this interaction with a different acidic site can be attributed to the lower intensity in these conditions.

The spectrum in Fig. 1b shows the situation after decarbonylation at 350°C for 6 h. Three weak bands are still visible in the carbonyl stretching region, which means that 350°C is

not sufficient to remove all bands from the stretching region.

Besides a decrease in band intensity in the carbonyl region during thermal treatment, the formation of new bands is observed between 1700 and 1200  $\text{cm}^{-1}$ . These bands can be assumed to be due to carbonate, bicarbonate or formate formed in interaction between released CO or  $\text{CO}_2$  with different surface sites. The bands were identified according to IR assignments given in the literature [27,32–37]. The two most intense bands, at 1394 and 1591  $\text{cm}^{-1}$ , indicate the presence of formate species on the surface and are assigned to C–H deformation mode and asymmetric O–C–O stretching vibrations, respectively. The corresponding symmetric O–C–O vibrations can be seen as a low shoulder at 1375  $\text{cm}^{-1}$ . The band at 1478  $\text{cm}^{-1}$  is a symmetric stretching vibration due to bicarbonate species. The peak observed around 1620 may be associated with the asymmetric O–C–O stretch of the bicarbonate species. The weak band at 1558  $\text{cm}^{-1}$  was not resolved.

### 3.1.4. Formation of surface oxides

The spectrum in Fig. 1c was recorded from a sample that was exposed to air during decarbonylation. On the basis of the earlier experiment (shown in spectrum b), the decarbonylation treatment could be expected to remove carbonyl bands almost totally. However, as can be seen, the intensity of the region around 2000  $\text{cm}^{-1}$  clearly increases instead. Wachs [38] has reported that some supported metal oxides have M = O overtone vibrations around 2000  $\text{cm}^{-1}$ . Spectrum c shows a broad band with maxima at wave numbers 1984 and 2005  $\text{cm}^{-1}$ . The shape and location of the band are in agreement with the spectra presented for rhenium and chromium oxide on alumina [38], and the increased intensity of the band around 2000  $\text{cm}^{-1}$  may, therefore, be explained by the formation of oxidized tungsten species.

It is interesting, however, that the wave numbers of these oxidized species do not differ clearly from those apparent in spectrum b where

decarbonylation was carried out under pure nitrogen. These findings indicate that, in carbonyl-based systems, thermal treatment at higher temperature leads to slight formation of oxidized surface species even under inert nitrogen atmosphere. The concentration of oxidized species was, nevertheless, much lower when the nitrogen flow was not contaminated with air. This observation is in agreement with the literature, where it is suggested that treatment over 200°C can lead to a redox reaction between metal complex and surface hydroxyls [16,18] and, as a consequence, the metal begins to oxidize.

Furthermore, heating under slight air exposure led to the appearance of a new weak band at 2127  $\text{cm}^{-1}$ , which could be associated with the CO interacted with oxidized tungsten particle ( $\text{CO} \cdots \text{WO}_x$ ). The IR assignment for similar structures has been reported at least for platinum oxide on alumina [39].

### 3.2. Effects of partial decarbonylation

To obtain more detailed information about surface reactions and sites by IR spectroscopy, we studied the carbonyl region after removal of more than one ligand. The bonding of  $\text{W}(\text{CO})_6$  and formation of subcarbonyls on partially or highly dehydroxylated  $\gamma$ -alumina has been shown to begin with the interaction of a carbonyl ligand with a Lewis acid site [13,22,24]. Interaction with the surface Lewis acid site increases the  $\pi$ -acid character of the involved CO. Moreover, a strong *trans* effect of the CO [40] favours a loss of the *trans* ligand with weaker  $\pi$ -bonding ability. Thus, a vacant coordination site is formed. The vacant site will then rearrange so as to lie in *cis* position to the CO at the Lewis site and will interact with the surface oxide or one of the basic OH group [22].

Additional loss of carbonyl via *cis* labilization may occur [41] and if it can be assumed that treatment at 200°C leads to  $\text{W}(\text{CO})_3$  surface complexes, as has been reported in the literature [16], the spectra in Fig. 2b and c can be ascribed

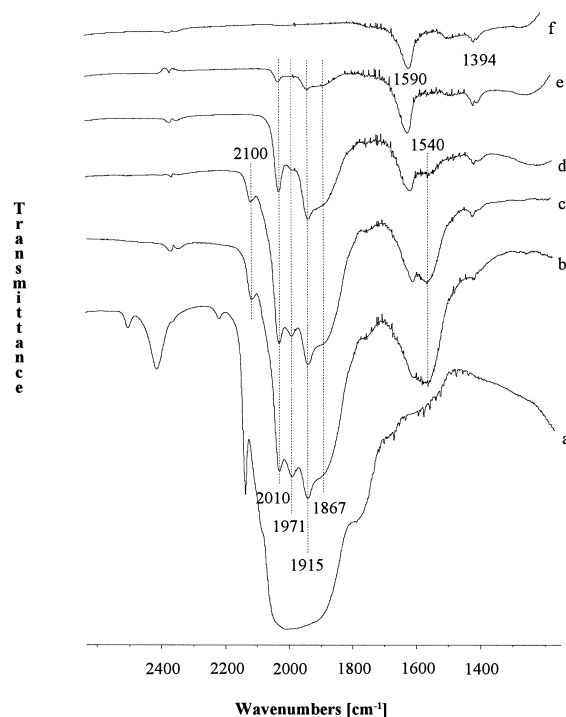


Fig. 2. Carbonyl region of  $\text{W}(\text{CO})_6$  supported on  $\gamma$ -alumina pretreated at 500°C (a) after deposition at 90°C/5 h/ $\text{N}_2$ , and after stepwise decarbonylation (b) at 200°C/5 h/ $\text{N}_2$ , (c) at 200°C/10 h/ $\text{N}_2$ , (d) at 350°C/5 h/ $\text{H}_2$ , (e) at 400°C/5 h/ $\text{H}_2$  and (f) 450°C/5 h/ $\text{H}_2$ .

to these three remaining carbonyls. It can be concluded that the three carbonyl ligands have been replaced by three surface oxy groups. Now, if the symmetry of the complex were  $C_{3v}$  [ $\text{W}(\text{CO})_3\text{L}_3$ ], the spectrum should exhibit only two vibrations: one for  $A_1$  and a second for degenerated E mode. However, as can be seen, spectra b and c are more complex than this. Furthermore, although the bands at 1590 and 1394  $\text{cm}^{-1}$  can be explained as due to carbonaceous species, there is still at least one carbonyl band, at wave number 1540  $\text{cm}^{-1}$ , which is too low to be due to free terminal ligand [13,21,22].

On the basis of IR and TPDE results, Kazusaka and Howe [12] have suggested that the decomposition pathways of adsorbed  $\text{W}(\text{CO})_6$  and  $\text{Mo}(\text{CO})_6$  are very similar. That being the case, the  $\text{W}(\text{CO})_3$  complex should interact with the surface in a similar way to its molybdenum analogue. Reddy and Brown [22]

have shown that the interaction of that partially decarbonylated species with the surface not only involves bonding via three surface oxo groups but also via the oxygen of one carbonyl ligand to Lewis acid site. A model for alumina-adsorbed  $W(CO)_3$  taking this fourth bonding into account is shown in Fig. 3. The bonding to Lewis acid site will convert the symmetry of the complex from  $C_{3v}$  to  $C_s$ , which has three IR active vibrations: two for  $A'$  and one for  $A''$ . For  $W(CO)_3$ , one would expect to see three bands in the carbonyl region, where the bands of the two terminal carbonyl ligands appear at higher frequency and the O-bonded CO has a band in lower region [22]. Moreover, the presence of several types of acidic site complicates the spectra. The stretching frequencies of subcarbonyl species would be expected to be lower than those of corresponding adsorbed hexacarbonyls [13].

We may now attempt to interpret the spectra in Fig. 2. It is known that interaction with acidic sites not only shifts the bands of the interacting CO to lower frequency, but also shifts the bands of the terminal ligands upward, and the more acidic the site, the greater the shift [13,21]. The band at  $2100\text{ cm}^{-1}$  may, therefore, be ascribed to terminal CO of a complex interacting with the most acidic, defective site. The fact that the intensity of the band at  $2100\text{ cm}^{-1}$  is weak, and that this band disappears first when the temperature of decarbonylation is increased, is in good agreement with the low concentration of defective sites. The two other bands expected this structure may be obscured by overlapping; moreover, the lower region is disturbed by moisture and carbonaceous species.

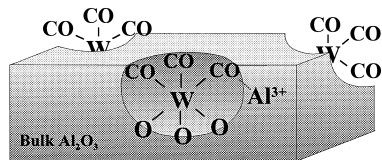


Fig. 3.  $W(CO)_3$  supported on alumina surface.

Interaction with tetrahedral cation site shifts the vibration of terminal ligand upward, but less effectively than interaction with defective site [13,21]. This, together with the strong intensity, suggests assignment of the band at  $2010\text{ cm}^{-1}$  to terminal CO ligand of  $W(CO)_3$  coordinated to tetrahedral Lewis site. Since the band at  $1915\text{ cm}^{-1}$  weakens during desorption parallel with the band at  $2010\text{ cm}^{-1}$ , we conclude that the band  $1915\text{ cm}^{-1}$  is also caused by the terminal ligand of the complex interacting with tetrahedral  $Al^{3+}$  site. The third band expected for the O-bonded CO ligand on tetrahedral aluminium cation is observed at  $1540\text{ cm}^{-1}$ .

The adsorption energy of the complex has been demonstrated to be greater in interaction with the tetrahedral than with the octahedral site [13,22]. The weaker and less persistent bands at  $1971$  and  $1867\text{ cm}^{-1}$  are accordingly ascribed to terminal ligands of  $W(CO)_3$  interacting via one CO with octahedral Lewis site. A band for oxygen-bonded CO on octahedral site was not observed. Reddy and Brown [22] have noted for  $Mo(CO)_3$  adsorbed on alumina that there are about 100 wave numbers between the bands of O-bonded CO at different sites. From this, we deduce that CO of  $W(CO)_3$  interacting with octahedral site should give a band a little above  $1600\text{ cm}^{-1}$ . This, however, presumably would be overlapped by the strong and fairly broad band of formate centred at  $1590\text{ cm}^{-1}$ .

The spectra in Fig. 2 show that the relations of the bands stay similar through the heating treatment and no new bands appear; evidently, then, the loss of the final three ligands proceeds without the formation of other intermediate forms. The formation of the dimeric form does not seem to be likely, and after 5 h at  $450^\circ\text{C}$ , all carbonyl bands have disappeared (spectrum f).

In general, the temperature required for decarbonylation of alumina-adsorbed  $W(CO)_6$  is considered to depend on the amount of metal complex. Only at very low initial surface loading is decarbonylation complete at a moderately low temperature [1,42]. At higher loading, the total removal of carbonyls reportedly does not

occur unless the temperature is at least 400°C [12]. Our findings are in good agreement with this.

To eliminate the above-mentioned oxide structure during the final decarbonylation, we treated the sample under reducing atmosphere. Comparison of the shapes of spectra 1b and 2d around 2000 cm<sup>-1</sup> reveals a clear dependence on the treatment atmosphere. Similar M = O oxide structures were evidently formed under nitrogen (spectrum 1b) as under slight air exposure (spectrum 1c), but this was not the case for hydrogen atmosphere (spectrum 2d). In addition, the formation of carbonaceous species is decreased when treatment is made under hydrogen, in agreement with the literature [35].

### 3.3. Hydroxyl region

Several models of slightly different emphasis have been proposed to describe the hydroxyl structure of alumina surface [43–46]. These models suggest the existence of about five kinds of OH configuration interacting with tetrahedral- and octahedral-coordinated aluminium. Noting that dehydroxylation also leads to the formation of three- and five-coordinated aluminium, Tsyganenko and Mardilovich [47] have recently argued that the number of different OH configurations would increase markedly during dehydroxylation. The existence and number of different hydroxyls would then depend on the stage of the dehydroxylation.

The OH groups remaining on partially dehydroxylated alumina play an important role in the surface reactions and some changes are also expected in the OH stretching region varying with the degree of tungsten coverage. Bilhou et al. [1] and Zecchina et al. [13] report that the OH region of  $\eta$ - and  $\gamma$ -alumina remains unmodified despite tungsten hexacarbonyl adsorption. Nevertheless, the spectra presented in Fig. 4 indicate that when the tungsten loading is increased gradually, in a controlled manner, some changes occur as a function of the adsorption pulses.

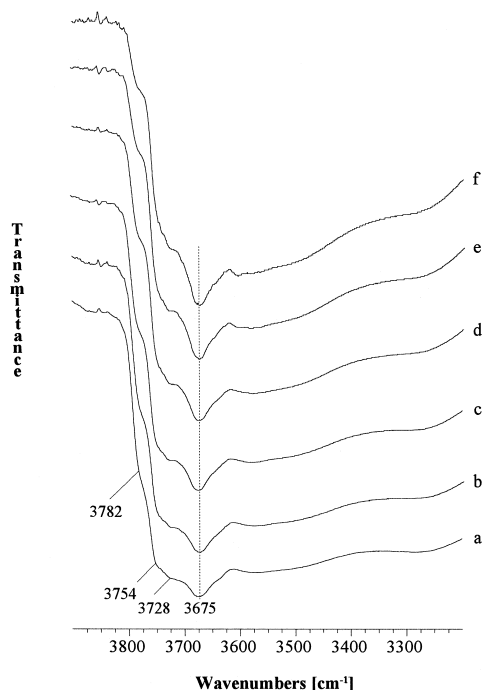


Fig. 4. Hydroxyl region of  $\gamma$ -alumina (a) after pre-treatment at 500°C, and after a (b) first, (c) second, (d) third, (e) fourth and (f) fifth successive preparation pulse comprising deposition at 90°C for 2 h and decarbonylation at 350°C for 6 h. The final tungsten content was  $\sim$  5.8 wt.% and the experiment was made under N<sub>2</sub>.

After vacuum treatment at 500°C, alumina exhibits four bands for isolated OH groups. The highest bands, at 3782 and 3754 cm<sup>-1</sup>, can be assigned to OH groups bonded to single Al atom on tetra- or octahedral sites. The band at 3728 cm<sup>-1</sup> is due to OH groups interacting with two aluminium atoms, while the a band at 3675 cm<sup>-1</sup> belongs to OH bonded to three Al atoms. The exact coordination of aluminium interacting with OH group is not considered in this study.

The spectra in Fig. 4b–e show that the wavenumbers of these four bands stay unchanged during successive deposition decarbonylation pulses, but the relative intensity (the shape of the region) changes with the tungsten loading. The OH bands at higher frequency weaken, especially the band at 3782 cm<sup>-1</sup>, causing the band at 3675 cm<sup>-1</sup> to stand out more clearly. The OH bands at highest frequency have com-



monly been assigned to the structures of most basic character [45,46], which leaves the band at  $3675\text{ cm}^{-1}$  to be assigned to the most acidic OH.

It is interesting that the band at  $3675\text{ cm}^{-1}$  also weakened in intensity during the deposition (spectra not shown). However, the phenomenon is reversible and decarbonylation restores the intensity.

The observed modest changes indicate that, despite several percent tungsten loading, the number of OH groups interacted with transition metal carbonyls is low compared with the total number of surface OH. At the same time, the marked and irreversible loss of intensity of the band at  $3782\text{ cm}^{-1}$  shows clearly that these interacting OH species are highly reactive in chemisorption. The finding is in good accord with the literature, where the intensity of the band near  $3780\text{ cm}^{-1}$  has been observed to be most easily influenced by admolecules [25,29,31,45,48]. The higher activity has been attributed to the greater accessibility of some OH groups [25,31].

The higher reactivity of the OH species at higher frequency is also in agreement with a decarbonylation mechanism based on the *trans* effect (see above). The vacant coordination site of the surface complex permits the binding of hydroxyl or oxy group provided that the group is basic enough. In addition, the accessibility of the OH species taking part in the interaction must be favourable.

The reappearance of the band at  $3675\text{ cm}^{-1}$  after decarbonylation shows that the interaction with these OH groups is physisorption rather than chemisorption. This would also be expected from the greater acidic character. These sites, we propose, interact with carbonyl complexes immediately after their deposition and facilitate the migration of admolecules over the surface to suitable sites where they can react and form stable chemical bonds.

At the higher tungsten loadings of this work, it is not impossible that some of the carbonyl complexes interact directly with the most basic

hydroxyls. The usually accepted reaction pathway for such nucleophilic attack on the carbon centre of carbonyl ligand and further formation of subcarbonyl based on *cis* labilization has been described well in the literature [22,24,41]. Nevertheless, there is no clear indication for this kind of interaction in the carbonyl stretching region of our spectra. Furthermore, Reddy and Brown [22] have shown for molybdenum hexacarbonyl that this is an important form of chemisorption only on hydroxylated alumina where the surface OH concentration is high.

#### 4. Conclusions

We used IR spectroscopy to study a gradual gas phase deposition process which allows the metal content to be varied over a wide range. The controllability of the process is good. The formation of tungsten carbonyl subspecies through loss of part of the CO ligands has been demonstrated in previous IR studies. However, we were able to obtain new information on the surface chemistry of alumina-adsorbed  $\text{W}(\text{CO})_6$  by carrying out IR studies at higher metal loading, with good control of deposition and decarbonylation.

The interaction of adsorbed tungsten pentacarbonyl with octa- and tetrahedral cation sites is suggested. The deposition and decarbonylation treatment also leads to the formation of several carbonaceous species on the alumina surface. Besides bands for linear  $\text{CO}_2$  and weakly interacted CO, bands for formate and bicarbonate were observed. The formation of formate is dominant after treatment at higher temperature. Use of hydrogen atmosphere during decarbonylation suppresses the formation of the carbonaceous species.

The formation of tungsten oxides is proposed for decarbonylation under nitrogen atmosphere at a higher temperature. The bands assigned to oxides became more intense when the nitrogen flow was doped with a small amount of air. Similar oxide bands were not observed when

thermal treatment were made under hydrogen flow.

When decarbonylation was adjusted to  $W(\text{CO})_3$  level, the IR spectra gave information about the interaction of the subspecies with different kinds of surface cation site. Besides binding to tetra- and octahedral sites, the binding of tungsten complex to an alumina defect site is suggested.

The region of isolated hydroxyl groups begins to change shape with increased tungsten loading. The most basic hydroxyls at higher wave numbers are most reactive in chemisorption, whereas the acidic OH groups take part only in physisorption.

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