Theoretical Study of the Stability of Carbene Intermediates Formed During the Hydrodechlorination Reaction of the $\text{CF}_x\text{Cl}_{4-x}$ Family on the Pd(110) Surface

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Received: 27 August 2009 / Accepted: 27 August 2009 / Published online: 25 September 2009
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Abstract In the present work the stability of the species CCl_2 , CFCl , CF_2 and CHF , which are produced during the hydrodechlorination reaction of the $\text{CF}_x\text{Cl}_{4-x}$ family, have been investigated on the Pd(110) surface by applying *ab initio* periodic Density Functional Theory. The most stable configuration for these carbenes on this surface is the short-bridge. Hollow positions have not been found as stationary points in most of the cases. For the chlorinated fragments, the optimisation of these hollow positions resulted in partial or full dechlorinated fragments. The most stable configuration for the carbenes (short-bridge) was compared to the least stable one (top) within different surface conditions in order to verify any change in this stability trend. Both geometries are equally affected by the surface modifications for most of the carbenes. The short-bridge is, however, more sensitive to the coverage increase in the CHF case. CHF has the strongest binding energy to the Pd(110) surface, whilst CF_2 has the least one. The stability trend of CHF , CFCl and CF_2 helped to better understand the selectivity of the hydrodechlorination reaction of the mono carbon CFC's, for example, the suggestion that CF_2 is the most important intermediate on

the hydrodechlorination of CF_2Cl_2 was confirmed by the calculations.

Keywords Dehydrochlorination · CFC · Theoretical chemistry · Pd surface

1 Introduction

Chlorohydrocarbons and chlorofluorohydrocarbons are related to ozone layer destruction and groundwater contamination. Not surprisingly the handling and destruction of these molecules have become an important environmental issue in the past few years.

The search of catalysts, which are able to dissociate the carbon–chlorine bond, is strongly desired and necessary. In addition, the understanding of the structure and reactivity of the intermediates from the dissociation of the chlorofluorocompounds should help to increase the activity and selectivity of the catalyst for such transformation.

The cleavage of the C–Cl bond has been studied by using different metal catalysts. The pure metals Pt, Pd, Cu and alloys combining Pt and Pd with Cu have been suggested to be excellent catalysts for the dechlorination reaction [1–33]. Within these studies the molecular size of the linear chlorocarbons was also well explored: C1 [5, 20, 24, 28, 30, 33], C2 [7, 21, 25–27, 34, 31] and C3 [7].

It is well accepted in the literature that the chlorine atom leaves the molecule more easily than fluorine atom. The C–Cl bond dissociation becomes also more facile with the increase of the number of chlorine atoms in the molecule, being easier for the CCl_2 group than for the CCl one [7, 11, 13, 21, 22, 25, 27].

Regarding the selectivity of the hydrodechlorination reaction on Pd it is higher for the formation of fully or

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partially dechlorinated products in the case of C2 fluorochlorocarbons [20, 21, 31, 35, 36] and for fully dehalogenated in the case C1 fluorochlorocarbons [20, 24, 30, 37–39]. Fully dehalogenated or partially dechlorinated molecules are not desirable, because the target is to substitute chlorine atoms of the CFC's molecules by hydrogen atoms.

The reaction selectivity is insensitive to the structure of the Pd surface, as demonstrated by Ribeiro et al. [36]. It seems, however, to be affected by dilution of Pd atoms on the catalyst surface after the introduction of an additional metal (Au, Pt or Ni) [24, 30, 40].

The CF_2 carbene is considered the most important intermediary of the hydrodechlorination of CF_2Cl_2 on Pd catalysts [20, 24, 32, 37–39]. It seems to be the key for this reaction selectivity. This reaction produces CF_2H_2 (83%) and methane (17%) [41]. However the selectivity of this reaction on Pd catalysts can be modified by the presence of chlorine on the catalyst [39]. The same authors also showed that F coadsorbed atoms were present in used catalysts but this atom did not influence the reaction kinetics.

The hydrodechlorination of another CFC molecule (CFCl_3) produces CFH_3 and methane. The selectivity towards methane is almost twice higher than the one observed for the parent (CF_2Cl_2) compound [41]. It is clear that the key for this selectivity resides on intermediaries produced during the dehalogenation reaction of this CFC: CFCl or CCl_2 .

There are still some open questions regarding the selectivity of the hydrodechlorination reaction of the CFC molecules and certainly they can be answered by understanding the reactivity of the reaction intermediaries. In order to obtain more insights of the hydrodechlorination reaction the stability of CHF , CF_2 , CFCl and CCl_2 carbenes on the Pd(110) surface have been investigated by means of periodical quantum chemical calculations. The analysis, at a molecular level, of the changes in the stability of these species upon different surface coverage offers an opportunity to confirm and to explain some of the current suggestions for the dechlorination mechanism on Pd catalysts.

2 Methods

All geometry optimizations have been performed using the Vienna Ab-initio Simulation Package (VASP) [42, 43]. This code carries out periodic Density Functional calculations (DFT) using pseudopotentials and a plane wave basis set. The DFT was parameterized in the local-density approximation (LDA), with the exchange-correlation functional proposed by Perdew and Zunger [44] and corrected for nonlocality in the generalized gradient approximations (GGA) using the Perdew-Wang 91 functional [45].

The interaction between the core and electrons is described using the ultrasoft pseudopotentials introduced by Vanderbilt [46] and provided by Kresse and Hafner [47].

The Pd surface is modeled by a periodic five layer-slab with the carbene fragment adsorbed on one side of the slab. One slab is separated from its periodic image in the z direction by a vacuum space, which is equivalent to ten metallic layers. Each metallic layer is composed by 9 Pd atoms (3×3 structure). The two bottom layers have been maintained frozen at their bulk distances in all optimisations.

In order to minimize the effect of stress that occurs due to the constraints in the slab model, the optimal bulk metal-metal distance was calculated. The calculated lattice parameter of 3.97 Å agrees well with experimental one of 3.92 Å [48].

In the slab model, these species are ordered over the bare surface in the following structure: $(3 \times 3) 1/9 \text{ ML}$. For some systems, the local coverage was higher than $1/9 \text{ ML}$ due to the presence of extra adsorbed atoms (Cl, F or H). These systems have been also optimised with the same original unit-cell.

The Brillouin-zone integrations have been performed on $3 \times 2 \times 1$ Monkhorst-Pack grid of k -points for all structures, which allows to reach convergence for the calculated energy. A spin restricted approach has been used, since spin polarization effects have been found to be negligible in other works using Pd surfaces [49–51]. The only exception was made for the case of calculations of the molecular radicals in the gas-phase.

3 Results

The dissociation of the $\text{CF}_x\text{Cl}_{4-x}$ family produces three different species on the Pd surface. Depending on the amount of F and Cl atoms in the CFC molecule, different carbene fragments can be produced. The decomposition of CF_3Cl leads to two different species: CFCl and CF_2 , whereas CFCl , CF_2 and CCl_2 are the possible products of the dissociation of CF_2Cl_2 and CFCl and CCl_2 are the ones possible from the dissociation of CFCl_3 . The reaction path for the generation of these species is shown in the Scheme 1.

However another carbene species can be produced during the hydrodechlorination process of the $\text{CF}_x\text{Cl}_{4-x}$ family; CHF . This could be the precursor of the completely dechlorinated molecules and methane, which are usually found in experimental studies [20, 21, 24, 30, 31, 35–39, 52].

3.1 Stability of the Interaction Modes of the CXY Species with the (110) Surface

Intuitively one would expect that the CXY species would interact with the Pd surface by keeping the tetrahedral

Scheme 1 Formation of CXY (X,Y = Cl, F) species during the hydrodechlorination reaction. The most probable dissociation path is highlighted in *bold*

configuration for the carbon, thus being bound to two Pd atoms of the metal surface. The carbene species could also exist on the (110) surface within different configurations: top, hollow, short-bridge and long-bridge. In a top configuration, only one Pd atom from the outmost layer

interacts with the carbon atom of the carbene fragment (T in Fig. 1a). In the short-bridge site (sB in Fig. 1a) two adjacent atoms in the outmost layer interact with the carbene, whereas in long-bridge site (IB in Fig. 1a) these two Pd atoms belong to two parallel rows. In the hollow site (H in Fig. 1a) the carbene sits just above the metal atom of the second layer. The hollow position can be observed in two different configurations, denominated in this study hollow 1 and hollow 2, see Fig. 1b, c, respectively. The main difference of these two positions is the orientation of the XCY plane; in the hollow 1 this plane is parallel to the $\langle \bar{1}10 \rangle$ direction of the surface, whereas in the hollow 2 the XCY plane is perpendicular to this direction. The stability of these distinct types of adsorption modes was evaluated for all four types of carbenes.

In Table 1 the relative energy difference (ΔE) between the top and the other configurations is presented. It is clear from the results that the short-bridge configuration is the most stable one. This has been also shown for another carbene species (CH_2), when adsorbed on different metal surfaces [53–57].

During the optimisation of these five configurations, three of them; top, short-bridge and long-bridge, resulted in a stable stationary point. In most of the cases both hollow positions either resulted on a short and long-bridge geometry or on a dissociated species. The dissociation was

Fig. 1 Representation of all different adsorption modes. **a** All four adsorption modes on [110] surface. **b** Hollow configuration on surface at $\theta = 1/9$. **c** Other possibility of the hollow configuration on surface at $\theta = 1/9$. **d** CCl_2 top configuration on surface at $\theta = 1/9$. **e** CF_2 top

configuration at $\theta = 1/9$. **f** CHF top configuration on surface at $\theta = 1/9$. **g** CFCI top configuration on surface at $\theta = 1/9$. **h** The second possibility for the CFCI top configuration on surface at $\theta = 1/9$

Table 1 Calculated energy difference between all distinct adsorption modes for all carbene species

Adsorption mode	CF ₂	CHF	CFCI	CCl ₂
Top	0.0	0.0	0.0	0.0
Short-bridge	−79	−125	−84	−76
Long-bridge	−52	−76	−63	−58
Hollow-1	− ^a	−62	− ^b	− ^c
Hollow-2	− ^d	− ^d	− ^b	− ^b

Energies are in kJ/mol

^a Similar to long-bridge configuration

^b The CXCl fragment was dissociated into CX + Cl species

^c The CXCl fragment was dissociated completely to C + X + Cl species

^d Similar to short-bridge configuration

either partial, forming CX and Y species, or total, forming C + X + Y species. Interestingly, the dissociation of the carbene at the hollow position only occurred for the CFCI and CCl₂, with the total dissociation found only for the latter case. The only stable stationary point, encountered for the hollow position, was verified for CHF, see Table 1.

The geometry optimisation of the hollow positions for the cases of CFCI and CCl₂ species confirms that thermodynamically these systems are more stable as Cl and CF/CCl fragments on the Pd surface than the carbenes. At this relative position on the (110) surface the chlorine atom of the carbene fragment can interact with the Pd atoms, thus facilitating the scission of the C–Cl bond. One may note that a full dissociation of CCl₂ species is only observed at the position hollow 1, in which both Cl atoms can interact with the Pd atoms of the surface.

The CCl₂ species in the top configuration orients the Cl–C–Cl plane onto the $\langle\bar{1}10\rangle$ direction because of an additional interaction with the Pd surface (via Cl), see Fig. 1d. This molecular orientation in relation to the surface is slightly altered for the cases of CF₂ and CHF, which is clearly due to the absence of the long C–Cl bond and the Pd–Cl interaction, see Fig. 1e, f respectively.

As expected the CFCI species acquires any of these two orientations, see Fig. 1g, h. The most stable situation is the one that has the FCCl molecular plane parallel to $\langle\bar{1}10\rangle$ direction, having the Pd–Cl interaction which is similar to CCl₂ species. All comparisons presented in Table 1 for the top CFCI species configuration is related to this most stable condition.

3.2 Stability of the CXY Species with the (110) Surface at the Short-Bridge Configuration

From the previous result the most stable configuration of the carbenes on the Pd(110) surface is the short-bridge. The

stability of this configuration could be, however, modified upon specific conditions on the surface, such as coverage and presence of certain co-adsorbed species. In order to analyse these possible changes, the stability of the short-bridge configuration was evaluated for different surface conditions and compared to the least stable top configuration. The choice for the top configuration, instead of the longbridge configuration, is due to the fact that the carbene in this geometry requires only one Pd atom to be bound to the surface, thus occupying less active metallic sites. The top configuration is expected to be less affected by the increase of coverage than the short and longbridge configurations.

All surface conditions that have been studied here are presented in the Fig. 2 for the CF₂ species at the short-bridge position.

3.2.1 Effect of Total Coverage

The first approach on the effect of the coverage was to increase the total coverage to values of 2/9 and 1/3 mL on the Pd(110) surface by adding chlorine atoms. Chlorine was chosen because it is the most likely species to be present during the hydrodechlorination reaction, as shown in several experimental studies [20, 21, 24, 30, 31, 35–39, 52], it is strongly bound to Pd surface at low/medium coverages [58–60] and it can be found at coverages up to 0.6 [58, 59].

In Fig. 3 the relative energy difference (ΔE) between the short-bridge and top configuration is presented for each of these four carbene species. It is clearly seen that the bridge configuration keeps being the most stable one, regardless of the species and coverage, see Table 2. This confirms that these carbene species indeed prefer the tetrahedral configuration on the metal surface.

The ΔE seems to be unchanged with the coverage for the CCl₂ and CFCI cases, therefore both short-bridge and top configurations are affected equally with the increase of the surface coverage. This can be explained by the steric hindrance of these fragments and chlorine adatoms. One may note that both Cl-fragments have a long C–Cl bond. For the CHF case, the bridge configuration seems to be more influenced by the chlorine adatoms. The ΔE is reduced by about 26% when the total coverage on the surface increases from 1/9 to 1/3 ML. This fragment should not be experiencing steric hindrance in any of these two configurations because it has short bonds (C–H and C–F), see Fig. 4a, b. The reason may be related to the reduction of the surface reactivity due to the presence of chlorine atoms. For example, Erley [58] indicated that the work function increases for Pd(110) and Pd(111) surfaces when chlorine coverage increases.

Fig. 2 Configuration of the short-bridge modes of the CXY species at $\theta = 1/9$, exemplified by CF_2 species. **a** Bridge configuration on bare surface. **b** Bridge configuration on surface covered by Cl at $\theta = 1/9$. **c** Bridge configuration on surface covered by H at $\theta = 1/9$. **d** Bridge configuration on surface covered by F at $\theta = 1/9$. **e** Bridge configuration on surface covered Cl at $\theta = 1/9$ and H at $\theta = 1/9$. **f** Bridge configuration on surface covered Cl at $\theta = 1/9$ and F at $\theta = 1/9$. **g** Bridge configuration on surface covered Cl at $\theta = 2/9$

Fig. 3 Effect of Cl coverage in the energy difference between bridge and top surface modes for all CXY species on Pd[110]

Since the short-bridge configuration interacts with two Pd atoms of the surface simultaneously, this effect is more pronounced than the one on the top configuration. Certainly this electronic effect should be also occurring to the previous carbene cases but the steric effects, perhaps, may be playing a major role in the latter fragments.

The CF_2 fragment seems to follow the same trend found for the CHF case, however the reduction of the ΔE is very small. It is also very unlikely that both configurations are suffering the effects of steric hindrance. The small

reduction of the ΔE may be an indication that this species is weakly bound to the surface, as proposed by experimental studies [20, 37, 38].

It is interesting to observe the Pd–C bond length trend in Table 3. The longest values are found for the CF_2 species, about 2.0 Å. The Pd–C bond length value seems to be quite similar for the other carbenes; around 1.98 Å. This agrees with the suggestion that CF_2 should be bound to the Pd surface weaker than the other carbenes (CHF, CFCl and CCl_2). In Fig. 1d, h it was presented that CFCl and CCl_2 species have an additional surface interaction at the top configuration. This can be evaluated by the Cl–Pd distance in Table 3. Upon increasing the surface coverage this distance increases due to the steric hindrance offered by the additional chlorine adatom in the same metal row, thus reducing the stability of this species on the surface.

3.2.2 Effect of Different Species on the Surface

As an extension of the previous section, the co-adsorption of different species, such as hydrogen and fluorine, on the Pd surface will be treated as well. The catalytic hydrogenolysis of the CFC family can also occur from the cleavage of the C–F bond. Although this is a rather difficult reaction compared to the dissociation of C–Cl bond, this dissociation is observed as well [20, 21, 24, 30, 35, 37, 39].

Hydrogen will certainly appear on the surface of the catalyst from two different sources. One is together with

Table 2 Calculated ΔE (shortbridge vs. top site) and binding energy (shortbridge site) for all carbene species at $\theta = 1/9$ with the surface covered by different species

Surface coverage	CFCI		CF ₂		CCl ₂		CHF	
	ΔE	Binding energy	ΔE	Binding energy	ΔE	Binding energy	ΔE	Binding energy
Clean	−74	−301	−79	−280	−76	−309	−125	−412
$\theta_H = 1/9$	−70	−293	−79	−277	−78	−307	−106	−386
$\theta_{Cl} = 1/9$	−71	−288	−74	−253	−72	−306	−102	−370
$\theta_F = 1/9$	−71	−274	−63	−251	−72	−281	−90	−367
$\theta_H = 1/9, \theta_{Cl} = 1/9$	−74	−273	−74	−248	−75	−279	−103	−363
$\theta_F = 1/9, \theta_{Cl} = 1/9$	−84	−294	−75	−268	−80	−311	−102	−387
$\theta_{Cl} = 2/9$	−74	−279	−68	−254	−73	−282	−93	−371

Energies are in kJ/mol

Fig. 4 Configuration of CHF at high halogen coverage. **a** CHF top configuration on surface covered Cl at $\theta = 2/9$. **b** CHF bridge configuration on surface covered Cl at $\theta = 2/9$. **c** Surface modifications due to high halogen coverage

the CFC stream and the other is as a “solid state” hydrogen, when hydrogen is already present on Pd, as observed by Rupprechter et al. [61]. This surface H is unlikely to be generated from the C–H bond scission, as shown from several isotopic studies with hydrogen and deuterium in chlorinated molecules [62], which indicated the formed C–H bonds are much more difficult to dissociate than to C–F and C–Cl bonds. In the present study, hydrogen is placed in all systems at a three fold hollow site, as seem to be the most stable situation on the Pd(111) surface [63].

3.2.2.1 Total Coverage of 2/9 Three different surface conditions have been studied within this condition; presence of H, F and Cl adatoms. The effect of the latter adatoms has already been explored in the previous section. The representation of these surface conditions is shown in Fig. 2b–d.

In Fig. 5 the ΔE between the short and top bridge configuration is again represented for each of these four carbene species. The bridge configuration is still the most stable at a coverage of 2/9, regardless of the carbene and surface species, see Table 2.

Table 3 Calculated bond lengths and atom distances for all carbene species at $\theta = 1/9$ with the surface covered by different species

Surface coverage	CFCl				CF ₂		CCl ₂			CHF		
	Bond distance				Bond		Bond distance			Bond		
	C–F (bridge site)	C–Cl (bridge)	C–Pd (bridge)	Cl–Pd (top)	C–F (bridge)	C–Pd (bridge)	C–Cl (bridge)	C–Pd (bridge)	Cl–Pd (top)	C–F (bridge)	C–H (bridge)	C–Pd (bridge)
Clean	1.37	1.78	1.99/1.97	2.68	1.36/1.36	2.01/2.00	1.77/1.77	1.98/1.98	2.59	1.38	1.10	1.99/1.97
$\theta_H = 1/9$	1.37	1.78	2.00/1.98	2.73	1.36/1.36	2.01/2.00	1.77/1.77	1.98/1.99	2.60	1.37	1.10	1.96/1.98
$\theta_{Cl} = 1/9$	1.37	1.76	1.99/1.98	2.69	1.36/1.36	2.00/2.00	1.76/1.77	1.98/1.98	2.58	1.37	1.10	1.98/1.96
$\theta_F = 1/9$	1.37	1.76	1.99/1.98	2.69	1.36/1.36	2.00/2.00	1.76/1.77	1.98/1.99	2.57	1.38	1.10	1.99/1.97
$\theta_H = 1/9$, $\theta_{Cl} = 1/9$	1.37	1.76	2.00/1.98	2.65	1.36/1.36	2.01/2.00	1.76/1.77	1.98/1.99	2.59	1.37	1.10	1.97/1.98
$\theta_F = 1/9$, $\theta_{Cl} = 1/9$	1.36	1.75	1.98/1.98	2.92	1.35/1.36	1.99/2.00	1.75/1.76	1.98/1.98	2.61	1.36	1.10	1.97/1.96
$\theta_{Cl} = 2/9$	1.36	1.75	1.99/1.98	3.79	1.36/1.35	2.00/1.99	1.75/1.76	1.98/1.99	3.93	1.37	1.10	1.97/1.96

Distances in Å

Comparing the values with the original difference at the bare surface condition, it is clearly observed that ΔE does not seem to be affected by the presence of an adatom for the cases of CFCl and CCl₂. The increase of the coverage does influence the stability of the short-bridge configuration in the CHF case, regardless of the adatom. The ΔE calculated for the CF₂ case is not affected by the presence of adatoms on the surface, except fluorine.

This influence of the fluorine on the ΔE is also observed for the CHF fragment case. This may be also related to modification of the electronic condition of the surface, similarly to the chlorine atom. One may observe that this effect may be also occurring with the other two carbene cases but the steric hindrance caused by the chlorine atom(s) of these molecules would have a major effect in the ΔE , as suggested before.

3.2.2.2 Total Coverage of 1/3 The co-adsorption of the carbenes with two different species simultaneously on the Pd surface was also investigated. Two new situations have been explored here: H/Cl and F/Cl on a Pd surface. Together with Cl/Cl co-population they form three systems with a total coverage of 1/3. Obviously, H/Cl and 2Cl are the desired population on the Pd surface during the catalytic hydrogenolysis of the CFC family. However, the condition in which cleavage of the C–F bond occurred before/after the rupture of a C–Cl bond was also studied, thus creating a Cl/F co-populated surface. The presence of fluorine and chlorine atoms was observed in used Pd catalysts after the hydrodechlorination reaction [39]. The representation of these surface conditions is shown in Fig. 2e–g.

In Fig. 6 the ΔE is again represented for each of these four carbene species. The bridge configuration continues to

Fig. 5 Effect of the presence of different species at $\theta = 1/9$ in the energy difference between bridge and top surface modes for all CXY species on Pd[110] **Fig. 6** Effect of the presence of different species at total $\theta = 2/9$ in the energy difference between bridge and top surface modes for all CXY species on Pd[110]

be the most stable one, regardless of the carbene and surface species at this coverage, see Table 2.

Comparing the values with the original difference at the bare surface condition, it is clearly observed that changes in ΔE by the presence of more adatoms can still be separated into two different groups of carbenes: CHF/CF₂ and CFCl/CCl₂. An interesting situation occurs for the CFCl and CCl₂ cases. The system F/Cl seems to favour slightly the bridge configuration. One would expect similar results to the one found for the 2Cl-Pd system. From Fig. 4b (for the case of CHF on the 2Cl-Pd surface) that the same Pd atom (marked by an arrow) is shared by the fragment at short-bridge geometry and the adatom, which are in the same metallic row. This may create a condition that the interaction between the carbene and the surface locally increases, even though the surface is less reactive. This may also occur with the top configuration, but the extra interaction with the surface (Pd-Cl) is lost due to steric effects, see Table 3. The effect is less pronounced for the CCl₂ case because this carbene suffers strong steric hindrance from the adatoms (mostly other chlorine atoms) because of its two long C-Cl bonds, see Table 3 for the Cl-Pd distance changes.

The CF₂ and CHF cases show that the increase of the coverage mostly influences the stability of the short-bridge configuration, being this effect more pronounced in the CHF case. Again this can be explained by the reduction of the surface reactivity, which would not strongly affect the CF₂ carbene that interacts weakly with the surface.

4 Discussion

4.1 Binding Energy

From the previous results it is clear to conclude that the bridge configuration is the most stable position for these carbenes regardless of surface conditions. To know the actual influence of coverage in this adsorption mode the binding energy was calculated by the following expression:

$$E_{\text{binding}} = E_{\text{system}} - (E_{\text{carbene}} + E_{\text{surface}}) \quad (1)$$

E_{carbene} is the energy of the carbene, calculated in gas-phase with its optimised structure. E_{surface} is the energy of the optimised surface geometry with all adsorbed species, except the carbene fragment.

Since the geometry of the gas-phase carbene is fixed to the one found in the original system, the binding energy is free of the influence of any molecular distortions suffered by the presence of the adatom(s). The binding energy of the short-bridge configuration is plotted in Fig. 7 and presented in Table 2. First one may observe that the CHF species has the highest binding energy value among all species, whilst CF₂ carbene has the lowest value. The result for CF₂

Fig. 7 Binding energy of the four different carbenes species at the short-bridge configuration with Pd surface within distinct surface populations

confirms the experimental findings that suggests that this fragment is the most reactive on the Pd surface [20, 38].

As a general trend the interaction energy of all carbenes seems to be equally influenced by the changes on the Pd surface. It is clear that the interaction energy is reduced when the surface is covered by halogens. However the binding energy is almost constant with an increase in coverage from 2/9 to 1/3. The most sensitive carbene for the presence of halogen adatoms on the surface is CHF, see Table 2.

It is interesting to observe that there is a clear trend in the binding energy within the carbene composition, CXY. The more electronegative the atoms X and Y are, the weaker the binding energy with the surface is, see Table 2. CCl₂ has a similar behaviour to CFCl, therefore one may consider grouping these carbenes into the following levels of binding energy: CHF > CFCl, CCl₂ > CF₂.

In Fig. 8 the local DOS diagram of the d-orbitals for Pd atoms of the bare surface, which are interacting with the carbene, is compared to the local DOS of the s,p orbitals of the C atom for CHF and CF₂. These carbenes were chosen because these fragments have the strongest and weakest binding energy on the Pd surface. It is clearly seen from Fig. 8b, c that the s and p orbitals of the carbon in the CHF have much higher energies than the ones for CF₂. This situation favours the interaction between the CHF species and the Pd surface, which explains the binding energy difference showed in Fig. 7. King et al. [57] showed a similar strong orbital interaction of the CH₂ fragment with Pt atoms at the same adsorption site on the Pt(110)(1 × 2) reconstructed surface.

Regarding the surface population when both fluorine and chlorine are present on the surface, the binding energy increases, see Fig. 7. This seems to be a rather common

Fig. 8 Interaction of the carbenes with the Pd surface. **a** DOS projected on d orbitals of the surface Pd atoms involved in the chemisorption. **b** DOS projected on s,p orbitals of the C atom in the

gas-phase CHF carbene. **c** DOS projected on s,p orbitals of the C atom in the gas-phase C₂ carbene

trend for all species. One may note that this had been verified in Fig. 6. This is a surprising result because the surface should be less reactive.

The reactivity of a given metal can be often changed by modifying the surface structure, by alloying or by introducing extra adsorbents on the surface. For instance when a surface undergoes a compressive or tensile strain, the metal d-band moves in energy downwards or upwards in relation to the Fermi level to maintain a constant filling [64]. Obviously this will change the reactivity of the atoms of the surface. One manner to quantify the change is to calculate the local average of d-electron energies, ε_d , the centre of d-band [64–67]. If the ε_d is closer to the Fermi level, the metal atom would be more reactive.

Mortensen et al. [68, 69] showed that the d-band of Ru atoms shifts downwards from the Fermi level due to the presence of S atoms adsorbed on the surface, which could be also expressed by the down shift of the ε_d of the d-band. In order to understand the reasons for the increase of the binding energy in the cases of Cl+F and 2Cl on Pd surface the d-band of the Pd atoms of the surface that interact with the CHF carbene were analysed. The choice for using the CHF system was due to the clear change in the binding energy trend with the surface coverage, see Fig. 7.

In Fig. 9 the local DOS diagram of the d-band for the two Pd atoms, which are interacting with the CHF carbene, is presented for the systems Cl + F, 2 Cl - Pd surface and for the bare surface. For these two systems the DOS of the Pd atoms was evaluated without the CHF fragment for two

different situations: (a) re-optimising the surface with adatoms and (b) keeping the original configuration of the surface with the adatoms.

Regardless of the adatoms on the surface the ε_d of d-band of the Pd atoms shifts downwards for the optimised systems (Fig. 9b, d) when compared to a bare Pd surface (Fig. 9a), similarly to what Mortensen et al. observed for S adsorbed on Ru [68, 69]. This indicates that the presence of halogen atoms reduces the reactivity of the surface. This effect is clearly observed in experiments [20, 41, 58, 59, 70] and confirms the results shown in the Figs. 3, 5, 6 and 7 for the CHF species. Conversely the center of the d-band shifts upwards in the case of the original geometry (Fig. 9c, e), indicating that the Pd atoms are slightly more reactive than the normal Pd surface.

This difference observed between optimised and original surfaces comes from the surface modifications that occurred upon the presence of all species. From Fig. 4c it is possible to observe that the Pd atom, which is shared by the CHF and F fragments, is clearly shifted upwards in the z-direction, being displaced from its original position. This displacement creates a local tensile strain, therefore shifting upwards the ε_d as compared to the optimised surfaces. Since the binding energy was calculated using this strained surface, a higher binding energy for these fragments is found. This phenomenon happens on the surface with 2Cl or Cl/F adatoms regardless of the carbenes species, as seen in Fig. 7. The accumulation of halogen adatoms on the surface may have two different effects on the surface

Fig. 9 Influence of the adatoms Cl and F in the reactivity of the Pd surface. **a** DOS projected on d orbitals of the bare surface Pd atoms involved in the chemisorption. **b** DOS projected on d orbitals of the Cl, F optimised surface Pd atoms involved in the chemisorption. **c** DOS projected on d orbitals of the Cl, F original surface Pd atoms

involved in the chemisorption. **d** DOS projected on d orbitals of the 2Cl optimised surface Pd atoms involved in the chemisorption. **(e)** DOS projected on d orbitals of the 2Cl original surface Pd atoms involved in the chemisorption

chemistry. One is to reduce the adsorption strength of the new coming molecules on the surface due to the modification of the reactivity of the metal surface. The other one is to increase the local binding energy of the already adsorbed fragments due to their neighbour environment.

4.2 Reactivity of the Carbene Species and Hydrodechlorination Catalysis

The CF_2 carbene can be generated by the decomposition of CFC's with more than two fluorine atoms, *viz.* CF_3Cl or CF_2Cl_2 . CFCl can be only formed from CFC's with two or three chlorine atoms. It is very unlikely that the CF_3Cl dissociation will form such species because it requires two consecutive C–F bond scissions. In the same way CCl_2 may be only produced from the dissociation of CFCl_3 , which would still require a C–F bond dissociation. The reaction paths for the generation of these species are shown in Scheme 1.

Based on the results of the previous sections, the CF_2 species binds most weakly to the Pd(110) surface. This means that this species is quite mobile on the surface, thus more susceptible to react with other surface species, *viz.* hydrogen or chlorine.

This is in line with several experimental observations that indicate that this carbene is the most important intermediary of the hydrodechlorination of CF_2Cl_2 on Pd catalysts [20, 24, 32, 37–39]. Additionally it explains the high selectivity towards CF_2H_2 in this reaction [20, 38]. The high mobility of CF_2 carbene will enable this fragment to find and to react with surface hydrogens to form the CF_2H intermediate prior to going through a dissociative process. This idea confirms the experimental result that in absence of surface hydrogen this species is further dissociated to carbon and fluorine [32]. This may also indicate that due to this weak interaction and absence of hydrogen the carbene diffuses on the surface until reaching defect sites, where it goes through a complete dissociation.

Wiersma et al. [39] showed that the selectivity of the hydrodechlorination reaction of CF_2Cl_2 on Pd catalysts can be modified by the presence of chlorine adatoms. One may note from Fig. 9 that the surface becomes less reactive, therefore consecutive dechlorination reactions may become difficult. This means that partially dechlorinated molecules could exist on the surface and follow the hydrogenation reaction. However the selectivity towards CF_2H_2 or methane should be certainly restored by removal of surface chlorine. Wiersma et al. [39] also indicated that both Cl

and F adatoms are present in used catalysts [39]. Moreover they indicate that fluorine had no influence in the kinetics. Based on the binding energy trend of the CF_2 one may expect an influence of the selectivity and kinetics upon fluorination of the surface. This has not been observed by these authors because the coverage of Cl in their experiment was much higher than of F.

Karpinski et al. [24, 30] showed that bi-metallic Pd catalysts (Pd–Pt and Pd–Au) give better selectivity towards CF_2H_2 for the same hydrodechlorination reaction. They suggested that this new Pd–Au and Pd–Pt assemblies may bind the intermediates less strongly than Pd–Pd, possibly affecting the CF_2 carbene. This effect is similar to the reduction of the binding energy upon changes on the surface conditions, as shown here.

CF_3Cl will form, upon C–Cl bond dissociation, CF_3 species. Very recently, Lin et al. [71] have shown by theoretical calculations that CF_3 species can dissociate on Cu(111) and Ag(111) surfaces with relatively low activation energies; 20 and 64 kJ/mol, respectively. This may indicate that this fragment would dissociate to CF_2 on Pd catalyst with a similar low activation energy. However, only the mono hydrogenated molecule (CF_3H) is found during this reaction [41]. This clearly indicates that the hydrogenation reaction of CF_3 species is much faster than the dissociation one. Consequently it is possible to suggest that CF_3 species may be as weakly bound to the Pd surface as the CF_2 fragment.

CFCl and CCl_2 species dehalogenate much easier than the other two carbenes (due to their Cl–C bonds), as seen by the results from the geometry optimisation of their hollow positions. This also confirms that C–Cl bond can easily break, even in a carbene. From Scheme 1 the CFCl fragment is certainly the preferred product of the dissociation of CFCl_3 molecule, taking into account two consecutive C–Cl bond scissions. The hydrodechlorination of this CFC molecule produces mostly CFH_3 and methane. The selectivity towards methane is almost twice higher than the one observed for the parent (CF_2Cl_2) compound [41]. This can be also explained by the current results. The CFCl fragment is not very mobile (not weakly bound to the surface), therefore it easily dissociates further, forming CF species on the surface. This species is probably the precursor of methane and CFH_3 in the hydrodechlorination reaction of CFCl_3 molecule.

CCl_2 may be also generated by dissociation of the CFCl_3 molecule, but it may be unlikely because the C–Cl dissociation is more facile than the C–F one. However, it is certainly formed during the CCl_4 dissociation. The hydrodechlorination of this molecule gives as main products: methane (31%) and CHCl_3 (49%) [70]. The mono and dichlorinated molecules, as well as hydrocarbons resulted from the growth of CH_x monomers, are also observed but

in lower amounts. The selectivity towards CHCl_3 may be explained by the reduction of reactivity upon surface chlorination, as shown in Fig. 9. The surface will be clearly covered and inhibited by chlorine atoms [36].

However CCl_3 can still decompose to CCl_2 . However this fragment can also further dissociate to form carbon species on the surface, as shown here. This may explain the reduced formation of mono and di-chlorinated molecules during this reaction. Similarly the carbon species will only produce light hydrocarbons, mainly methane, because Pd is not very active for Fischer-Tropsch synthesis [52].

The great stability of the CHF carbene on the Pd surface may help to explain the selectivity towards methane in the hydrodechlorination reaction of CFC's. This carbene is the most stable from the ones studied here. CHF carbene may be formed from the dissociation of the CF_2H species or from the hydrogenation of CF species. The participation of this species in the formation of methane during the hydrodechlorination of CF_2Cl_2 seems to be unlikely because both CF_2H and CHF species must go through consecutive defluorination reactions.

The formation of CHF carbene gives, however, some insights on the selectivity of the hydrodechlorination of CFCl_3 . As shown previously, CF species will be formed on the catalyst during this reaction. If CF is hydrogenated, it will form the CHF carbene. The stability of CF may not change upon modification of the surface composition, as its parent CF_2 (Fig. 7). CHF is very sensitive to these modifications, for example, in the presence of H and Cl adatoms (possible condition during hydrodechlorination) the binding energy of this carbene to the Pd surface is reduced about 12%, see Table 2. Therefore CHF may be more mobile than CF thus get further hydrogenated to form CFH_3 .

5 Conclusions

In the present work the stability of the species CXY (X = Cl, F and Y = Cl, F, H) that are produced during the hydrodechlorination reaction of the $\text{CF}_x\text{Cl}_{4-x}$ family on Pd(110) surface has been investigated by applying *ab initio* periodic Density Functional Theory.

The most stable configuration for these carbenes seems to be the short-bridge on the Pd(110) surface. Interestingly hollow positions have not been found as stationary points, except for the case of CHF species. For the chlorinated fragments the optimisation of these hollow configurations resulted in partial or full dechlorinated fragments. This indicates that the scission of C–Cl bond on surface defects (hollow positions on (110) surfaces) is facile.

The most stable short-bridge configuration was compared to the least stable geometry (top) within different surface conditions. The short-bridge configuration is the

most stable regardless of surface condition. Both configurations are equally affected by the surface changes for most of the carbenes with the exception of the CHF carbene, where the short-bridge configuration is more sensitive to the coverage increase.

The CHF species is the most strongly bound carbene on the Pd(110) surface, whilst CF₂ is the least one. The result for the latter fragment confirms the experimental observations that CF₂ is the most important intermediate on the hydrodechlorination of CF₂Cl₂. CHF and CFCl showed to be important keys for understanding the selectivity of the hydrodechlorination of CF₃Cl. Finally, CCl₂ carbene does not seem to participate in the hydrodechlorination of CFC's but its formation may help the explanation of the selectivity of the hydrodechlorination of the CCl₄ molecule.

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References

- Lin J-L, Bent BE (1992) *J Phys Chem* 96: 8529
- Lin J-L, Bent BE (1993) *J Phys Chem* 97:9713
- Cassuto A, Hugenschmidt MB, Parent Ph, Laffon C, Tourillon HG (1994) *Surf Sci* 310:390
- Ohnishi R, Wang W-L, Ichikawa M (1994) *Appl Catal A Gen* 113:29
- Karpiński Z, Early K, d'Itri JL (1996) *J Catal* 164:378
- Yang MX, Eng J Jr, Kash PW, Flynn GW, Bent B, Holbrook MT, Bare SR, Gland JL, Fischer DA (1996) *J Phys Chem* 100:12431
- Yang MX, Sarkar S, Bent BE, Bare SR, Holbrook MT (1997) *Langmuir* 13:229
- Yang MX, Kash PW, Sun D-H, Flynn GW, Bent B, Holbrook MT, Bare SR, Fischer DA, Gland JL (1997) *Surf Sci* 380:151
- Rocheffort A, Martel R, McBreen PH (1998) *Surf Sci* 414:38
- Jugnet Y, Prakash NS, Bertolini JC, Laroze SC, Raval R (1998) *Catal Lett* 56:17
- Chan C, Gellman AJ (1998) *Catal Lett* 53:139
- Zhou G, Chan C, Gellman AJ (1999) *J Phys Chem B* 103:1134
- Buelow MT, Zhou G, Gellman AJ, Immaraporn B (1999) *Catal Lett* 59:9
- Chan ASY, Turton S, Jones RG (1999) *Surf Sci* 234:433
- Laroze SC, Haq S, Raval R, Jugnet Y, Bertolini JC (1999) *Surf Sci* 193:433
- Jenks CJ, Bent BE, Bernstein N, Zaera F (2000) *J Phys Chem B* 104:3008
- Lowry GV, Reinhard M (2000) *Environ Sci Technol* 34:3217
- Benitez JL, del Angel G (2000) *React Kinet Catal Lett* 70:67
- Cabibil H, Ihm H, White JM (2000) *Surf Sci* 447:91
- Ramos ALD, Schmal M, Donato AGA, Somorjai GA (2000) *J Catal* 192:423
- Thompson CD, Rioux RM, Chen N, Ribeiro FHJ (2000) *Phys Chem B* 104:3067
- Rioux RM, Thompson CD, Chen N, Ribeiro FH (2000) *Catal Today* 62:269
- Bloxham LH, Haq S, Mitchell C, Raval R (2001) *Surf Sci* 389:191
- Bonarowska M, Malinowski A, Juszczak W, Karpiński Z (2001) *Appl Catal B Environ* 30:187
- Rioux RM, Chen N, Ribeiro FH (2002) *J Catal* 211:192
- Jugnet Y, Bertolini J-C, Barbosa LAMM, Sautet P (2002) *Surf Sci* 505:153
- Barbosa LAMM, Sautet P (2002) *J Catal* 207:127
- Padmasri AH, Venugopal A, Krishnamurthy J, Rao KSR, Rao PK (2002) *J Mol Catal A Chem* 181:73
- Rioux RM, Chen N, Ribeiro FH (2004) *Appl Catal A Gen* 271:85
- Legawiec-Jarzyna M, Śrebrowata A, Juszczak W, Karpiński Z (2004) *Catal Today* 88:93
- Murwani IK, Kemnitz E, Skapin T, Nickkho-Amiry M, Winfield JM (2004) *Catal Today* 88:153
- Borovkov VY, Kulkarni PP, Kovalchuk VI, D'Itri JL (2004) *J Phys Chem B* 271:85
- Bae JW, Jang EJ, Lee BI, Lee JS, Lee KH (2007) *Ind Eng Chem Res* 46:1721
- Barbosa LAMM, Loffreda D, Sautet P (2002) *Langmuir* 18: 2625
- Ribeiro FH, Gerken CA, Somorjai GA, Kellner CS, Coulston GW, Manzer LE, Abrams L (1997) *Catal Lett* 45:149
- Ribeiro FH, Gerken CA, Rupprecher G, Somorjai GA, Kellner CS, Coulston GW, Manzer LE, Abrams L (1998) *J Catal* 176:352
- Coq B, Cognion J-M, Figuéras F, Tournigant D (1993) *J Catal* 141:21
- Deshmukh S, D'Itri JL (1998) *Catal Today* 40:377
- Wiersma A, van de Sandt EJAX, den Hollander MA, van Bekkum H, Makkee M, Moulijn JA (1998) *J Catal* 177:29
- Śrebrowata A, Juszczak W, Kaszkur Z, Karpiński Z (2007) *Catal Today* 124:28
- Chen N, Rioux RM, Barbosa LAMM, Ribeiro FH (2009). (to be submitted)
- Kresse G, Furthmüller J (1996) *Comp Mater Sci* 6:15
- Kresse G, Furthmüller J (1996) *Phys Rev B* 54:169
- Perdew J, Zunger A (1981) *Phys Rev B* 23:8054
- Perdew J, Wang Y (1986) *Phys Rev B* 33:8800
- Vanderbilt D (1990) *Phys Rev B* 41:7892
- Kresse G, Hafner J (1994) *J Phys Condens Matter* 6:8245
- Lide DR (ed) (1998) *Handbook of chemistry and physics*, 75th edn. CRC, New York
- Loffreda D, Simon D, Sautet P (1998) *Chem Phys Lett* 291:15
- Loffreda D, Simon D, Sautet P (1999) *Surf Sci* 425:68
- Delbecq F, Sautet P (1999) *Surf Sci* 442:338
- van Barneveld WAA, Ponc V (1984) *J Catal* 88:382
- Minot C, van Hove MA, Somorjai GA (1982) *Surf Sci* 127:441
- Paul J-F, Sautet P (1998) *J Phys Chem B* 102:1578
- Papioan G, Nørskov JK, Hoffmann R (2000) *J Am Chem Soc* 122:4129
- Michaelides A, Hu P (2001) Theoretical aspects of heterogeneous catalysis. In: Nascimento MA (ed) Kluwer, Dordrecht
- Petersen MA, Jenkins SJ, King DA (2004) *J Phys Chem B* 108:5909
- Erley W (1980) *Surf Sci* 94:281
- Erley W (1982) *Surf Sci* 114:47
- Hunka DE, Herman DC, Lopez LI, Lormand KD, Land DP (2001) *J Phys Chem B* 105:4973
- Rupprecher G, Somorjai GA (1997) *Catal Lett* 48:17
- Campbell JS, Kemball C (1961) *Trans Faraday Soc* 57:809
- Mitsui T, Rose MK, Fomin E, Ogletree DF, Salmeron M (2003) *Surf Sci* 540:5
- Hammer B, Nørskov JK (2000) *Adv Catal* 45:71
- Ruban A, Hammer B, Stoltze P, Skriver HL, Nørskov JK (1997) *J Mol Catal A* 115:421
- Hammer B, Morikawa Y, Nørskov JK (1996) *Phys Rev Lett* 76:2141
- Hammer B, Nielsen OH, Nørskov JK (1997) *Catal Lett* 46:31

68. Mortensen JJ, Hammer B, Nørskov JK (1998) *Phys Rev Lett* 80:4333
69. Mortensen JJ, Hammer B, Nørskov JK (1998) *Surf Sci* 414:315
70. Chen N, Rioux RM, Barbosa LAMM, Ribeiro FH (2009). (to be submitted)
71. Lin JS, Chou W-C (2008) *J Phys Chem C* 112:768