Bonding of Saturated Hydrocarbons to Metal Surfaces

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The adsorption of octane on Cu(110) was studied by x-ray absorption and x-ray emission spectroscopy, in combination with spectrum calculations in the framework of density functional theory, as a model system for alkane adsorption on transition metals. Significant electron sharing between the adsorbate and metal surface and involvement of both bonding and antibonding C-H molecular orbitals in the molecule-metal bond was found. The calculations were extended to the case of octane adsorbed on Ni(110), and the position of the metal d band was found to be important for the bonding. The results were generalized to show that this is important for the efficiency as an alkane dehydrogenation catalyst.

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Many catalytic processes of industrial importance involve conversion of saturated hydrocarbons to various products [1]. Most often the first step involves breaking of a C-H bond in the molecule, which is a strongly activated process [2]. It has been known for a long time that the C-H bond is activated already in the adsorbed molecular state [3-10]. The adsorption energy of saturated hydrocarbons is close to the sublimation energy of the condensed solid and has usually been denoted physical adsorption involving mainly dispersion forces in the molecule-surface interaction. However, with vibrational spectroscopy a substantial softening of the C-H vibration [3–9] has been seen as well as a metal-induced feature (M^*) in the x-ray absorption spectra (XAS) of adsorbed saturated hydrocarbons [10]. Both of these observations indicate that a simple physical adsorption picture is too simplified and there should also be some chemical interactions involved in the adsorption process. Recently, it was shown for octane adsorbed on Cu(110), using a combination of x-ray emission spectroscopy (XES) and XAS together with density functional theory (DFT) calculations of spectra, that there are rather large internal geometry distortions and a relatively short H-Cu bond distance [11]. The C-C bond was shortened and the C-H bond pointing towards the surface elongated due to the Cu-H interaction. This means that the molecule has taken a small step towards dehydrogenation. These changes are very costly according to the total energy DFT calculations indicating interactions of importance not included in the theory. The question is: How can we understand the electronic structure of the surface interaction that leads to such a surprisingly large internal rehybridization of the molecular structure? Furthermore, based on that knowledge, can we predict how the rehybridization is affected when the adsorption occurs on a different, more reactive metal?

The bonding of saturated hydrocarbons to metals has been investigated theoretically previously by Wöll *et al.* [12] using cyclopropane on a Cu(111) surface as their model system. It was proposed that the bonding involves backdonation from the metal into unoccupied molecular orbitals of Rydberg character. This is distinctly different from the agostic bonding known from organometallic chemistry, which is traditionally thought of as a dative covalent bond involving donation from the C-H group to the metal [13]. Cyclopropane is not an ideal model system for alkanes since the molecule is very strained and not flexible enough to undergo the changes in the internal geometry necessary to open the bonds for interaction with the surface. This will lead to a longer adsorbatesurface distance, which in turn will allow the surface to interact mainly with the large radius unoccupied orbitals. The smaller surface interaction in cyclopropane than with other saturated hydrocarbons can also be seen from the lack of softening in the vibrational modes [14,15].

In the present paper, we propose a bonding model for saturated hydrocarbons on metal surfaces involving both the occupied and unoccupied C-H orbitals based on XAS, XES spectra, and DFT calculations. Adsorption on a Cu substrate is a good model system for this purpose since the *d*-band interaction appears entirely in the occupied states, making the effect more clearly visible and the analysis of the electronic structure easier. We find that, upon adsorption on Ni, the interaction with the 3*d* band contributes to the bonding, which brings the molecule closer to the surface, and increases the rehybridization of the molecular orbitals and allows for C-H bond activation. This is what makes Ni a better dehydrogenation catalyst.

The experiments were performed at beam line I511 at the Swedish national synchrotron radiation facility MAX-Lab. The octane monolayer was prepared by condensing octane on a clean Cu(110) crystal and annealing the sample to 250 K, to remove the multilayers. The resolution of the XAS and XES spectra was 100 meV and 1 eV, respectively. DFT cluster calculations were performed with the DeMon [16] code for the XES and XAS spectra and periodic calculations with DaCapo [17] for the local p density of states. Gradient corrected functionals were used for both exchange and correlation for all calculations. The computed oscillator strengths and local p density of states were broadened with Gaussians to obtain the spectra. The local p density of states and XES calculations were performed for the ground state, whereas the XAS calculations were performed with a half occupied core orbital.

The occupied and unoccupied local p electronic structures of the carbon were measured using XES and XAS, respectively. Angle resolved measurements were performed to separate orbitals of different symmetry. The spectra are projected onto the three high-symmetry directions of the surface, along the Cu rows (p_x) , in the surface plane, orthogonal to the rows (p_y) , and out-of the surface plane (p_z) . The corresponding spectra are shown in Fig. 1, together with computed XES and XAS spectra. Note that both the XES and XAS spectra are shown in binding energy scale relative to the Fermi level. The negative values show unoccupied states.

The C 1s XAS is a sensitive probe of the orientation and internal structure of the adsorbate [11,18]. Shown in the right part of Fig. 1 are the XAS spectra. The top spectrum, showing the p_x contribution, is characterized by a main feature at -8.8 eV binding energy, with a shoulder on the high binding energy side, and in the p_y spectrum there is a main feature at -6.8 eV. Both these features can be assigned to different C-C σ^* shape resonances. There are spectral features around -3.5 eV binding energy both in the p_y and p_z spectra, assigned to transitions into C-H^{*} orbitals. The p_z spectrum also shows significant intensity



FIG. 1 (color online). Experimental and theoretical symmetry-resolved XES and XAS spectra of n octane adsorbed on Cu(110). The spectra are projected along the three high-symmetry directions of the surface. The alignment of the n-octane molecule on the surface is shown in the inset.

right at the Fermi level, previously denoted M^* [10]. The XAS fine structure is discussed in more detail elsewhere [19]. The positions and intensities of the C-C σ^* shape resonances are sensitive to the C-C bond length. The geometry of the adsorbed molecule was determined by systematically computing theoretical XAS spectra for different geometries, and determining which one best represents the experimental data. We have found that for weakly adsorbed systems the molecular orbital structure provides a more sensitive measure of the geometry than the total energy [11]. The structure of the carbon skeleton was determined by fitting the C-C σ^* shape resonances in the XAS spectra to the experiment. Based on this, the C-C bond length was determined to be 1.49 Å [11], which is shorter than for the optimized isolated molecule (1.53 Å).

The XES spectra in the left panel of Fig. 1 show the occupied C 2p projected density of states. All these spectra are characterized by a broad feature around 8 eV binding energy. This large width is typical for alkanes, and arises due to band formation [20] and vibronic coupling [21] of the C 2p derived molecular orbitals. The p_{z} spectrum, however, shows an additional feature at 5 eV appearing as a consequence of the interaction with the metal surface. We denote this feature M. The occupied metal-induced states are not sensitive to changes in the C-C skeleton of the molecules, but to the moleculesurface distance as well as both bond length and direction of the C-H bonds. In order to reproduce the M feature, the molecule had to be pushed in to a C-Cu distance of 2.7 Å and the C-H bonds pointing towards the surface were elongated from 1.10 to 1.18 Å, and rotated towards the surface [11]. What is the nature of this new occupied state and can this be connected to the surface chemical bond?

An investigation of the molecular orbitals shows that the new *M* band is formed in the region of the Cu *d* band. Figure 2 shows a schematic picture of the orbital rearrangement. The high binding energy region of the XES spectra consists of orbitals, resembling the orbitals in gas phase octane, but with a small contribution of metal states. The new M band has mainly metal character, but also some carbon character as is evident from the XES. The octane orbitals contributing to this band are mainly the bonding C-H orbitals, since these are closer in energy to the Cu d band, but also to a smaller extent antibonding C-H* orbitals. The band, which is completely occupied, is both bonding and antibonding with the surface, leading to a net repulsion. Also the much broader Cu sp band interacts with the octane orbitals, leading to an extended weak band. The unoccupied part of this band can be seen in the XAS spectra. This indicates that all bonding and antibonding states are not fully occupied. Can we anticipate a potential covalent bonding?

Figure 3 shows the difference in charge density as the molecule is allowed to interact with the surface. We observe small but significant changes in the charge density.



FIG. 2. A schematic figure showing the interaction between the C-H orbitals and the metal d band, which leads to a strong mixing of molecular orbitals.

Along the C-H plane, there is a polarization of the C-H bonds towards the C atoms and charge depletion close to the hydrogen atoms. This is part of the breaking up of the C-H bonds due to mixing of C-H bonding and antibonding orbitals. This mixing leads to a weakening of the C-H bonds and results in the observed elongation of the C-H bonds pointing towards the surface. Along the CuH plane, there is a loss of charge on the H atoms, and a build up of charge between the H and the Cu atoms, which means that there is electron sharing between the adsorbate and substrate. From a closer inspection we can derive that it is mainly the Cu p_z states that are involved in the bonding. Furthermore, there are some changes in the substrate, which can be related to an *spd* rehybridization in the Cu. The net charge does not increase on the molecule, indicating that the bonding model suggested by Wöll et al. [12] is not appropriate for a nonstrained molecule. Their model does not allow for much interaction, and the adsorbate-surface distance is too long to allow for any interaction with the relatively small bonding C-H orbitals. Based on our charge density difference plots, we conclude that the interaction is a combination of both donation and backdonation, involving the Cu 4sp band. Even though the bond is weak, it is likely that this is the driving force behind the changes observed in the structure of the molecule.

As shown in previous work by Hammer and Nørskov [22], the nobility of metals is directly related to the position of the metal d band, with respect to the Fermi level. Can we predict the differences in interaction of octane with different transition metals, based on that picture?

In Fig. 4, computed carbon local p densities of states, projected along the out-of-plane (p_z) direction, are shown for octane adsorbed on both Cu and Ni. The main spectral difference between the two substrates is

Density difference octane/Cu(110)



FIG. 3 (color online). Charge density difference plotted along the C-H plane (top) and the CuH plane (bottom).

the position of the 3d metal-induced states (*M*), which follow the position of the metal *d* band. In Cu, these states are entirely below the Fermi level, leading to a net repulsion in the interaction with the 3d contribution. However, in the case of Ni, the antibonding states continue above the Fermi level, and this interaction can start to contribute to the adsorption energy. In this case, we can anticipate that the molecule will move closer to the surface, due to the increased bonding, leading to further rehybridization and weakening of the C-H bonds. As the *d* band moves towards and over the Fermi level, this increases the possibility for charge donation to the surface, and formation of a more dative bond similar to the agostic bonding in organometallic compounds.

From these results we can predict, in accordance with Ref. [22], that when we move further to the left in the periodic table the bonding will become even stronger, and all C-H bonds will be broken, depositing strongly bound carbon on the surface, thus yielding a less efficient catalyst. It has been seen in dehydrogenation reactions of cyclohexene on Pt, where a monolayer of Au increases the rate for this reaction significantly [23]. The same is also true for methane dissociation in steam reforming reactions on Ni. The main problem with this catalyst is that it also catalyzes graphite formation, which poisons



FIG. 4 (color online). The calculated local p density of states projected onto the out of plane (p_z) direction for octane on Cu and Ni.

the catalyst. This problem can be overcome by alloying the Ni with Au [24]. From our present results, this effect can be understood on an electronic structure level. The Ni d band crosses the Fermi level, giving rise to a strong adsorbate-substrate bond. The Au lowers the d band in the compound, causing a weakening of this bond. By finetuning the Au-Ni ratio, the d band can be positioned high enough to allow for breaking of the C-H bond and low enough not to form graphite.

In conclusion, our study shows significant electron sharing between the adsorbate and metal surface. We show that both bonding and antibonding C-H orbitals are involved in the interaction, which involves strong orbital mixing. Furthermore, we discuss the bonding of alkanes on different transition metals, where we find that the position of the metal *d* band is important for the bond strength, as well as the efficiency of the substrate as a dehydrogenation catalyst.

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