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The electronic structure effect in heterogeneous catalysis

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Using a combination of density functional theory calculations and X-ray emission and absorption spectroscopy for nitrogen on Cu and Ni surfaces, a detailed picture is given of the chemisorption bond. It is suggested that the adsorption bond strength and hence the activity of transition metal surfaces as catalysts for chemical reactions can be related to certain characteristics of the surface electronic structure.

KEY WORDS: electronic structure; chemical bonding; density functional theory; X-ray spectroscopy.

1. Introduction

One of the most fundamental properties of a metal surface is its ability to form bonds with atoms and molecules from the surroundings. The bonding ability determines the state of the surface when exposed to a gas or liquid, and it determines the ability of the surface to act as a catalyst. During catalysis, the surface makes chemical bonds to the reactants and helps in this way breaking intramolecular bonds and forming new ones. Transition metals are used extensively as catalysts and the variation in the catalytic activity for a given reaction is determined largely by the differences in the strength of the adsorbate-surface interaction from one metal to the next [1,2].

This importance of the adsorbate–surface bond strength determining the catalytic activity of a given surface is illustrated in figure 1. Here it can be seen how the catalytic activity of different transition metals as catalysts for ammonia synthesis is given by the strength of the nitrogen–surface bond [3]. The reason is that the ability of the surface to bond to a nitrogen atom also determines the ability of the surface to stabilize the transition state for the dissociation of the N–N bond. The maximum in the catalytic rate for an intermediate metal–nitrogen bond strength thus represents the optimal compromise between having a low activation barrier for dissociation of N_2 (favored by a strong N–surface bond) and being able to further react the adsorbed nitrogen to NH_3 (favored by a weak N–surface bond). This is also know as the Sabattier principle [4], and it applies to a range of different catalytic processes [1,2]. Understanding which parameters determine the catalytic activity is therefore closely related to understanding the origin of variations in adsorption bond strengths.

In the present report, we will focus on understanding trends in adsorbate–surface interactions and we will discuss a particularly simple picture that was originally developed to describe the difference in reactivity for hydrogen dissociation on metal surfaces [5]. We will show that it applies quite generally, and in particular we will show that it can be validated through an experimental determination of the electronic structure of both occupied and unoccupied adsorbate states in an atom specific way.

2. Methods

The experimental spectra were obtained at beamline 10-1 at Stanford Synchrotron Radiation Laboratory (SSRL), USA and at beamline 22 at MAX-lab, Sweden [6–8]. The XE spectra were recorded using a grazing incidence spectrometer with a movable multichannel-based detector with an overall resolution of 0.5 eV [9]. Angle resolved measurements together with a subtraction procedure were performed to separate orbitals of different symmetry [9,10]. The XA spectra were recorded using a partial electron yield detector with a retardation voltage of 350 V and were normalized to the incidence flux to the sample. The overall resolution was 0.2 eV. The nitrogen c (2×2) overlayer on Cu(100) was prepared by low energy ion bombardement in a N_2 atmosphere at room temperature followed by annealing to 300 °C. The nitrogen p4g (2×2) overlayer on Ni(100) was prepared by decomposition of NH_3 at 200 °C. The

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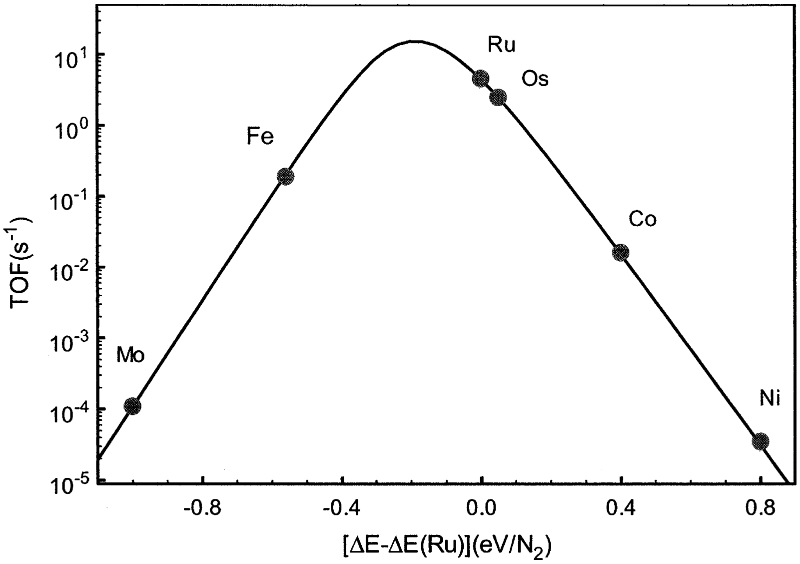

Figure 1. Calculated rate of ammonia synthesis per surface atom per second (turn over frequency, TOF) for different transition metals plotted as a function of the N–metal bonds strength (the dissociative chemisorption energy), from Ref. [2].

overlayer structure of all preparations was controlled by low energy electron diffraction (LEED).

The calculations were performed within a plane wave pseudopotential implementation [11]. We used the ultrasoft pseudopotentials to represent the ionic cores, allowing for a good treatment of first-row atoms and transition metals with a relatively limited plane wave basis. The plane wave cut-off in the calculations was 25 Rydberg in all cases, except for the cobalt surface, in which case a cut-off of 35 Rydberg was chosen, due to the hardness of the corresponding pseudopotential. All total energy calculations were performed with the RPBE exchange–correlation functional [12] on periodically repeated stepped metal slabs. The surface coverage of the adsorbates was 1/6 in all cases, and the slab thickness was 9 layers in the [211] direction for the fcc metals and 11 layers in the [210] direction for the bcc metals. In the case of the hcp metals (Ru and Co), the adsorption was modeled by using the same type of fcc (211) slabs as for the fcc metals. The fcc-and the bcc-surfaces exposed a terrace of close-packed atoms, the (111) and (110) layers respectively, and the uppermost close-packed layer, including the step atoms were in all cases fully relaxed together with the adsorbate atom/molecule. The lattice constants were chosen as the calculated bulk lattice constant for the respective metals in their ground state structure using the RPBE functional. Between the metal slabs we introduced at least 8 Å of vacuum, and the interaction between the dipole moments of the periodically repeated slabs was decoupled, by the introduction of a dipole layer in the vacuum between the slabs. We used a **k**-point sampling of 4 × 4 × 1 Monkhorst–Pack special points in the x, y, and z directions respectively; the number of **k**-points was reduced to 8 **k**-points in the irreducible Brillouin zone by time-inversion symmetry. The spectra were obtained from 6 layer slab models of the fcc-(l00)-c(2 × 2)-N adsorption systems. Three layers were relaxed, the slabs were separated by 12 Å of vacuum, and a 8 × 8 × 1 **k**-point mesh was used. The Kohn–Sham wave-functions were projected onto the pseudopotential p_x and p_z-operators and the energy-dependent overlap-terms obtained were broadened with 1 eV broad Gaussian functions.

3. Results and discussion

We will consider nitrogen bonding to different 3d transition metals to illustrate our approach. It is clear from figure 1 that understanding trends in nitrogen chemisorption energies is essential to an understanding of the effects leading to ammonia catalysis. The general picture that we derive is, however, more general than that.

The chemisorption energy of nitrogen calculated using density functional theory [12,13] is well correlated with the average energy of the metal valence d-bands, see figure 2. The higher in energy the d states are the stronger the N–surface bond. This effect can be understood qualitatively in the following way. Consider an adsorbate valence state, in the present case one of the 2p levels of N, interacting with the valence states on a transition metal as illustrated in figure 3. The valence states of the transition metal surface atoms can be divided up into the free-electron-like s electron states and the more localized d electron states. We can imagine including the coupling between the nitrogen 2p state to the metal s states first and then switching on the coupling to the metal d states later. The coupling to the

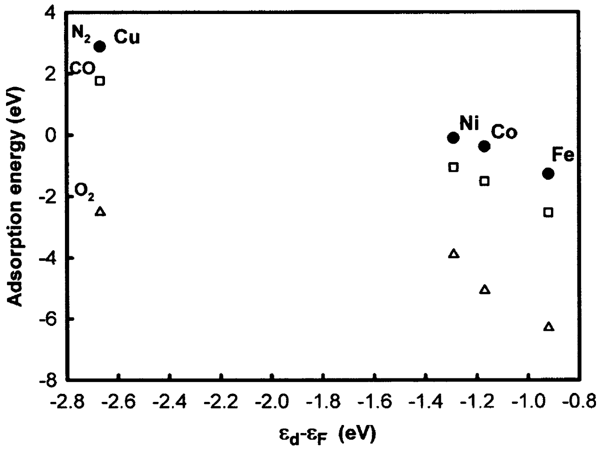

Figure 2. Calculated dissociative nitrogen, carbon monoxide, and oxygen chemisorption energies over different 3d transition metals plotted as a function of the center of the transition metal d bands.

broad s band leads to a broadening and shift of the adsorbate states [14,15], see figure 3. There may be a large energy involved in this interaction, but since all the transition metals have a half-filled s band in the metallic state and since the band is broad, there will only be small differences in this interaction from one metal to the next. The differences between the different transition metals must be associated primarily with the d states. The interaction of the adsorbate states with a narrow distribution of states will give rise to the formation of separate bonding and anti-bonding states just as in molecules. When bonding and anti-bonding states are formed, the strength of the bond will depend on the relative occupancy of these states. If only the bonding states are filled, there will be a strong bond, whereas if the anti-bonding states are also, filled the bond becomes considerably weaker.

In a molecule, the occupancy of the anti-bonding states depends on the number of electrons in the system. This is different at a metal surface. Here there is an infinite sea of metallic electrons and the occupancy of the anti-bonding states depends only on the energy of these states relative to the Fermi level. Since the energy of the d states relative to the Fermi level varies substantially from one metal to the next, the number of anti-bonding states that are above the Fermi level, and thus empty, will depend on the metal in question. As the d states shift up energy, the strength of the adsorbate metal bond should increase as observed in figure 2.

In figure 4 we consider the picture in more detail for Cu and Ni. The two metals are neighbors in the periodic table, yet their ability to interact with e.g. nitrogen differs substantially, see figure 2. Cu has d bands well below the Fermi level, and the anti-bonding states at the top of the d bands end up below the Fermi level and are filled. The d-contribution to the bond is therefore not attractive. For Ni, on the other hand, the anti-bonding states at the top of the d bands are partly above the Fermi level and the interaction is much more attractive.

This picture can be verified in detail by X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS), see figure 4. These spectroscopies provide an atom specific projection of the occupied (XES) and unoccupied (XAS) electronic states [9,10]. Since the decay process in XES and the excitation process in XAS are dipole dominated and the transitions are governed by the overlap with the N ls core orbital, only the N2*p* valence electrons contribute to the intensity. Furthermore, using angle-resolved measurements the different p_x, p_y and p_z components of the electronic structure can be separated. Figure 4 shows angular resolved XE and XA spectra on a common energy scale with respect to the Fermi level of N adsorbed on Ni(100) and Cu(100) with a coverage of half a monolayer [6–8]. In the XE spectra of N adsorbed on Cu, both the p_{xy} and p_z components exhibit two strong peaks, representing the bonding and antibonding states. In the XA spectra, on the other hand, no strong peaks are observed. For N adsorbed on Ni we only observe one strong peak at high binding energy in the XE spectra, due to occupied bonding p_{xy} and p_z states. The

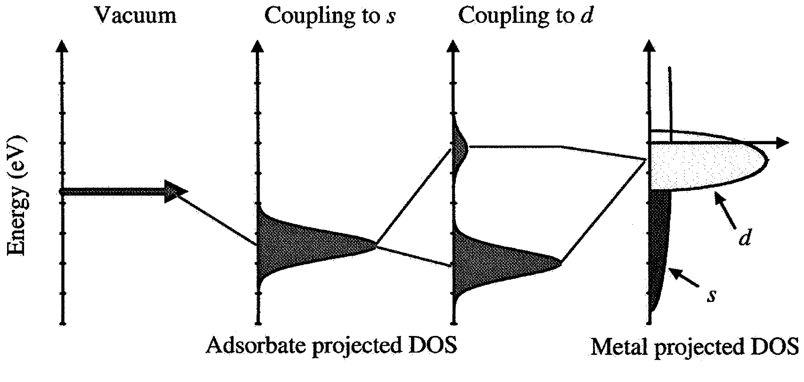

Figure 3. Schematic illustration of the formation of a chemical bond between an adsorbate valence level and the s and d states of a transition metal surface.

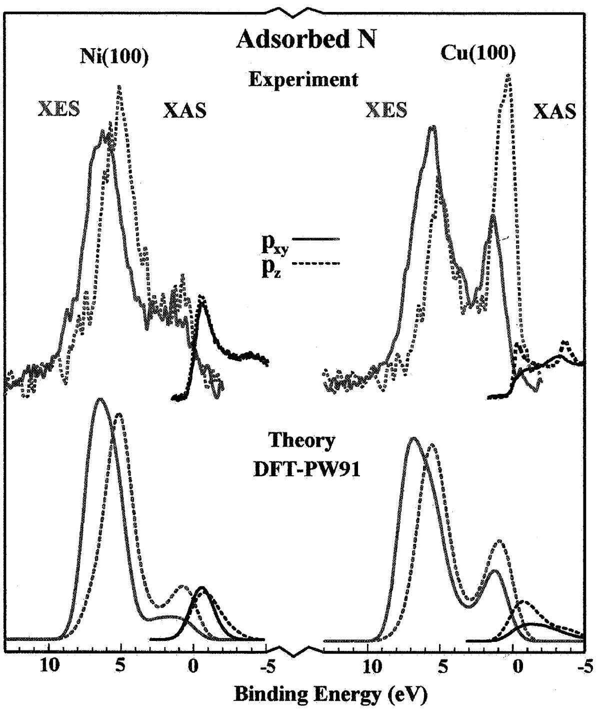

Figure 4. Top: Comparison of the XES (occupied states) and XAS (unoccupied states) spectra of atomic N adsorbed on Ni(l00) in and Cu(100) with separated p components. The intensity scaling between the XES and XAS spectra is arbitrary. Bottom: Calculated density of states projected onto the p_x and p_z valence states of N chemisorbed onto a Cu(100) and Ni(100) surface in the c(2 × 2) structure. Filled states below the Fermi level are shown in red while empty states are shown in blue. In order to make the comparison to the experimental results clearer the spectrum has been broadened by the experimental energy resolution of ~1 eV.

antibonding states can now be seen in the XA spectra directly above the Fermi level.

It is clear from figure 4 that there is a very close correspondence between the calculated and the measured spectra. Both the calculated one-electron (Kohn–Sham) spectra and the experimental spectra show peaks below and just above the d bands. From the DFT calculations we can further confirm that the lower-lying states have bonding metal-d–N-2p character whereas the high-lying states have anti-bonding character. Both the DFT results and the experiments show that the anti-bonding states are filled for Cu and partially empty for Ni. By combining the DFT calculations with very detailed experimental observations, we have therefore established strong support for the notion that the difference in the bonding ability of Cu and Ni is related to the degree of filling of the anti-bonding metal-d related states.

The observations described above, provide a fairly complete picture of an important electronic factor in heterogeneous catalysis: The catalytic activity of transition metals for ammonia synthesis is correlated with the strength of the nitrogen–surface bond. The bond strength in turn is determined by the filling of the anti-bonding N 2p–metal d states and the average energy of the metal d states relative to the Fermi level provides a good indicator of the filling. The physical picture has been derived by a combination of density functional calculations, simple models and atom specific spectroscopy measurements.

4. Conclusion

The nitrogen results discussed here are indicative of the behavior of many other systems. This is illustrated in figure 3 and it has been shown in a number of studies that bond strengths and activation energies scale with the d band center [11]. Since adsorption bond strengths are also found quite generally to be a good descriptor of catalytic activity [1, 2], we conclude that the metal d band energy is in general a good indicator of the catalytic reactivity of transition metal surfaces.

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