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Correlations between the Heat of Adsorption and the Position of the Center of the D-Band: Differences between Computation and Experiment

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Previous DFT computations have shown that there should be a correlation between the calculated heat of adsorption of gases such as hydrogen, carbon monoxide, and ethylene and the energy of the center of the d-band. This paper considers whether the trends expected from the calculations agree with the available data. It is found that experimental heats of adsorption of CO on platinum single crystals increase linearly with increases in the energy of the center of the d-band as expected theoretically, but the slope is about one-third of that expected theoretically. Experimental heats of adsorption of hydrogen on platinum show a small *decrease* as the energy of the center of the d-band becomes less negative. By comparison, recent DFT calculations suggest a substantial *increase*. Experimental heats of adsorption of ethylene on platinum also show a small *decrease* as the energy of the center of the d-band becomes less negative. By comparison, recent DFT calculations suggest a substantial *increase*. Interestingly, the heat of adsorption of oxygen, and the heat of dissociative adsorption of ethylene, do follow the trends expected from the model, although no quantitative comparison is possible. Overall, calculated and experimental heats of adsorption differ by as much as 90 kJ/mol. Ours is the fifth recent paper that shows significant differences between careful experiments and careful DFT calculations. We suggest, therefore, that the functionals used to model adsorption need improvement.

Introduction

Over the years, there have been many attempts to correlate catalytic properties to easily calculated properties. Years ago people developed correlations. For example, Sachler and Farhenfort[1] and Tanaka and Tamaru[2] showed that there was a relationship between catalytic properties and heats of formation of bulk compounds. Sinfelt[3] developed correlations between catalytic properties and the percentage d-character. More recently, Masel[4] noted that the jellium model implied that there is a correlation between heats of adsorption and the interstitial electron density of the metals. Recent investigators have used DFT calculations to understand adsorption. For example, Hammer and Nørskov[5,6] suggested that heats of adsorption of molecules such as CO and ethylene could be understood based on two parameters: the energy of the center of the d-band relative to the Fermi level and the strength of the Pauli repulsions. At this point, all of the correlations have been proposed on theoretical grounds and have not been tested experimentally, so we do not know whether the correlations work in practice. In a larger way, we do not know whether the current generation of DFT calculations is adequately representing adsorption.

The objective of this paper is to determine whether the trends expected theoretically are observed experimentally. In recent years, calorimetric methods have allowed accurate heats of adsorption to be measured. Vibrational and TPD data exist for many of the molecules. Therefore, there exists the opportunity to ask whether there is any correlation between theory and experiment. In this paper, we will compare theory and experiment to see if the trends expected theoretically are observed experimentally.

Data Sources. This paper will use only data that have been published previously. The calorimetric data for heats of adsorption are from the reviews of Brown, Kose, and King,[7] Cerny,[8] Brennan and Hayes,[9] and Kyser and Masel.[10,11] Vibrational data are from Yagasaki and Masel,[12] and Masel.[4] TPD data are from Thomas et al.,[13] Lee et al.,[14] Benziger,[15] Ford et al.,[16] and Ruggiero and Hollins.[17] All of the data show variations in the heat of adsorption with coverage. In the comparison here, we considered the zero coverage limit of the calorimetric and vibrational data. The TPD data often show some anomalies at coverages below 0.02 monolayers (ML), so we arbitrarily considered the heat of adsorption at a coverage of 0.1 ML. The energy of the center of the d-band and the strength of the Pauli repulsion is from Hammer and Nørskov,[6] Hammer, Nielsen, and Nørskov,[6] or Pallassandra and Neurock,[18] or Watwe et al.[19] All other metal properties were from Papaconstantopoulos.[20]

Results: Carbon Monoxide

As a start of our effort, it is useful to consider whether there is a correlation between the binding of carbon monoxide and any of the bulk properties considered by previous investigators. To put this work in perspective, Masel[4] noted that the binding of CO is particularly difficult to model. The molecule is held via a mixture of polarization forces, delta bonds, and nonlocal exchange. Surfaces relax when CO adsorbs. Nevertheless, Hammer and Nørskov[5] proposed a simple model of bonding process, in which they assumed that the main interaction was back-donation of electrons into the antibonding orbitals of the adsorbed CO. Hammer and Nørskov then used perturbation

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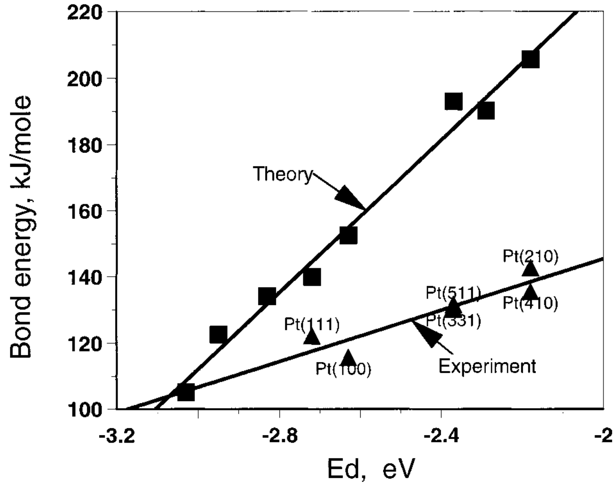

Figure 1. Plot of the heat of adsorption of CO on several faces of platinum (▲) measured by our group[13,16] using TPD and (■) calculated by Hammer, Nielsen, and Nørskov[6] against the energy of the center of the d-band of the surface atoms as reported by Hammer, Nielsen, and Nørskov.[6]

TABLE 1: Heat of Adsorption of CO on Pt(111) Measured by a Variety of Techniques

technique	measured heat of adsorption kJ/mol	reference
TPD-β Plot	122	13
TPD-Arrhenius plot	130	14
single crystal calorimetry	135 ± 12	10, 11
isosteric heat	135	43
DFT calculations	138	6
film calorimetry	187	7

theory to suggested that there are two key factors which determine the strength of the binding of molecules with metals: the energy of the center of the d-band relative to the Fermi level and the strength of the Pauli repulsions. They then showed that the heat of adsorption of gases on transition metals should linearly increase as the energy of the center of the d-band increases, while the heat of adsorption decreases linearly with the strength of the Pauli repulsions.

Figure 1 shows a plot of the heat of adsorption of CO on a number of single-crystal surfaces that we have measured by TPD β-plots[13] as a function of the position of the center of the d-band on the adsorption site as reported by Hammer, Nielsen, and Nørskov.[6] In the plots we assumed that the d-band position on a step was the same as in Pt(211) and a kink was the same as in Pt(11 8 5). Hammer, Nielsen, and Nørskov's[6] calculations for the binding energy of CO on platinum are also shown on the figure. Notice that the experiments show the trends expected from the theory in that heat of adsorption measured by TPD increases approximately linearly with the position of the center of the d-band. In previous work,[13,14] we noted that it was hard to find any variable that correlated to our data. The results in Figure 1 show that the energy of the center of the d-band is a good correlating variable. Still, the slope of the data is about 1/3 of that expected theoretically. We only observe a 17 kJ/mol variation in the heat of adsorption of CO with changing face, whereas the theory predicts a 100 kJ/mol variation. Therefore, it appears that there is a significant difference between theory and experiment.

We have also analyzed our data by a variety of different methods. Table 1 summarizes our findings for Pt(111). We find that the absolute value of the measured heat of adsorption varies by ±10 kJ/mol according to how we analyze the data, but the differences between the heat of adsorption on one face and on another are independent of how the data are analyzed. For example, the heat of adsorption of CO on Pt(111) measured by varying the heating rate, and constructing a β-plot, gives a value of 122 kJ/mol.[13] If we instead construct an Arrhenius plot using the initial rate method[4] we estimate a heat of adsorption of 130 kJ/mol.[14] Calorimetry gives 135 kJ/mol,[10,11] as does isosteric heat measurement. Importantly though, the heat of adsorption of CO on Pt(111) is always about 15 kJ/mol lower than that on Pt(410), independent of whether we construct β-plots or Arrhenius plots. Physically, at low coverages, the peak shapes are similar in all of the TPD data. Consequently, the differences between the measured heat of adsorption and different crystal faces are the same, no matter how we analyze the data.

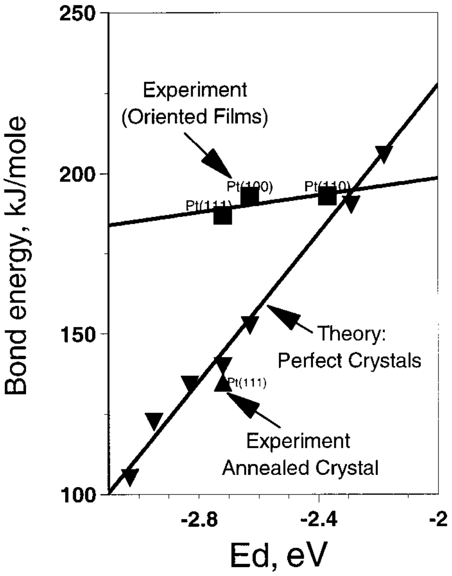

Figure 2. Plot of the heat of adsorption of CO on Pt, Pd, Ni, and Rh measured calorimetrically against the energy of the center of the surface d-band as reported by Hammer and Nørskov. (▲) Our measurements of the heat of adsorption of CO on a Pt(111) crystal.[10] (■) King's measurements of the heat of adsorption of CO on oriented metal films.[7] (▼) Calculations of Hammer, Nielsen, and Nørskov for CO on several faces of platinum.[6]

There is one data set, however, that is different from the rest, so we want to consider it, too. King and co-workers[7] used calorimetry to measure the heat of adsorption of CO on a series of platinum *films* that were roughly oriented in the (111), (100), and (110) directions. Table 1 shows that these measurements give higher heats of adsorption than all of the other techniques, probably because the evaporated films contain more adatom defects than well annealed single crystals. Figure 2 is a plot of King's data versus the energy of the center of the well annealed *surface* d-band as reported by Hammer and Nørskov.[5] Our own data[10,11] for the calorimetric heat of adsorption on a well annealed Pt(111) single crystal is included for comparison, as are the calculations of Hammer, Nielson and Nørskov[6] for the heat of adsorption of CO on platinum as a function of the position of the *surface* d-band.

King also finds some evidence that the heat of adsorption of CO on various platinum surfaces increases as the center of the d-band increases, but again the shift is much smaller than that expected theoretically. King observes a 6 kJ/mol variation in the heat of adsorption with crystal face compared to the 100 kJ/mol variation expected theoretically. One does not want to push this comparison too far, because King is measuring data for a film, not a well annealed single crystal. King finds a heat of adsorption of CO on Pt(111) oriented film of 187 kJ/mol

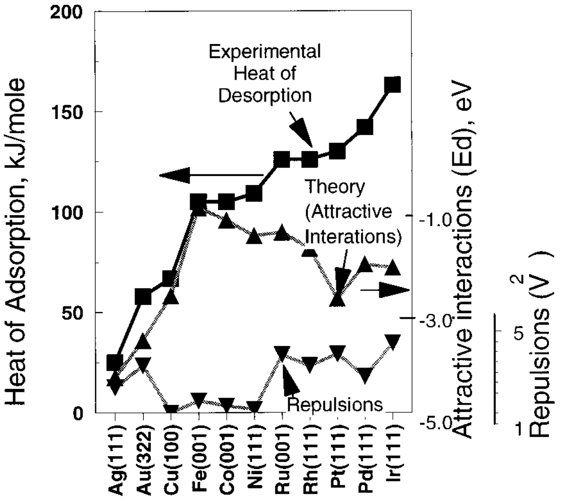

Figure 3. Plot of the heat of adsorption of CO on several faces of metals measured via TPD[15,16,17] (■); Hammers and Nørskov's results[5] for the energy of the center of the d-band of the bulk metal (attractive interactions, ▲) and Pauli repulsions (▼) are also shown.

compared to a calculated value of 138 kJ/mol for Pt(111)[6] and our own calorimetric measurements on well annealed single crystals[10] of 135 ± 12 kJ/mol. Consequently, one would not want to draw strong conclusions from King's results. Still, King's measurements verify the findings in Figure 1 that measured variations in heat of adsorption follow the trends expected theoretically, in that the heat of adsorption varies approximately linearly with the energy of the center of the d-bands. However, the variations with changing face are considerably smaller than those expected theoretically.

In a larger way, the heat of adsorption of CO has also been measured on several faces of palladium, nickel, and other metals by TPD and isosteric heats.[21] In all cases one finds at most a 20 kJ/mol variation in the heat of adsorption with changing crystal face. The data generally follow the trend that rough surfaces bind CO more strongly than smooth ones, as expected theoretically. However, there are exceptions.[22] The experimental variations are always much smaller than those expected theoretically. Our conclusion is that the heat of adsorption measured in careful experiments varies much less with changing face than that expected from careful DFT calculations.

Next, we wish to consider whether the variation in the heat of adsorption of CO with changing metal correlates with the energy of the center of the d-band and the strength of the Pauli repulsion, as was suggested by Hammer and Nørskov. Figure 3 shows a plot of the heat of adsorption of CO on several metals measured via TPD[14] versus the energy center of the d-band for *bulk* metals and the strength of the Pauli repulsions as reported by Hammer and Nørskov.[5] We have ordered the points so that the experimental heats of adsorption increase. We find that the model of Hammer and Nørskov reproduces the trends on the left side of the plot, but not those on the right side of the plot. According to Hammer and Nørskov, the attractive interactions due to the interaction with the d-bands are largest at iron, while the Pauli repulsions are smallest there. Consequently, according to eq 1 in Hammer, Morika, and Norskov, one would expect the heat of adsorption of CO to be larger on iron, than, for example, on platinum or iridium. Unfortunately, the experiments show the opposite trend, which suggests a difficulty with the model.

Table 2 gives a quantitative comparison between computation and experiment. Generally, the computations predict that the heat of adsorption of CO on Rh(111) is unusually large, the heat of adsorption on Pt(111) is unusually small, and the variations between the metals shown are as large as 80 kJ/mol. The experiments show much smaller variations with changing metal, and, importantly, platinum binds CO more strongly than either ruthenium of rhodium. Care is needed because the differences in the experiment are comparable to the uncertainties in Table 1. Still, the experiments show that CO desorbs from rhodium and ruthenium at lower temperatures than it does from platinum or palladium, so there is no doubt that, experimentally, CO binds more strongly to platinum and palladium than it does to rhodium or ruthenium even though the calculations predict the opposite behavior.

TABLE 2: Comparison of Heats of Adsorption of CO on Various SurfacesCalculated Using the PW91 and RPBE Functions to Those Measured Experimentally

surface	DFT with the PW91 functional, kJ/mol	DFT with the RPBE functional, kJ/mol	experiment 15
Ni(111)	192[a]	144[a]	109
Rh(100)	220[a]	175[a]	126
Ru(001)	194[b]		126
Pt(111)	138[c]		134
Pd(111)	200[a]	151[a]	142

[a] Reference 45. [b] Reference 46. [c] Reference 6.

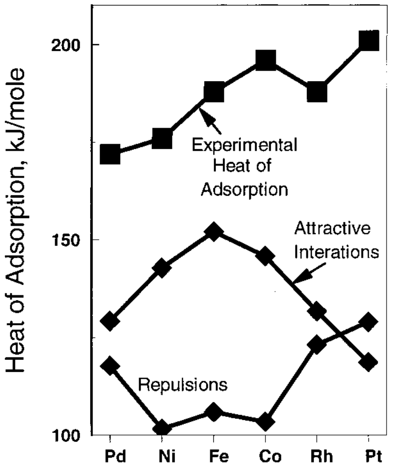

Figure 4. Plot of Brennan and Hayes's[9] measurements of the heat of adsorption of CO adsorption on several metals. Hammer and Nørskov's results[5] for the energy of the center of the d-band of the bulk metal (attractive interactions) and Pauli repulsions are also shown.

We have also considered Brennan's[9] calorimetric measurements of the heat of adsorption of CO on extended metal films. Figure 4, shows a plot of Brennan's measurements of the heat of adsorption of CO adsorption on platinum, palladium, nickel, rhodium, cobalt, and iron, and the energy of the center of the d-band of the bulk metal, and the strength of the Pauli repulsions as reported by Hammers and Nørskov. Brennan's data show very small changes in the heat of adsorption with changing metal. Again, the data and the theory show opposite trends in moving from iron to platinum.

Finally, we have also considered King's calorimetric measurements of the heat of adsorption of CO on extended metal films.[7] Figure 5 shows a plot of Kings' measurements of the heat of adsorption of CO adsorption on several faces of platinum, palladium, and nickel, the energy of the center of the d-band of the bulk metal, and the strength of the Pauli repulsions as reported by Hammers and Nørskov. Kings' data show very small changes in the heat of adsorption with changing metal. Again, the data and the theory show opposite trends on the right side of the figure.

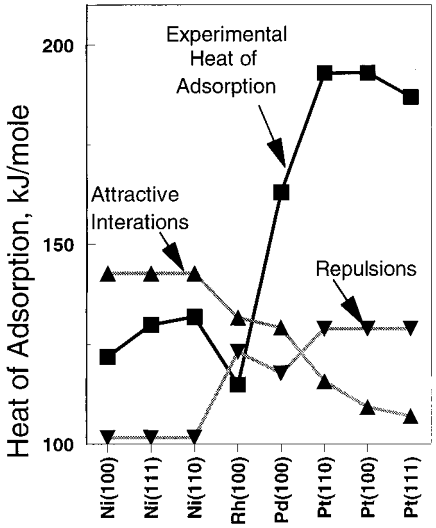

Figure 5. Plot of King's measurements[7] of the heat of adsorption of CO adsorption on several metals. Hammer and Nørskov's results for the energy of the center of the d-band of the bulk metal (attractive interactions, ▲) and Pauli repulsions (▼) are also shown.

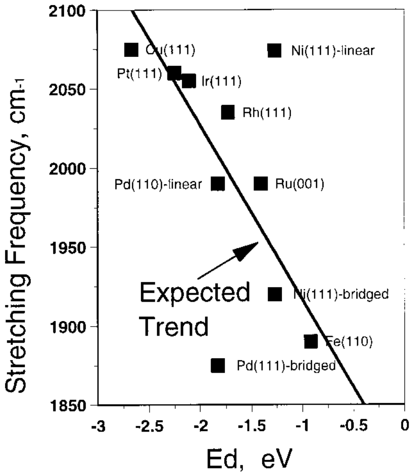

Figure 6. Plot of the vibrational frequency of adsorbed CO on several transition metals[4] against the energy of the center of the d-band of the bulk metal as reported by Hammer and Nørskov.[5]

The implication of Figures 1 through 5 and Table 1 is that there are important trends in the experimental data that are not reproduced with careful DFT calculations.

To try to understand why the models failed, we also considered how the vibrational frequency of adsorbed CO varies over the d-band metals. Recall that the vibrational frequency of adsorbed CO is sensitive to minute alternations in the degree of pi-back-donation.

Figure 6 is a plot of the vibrational frequency of adsorbed CO reported by Masel[4] versus the energy of the d-band of the metal as reported by Hammer and Nørskov.[5] Notice that there is a reasonable correlation between the vibrational frequency of adsorbed CO and the energy of the center of the d-band. In many cases, two different bands are seen with the same metal. We included a few of those cases where the theory reflected the wrong preferred binding site. However, the trend is that there is a good correlation between the energy of the center of the d-band and the vibration frequency of the adsorbed CO. The implication of Figure 6 therefore, is that Hammer and Nørskov's model is correctly predicting the trends in the degree of pi-back-binding of the adsorbed CO with changing metal, even though the model does not correctly predict the trends in the heat of adsorption of the adsorbed CO.

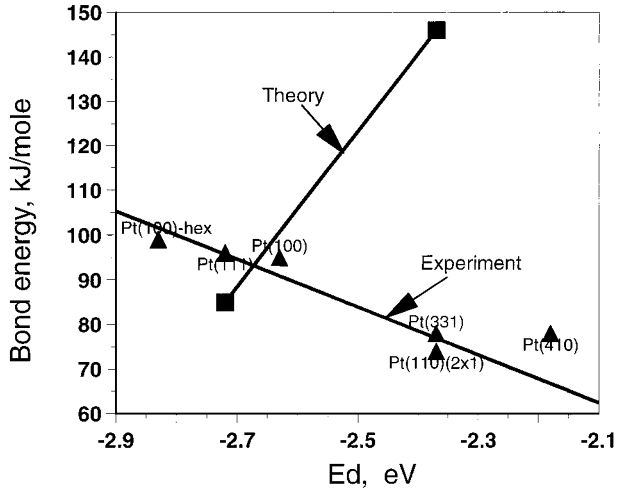

Figure 7. Plot of the heat of adsorption of H_2 on several faces of platinum (▲) measured by our group[13,14,16] using TPD and (■) calculated by Watwe[19] against the energy of the center of the d-band of the surface atoms as reported by Hammer, Nielsen, and Nørskov.[6]

Results: Hydrogen

Next, we wish to consider whether there is a correlation between the heat of adsorption of hydrogen and the energy of the center of the d-band as suggested by Nordlander, Holloway, and Norskov[33] and Pallassana et al.[34] Figure 7 shows our measurements[13,14,16] of the heat of adsorption of hydrogen at low temperature on several faces of platinum versus the energy of the center of the d-band on each surface estimated as described above. Watwe et al.'s[19] calculations for hydrogen adsorption on Pt(111) and Pt(211) slabs are included for comparison. The data show that the heat of adsorption slightly decreases as the energy of center of the d-band increases. By comparison, the calculations show a substantial increase. The experiments show that hydrogen binds more strongly to Pt(111) than to surfaces with (111) steps and (111) terraces (e.g., Pt(110)). However, the computations show the opposite behavior.

We have included only our own data in the figure, but McCabe and Schmidt[23] have also measured the variation in the heats of adsorption of hydrogen with crystal face. McCabe and Schmidt confirm the trends in Figure 7: a lower heat of adsorption of hydrogen on Pt(110) than on Pt(111).

Results: Ethylene

Next, we wish to consider whether there is a correlation between the heat of adsorption of ethylene measured at about 100 K and bulk properties. Recall that ethylene is another molecule that shows complex binding on surfaces.[12] The nature of the adsorbed intermediates varies strongly with surface structure. Stepped surfaces show behavior very different from that of closed packed planes. Nevertheless, Pallassana and Neurock[18] proposed that the trends in the binding could be understood via Hammer and Nørskov's model.[5] In particular, they proposed that there would be a simple correlation between the calculated heat of adsorption of ethylene and ethylidyne on transition metal surfaces and the position of the center of the d-band.

Figure 8 shows our measurements of the heat of adsorption of ethylene at low temperature on several faces of platinum

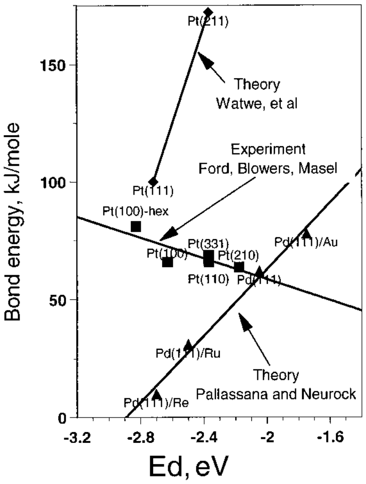

Figure 8. Plot of the heat of molecular adsorption of ethylene on several faces of platinum against the energy of the center of the d-band of the bulk metal as reported by Hammer, Nielsen, and Nørskov.[7] (■) Our data for the heat of molecular adsorption of ethylene on platinum as measured by TPD.[14] (◆) Calculations of Watwe et al. for ethylene on platinum.[19] (▲) Calculations of Pallassana and Neurock[18] for ethylene on palladium monolayers on various substrates.

measured near 100 K with TPD versus the energy of the center of the d-band on each surface estimated as described above. Pallassana and Neurock's calculations for palladium[18] and Watwe's calculations for hydrogen adsorption on Pt(111) and Pt(211) slabs[19] are included for comparison. The data show that the heat of adsorption slightly decreases as the energy of center of the d-band increases. By comparison, the calculations show a substantial increase. The data and calculations are not directly comparable. During the TPD experiment, only a fraction of the ethylene desorbs from the surface. Other ethylene molecules react. The TPD experiment sees only the molecules that desorb and not those that react. Also, Pallassanca and Neurock's calculations are for metal overlayers, and not extended single crystals. Still, the experiments do not show the trends expected from the theory.

We have also measured the vibrational frequency of the adsorbed ethylene at 100 K using EELS. Generally, two forms of adsorbed ethylene are observed spectroscopically at 100 K: di-sigma ethylene and a more weakly pi-bound ethylene.[12] On Pt(111) and Pt(100), only di-sigma ethylene is observed at 100 K.[24] In contrast, a mixture of di-sigma and pi-bound ethylene is seen on Pt(110)[25] and Pt(311) at 100 K,[26] whereas only pi-bound ethylene is seen on Pt(210) at 100 K.[27] The EELS measurements show that at 100 K, ethylene is interacting more weakly with close-packed surfaces than with stepped surfaces, in agreement with the results in Figure 8, and in disagreement with the calculations of Watwe et al.[19] and the trends expected from the calculations of Pallassana and Neurock.[18]

To see if the trends above carry over to other systems, we have also examined the heats of *dissociative* adsorption of ethylene on several faces, as measured calorimetrically by King and co-workers.[7] Figure 9 shows a plot of the heat *dissociative* adsorption of ethylene measured calorimetrically at 300 K versus the energy of the center of the surface d-band as reported by Hammer and Nørskov.[5] Our own calorimetric measurements[11] are included for comparison. Again, there is about a 50 kJ/mol difference between King's measurements and the theory for ethylene on Pt(111), whereas our own measurements are much closer to the theory. King's measurements on platinum show the trends expected in the theory, in that the heat of adsorption increases as the energy of the center of the d-band increases.

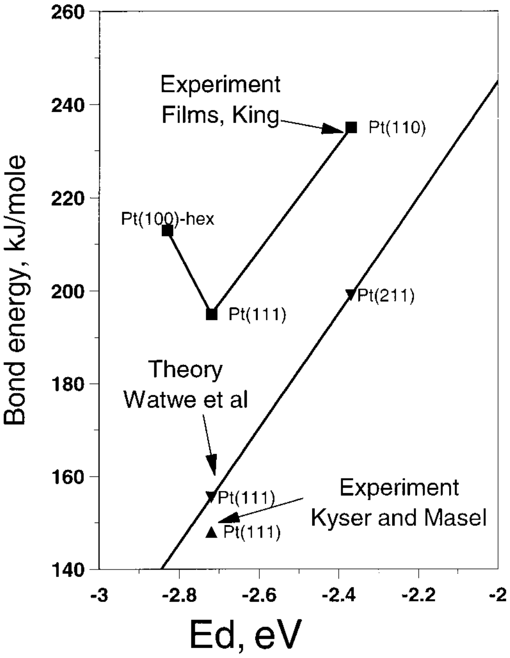

Figure 9. Plot of the heat of dissociative adsorption of ethylene against the energy of the center of the d-band of the bulk metal as reported by Hammer and Nørskov.[5] (■) King's data for the heat of molecular adsorption of ethylene at 300 K, as measured by calorimetry.[7] (▼) Calculations of Watwe et al. for ethylene on platinum.[19] (▲) Calorimetric measurements of Kyser and Masel.[11]

However, he observes the opposite trend on other metals. There is a subtle problem with Figure 9 in that the form of ethylene is different on the various surfaces. Ethylene adsorbs molecularly at 300 K on Pd(100), whereas ethylidyne forms on Pt(111), hex-Pt(100), Pt(110), or Ni(110), and vinylidene or vinyl species form on Ni(100), Pt(100)(1 × 1) or Rh(100).[12] If we examine only the surfaces where ethylidyne forms, we find that the data show an effect opposite of that which is expected from the calculations of Watwe et al.,[19] in that the bond energy goes down as the d-bands shift to lower energy.

Results: Oxygen

Next, we consider whether there is a correlation between the heat of dissociative adsorption of oxygen and the bulk properties. Recall that the binding of atomic oxygen is thought to be much simpler than the binding of ethylene or carbon monoxide. Chakraborty, Holloway, and Nørskov[28] showed that electrons flow from the metal into the antibonding orbitals of the oxygen. Polarization forces and local bonds play a much smaller role.[33] Consequently, if Hammer and Nørskov's model would work anywhere, it should work for oxygen.

Figure 10 shows a plot of the heat adsorption of oxygen on single crystal surfaces measured calorimetrically by King and co-workers[7] versus the energy of the center of the d-band as reported by Hammer and Nørskov.[5] In this case, there is considerable scatter in the data because the heat of adsorption varies significantly with surface structure, but the trend in the data follows the trend expected in the model.

Discussion

The results here did not come out as we had expected. In the previous literature, Hammer, Nielson and Nørskov,[5] Pallassana and Neurock,[18] and Pallassana et al.[34] have done careful DFT calculations showing that theoretically the heats of adsorption of carbon monoxide, hydrogen, and ethylene should increase

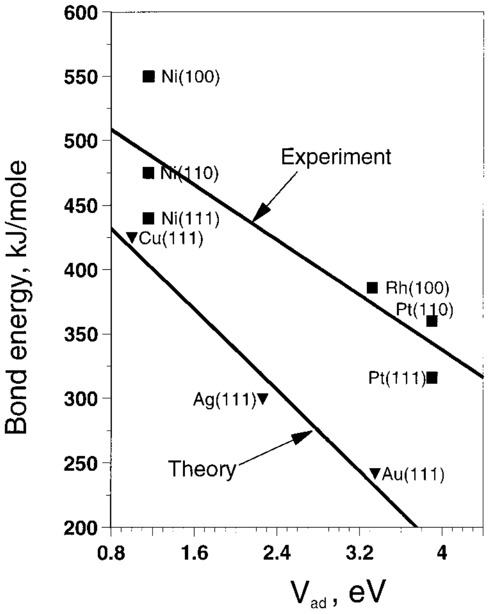

Figure 10. Plot of the heat of adsorption of oxygen on single crystal films measured calorimetrically by King and co-workers[7] (■) versus the energy of the center of the d-band as reported by Hammer and Nørskov.[5] (▼) Calculations of Nordlander, Holloway, and Nørskov.[33]

as the energy of the center of the d-band becomes less negative. We were expecting to observe a similar trend in the experiments. The carbon monoxide TPD data in Figures 1 and 2 show that the variation in the heat of adsorption with changing face shows some correlation to the theory in that the heat of adsorption increases as the energy of the center of the d-band increases. Still, the variations are much smaller than expected theoretically. The hydrogen data in Figure 7 show that the heats of adsorption of hydrogen on platinum show a small *decrease* as (111) oriented steps are added to the surface, whereas Watwe et al.'s DFT slab calculations suggest a substantial *increase*. The data in Figure 8 show that the heat of adsorption of ethylene on platinum shows a small *decrease* as the energy of the center of the d-band becomes less negative. By comparison, Watwe's DFT slab calculations suggest a substantial *increase*. The results in Figures 3−5 and Table 2 show that the experimental trends in the heats of adsorption with changing metal are not reproduced by the calculations. Clearly, there are substantial differences between theory and experiment that need to be explained.

The oxygen data show the trends expected from the theory. Unfortunately, there is no calculation to directly compare to experiments, so we do not know whether the magnitude of the variation is correct.

We believe that the measurements are reliable. We have examined several different data sets, including our own and several others. The experiments have a consistent trend: our work,[13,14] isosteric heat data,[21] and results from King's group[7] show only small changes in the heat of adsorption of CO with crystal face and somewhat larger variations between metals. Both our work[13,14,16] and results from McCabe and Schmidt[23] see a decrease in the binding of hydrogen on stepped surfaces. Our observation of a weakening of the ethylene bond with increasing step density is confirmed spectroscopically.[24−26] The TPD data in Figures 1, 7, and 8 were analyzed by constructing β plots. However, we have also analyzed the data via the initial rate method, and by fixing the preexponentials at 10^{13}/sec as summarized in Table 1 we observe the same trends. All of the trends in the experiments have been confirmed by (i) doing the measurements using two different techniques, (ii) doing the same measurements in two different laboratories, or (iii) both. Therefore, we believe that the experiments are reliable.

We also believe that the DFT calculations were done properly. We are comparing our data to some of the best DFT calculations in the literature. The calculations in refs 5, 6, 18, 28, 29, 34, 45, and 46 were done properly. The exchange/correlation functionals are some of the best in the literature; the cutoffs were appropriate. In all cases, slabs, not clusters, were used to represent the surface. Surface relations of the top layer of atoms were considered. It is clear that the calculations were carefully done, even though the calculations show trends that are not reproduced in the experiments.

Our conclusion, therefore, is that there is a real difference between the heats of adsorption measured in careful experiments and those predicted by careful DFT calculations. That was not the result we expected when we started this work.

We are not alone in making these observations. Several recent papers have shown substantial differences between careful experiments and careful DFT calculations. Recently, Feibelman et al.[29] noted that all of the available DFT calculations predict that CO should be bridge-bound on Pt(111) even though several different experimental techniques show linear bound CO instead. In a previous paper, we found[30] that the electronic structure of CO adsorbed on platinum measured by UV/HREELS differs substantially from that in the best calculations. More recently, Hoeft et al.[35] found that the geometry of CO and NO on NiO differs substantially from that expected from careful DFT calculations. Pichierri et al.[36] found that the binding site of ethylene is incorrectly predicted. Our results, here, represent a fifth case in which careful experiments give results that are substantially different from those expected from careful DFT calculations.

We suggest that the difficulty must be associated with an unforeseen weakness in the calculations. Many independent experiments are showing significant differences between calculation and experiment. Different laboratories have reproduced the experimental results. If there were an experimental artifact, then one would not expect it to be reproduced by so many different techniques, and in so many different laboratories. Clearly, there is a real difference between calculation and experiment that needs to be explained.

We suspect that there is something that we do not understand that is causing the experiments to differ from the calculations. The current generation of DFT calculations use empirical approximations for the exchange−correlation functional which might or might not be accurate. Also, the calculations approximate surfaces as thin slabs with incomplete relaxations. Evidently, some combination of incorrect geometry and inadequate functionals are causing the DFT careful calculations to predict trends that are different from those seen in careful experiments.

Our previous spectroscopic results[30] give clues as to the origin of the failure. Recall that the binding of CO is thought to mainly be associated with (i) an interaction between the 4σ orbital in the CO and the s-band of the metal, (ii) an interaction between the 5σ orbital in the CO and the s- and d-bands in the metal, and (iii) an interaction between the $2\pi^*$ orbital in the CO and the d-bands in the metal. Hammer, Neilsen, and Nørskov[6] examined the bonding of CO on platinum in some detail, and concluded that 4σ and 5σ interactions were weak and the main bond was due to an interaction with the $2\pi^*$ orbital. Experimentally though, our UV/HREELS measurements[30] seem to indicate that the main bond is associated with the 4σ and 5σ

interactions and the interaction with the $2\pi^*$ orbital is weak. Our measurements are on platinum, but similar data exist on copper and nickel.[31,32] Therefore, it seems that the calculations are overestimating the interaction of the d-electrons with the $2\pi^*$ orbital in the CO and underestimating the strength of the 4σ, 5σ interactions. CO on platinum is a special case, in that Feibelman et al.[29] have noted that the binding site of CO is incorrectly predicted. Clearly, there are significant differences between theory and experiment that need to be resolved.

In Figure 1 we find that both theory and experiment show a correlation to the energy of the center of the d-band, but the experimental variations are only about a third of those expected based on the work of Hammer, Nielson, and Nørskov.[6] Therefore, in effect, the measurements suggest that the interaction between the d-electrons in platinum and the $2\pi^*$ orbital in the CO are only about a third of those expected theoretically. We also observe significant differences in the heat adsorption of CO with changing metals, as indicated in Table 2.

At first we thought that CO might be a special case, but in fact we also find that the trends in ethylene adsorption on platinum and hydrogen adsorption on platinum are not reproduced in the calculations. Experimentally, the heat of adsorption of ethylene decreases as the surface becomes rougher, but the computations show a strongly increasing trend. Physically, heats of adsorption are different on stepped surfaces than on closed packed planes because of two key effects: (i) the center of the d-band shifts to lower energy as steps are created,[6] and (ii) the average electron density and work function of a surface decreases when steps are created.[14] Hammer and Nørskov[6] showed that the first effect produces an increase in the strength of the adsorbate−surface bond as steps are added to the surface. Masel[4] noted that the second effect produces a decrease in the strength of the adsorbate−surface bond as steps are added because there are fewer electrons available for bonding. Pallassana et al.[18,34] suggest that during ethylene adsorption the first effect dominates, so the heat of adsorption should increase as steps are added. However, the experiments show a decrease. Yagasaki and Masel[12] have shown that the decrease in the binding energy is proportional to the decrease in the electron density of the surface. In effect, the computations are overestimating the effect of the change in the energy of the d-bands, and/or underestimating the effect of the decrease in the surface electron density, again consistent with the idea that the d-bonding is overestimated in the current calculations.

The hydrogen results are similar. Again, the experiments show a decrease in the binding energy of hydrogen when (111) steps are added to the surface, but the computations show a strongly increasing trend. In effect, the computations are putting too much bonding on stepped surfaces, again consistent with the idea that the d-bonding is overestimated in the current calculations. We want to emphasize that these are the best calculations in the literature and so it is disappointing that the experimental trends are not being reproduced by the calculations.

We do not know why the theory fails to reproduce the experimental trends, but one possibility is that the calculations have predicted the wrong trends with changing face because many of the calculations have not properly considered surface relaxations. Some of the calculations in refs 5, 6, 18, 28, 29, and 34 were done on unrelaxed surfaces. Others allowed only the first layer to relax. Platinum relaxes by as much as 0.2 Å, and the relaxations are significant down to the fifth layer. In previous work, we have found that the electronic structure of platinum changes substantially during the relaxation process, so binding on an unrelaxed surface is quite different from binding on a relaxed surface.[14] In unpublished work, Neurock found that the heat of adsorption of ethylene changes substantially as surfaces relax. The heat of adsorption increases as the surface gets rougher on unrelaxed surfaces, but the effect is much smaller with relaxed surfaces. Clearly, the calculations need to include surface relaxations, before the trends are reliable.

Relaxations cannot be the whole story, however, because the calculations of data in Figure 3 and Table 1 were all taken on surfaces that do not relax substantially, and the data still show trends different from those that were expected theoretically. Further, Hammer et al.[6] found that relaxations reduce the binding energies of CO on Pt(211) by only 10 kJ/mol, which is not enough to account for the differences between calculation and experiment. Also, the binding site of CO on Pt(111) is not properly predicted[26,29] even though the Pt(111) surface does not relax substantially. Therefore, one also has to consider whether there is a more fundamental problem in the current generation of surface DFT calculations.

One possibility is that the functionals used in the DFT calculations are not adequately representing the interactions between adsorbates and transition metal surfaces. Recall that practical DFT calculations use approximations to the exchange/correlation functional.[36−39] Most modern calculations of adsorbate properties, including those in refs 5, 6, 18, 28, 29, 34, 45, 46, and 47 use the local density approximations with gradient corrections (i.e., GGA). GGA usually does a good job on metals. Still, the functional does not include any terms in the second derivative of the electron density,[42] any exact exchange contributions[41] or any connection for the self-interaction correction.[40] Consequently, the functional would not be expected to do as good of a job on exchange proportional to the second derivative of the electron density, i.e., delta bonding. Yet, classically, delta bonding is quite important to the bonding of CO and ethylene on transition metals.[40−42] Functionals that describe the key features of the delta bonding exist in the literature,[40−42] but so far those functionals have not yet been used to model adsorption or reaction on solid surfaces. At this point, it is unclear whether the functionals need improvement, or some other part of the calculation needs to be changed. Still, the calculations of Hammer, Neilsen, and Nørskov and Pallassana and Neurock are some of the best in the literature, and show clear discrepancies with experimental trends that have been reproduced in several different laboratories. Certainly, an inadequate functional would explain the substantial difference between calculations and experiments.

Summary

In summary then, in this paper we examined the variation in the heat of adsorption of CO, H_2, O_2, and ethylene with changing metal and changing face. The results show a substantial difference between careful experiments and careful calculations. The heat of adsorption of CO on platinum was found to increase as the center of the d-band shifts, but the variation was a factor of 3 less in the experiments than in the calculations. The heat of adsorption of ethylene and hydrogen decrease as (111) steps are added to the surfaces, but the calculations show the opposite trends. All of the experimental trends have been reproduced by at least two laboratories, supporting their validity. These results suggest that there is something that we do not understand about adsorption of gases on surfaces. Either, the effects of surface relaxations are much larger than previously supposed, or the functionals used to model adsorption need improvement. We favor the latter, because this is the fourth recent paper that has found a substantial difference between careful experiments and careful DFT calculations.

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