# Nature of adsorbed species during the reduction of $CrO_3/SiO_2$ with CO

## *In situ* FTIR spectroscopie study

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*In situ* FTIR spectra of adsorbed CO on $CrO_3/SiO_2$ catalysts have been investigated at elevated temperatures to elucidate the nature of the species formed during the reduction process with CO. The results show the formation of three species: bicarbonates, monodentate carbonate and inorganic carboxylate. The reduction of $CrO_3/SiO_2$, which occurs through the formation of surface bicarbonate and carboxylate compounds, starts near 100 °C.

## 1 Introduction

Chromium(vi) supported on silica is one of the most studied and controversal catalytic systems used industrially for production of polyethylene.[1] Phillips catalysts ($Cr/SiO_2$) are well known but some basic questions are still unresolved. One area of disagreement centers on the valence state of the active chromium center. Hexavalent chromium does not catalyze the polymerization of ethylene[2] and the active oxidation state of $Cr/SiO_2$ during industrial production of polyethylene is achieved through a reduction procedure, but details remain unknown.

Among the different approaches used to produce reduced chromium oxides supported on silica thermal reduction with CO is convenient. CO reduction of $Cr/SiO_2$ catalysts results in the formation of traces of $Cr^{5+}$ as well as $Cr^{3+}$ and $Cr^{2+}$, their relative proportion depending on the reduction temperature and time.[3] Three types of $Cr^{II}$ ions have been found (A, B and C), having two, three and four oxygen ligands, respectively, so that the ability to coordinate additional ligands is in the order A > B > C.[4]

Although CO adsorbed on $Cr/SiO_2$ has previously been extensively studied by spectroscopy,[4–14] all previous work was focussed on the oxidation state and coordination environment of chromium after CO reduction. No data on the mechanism of reduction of $Cr^{6+}$ are available in the literature. Indeed, the IR spectra were taken at room temperature and focussed on the carbonyl region (2300-1800 $cm^{-1}$). The aim of this work is to throw some light on the nature of the species formed during the reduction process of $CrO_3/SiO_2$ with CO. This has been done by performing *in situ* IR investigations of adsorbed CO in the region 1800-1200 $cm^{-1}$, during thermal heating of $Cr/SiO_2$ in CO from room temperature to 400 °C. The adsorption of CO at elevated temperatures was also followed as a function of time.

## 2 Experimental

A $CrO_3/SiO_2$ catalyst was prepared by impregnating silica (Candea, surface area = 800 $m^2 g^{-1}$) with an aqueous solution of chromium(vi) trioxide ($CrO_3$). An amount of solution equal to the pore volume (1.2 ml $g^{-1}$), was mixed with the support under continuous stiring. The Cr content, determined by ion coupled plasma (ICP) analysis, was 0.5 wt.%. Pellets of com-

pressed powder ($\varkappa$20 mg $cm^{-2}$) were introduced in the IR cell and activated following a procedure consisting of a treatment at 400 °C in $O_2$ flow for 2 h and then in He flow for 1 h. *In situ* IR measurements were recorded on a Nicolet 730 FTIR spectrophotometer using a home-made cell connected with an evacuation-gas manipulation system. This conventional cell with $CaF_2$ windows and a furnace is applicable for *in situ* thermal treatments to *ca.* 400 °C. The temperature was controlled by an electronically steered heating system and circulating tap water cooled the $CaF_2$ windows. The temperature was measured to an accuracy of ± 3 °C.

100 scans were collected in the wavenumber range 4000-400 $cm^{-1}$ (resolution = 4 $cm^{-1}$). An IR spectrum obtained under He flow was used as the background to which the spectrum, after treatment by CO, was ratioed.

We should note here that we have also carried out preliminary experiments in the diffuse reflectance mode using a commercial DRIFT cell from Spectratech, which offers the possibility of *in situ* pretreatments up to 550 °C. However, DRIFT experiments are difficult to obtain with low Cr loaded samples, and only those performed on samples with loading >4 wt.% present exploitable data. Since the industrial catalysts have a Cr loading close to 0.5 wt.%, we preferred to perform our experiments in the transmission mode using a conventional cell. We also found that in experiments carried out at different temperatures on the support the silica does not adsorb CO under our experimental conditions.

## 3 Results

### 3.1 Adsorbed species formed during the reduction of $Cr/SiO_2$ with CO

At room temperature, the interaction of CO with $CrO_3/SiO_2$, calcined and evacuated at 673 K, shows no IR bands due to adsorbed CO. Introduction of CO at 100 °C immediately gives three strong bands at 1642, 1584 and 1443 $cm^{-1}$ and three weak bands at 1227, 1385 and 1371 $cm^{-1}$, (Fig. 1). All these bands grow quickly with time and after 25 min six distinct peaks are visible.

In order to distinguish the different species contributing to the IR spectrum the variation of the five most important bands with CO adsorption time is presented in Fig. 2 with the 1584 $cm^{-1}$ band taken as the reference. The bands at 1584 and 1385 $cm^{-1}$ grow at the same rate; hence their intensity ratios remain the same. The relative intensities of the bands at 1227, 1642 and 1443 $cm^{-1}$ show the same behavior. They all decrease in a similar manner with increasing adsorption time.

**Fig. 1** *In situ* FTIR spectra of the adsorbed species following CO reduction of 0.5% $Cr/SiO_2$ at 100 °C
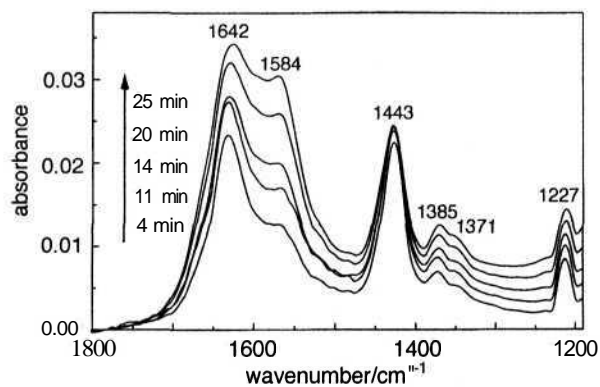


**Fig.** *4* *In situ* FTIR spectra of the adsorbed species following CO reduction of 0.5% $Cr/SiO_2$ at 200 °C

On this basis the six bands are classified into two groups, arising from two surface species. The species labelled A is characterized by bands at 1642, 1443 and 1227 $cm^{-1}$ and species B is characterized by bands at 1584 and 1385 $cm^{-1}$.

Fig. 3 displays a series of IR spectra of adsorbed CO during heating under CO flow from 100 to 200 °C. Species A (1642, 1443 and 1227 $cm^{-1}$), dominant at 100 °C, has almost completely disappeared at 200 °C. Species B (1584, 1385 $cm^{-1}$) becomes the dominant species, but a third band at 1371 $cm^{-1}$ starts to grow. A new species with a band at 1457 $cm^{-1}$, also grows at the expense of species A. Finally, a very weak band at 1506 $cm^{-1}$ starts to be visible at 150 C and grows very slowly with temperature.

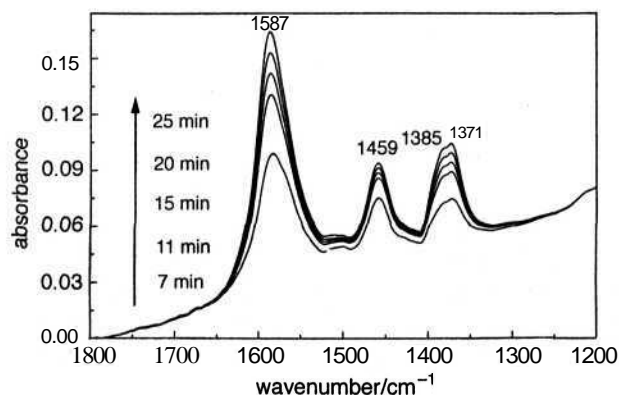At 200 °C, the spectrum is composed of four strong bands at 1587 and 1385 $cm^{-1}$ (species B), 1459 and 1373 $cm^{-1}$, and a very weak band at 1509 $cm^{-1}$. All these bands, except that at 1509 $cm^{-1}$, increase with **adsorption** time as shown in Fig. 4. In an attempt to assign the 1459 and 1373 $cm^{-1}$ bands, we compare (Fig. 5) the time dependence of their intensities relative to the band at 1587 $cm^{-1}$. Fig. 5 shows that their intensity variation is similar and different from that of the 1587 $cm^{-1}$ band. This implies that the bands at 1459 and 1373 $cm^{-1}$ can be ascribed to a new species C.

Fig. 6 quantitatively illustrates the evolution of the three main bands at 1642, 1584-1589 and 1371-1373 $cm^{-1}$, which are taken as representative of the three species A, B and C, respectively. The bands at 1373 and 1585 $cm^{-1}$ grow more than threefold with increasing adsorption temperature in the range 100–200 °C, while the band at 1642 $cm^{-1}$ decreases in intensity by a factor of two.
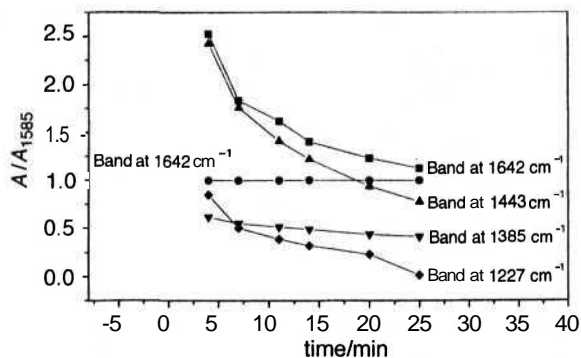


Fig. 2 Variations of FTIR band intensities of the adsorbed species at 100 °C as a function of time
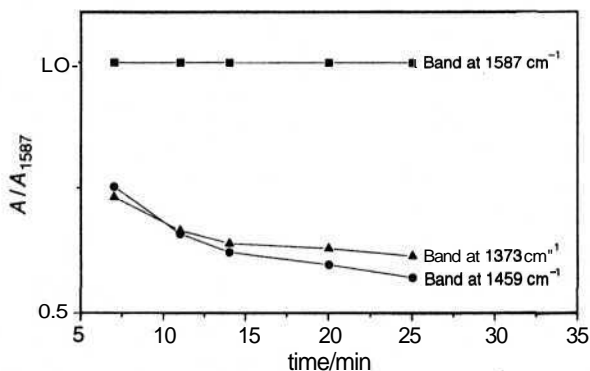


Fig. 5 Variations of FTIR band **intensities** of the adsorbed species at 200 °C as a function of time
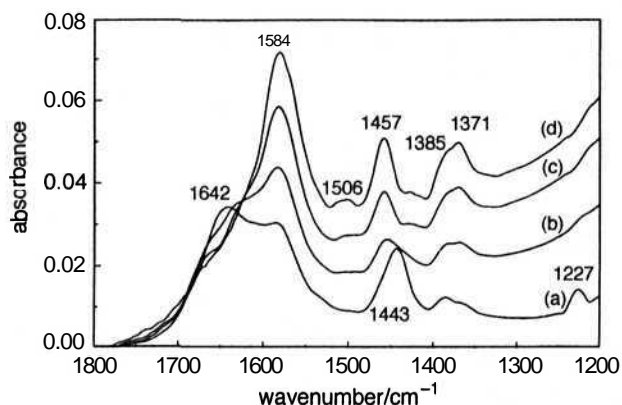


Fig. 3 *In situ* FTIR spectra of the adsorbed species following CO reduction of 0.5% $Cr/SiO_2$ at elevated temperatures: (a) 100 °C, (b) 125 °C, (c) 150 °C, (d) 175 °C
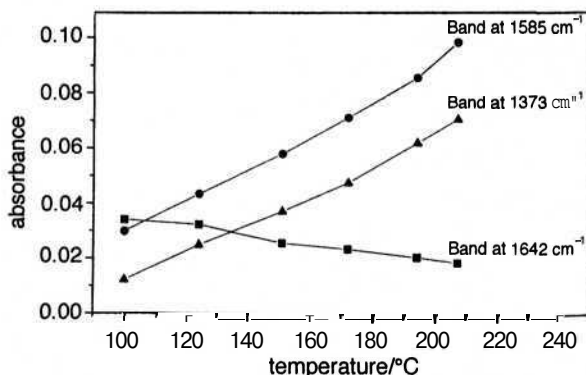


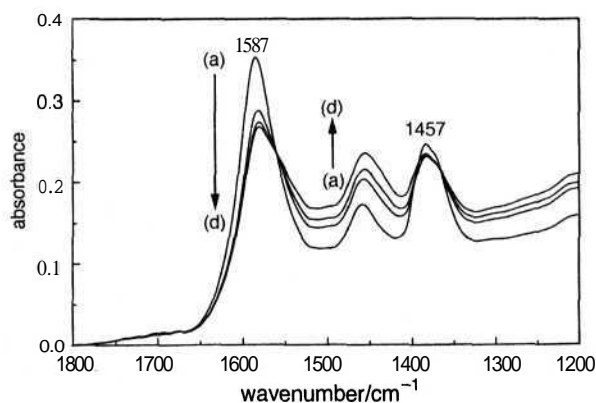Fig. 6 Variations of FTIR band intensities under CO flow from 100 to 200 °C

Fig. 7 *In situ* FTIR spectra of the adsorbed species following CO reduction of 0.5% **Cr/SiO$_2$**: (a) **320 °C,** (b) **360 °C,** (c) **375 °C,** (d) **390 °C**



Fig. 8 *In situ* FTIR spectra of the adsorbed species formed at the first stage (4 **min).** (a) Adsorption at 100 °C; (b) adsorption at 400 °C.

Upon heating in CO from 200 to 300 °C, the bands due to species B and C grow in intensity, with those of B at a higher rate. Above 300 °C, the bands of species B (1585 cm$^{-1}$) decrease and those of species C (1456 cm$^{-1}$) continue to increase in intensity (Fig. 7). These results suggest that the thermal stability of species C is higher than of species B.

### 3.2 Influence of the temperature on the formation of the different adsorbed species

To study the influence of the adsorption temperature on the formation of the three species (A, B, C), three adsorption experiments were performed at 100, 200 and 400 °C on fresh samples. Each sample was pretreated at 400 °C in an **O$_2$** flow for 2 h and then in a He flow for l h prior to CO adsorption. Fig. 8 displays the spectra recorded in the first stage of adsorption (4 min after CO was introduced). This figure clearly shows that (i) species A (bands at 1642, 1443 and 1227 cm$^{-1}$) is dominant at **100°C** and (ii) at **400 °C,** only species B (bands at 1584 and 1384 cm$^{-1}$) is detected. After 30 min, the spectra recorded at 200 and 400 °C indicate the coexistence of species B and C. However, at 100 °C species B coexists with species A. It is also important to note that when the temperature is increased from 100 to 200 °C, the intensities of the bands due to species B increase by a factor of ten. These results are in full agreement with our previous data: at low temperature species A is dominant and B grows slowly with time. The formation of species B is accelerated with an increase of temperature. Species C is only formed at high temperature and grows at the expense of species B. These results suggest the transformation

$$A \xrightarrow{\text{heat}} B + C$$
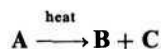
### 3.3 Thermal stability of the different adsorbed species

The desorption of adsorbed CO was undertaken starting from 200 °C to examine the thermal stability of the surface species. After achieving a steady-state adsorption at **200 °C,** the sample was heated in an He flow from 200 to 400 °C. Between 200 and **300°C,** all the bands are almost unaffected. Above 300 °C, the bands of species B decrease strongly and at 400 °C, their intensity is already halved. On the other hand, the bands of species C start to decrease slowly at 380 °C. These results confirm the conclusion that the bands at 1584-1589 (B), 1457-1459 (C), 1383-1385 (B) and 1371-1373 (C) cm$^{-1}$ arise from two kinds of surface species distinguished by their difference in behavior when subjected to evacuation. The variation of the two species B and C characterised by the bands at 1588 and 1457 cm$^{-1}$, respectively, is illustrated more clearly in Fig. 9.
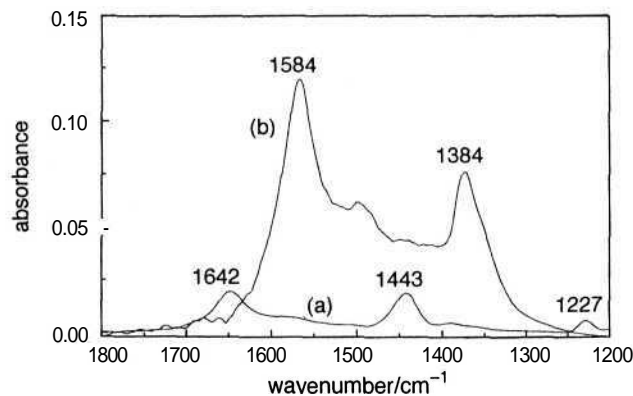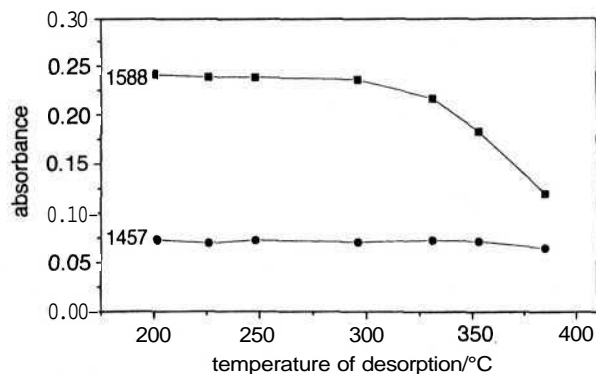


**Fig.** 9 Variations of FTIR band intensities of the adsorbed species at 200 °C during desorption in He flow

Species C is more stable than species B and consequently, the order of thermal stability of the three species detected is A < B < C.

## 4 Discussion

### 4.1 Assignment of the bands

On the basis of spectral investigations of various carbonate and carboxylate compounds (mainly bulk solid spectra), the following scheme (Table 1) has been proposed by Davidov[15] to interpret the spectra of surface carbonate and carboxylate compounds.

On supported **CrO$_3$** no detailed data are available to our knowledge, but on α-**Cr$_2$O$_3$**, Zecchina *et al.*[16] have reported **IR** studies of **CO$_2$** adsorption. Table 2 lists some assignments

**Table 1** Summary of the adsorbed surface carbonate and carboxylate species and their band positions and assignments for CO adsorbed on transition-metal **oxides**[15]

| species | band position/cm$^{-1}$ (assignment) |
|---|---|
| inorganic carboxylate | 1560-1630 ($\nu_{as}COO^-$); 1350-1420 ($\nu_s COO^-$) |
| **non-coordinated** carbonate | 1450-1420 ($\nu_{as}CO_3^{2-}$); 1090-1020 ($\nu_s CO_3^{2-}$) |
| **monodentate** carbonate | 1530-1470 ($\nu_{as}COO^-$); 1370-1300 ($\nu_s COO^-$) 1080-1040 ($\nu C=O$) |
| bidentate carbonate | 1530-1620 ($\nu C=O$); 1270-1250 ($\nu_{as}COO$) 1030-1020 ($\nu_s COO$) |
| bridged carbonate | 1620-1670 ($\nu C=O$); **1220–1270** ($\nu_{as}COO$) 980-1020 ($\nu_s COO$) |

**Table 2** Assignments of carbonate-like surface species observed after $CO_2$ adsorption on $\alpha$-$Cr_2O_3$ [16]

| wavenumber/cm$^{-1}$ | assignment |
|---|---|
| 1560, 1340 | bidentate carbonate |
| 1590, 1305 | bidentate carbonate |
| 1635, 1285 | bidentate carbonate |
| 1490, 1365 | monodentate carbonate |
| 1620, 1430, 1225 | bicarbonate |
| 1630, 1440 | carboxylate |

of carbonate-like species related to the present work. By comparing our results presented above with those presented in Tables 1 and 2, one can assign species C to monodentate carbonate: 1458 cm$^{-1}$ for $\nu_{as}COO^-$ and 1373 cm$^{-1}$ for $\nu_s COO^-$. These two bands cannot be ascribed to bidentate carbonate since it is known that the splitting is smaller in the monodentate complex than in the bidentate complex.[15] Indeed, Nakamoto[17] demonstrated that the difference between $\nu(C-O^1)$ and $\nu(C-O^2)$ is ca. 100 cm$^{-1}$ for a monodentate complex but > 200 cm$^{-1}$ for a bidentate complex. For carboxylate species, symmetric and antisymmetric stretching vibrations are usually found in the regions 1350-1420 and 1550-1630 cm$^{-1}$, respectively (Table 1). For $\alpha$-$Cr_2O_3$,[15] $\Delta\nu(=\nu_{as}-\nu_s)$ is ca. 200 cm$^{-1}$. Then, the bands near 1585 and near 1385 cm$^{-1}$, previously grouped as species B may be attributed to inorganic carboxylate rather than to carbonate species.

Zecchina et al.[16] have reported three bands (1620, 1430, 1225 cm$^{-1}$) attributed to bicarbonate species (Table 2). The same species have also been observed on other oxides ($Al_2O_3$, $ZrO_2$, ZnO).[18-20] Then, we propose to assign species A (1642, 1444, 1227 cm$^{-1}$) to a bicarbonates species; the antisymmetric mode being at 1642 cm$^{-1}$ and the symmetric mode at 1444 cm$^{-1}$. The 1227 cm$^{-1}$ peak corresponds to the OH bending mode. Owing to very weak transmission in the high frequency region, it has not been possible to observe the OH stretching mode that is expected at ca. 3600 cm$^{-1}$.

The other factor that must be taken into account in the analysis of differences between carbonate and carboxylate compounds is their thermal stability. It is known that monodentate carbonates are more thermally resistant than bicarbonate species.[18-20] This is in accord with our assignment of species A to a bicarbonate and C to monodentate carbonate. On the other hand, in many studies concerning the adsorption of CO on oxides,[17,21-24] it is shown that inorganic carboxylates are less thermally resistant than monodentate carbonates. This tendency reinforces our assignment of species B to inorganic carboxylate. Table 3 summarizes the assignment of the different bands.

IR spectroscopie studies of CO adsorption on MgO,[25] CaO and SrO[26] have shown that adsorbed CO gives rise to a large number of bands attributed to carbonate species and some unusual polymeric CO species. Furthermore, the polymeric species were sensitive to oxygen, being destroyed upon exposure to $O_2$, however, no apparent change in our spectra of adsorbed CO was found after exposure of the sample surface preadsorbed with CO to an oxygen flow for 30 min at 200 or 400 °C. We therefore rule out the possibility of polymeric CO

**Table 3** Summary of the adsorbed surface species and their band positions and assignments for CO treated $CrO_3/SiO_2$ catalysts

| surface species | band positions/cm$^{-1}$ (assignment) |
|---|---|
| bicarbonate | 1227 ($\nu$O-H), 1442-1446 ($\nu_s$COO); 1642-1648 ($\nu_{as}$COO) |
| monodentate carbonate | 1371-1376 ($\nu_s COO^-$), 1453-1459 ($\nu_{as}COO^-$) |
| inorganic carboxylate | 1381-1386 ($\nu_s COO^-$), 1585-1589 ($\nu_{as}COO^-$) |

species in the present study.

The band at 1509 cm$^{-1}$ is very weak and not regularly observed and has not been assigned.

### 4.2 Mechanism of the reduction of $CrO_3/SiO_2$ with CO

According to our model,[27] the reduction process of supported $CrO_3$ with CO is a two-step mechanism:

$$Cr_a + CO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Cr_a(CO)_{ads} \xrightarrow{k_2} Cr^{m+}(CO_2)_{ads} \quad (m < 6)$$
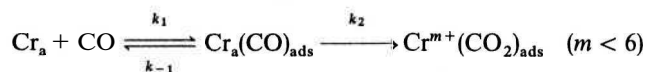
where $Cr_a$ represents anchored $Cr^{6+}$ [chromate or di(poly)chromate species].

The first step is the adsorption of CO on the surface at some unspecified site, resulting from in its activation. The second step, the actual reduction of $Cr^{6+}$, is rate determining and occurs with formation of surface carboxylates, which decompose to $CO_2$. The oxygen comes from the chromate or di(poly)chromate species. On the other hand, we have found that the rate constant $k_2$ is at least 100 times smaller than $k_1'$ ($k_1' = fc^{\wedge}CO]"$). This implies that the intermediate $Cr_a(CO)_{ads}$ accumulates and can be detected spectroscopically.

The first step which is the activation of the reducing agent[28] corresponds to the formation of bicarbonate species. Then, the bicarbonates are converted into carboxylate species inducing the reduction of $Cr^{6+}$ ions. At moderate temperatures (100, 200 °C), at the first stage of adsorption, the bicarbonate species dominate (Fig. 8, Table 4) but are no longer detectable at 400 °C. We propose that their formation and conversion into carboxylates is very rapid.

Since $Cr^{6+}$ (d°) ions cannot bind to carbon to form carboxylates the formation of carboxylate species indicates that reduction of supported chromium oxide has already commenced. We have found that carboxylate species start to form at 100 °C and their highest concentration is observed at 300 °C. This result is in good agreement with observations reported by Finch.[29] Indeed, using TPR, Finch has shown that the onset of reduction of $CrO_3/SiO_2$ with CO occurs at ca. 100 °C. On the other hand, using EPR spectroscopy we have confirmed the absence of $Cr_2O_3$ clusters prior to CO adsorption (calcined sample). This rules out the possibility that carboxylate formation is only due to the interaction of CO with the $Cr_2O_3$ surface. On the other hand, monodentate carbonate species result from the re-adsorption of $CO_2$ on reduced chromium ions, as previously proposed for $\alpha$-$Cr_2O_3$.[16]

In conclusion, we propose the following scheme: (i) CO interacts with chromate or di(poly)chromate sites and with surface hydroxy group to form bicarbonate species; (ii) these intermediate species are then converted into carboxylate species; (iii) two electrons are consumed by $Cr^{n+}$ ($n = 6$, 5) cations which are consequently reduced [$Cr^{(n-2)+}$].

## 5 Conclusions

The following conclusions can be made from this work.

(1) CO reduction of $CrO_3/SiO_2$ commences at 100 °C.

(2) The reduction process occurs through the formation of surface bicarbonate and carboxylate species.

**Table 4** Evolution of the adsorbed species during the reaction as a function of the reduction temperature

| $T/°C$ | after 4 min | after 30 min |
|---|---|---|
| 100 | bicarbonate | bicarbonates/carboxylates |
| 200 | bicarbonate/carboxylate | carboxylates/monodentate carbonate |
| 400 | carboxylate | carboxylates/monodentate carbonate |

(3) The first step of reduction, the activation of CO, consists of the formation of bicarbonate species which are quickly converted to carboxylate adsorbed on reduced chromium ions $[Cr^{(n-2)+}]$ in accord with our model.[27]

(4) Inorganic carboxylates are the dominant adsorbed species, and can be considered as a probe for the course of the reduction process on supported chromium oxide.

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