Strain and coordination effects in the adsorption properties of early transition metals

Sebastian Schnur and Axel Groß

Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm, Germany

Strain and coordination effects in the adsorption on early transition metals were studied using density functional theory. We show that, in contrast to late transition metals, early transition metal surfaces with a less than half-filled local d-band exhibit lower adsorption energies upon lattice expansion and on low-coordinated sites, in agreement with predictions based on the d-band model. This demonstrates that the d-band model can be extended to early transition metals. Implications of these results for hydrogen storage materials are discussed.

Strain and coordination effects in late transition metals have recently attracted a lot of attention as they can significantly change the electronic and catalytic properties of these metal surfaces [1–7]. Strain effects occur, e.g., when a metal is grown pseudomorphically on another metal with a different lattice constant. Tensile strain of 1.5% can for example lower the dissociation barrier of CO by up to 0.2 eV [2] which would enhance the dissociation rate constant by more than three orders of magnitude at room temperature. Considerations based on effective strain are also important to understand the reactivity of metallic compounds such as surface alloys [8]. The effects of a reduced coordination can be even more dramatic. In a combined experimental and theoretical study it was shown that the N_2 dissociation rate at the steps of a Ru surface is at least nine orders of magnitude higher than on Ru(0001) terraces [9].

The qualitative trends found in the catalytic activity as a function of the strain or the coordination of the substrate atoms can be nicely explained [10] invoking the d-band model [11]: tensile strain for example leads to a narrowing of the metal d-band due to the reduced overlap of the wave functions. If the d-band is more than half-filled, i.e., if the metal is a late transition metal, then the band narrowing leads to an increased population of the d-band. Because of charge conservation, the d-band moves up in order to preserve its degree of d-band filling. According to the d-band model, an upshift of the d-band leads to a lower occupation of anti-bonding states in the molecule-surface interaction thus raising the interaction strength. Using perturbation theory, a linear relationship between the d-band center shift $\delta\varepsilon_d$ and the change in the chemisorption strength ΔE_d [12, 13],

$$\Delta E_d = -\frac{V^2}{|\epsilon_d - \epsilon_a|^2}\,\delta\varepsilon_d\;,\qquad(1)$$

can be derived, where ϵ_a is an electronic adsorbate level and V is a coupling matrix element that is assumed to be constant for similar situations. It is important to realize that the higher binding to lower coordinated sites at nanostructured surfaces can be explained by a similar reasoning [7]: A lower coordination, i.e., a smaller num-
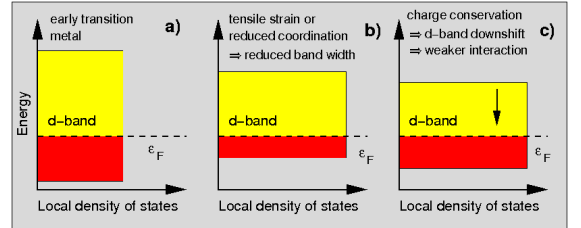

FIG. 1: Illustration of the effect of tensile strain or reduced coordination on the width and position of the d-band of an early transition metal: a) less than half-filled d-band; b) reduced width of the d-band due to a smaller overlap or lower coordination; c) downshift of the d-band because of charge conservation.

ber of nearest neighbors also leads to a band narrowing and a subsequent upshift of the d-band center.

Using the same line of arguments, for early transition metals with a less than half-filled d-band, tensile strain or reduced coordination should have the opposite effect on the d-band center, as illustrated in Fig. 1: the band narrowing caused by tensile strain or lower coordination should lead to a down-shift of the d-band center and thus to a reduced interaction with adsorbates. Hence the dependence of adsorption energies on the strain and coordination should have the opposite behavior in early transition metals compared to late transition metals.

However, the study of strain and coordination effects has almost exclusively focused on late transition metals because these are the typical catalytically active metals. Here we present a systematic theoretical study based on density functional theory (DFT) addressing strain and coordination effects in the adsorption on some early transition metals. We have used hydrogen and CO chemisorption energies as a probe of the interaction strength. Thus we check whether the d-band model that has been very successfully in explaining and predicting trends for late transition metals [14] can also be extended to early transition metals. We particularly focus on the light 3d transition metals since some of them such as titanium have recently also been discussed as promising materials in compounds for hydrogen storage

devices [15, 16]. Hence an understanding of strain and co-ordination effects in early transition metals can also be beneficial for the design of improved hydrogen storage devices. Furthermore, these findings are important for an analysis of hydrogen embrittlement in metallic compounds containing early transition metals [17].

We performed periodic DFT calculations using the Vienna ab initio simulation package (VASP) [18]. The exchange-correlation effects were described within the generalized gradient approximation (GGA) using the Perdew-Burke-Ernzerhof (PBE) functional [19], but additional calculations with the RPBE functional [20] were performed to check the trends. The ionic cores were represented by projector augmented wave (PAW) potentials [21] as constructed by Kresse and Joubert [22]. The plane wave basis was expanded up to a cutoff energy of 400 eV for CO adsorption and 350 eV for hydrogen adsorption. The reported adsorption energies were determined in (2×2) surface unit cells corresponding to a coverage of $\theta = 0.25$.

Since in the case of early transition metals only few d states are occupied, special care is required in order to take the unoccupied portion of the d band into account. Therefore, a rather fine mesh of at least $13 \times 13 \times 1$ **k**-points was used in all calculations and the number of bands was increased to make sure that all relevant states above the Fermi level are included. To avoid picking up any irrelevant noise above the actual d-band due to the projection scheme, the integrals necessary to determine the d-band centers were truncated at the upper edge of the d-band.

All considered surfaces are modeled by a slab of five layers. The slabs are separated by at least $10\,\text{Å}$ of vacuum. The adsorption energies are determined via

$$E_{\text{ads}}^{\text{H}} = E_{\text{slab}+\text{H}} - \left(E_{\text{slab}} + \frac{1}{2}E_{\text{H}_2}\right) \qquad (2)$$

$$E_{\text{ads}}^{\text{CO}} = E_{\text{slab}+\text{CO}} - \left(E_{\text{slab}} + E_{\text{CO}}\right) \qquad (3)$$

where E_{slab} and $E_{\text{slab}+\text{X}}$ are the total energies of the slabs without and with the adsorbate.

TABLE I: Lattice parameters, d-band center ϵ_d and the root mean square deviation (RMSD) in eV as an indicator of the d-band width at the close-packed surfaces of the d-band metals considered in this study.

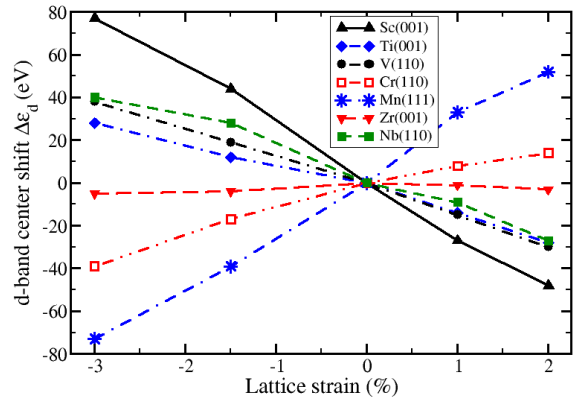| Substrate	Crystal structure	Lattice constant Å	d-band center (eV)	d-band RMSD (eV)
Sc(001)	hcp	a=3.31/c=1.55	1.916	1.618
Ti(001)	hcp	a=2.98/c=1.62	1.274	1.723
V(110)	bcc	3.00	0.860	1.852
Cr(110)	bcc	2.84	-0.111	1.821
Mn(111)	fcc	3.50	-0.528	1.749
Zr(001)	hcp	a=3.28/c=1.58	1.629	2.330
Nb(110)	bcc	3.31	1.335	2.435

FIG. 2: Calculated shift of the d-band center as a function of the lattice strain for several transition metal surfaces.

In table I, we have collected some basic data of the early $3d$ metals Sc, Ti, V, Cr, Mn and the early $4d$ metals Zr and Nb considered in this study. In general, we have selected the densely packed surfaces of the metals because these show usually the largest strain effects. The increasing population of the surface d-band from Sc to Mn is reflected in the significant downshift of the d-band center. With respect to Mn we note that Mn exists in five allotropic forms with partly rather complex geometric and magnetic structures [23]. Since we are only interested in trends here, we have just considered a non-magnetic fcc(111) surface of Mn. Note that for Cr(110) and Mn(111) the local d-band center at the surface is already below the Fermi energy in spite of their atomic $3d^5 4s^1$ and $3d^5 4s^2$ configuration, respectively. This indicates that there is an $s \rightarrow d$ transfer in these metals.

In order to determine strain effects we have used slabs with lateral lattice constants corresponding to 3% and 1.5% compression, no strain, and 1% and 2% expansion, respectively. Indeed we find for all considered metals a narrowing of the d-band with lattice expansion, as reflected in a decreasing root mean square deviation from the d-band center. The resulting shifts of the d-band centers as a function of lattice strain are plotted in Fig. 2. The early d-band metal surfaces Sc(001), Ti(001), V(110) and Nb(110) show the expected trend, a down-shift of the d-band center upon expansion. Unexpectly, the d-band-center of Zr(001) does not depend on the lattice strain whereas Cr(110) and Mn(111), whose d-band center at the surface is below the Fermi energy, show the trend typical for late transition metals.

The corresponding changes in the H and CO adsorption energies as a function of the lattice strain are plotted in Fig. 3. Hydrogen usually prefers high-coordinated adsorption sites on metal surfaces. Therefore we chose the most favorable adsorption sites for hydrogen. CO, in contrast, exhibits different energetically favorable adsorption sites. Since we regard the adsorption energy as
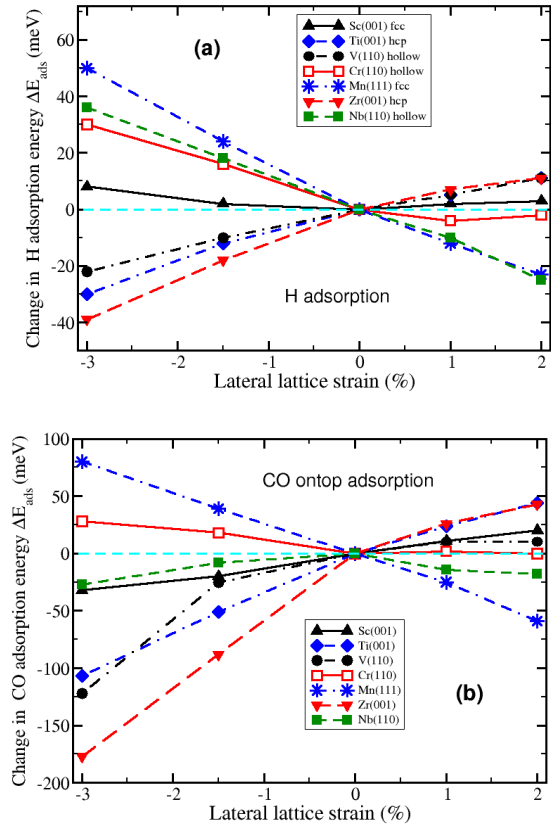
FIG. 3: Calculated change of the adsorption energies for H at the most favorable sites (a) and for CO at the ontop sites (b) as a function of the lattice strain for several early transition metal surfaces.
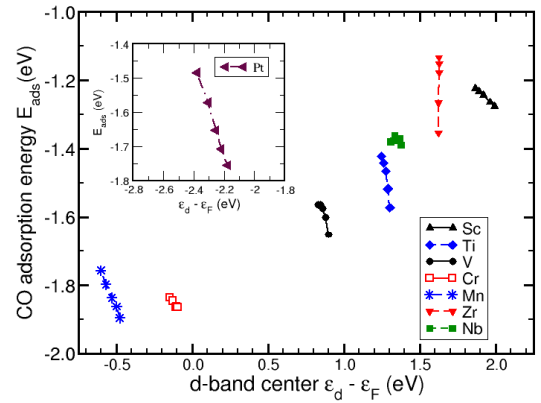
FIG. 4: CO adsorption energies at the ontop sites of the strained early transition metal surfaces as a function of the local d-band center. The inset shows the corresponding data for the CO adsorption on Pt surfaces using the same scale.

a probe of the local reactivity, we consider here only CO adsorption at the ontop sites. Thus the trends for the different metals can be better compared and we also avoid problems related to the site preference [24]. Note that according to our definition of the adsorption energies energetically favorable adsorption is reflected by negative numbers. Hence, more positive adsorption energies correspond to a *weaker* binding of the adsorbates.

Inspecting Fig. 3, the following trends are obvious both for hydrogen as well as for CO adsorption. On the early transition metals Ti, V and Zr of the fourth and fifth group with two or three d electrons, H and CO binding becomes weaker upon lattice expansion. Sc exhibits the expected trend for CO adsorption, the H adsorption energies, however, are within our accuracy independent of the lattice strain. For Mn and Cr, the interaction strength increases upon lattice expansion, i.e., they behave similar to late transition metals which is not surprising regarding that their local d-band at the surface is more than half filled (see Table I). Only the Nb results do not follow the expected trends.

In order to check whether the computed adsorption energies are consistent with the predictions of the d-band model according to Eq. (1), we plotted in Fig. 4 the calcu-

lated CO adsorption energies as a function of the d-band center for the strained surfaces. For comparison, we included in the inset of Fig. 4 the CO adsorption on the corresponding Pt substrates using the same scale of the axes. Indeed, for all considered early transition metals except for Nb and Zr we find an approximate linear relationship between the shift of the d-band center and the change in the interaction energy with a slope that is comparable to the case of Pt. For hydrogen adsorption, we obtain the same trends.

The width of the d-band can not only be modified by straining the lattice but also by changing the coordination of the metal atoms. Hence we have also considered CO adsorption on low-coordinated sites, namely ontop of the step atoms of the fcc(211) surface and the equivalent terminations for the hcp and bcc metals. These surfaces exhibit hexagonal microfacets at the steps. In addition, CO adsorption energies ontop of single adatoms in a 2×2 arrangement were calculated. The corresponding changes in the adsorption energies with respect to the adsorption at the close-packed surfaces are plotted in Fig. 5. Except for the CO adsorption at the step sites of Mn and Zr we find for all considered early transition metals that the CO binding to low-coordinated sites is weaker than the binding to the high-coordinated terrace atoms.

It is important to note that on all considered early transition metal surfaces the d-band center is downshifted at the low coordinated adatoms. This is also true for Mn and Cr with a more than half-filled d-band, thus explaining the weaker bonding ontop of the single adatoms. In contrast, at the step atoms the d-band center is almost unchanged with respect to the flat surfaces for these two metals.

At first sight, the trends found in the adsorption energy as a function of the coordination seem to be surprising. Within a local view of chemical bonding, the bond or-
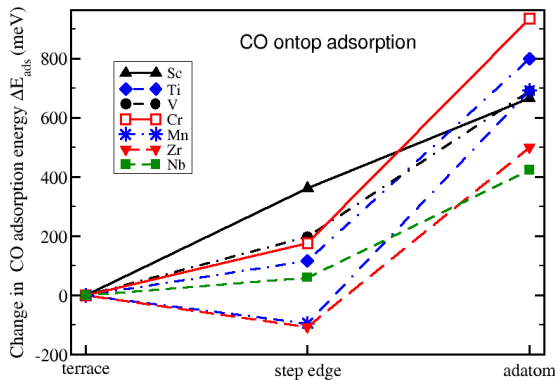
FIG. 5: Calculated change of the adsorption energies CO at the ontop sites of a step edge atom and an adatom with respect to the adsorption on the close-packed terraces.

der concept predicts that lower-coordinated sites should show a stronger interaction with adsorbates than higher-coordinated sites in order to conserve the bond order. For late transition metals, this is usually the case [7], as we have explicitly checked for Pt. Early transition metals, however, obviously do not follow this trend. However, there is another point of view within the framework of the effective medium theory [25]: there is an optimum charge density for the binding of adsorbates, and apparently low-coordinated early transition metals cannot provide this optimum charge density.

Our general findings are useful for understanding trends in the interaction of hydrogen with early transition metal clusters. For example, DFT calculations found a general increase in the hydrogen binding strength to small Ti clusters as a function of the cluster size [16]. Furthermore, the chemisorption of hydrogen on small Ti clusters becomes stronger with growing hydrogen coverage at small to moderate coverages [26]. In both cases, the effective coordination of the early transition metal atoms increases, either because of the growing cluster size or because of the growing hydrogen coverage. This causes a stronger bonding, in contrast to late transition metals.

Similar results were found in DFT calculations addressing nanomaterials decorated by early transition metals [15, 27]. A single Ti atom adsorbed on a carbon nanotube can bind up to four hydrogen molecules, and the energy gain for the involved successive adsorption events remains substantial [15]. This is also true for Sc and V atoms adsorbed on carbon nanotubes [28].

In conclusion, using periodic DFT calculations we have shown that the d-band model can be used to explain and predict trends in the adsorption energy on early-transition metal substrates. Because of the less than half-filled d-band the dependence on the lattice strain and the coordination is opposite to the one found for late transition metals. These findings may help to fine-tune the hydrogen storage capabilities of compounds containing early transition metals.

[1] M. Gsell, P. Jakob, and D. Menzel, Science **280**, 717 (1998).
[2] M. Mavrikakis, B. Hammer, and J. K. Nørskov, Phys. Rev. Lett. **81**, 2819 (1998).
[3] A. Schlapka, M. Lischka, A. Groß, U. Käsberger, and P. Jakob, Phys. Rev. Lett. **91**, 016101 (2003).
[4] A. Roudgar and A. Groß, Phys. Rev. B **67**, 033409 (2003).
[5] J. Greeley, W. R. Krekelberg, and M. Mavrikakis, Angew. Chem. Int. Ed. **43**, 4296 (2004).
[6] L. A. Kibler, A. M. El-Aziz, R. Hoyer, and D. M. Kolb, Angew. Chemie, Int. Ed. **44**, 2080 (2005).
[7] A. Groß, J. Comput. Theor. Nanosci. **5**, 894 (2008).
[8] S. Sakong, C. Mosch, and A. Groß, Phys. Chem. Chem. Phys. **9**, 2216 (2007).
[9] S. Dahl, A. Logadottir, R. C. Egeberg, J. H. Larsen, I. Chorkendorff, E. Törnqvist, and J. K. Nørskov, Phys. Rev. Lett. **83**, 1814 (1999).
[10] A. Ruban, B. Hammer, P. Stoltze, H. L. Skriver, and J. K. Nørskov, J. Mol. Catal. A **115**, 421 (1997).
[11] B. Hammer and J. K. Nørskov, Surf. Sci. **343**, 211 (1995).
[12] B. Hammer, O. H. Nielsen, and J. K. Nørskov, Catal. Lett. **46**, 31 (1997).
[13] V. Pallassana, M. Neurock, L. B. Hansen, B. Hammer, and J. K. Nørskov, Phys. Rev. B **60**, 6146 (1999).
[14] B. Hammer and J. Nørskov, Adv. in Catal. **45**, 71 (2000).
[15] T. Yildirim and S. Ciraci, Phys. Rev. Lett. **94**, 175501 (2005).
[16] T. J. D. Kumar, P. F. Weck, and N. Balakrishnan, J. Phys. Chem. C **111**, 7494 (2007).
[17] A. Pundt and R. Kirchheim, Annu. Rev. Mater. Res. **36**, 555 (2006).
[18] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11169 (1996).
[19] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).
[20] B. Hammer, L. B. Hansen, and J. K. Nørskov, Phys. Rev. B **59**, 7413 (1999).
[21] P. E. Blöchl, Phys. Rev. B **50**, 17953 (1994).
[22] G. Kresse and D. Joubert, Phys. Rev. B **59**, 1758 (1999).
[23] J. Hafner and D. Spišák, Phys. Rev. B **72**, 144420 (2005).
[24] P. J. Feibelman, B. Hammer, J. K. Nørskov, F. Wagner, M. Scheffler, R. Stumpf, R. Watwe, and J. Dumesic, J. Phys. Chem. B **105**, 4018 (2001).
[25] J. Nørskov, Rep. Prog. Phys. **53**, 1253 (1990).
[26] P. Tarakeshwar, T. J. D. Kumar, and N. Balakrishnan, J. Phys. Chem. A **112**, 2846 (2008).
[27] R. Stumpf, R. Bastasz, J. A. Whaley, and W. P. Ellis, Phys. Rev. B **77**, 235413 (2008).
[28] E. Durgun, S. Ciraci, and T. Yildirim, Phys. Rev. B **77**, 085405 (2008).