IDENTIFICATION AND STABILITY OF CH_3, CH_2, AND CH SPECIES ON Co AND Ni SURFACES, A PES INVESTIGATION

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CH_3, CH_2, CH, and C, adsorbed on polycrystalline Co or Ni, are idenified and characterized by XPS and UPS with respect to peak positions and temperature regimes of existence. The species are generated by adsorption and subsequent dissociation of CH_3Cl or CH_2Cl_2. Due to the early dissociation of the C–Cl bond it is possible to study the CH_n species and their stepwise dehydrogenation without interference. Constant and temperature independent peak positions over ranges of at least 50 K on Co and of about 40 K on Ni indicate that the peak maxima used for identification are generated by the respective single species and not by superimposition of two or more peaks of species drifting through the dehydrogenation.

1. Introduction

Alcohols are known to be an important share of the reaction products of CO hydrogenation over metal catalysts [1]. The addition of primary alcohols to a CO/H_2 feed stream is reported to yield long chained hydrocarbons [2,3]. In a number of studies on alcohol adsorption and reaction alcohols were observed to form alkoxy species [4–20] and it was suggested that these alkoxy species were important intermediates in Fischer–Tropsch synthesis, as they reacted to form hydrocarbons and oxygen containing products. However, in studies of the reactions of methanol on Ni and Co polycrystalline foils a significant switch in the mechanism was found in dependence on the flux of the methanol over the catalyst: by administering a very high methanol flux to the catalyst – realized by application of the high intensity of a supersonic nozzle beam – and also in the presence of excess hydrogen an early rupture of the C–O bond was observed; then CH_3 and OH (or O) are the primary products of the reaction [18–20]. The rather sharp transition between the two mechanisms shows that results obtained in static experiments with low covered surfaces cannot be

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transferred by linear extrapolation to higher pressure regimes. Furthermore, the formation of CH_3 and its further reactions demand for means to identify the CH_3, CH_2, CH, and C species. This was done in the present study for Co and Ni. There is a number of results on PES of hydrocarbon species scattered in the literature, to be extracted from studies of adsorption of molecules dissociating into CH_n or C_mH_n [21–27], however, with respect, to the C_1 species these results are incomplete and somewhat contradictory; hence, a systematic PES investigations was done.

2. Experimental

The UHV apparatus has been described earlier [15,16]. An effusion beam is used in order to introduce the reactants to the surface. The surface can be cooled down to liquid nitrogen temperature and heated up to 850 K. A quadrupole mass spectrometer is used for monitoring desorbing particles, a PE spectrometer for analysis of the surface and the surface species. UPS: 21.21 eV, 0.003 eV resolution; and 40.81 eV, 0.017 eV resolution; XPS: 1486.6 eV, 0.9 eV resolution. The hemispherical analyzer has a resolution of 0.2 to 0.5 eV according to the mode of operation. The experiments are done in the following pattern: the spectroscopically controlled clean Co or Ni surface is cooled down to liquid nitrogen temperature and then covered with CH_3Cl or CH_2Cl_2 by single exposure to the effusion beam (beam pressure about 10^{-7} mbar of chloride; exposure time 40 s for CH_2Cl_2 and 120 s for CH_3Cl). Without further admission of chloride stepwise raised temperatures are adjusted up to 600 K and the PE spectra of the surface species taken at constant temperatures.

Since several C 1s binding energies lie also in the range of oxygenated compounds, particular care is given to the control of those species. This is done after adsorption and during decomposition by XPS monitoring of the O 1s region and by quadrupole monitoring of desorption of CO or CO_2. From this the presence of oxygenated species can be ruled out. Furthermore, $CO_{2\ ads}$ and, in particular, CO_{ads} are clearly discernible from $CH_{n\ ads}$ in He II spectra.

3. Results and discussion

First the spectra of the experiments with Co will be presented and discussed in detail. General arguments which give essential support to the details will be compiled and presented thereafter. The results with Ni are basically identical though the temperature regions of the presence of a species are smeared out in comparison to the rather clearly separated intervals on Co.

3.1. CH₂Cl₂ on Co

The XP spectrum of CH_2Cl_2 adsorbed on polyscrystalline Co and the subsequent evolution of species is shown in fig. 1. At 95 K the C 1s peak is situated at 288.2 eV, the Cl 2s peak at 271.8 eV. No change in the spectrum occurs up to a surface temperature of 140 K. These two peaks are attributed to molecularly condensed (frozen) CH_2Cl_2. Upon heating to 150 K the C 1s peak is shifted to 286.2 eV, a broad peak centered around 269.6 eV is observed in the Cl 2s spectrum; the change of the spectrum is accompanied by a substantial desorption of CH_2Cl_2. Hence, the residual species in taken for $CH_2Cl_{2\ ads}$ in the major concentration (see UPS results below). With further temperature increase the position of the Cl 2s peak is shifted again to lower energies: at 180 K a double peak indicates the presence of two surface species; at 210 K a peak of normal width is formed at 268.9 eV. This peak stays in constant position, FWHM, and intensity from as low as 210 K up to 800 K. It indicates that the C–Cl bond is broken and Cl_{ads} on Co is formed as low as 180 K. Cl_{ads} can be removed by Ar sputtering only; any desorption of HCl, Cl_2 or other Cl containing species was carefully checked and can be ruled out within the temperature limits of the apparatus (850 K).

In contrast to the constant Cl 2s peak, the C 1s peak shifts in the given temperature range indicating thereby further reactions of the $CH_{2\ ads}$. The only gaseous product of these reactions is H_2, i.e., gradual dehydrogenation of $CH_{2\ ads}$ occurs.

At 150 K after desorption of the condensed CH_2Cl_2 the position of the C 1s peak is 286.2 eV; it is attributed to chemisorbed CH_2Cl_2. Above 180 K a large shift of both peaks indicates the dissociation of the molecule

$$CH_2Cl_{2\ ads} \rightarrow CH_{2\ ads} + 2\ Cl_{ads}. \tag{1}$$

The formed $CH_{2\ ads}$, characterized by a C 1s peak at 284.9 eV, is detectable up to 470 K. Above 180 K a broad peak indicates the formation of a second species, at about 270 K this process is completed; a well resolved peak at 283.8 eV indicates the completion of H abstraction according to

$$CH_{2\ ads} \rightarrow CH_{ads} + H_{ads}. \tag{2}$$

The CH_{ads} species is dehydrogenated at 470 K. The peak at 283.2 eV for the C_{ads} formed is in accordance with the values found earlier, e.g. refs. [16,18,26];

$$2\ CH_{ads} \rightarrow 2\ C_{ads} + H_2. \tag{3}$$
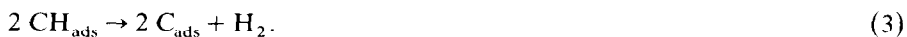
The reactions given in eqs. (2) and (3) are neatly supported by the evolution of hydrogen from the surface: the amount of hydrogen generated at about 270 K is stored on the surface and desorbs at 400 K; this temperature is well known from a number of hydrogen adsorption studies. A second substantial emission of hydrogen is observed far beyond the 400 K desorption at about 470 K. This
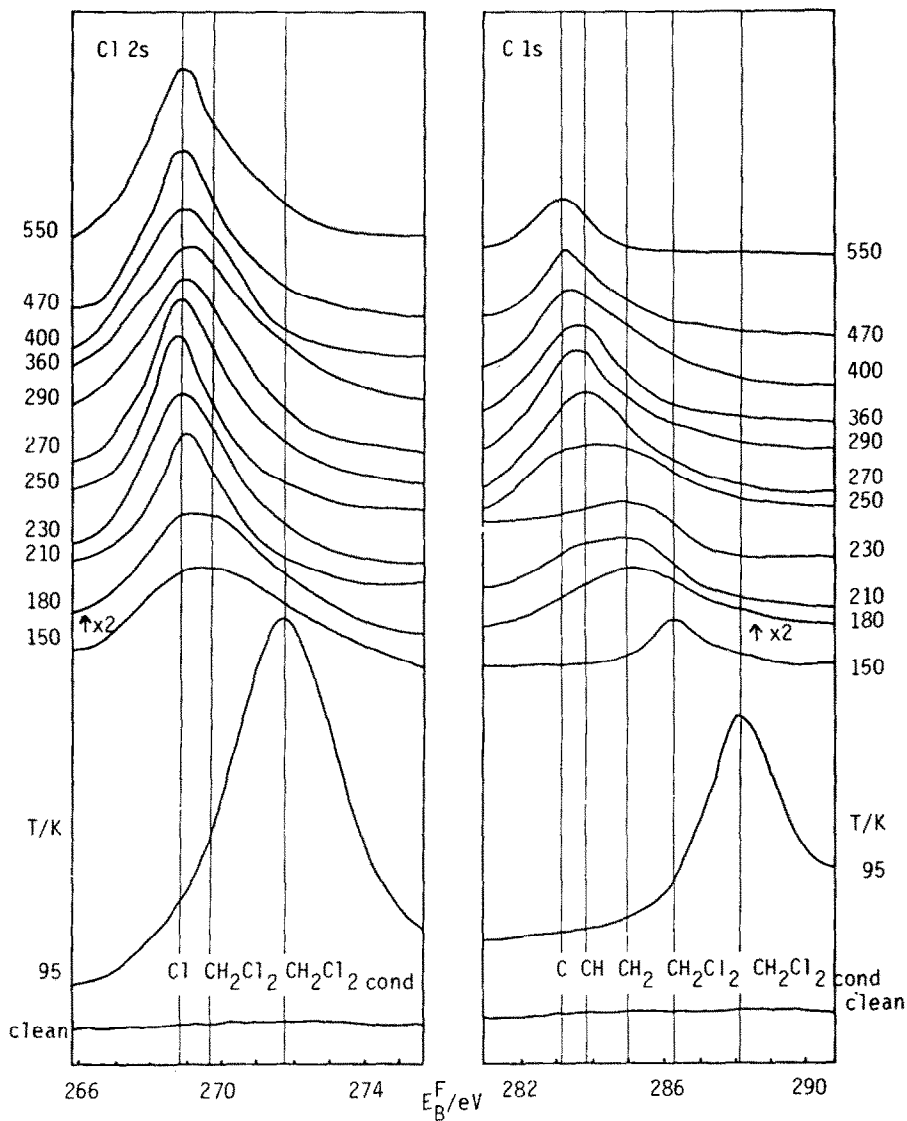
Fig. 1. 1486.6 eV spectra of CH$_2$Cl$_2$ and the reaction products on Co. (The spectra of 180 K and above are registered with double sensitivity.)

hydrogen cannot have been kept adsorbed by Co, it is the hydrogen set free by the reaction according to eq. (3).

The He I spectra of the CH$_2$Cl$_2$ adsorption and decomposition essentially support the XPS findings; due to the different emission coefficients of the

different orbitals the regimes of dominance of a peak (species) do not corre-
spond strictly in every detail. Two peaks at 5.5 and 8.9 eV, of constant position
and intensity from 95 to 140 K, indicate the undissociated adsorbed CH_2Cl_2.
At 150 K and above a drastic decrease of these peaks occurs due to desorption
of the condensed CH_2Cl_2. Above 150 K the 8.9 eV peak is no longer
detectable; from this it is concluded that the 5.5 eV peak contains the lone pair
electron level of Cl_{ads}. At 180 K only one nearly symmetric peak is observed at
5.5 to 5.6 eV, it is not changed up to 570 K; however, a shoulder at 5 eV starts
to emerge from it. The shoulder reaches maximum intensity at 270 K and
decreases on going to higher temperatures. Taking into account the XPS results
the peak at about 5 eV is attributed to CH_{ads} in good agreement with ref. [26].
It is unfortunate but supported by the CH_3Cl results (see below) that the peak
of the lone pair orbital of Cl_{ads} and the peak of $CH_{2\,ads}$ overlap significantly at
5.5 eV.

3.2. CH_3Cl on Co

The XP spectra of adsorption, dissociation and dehydrogenation of CH_3Cl
on polycrystalline Co are given in fig. 2. At 90 K the C 1s peak is situated at
287.4 eV, the Cl 2s peak at 272.2 eV. The situation is similar to the one just
outlined for CH_2Cl_2; however, it will be seen that the $CH_{2\,ads}$ species
generated by dehydrogenation of $CH_{3\,ads}$ is a very unstable and short living
species. At 130 K the peaks are shifted to 286.8 eV for C 1s and 270.5 eV for
Cl 2s, the shift is accompanied by a decrease in peak intensity and by
substantial desorption of CH_3Cl. Hence, these peaks are attributed to chemiso-
rbed CH_3Cl_{ads} which is not yet dissociated. At about 170 K a large shift of
both peaks is observed. The Cl 2s peak is broadened and shifted to 269.5 eV
and furthermore at 190 K to 268.9 eV. At that position the peaks stays
constantly and is of well developed shape and FWHM. This is the peak of
Cl_{ads}, hence, CH_3Cl must be dissociated at that temperature:

$$CH_3Cl_{ads} \rightarrow CH_{3\,ads} + Cl_{ads}. \tag{4}$$

This means that the C 1s peak at 285.8 eV, observed at 170 K, must be
attributed to $CH_{3\,ads}$. This species gradually is dehydrogenated with further
heating, as indicated by a decrease in intensity, to form a shoulder at higher
temperatures. At 330 K even this shoulder no longer is detectable. Above 170
K decomposition of $CH_{3\,ads}$ sets in, indicated by a sequence of twin peaks and,
later on, of broad double or triple species peaks. This evolution comes to an
end at 570 K by formation of C_{ads}, the C 1s peak is located at 283.2 eV. Of
particular interest is the evolution in the temperature range of 190 to 250 K.
The spectra show twin peaks with maxima at 285.8 and 283.8 eV, attributed to
$CH_{3\,ads}$ and, according to the results with CH_2Cl_2 (fig. 1), to CH_{ads} whereas
only minor intensity, if any, is found in the position of the $CH_{2\,ads}$ (284.9 eV).
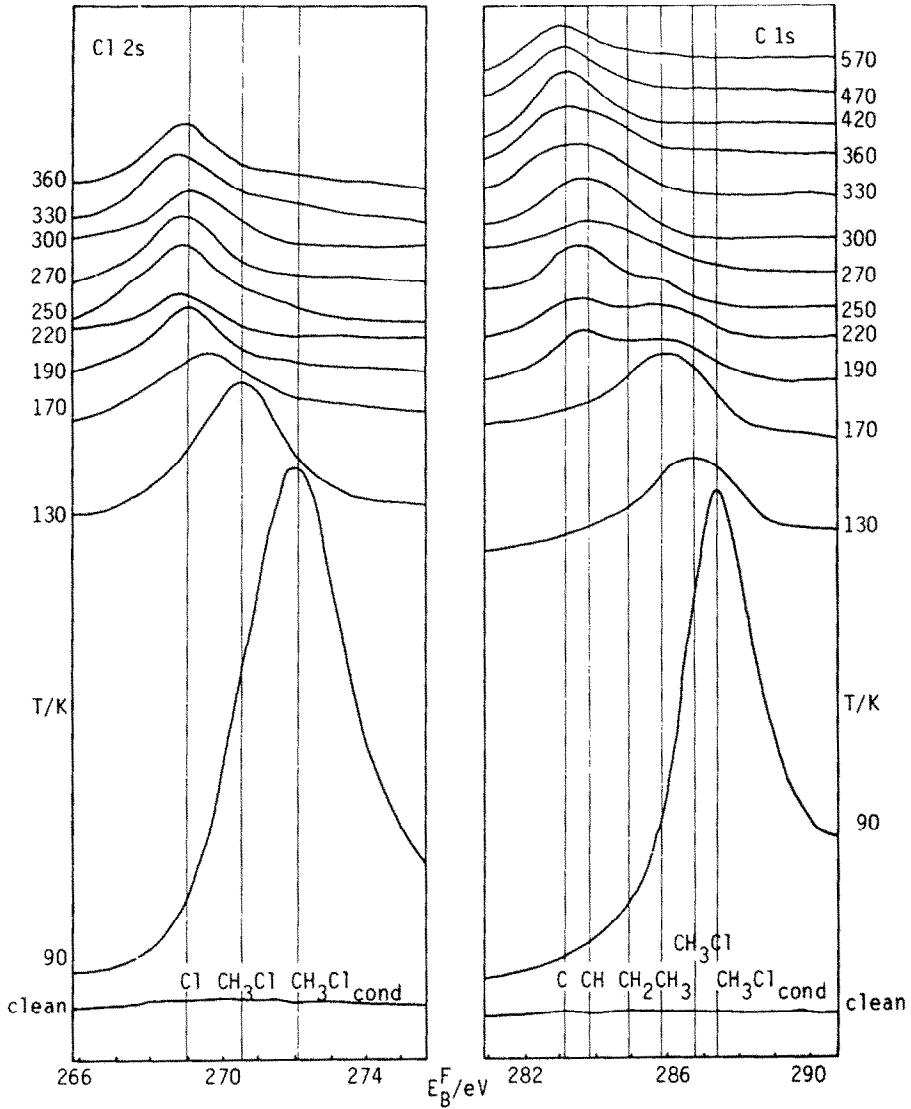
Fig. 2. 1486.6 eV spectra of CH_3Cl and reaction products on Co.

This of course is due to the higher temperature necessary in order to dissociate $CH_{3\,ads}$ according to

$$CH_{3\,ads} \rightarrow CH_{2\,ads} + H_{ads} \qquad (5)$$

in comparison to the dissociation of $CH_2Cl_{2\,ads}$ according to eq. (1). The

former reaction – eq. (5) – occurs at 190 K, the latter – eq. (1) – at 150 to 160 K. The temperature range of CH$_{ads}$ is rather expanded; the 283.8 eV peak is clearly present from 190 to 360 K. Above 470 K only C$_{ads}$ remains on the surface. Like in the experiments with CH$_2$Cl$_2$ the PE spectroscopic evidence is matched by a corresponding evolution of hydrogen well above the desorption temperature of 400 K.

The He II spectra (fig. 3) thoroughly corroborate the findings with XPS. At 90 K molecularly adsorbed CH$_3$Cl is indicated by two peaks at 5.8 and 9.6 eV. Going to 120 K the intensity of these peaks is decreased by desorption of CH$_3$Cl. At 150 K already a new peak emerges at 6.8 eV, increasing with further temperature increase up to 160 K, accompanied by a simultaneous decrease of the 9.6 eV peak. The 6.8 eV peak is attributed to CH$_{3\,ads}$, which according to the clear difference in peak energy with respect to CH$_3$Cl$_{ads}$ can be detected at lower temperature in UPS than in XPS. The temperature region in which CH$_{3\,ads}$ is the dominant species in both spectra is 170 to 180 K (figs. 2 and 3). CH$_{3\,ads}$ is detectable by UPS up to 310 K in accordance with the XPS findings. The attribution of the 6.8 eV peak to CH$_{3\,ads}$ is supported by experiments on the dissociative adsorption of dimethylether on Fe [28]. In the temperature range between 130 and 150 K the well known feature of CH$_3$O$_{ads}$, identified by two peaks at 10.1 and 5.8 eV [16] is accompanied by a 6.9 eV peak. The fact that those three peaks must be attributed to two species is clearly shown by the different intervals of temperature of further decomposition of the species. On Co, above 220 K a shoulder at 5.1 eV starts to emerge on the low energy side of the 5.5 eV peak of Cl$_{ads}$; it indicates the formation of CH$_{ads}$ which at still higher temperatures is decomposed to form C$_{ads}$, identified by a 4.8 eV peak. Due to the overlap of CH$_{2\,ads}$ and Cl$_{ads}$ in the UP spectrum, apart from a slight rise and fall of the intensity of that peak due to the intermediate generation of CH$_{2\,ads}$ no clear temperature limits on the stability of CH$_{2\,ads}$ can be gained from UPS.

3.3. General support of the outlined identification

3.3.1. Influence of Cl$_{ads}$ on the position of PE peaks

Since a rather high coverage of Cl$_{ads}$ is present during part of the experiments (after dissociation of CH$_3$Cl or CH$_2$Cl$_2$, respectively) the surface dipole and the extramolecular relaxation/polarization (ERP shift) might be changed by Cl$_{ads}$. This would mean that peak positions of CH$_{n\,ads}$ species, identified in this work, could not be used in general. In order to inspect this point a comparison of peak positions of species generated in chlorine free experiments and of the present experiments is necessary. Such a comparison is possible for UPS and XPS peaks as well for C$_{ads}$, CH$_3$OH$_{ads}$ and CH$_{3\,ads}$ on Co [19] and for C$_{ads}$, CH$_3$OH$_{ads}$ and CH$_{3\,ads}$ on Ni [20]. No energy shift is observed in the manifold peaks of these species, hence, it can be concluded that also the peaks

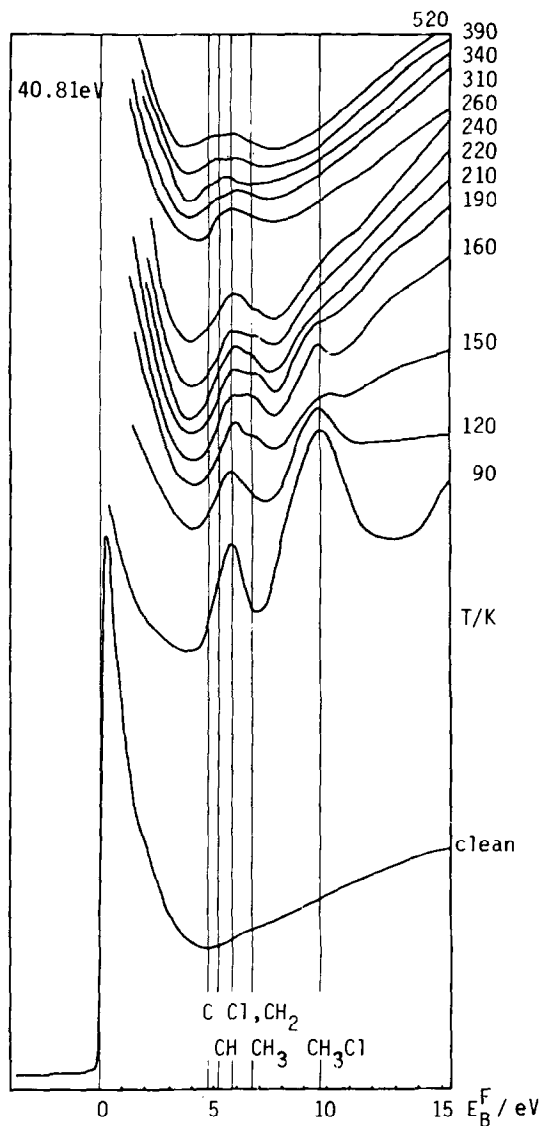Fig. 3. 40.81 eV spectra of CH_3Cl and reaction products on Co.

of the various $CH_{n\ ads}$ species are not shifted, i.e., the peak positions identified in this study can be generalized. In addition, the position of the peak of $CH_{3\ ads}$ is identical whether it has been generated by dissociation of CH_3Cl, CH_3OH, or CH_3OCH_3.

The dehydrogenation reactions of $CH_{n\ ads}$, on the other hand, might be

Table 1

Characteristic PE line energies for species adsorbed on polycrystalline Co; the electron binding energies are referenced to the Fermi level of the metal; the temperature regimes where a species is visible and dominant are stated

	XPS 1486.6 eV E_B^F (eV)	UPS 40.81 eV E_B^F (eV)	Temperature regime (K)
CH₃	285.8	6.8–6.9	170–250 150–300
CH₂	284.9	~ 5.5	180–230 [a] 180–360 [a]
CH	283.8	5.0–5.1	200–360 190–450
C	293.3	4.7	360–570
Cl	268.9	5.5	210–800

[a] In CH₂Cl₂ experiments only (see text).

affected by the presence of Cl$_{ads}$, i.e., the temperature intervals given in tables 1 and 2 might be somewhat different from those of clean metal surfaces. However, there is a number of experimental hints that the influence of Cl$_{ads}$ on adsorbed species is smaller than that on incoming reactants prior to chemisorption [29].

Table 2

Characteristic PE line energies for species adsorbed on polycrystalline Ni; the electron binding energies are referenced to the Fermi level of the metal; the temperature regimes where a species is visible and dominant are stated

	XPs 1486.6 eV E_B^F (eV)	UPS 40.81 eV E_B^F (eV)	Temperature regime (K)
CH₃	285.6–285.8	6.5	170–210 150–380
CH₂	285.0–285.2	5.5–5.8	220–260 180–420
CH	283.8–284.0	5.2	270–470 200–650
C	283.5	4.3	480–850 300–850
Cl	268.9	5.8	180–850

3.3.2 Dissociation of the C–Cl bond and dehydrogenation of $CH_{n\ ads}$

An inspection of the peak widths shows that essentially the dissociation of the C–Cl bond is completed before the dehydrogenation reactions of the $CH_{n\ ads}$ species occur. In particular, the overlap of both reactions is so small that the identification of the $CH_{n\ ads}$ species is not blurred. The transition from condensed to adsorbed chlorides and the dissociation of the C–Cl bond are manifested in the Cl 2s spectra by broad peaks due to the superimposition of the peaks of the different species. Natural peak width is restored as soon as the dissociation is completed and Cl_{ads} is the only Cl containing species at the surface. This is different on the C 1s side of the spectra due to the overlap of regimes of existence of the different $CH_{n\ ads}$ species, e.g., the spectrum at 250 K in the CH_2Cl_2 experiment (fig. 1) or the spectra from 190 to 270 K in the CH_3Cl experiment (fig. 2). However, the possibility (and need) to discuss dehydrogenated species with a still intact C–Cl bond is ruled out by these results. Furthermore, there is no spectroscopic evidence for a transition of CH_3Cl_{ads} into a CH_2Cl_{ads} species as a comparison of the XP and the UP spectra shows.

3.3.3. Attribution of peak positions to single $CH_{n\ ads}$ species

In consequence of the before stated it is necessary to point out that there is always a clear temperature regime with a stable position of the peak maximum: e.g., 170 to 250 K for the 285.8 eV peak, 190 to 300 K for the 283.8 eV peak, and 360 to 570 K for the 283.2 eV peak in the CH_3Cl experiment (fig 2); 180 to 230 K for the 284.9 eV peak, 270 to 360 K for the 283.8 eV peak, and 470 to 550 K for the 283.2 eV peak in the CH_2Cl_2 experiment (fig. 1). (These are not the temperature regimes of detectability but of stable peak maximum.) Temperature regimes of at least 50 K with stable peak maxima mean of course that the maxima are generated by a single species and not by a superimposition of peaks of two species being simultaneously present at the surface. Since the simultaneous presence of two species would be influenced by the temperature increase – by either increase of rate or shift of equilibrium constant of the H dissociation – as in fact can be seen by the twin peak spectra in the range from 190 to 250 K in the CH_3Cl experiment (fig. 2), a constant position of the peak maximum over these wide temperature ranges could not be expected – nor computed in model calculations – by superimposition of two peaks with coupled surface concentrations. Hence, in fact, these stable positions within large temperature intervals show that there occurs a stepwise dehydrogenation – with the one exception of the rather small regime of $CH_{2\ ads}$ in the CH_3Cl experiment. The subsequent dehydrogenation steps are separated by large temperature intervals – at least on Co and Ni.

3.3.4. Comparison of binding energy differences of adsorbed CH_n species with calculated values

It is reasonable to compare the difference in binding energies of the adsorbed

CH_n species with the differences of theoretically calculated energies of the respective free species [30]. In fact the valence levels of singlet methylene $1B_2$ and pyramidal methyl 1E differ by 0.7 eV; also the triplet methylene $1B_2$ and the planar methyl 1E' show that difference of 0.7 eV. Though this difference is in the right direction and in a proper order of magnitude other experiments and calculations, e.g., on acetylene, ethylene, and ethane [31], as well as our own results on CO and CH_3OH show that the trends in C 1s core level binding energy in gas phase molecules are in a direction opposite to that observed in adsorbed species. This reversion might be due to the fact that the metal surface is a very appropriate ligand; hence, loss of hydrogen of a surface species might be a substitution by metal rather than a real reduction of bonds. It is a general observation that by dissociative adsorption electron binding energies are shifted to lower values with respect to nondissociative adsorption due to the higher amount of charge transfer from the metal to the dissociated species.

4. Conclusion

It has to be stressed that XPS and UPS and hydrogen desorption combine to a uniform and self-consistent picture; the CH_2Cl_2 experiment not only is consistent with but fills the gap left by the CH_3Cl experiment. Due to the early dissociation of the C–Cl bond, it is possible to generate $CH_{3\,ads}$ and $CH_{2\,ads}$. Fortunately, for a straightforward identification the reaction temperatures of further dehydrogenation are separated by large intervals, at least 50 K on Co, still about 40 K on Ni. Within these intervals the different species are stable and can be characterized by temperature independent peak positions. The results on Co are summarized in table 1, those on Ni in table 2. Not only a clear spectroscopic analysis is possible but the dehydrogenation reactions and the ranges of stability of the C_1 species are explored. These results are necessary in order to study reactions involving those species.

Acknowledgements

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