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Research Article

Spin Effects in Chemisorption and Catalysis

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Cite This: *ACS Catal.* 2023, 13, 3456−3462

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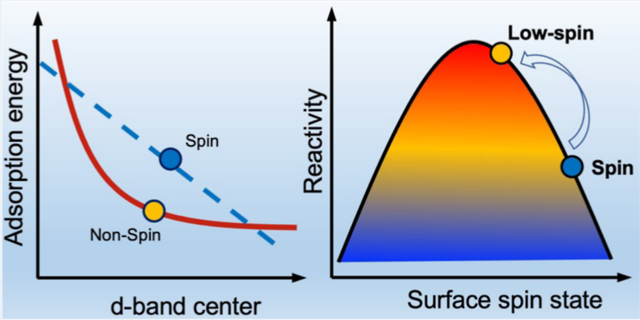
ABSTRACT: In this work, we show using density functional theory calculations that controlling the spin state of the surface of magnetic metals has a substantial effect on their chemical properties. For a range of adsorbates, the adsorption energy is shown to be stronger on non-spin polarized surfaces than on spin polarized ground state surfaces. This is true for Fe, Co, and Ni surfaces, and the result is the same for three commonly used exchange−correlation functionals. We further discuss the origin of the effect in terms of the surface electronic structure and show that a simple model based on the d-band model of adsorption can explain the effect. Finally, we discuss how spin effects may be used to control surface reactivity and provide guidance on how to alter the surface spin state, e.g., adding a metal promotor.



KEYWORDS: *spin effect, d-band model, surface spin state, reactivity, promoter*

INTRODUCTION

Ammonia synthesis catalysts are usually promoted by the addition of alkali metals.[1−6] This effect has been explained as primarily stemming from an electrostatic interaction between the partially ionized alkali adsorbate and different intermediates—the slightly negatively charged transition state for N_2 dissociation is stabilized, whereas adsorbed NH_x intermediates with an opposite dipole moment are destabilized. The former increases the rate of N_2 dissociation, while the latter effect decreases the coverage of intermediates blocking N_2 dissociation.[7−9] There has, however, been some remarkable data in the literature that cannot be explained that way. This includes the finding that a Ba promoted Co catalyst can have rates of ammonia synthesis higher than the usual Fe or Ru based catalysts in spite of the fact that Co by itself is quite unreactive for this process.[10,11] It also includes several recent findings that Li, Ca, La, and Ce can act as efficient promotors.[12−15]

It has been suggested that the origin of the "unusual" promotion of Co is mediated by the Co spin in the active site.[9] The explanation has two steps: first, it is found that the energy of adsorbed N and of the N_2 dissociation transition state is lower (more stable) on non-spin polarized Co than on spin polarized Co. Second, certain adsorbed promoters like Cs, Li, Ba, Ca, La, and Ce are found to lower the spin moment in their vicinity, hence stabilizing the adsorbed N and N−N transition state.

In the following, we explore the generality of this spin effect for different transition metals and a range of different adsorbates. We do that by calculating the difference between adsorption energies on spin-polarized and non-spin polarized surfaces as a measure of the strength of the spin mediated promotion effect. The conclusion is that the effect is very general; the effect is found on Ni, Co, and Fe surfaces and for all adsorbates studied although the degree of the effect is adsorbate-dependent. We also show that the effect is independent of the exchange−correlation functional used.

RESULTS

Spin Effects in Adsorption Energies. To determine the effect of the surface spin state on the adsorbate adsorption energy, two Co(1015) surfaces with distinct spin moments, namely, spin (ground state spin moment) and non-spin polarized were introduced for comparison. Here, non-spin polarized results have been obtained by setting the spin to zero on all Co atoms in the system and recalculating the lattice constant. Computational details can be found in the Methods section as shown in the Supporting Information.

Figure 1a shows that the CO adsorption energy on non-spin polarized Co is stronger than that on the spin polarized Co, suggesting that decreasing the spin moment of Co atoms can increase the affinity for CO adsorption. Figure 1b shows that the N bonding to spin polarized Co becomes relatively stronger at high coverage (>0.5ML) as a result of the fact that

Received: December 22, 2022
Revised: February 7, 2023

https://doi.org/10.1021/acscatal.2c06319

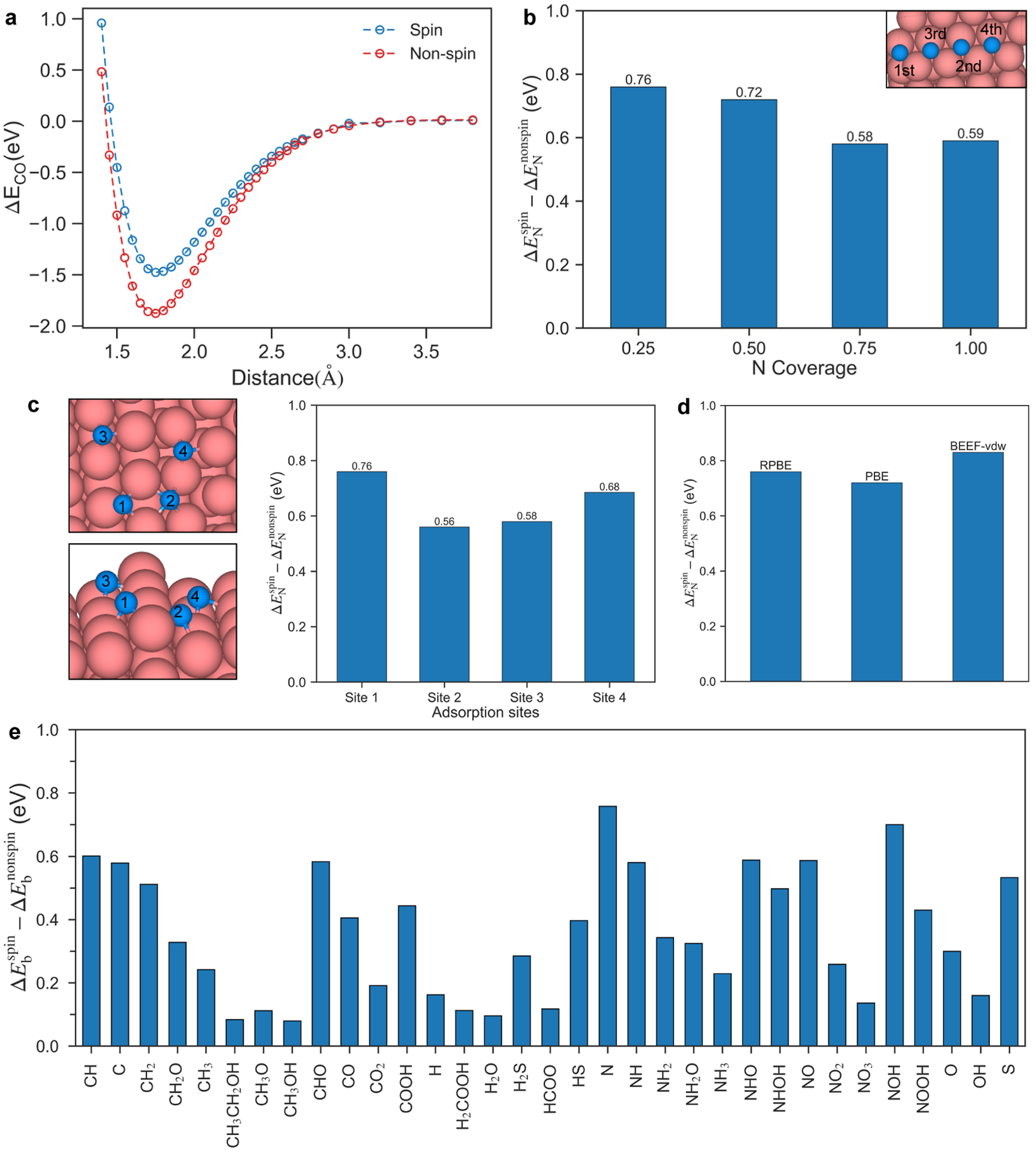


Figure 1. Spin effect on the adsorption energy on Co surfaces. (a) Potential energy diagram for the chemisorption of CO in the top site of a spin polarized and non-spin polarized HCP Co(1015) surface (surface structures in Figure S1). The potential energy is shown as a function of the distance between the outermost Co surface layer and the C atom of CO. (b) Energy difference (spin polarized minus non-spin polarized surface) in N adsorption as a function of coverage on Co(1015). 1ML represents full coverage of N atoms in face-centered cubic (fcc) sites along the step. The order of N adsorption is illustrated in the inset, where red and green spheres represent Co and N atom, respectively. (c,d) Energy difference in N adsorption as a function of the adsorption site and applied exchange−correlation functional. (e) Energy difference for various adsorbates at the most stable adsorption sites on Co(1015).

already adsorbed N reduces the spin moment of Co surface atoms in the vicinity.[16] Moreover, the effect on Co is found to be independent of the adsorption site and employed functional (Figure 1c,d). As a main result, Figure 1e shows that there is a spin effect on the adsorption energy for a broad range of adsorbates.

We also find a spin effect on the adsorption energy on other magnetic 3d transition metals (Ni and Fe). Although the adsorption energy difference between spin and non-spin polarized surfaces is different for various adsorbates, all adsorbates studied in Figure 2 showed a stronger bonding to non-spin-polarized surfaces than to the ground state magnetic phase. We further found that, both for adsorbed N and the N_2 dissociation transition state, the adsorption energy difference between spin and non-spin polarized surfaces scales well with the spin moment of surface, as shown in Figure 3 (and Figure S2 for other adsorbates). This is direct evidence that the adsorption energy decreases as the spin moment decreases. A similar effect was found in ref 9 for Co surfaces with different promoters. Others have found similar effects for selected adsorbates using model Hamiltonians.[17]

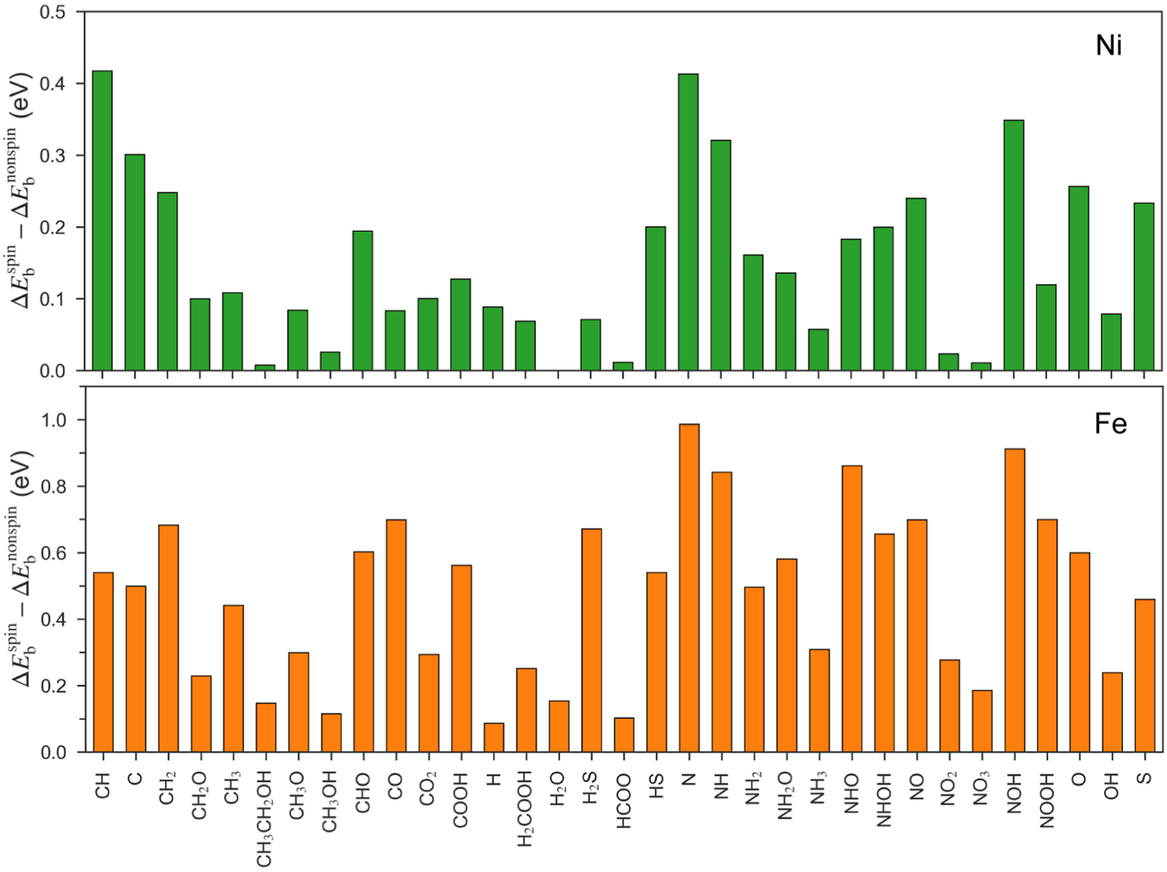


Figure 2. Spin effect on Ni and Fe. The chemisorption energy difference for various adsorbates at the most stable adsorption sites between spin and non-spin polarized fcc Ni(211) and body-centered cubic Fe(211) surfaces.

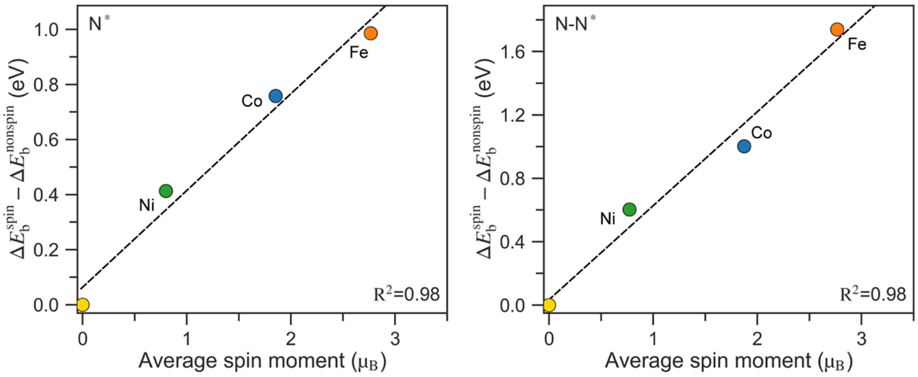


Figure 3. Relations between spin moment and adsorption energy difference. The chemisorption energy difference for the N adsorbate (N*) and N_2 transition state (N−N*) as a function of the spin moment on metals. The yellow point means the spin moment is zero, where the adsorption energy difference is zero.

Note that the above calculations were performed on the stepped surfaces, which is considered to be the active sites for many thermal reactions, such as ammonia synthesis and[18] methanol synthesis for CO/CO_2 hydrogenation.[19] Also, we have confirmed that the spin effect exists on the terraced metal surfaces (Table S1). We therefore conclude that the spin effect on magnetic metals is quite general.

Origin of Spin Effects. We now move to explore why the spin state of surface has such a substantial impact on the adsorbate chemisorption energy. One simple way to rationalize the effect is based on the d-band model.[20−23] It is found quite generally that variations in adsorbate chemisorption energies over various metals are correlated to variations in the metal d-band center—the higher the d bands are in energy relative to the Fermi level, the stronger the bond. We illustrate that in Figure 4a for N adsorption on the 3d series (and for C, O, H, and S adsorption in Figure S3). The rationale is that the higher in energy the d states, the higher in energy the antibonding adsorbate-metal d states are, and hence the more the antibonding states are shifted above the Fermi level and become unoccupied. The results in Figure 4a (and Figure S3) are for non-spin polarized surfaces. To estimate the adsorption energy of the spin polarized surfaces, we take the average of the adsorption energy corresponding to the d-band center for the

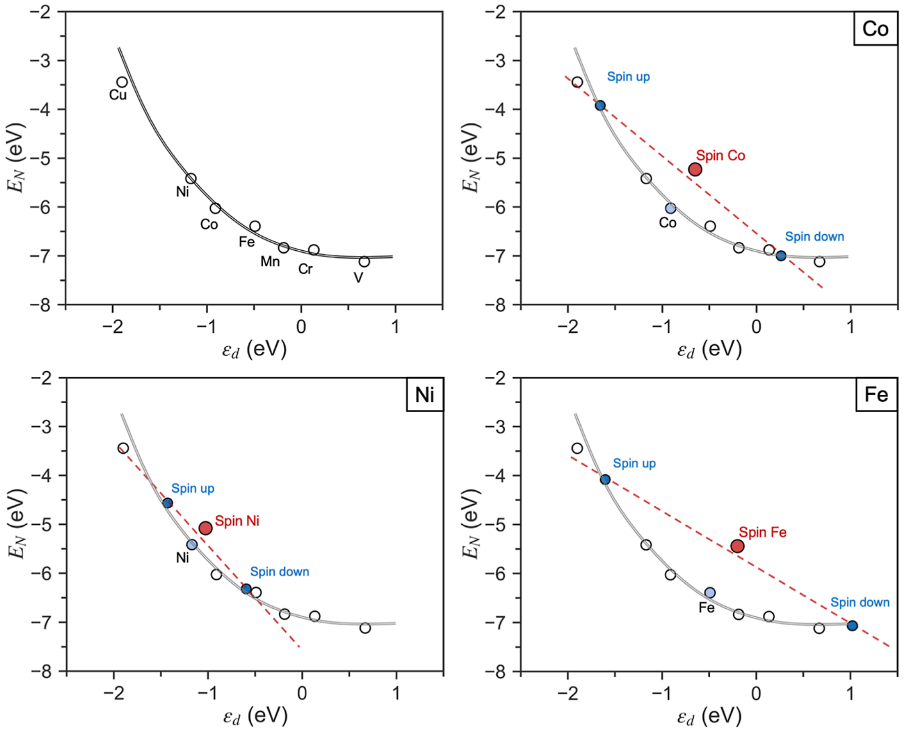


Figure 4. Non-linear relationship between chemisorption energy and d-band center. (a) Calculated N binding energy on the stepped surface of the 3d transition metals shown as a function of the d-band center on the pristine surface. (b−d) explanation for the weak adsorption of N on spin polarized Co, Ni, and Fe surfaces (details in Figures S3−S8 and Tables S2,S3).

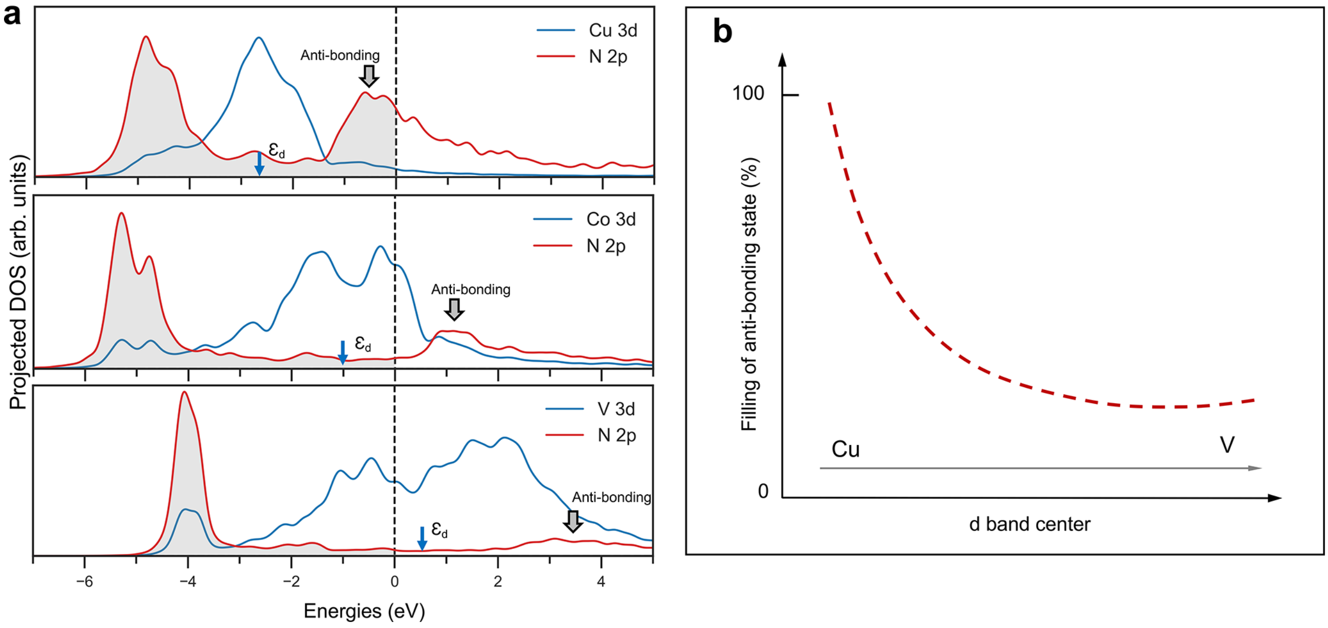


Figure 5. Origin of the non-linear behavior between adsorption energy and d band center. (a) Projected density of states (DOS) for N atomically chemisorbed on the step surface of Cu, Co, and V. The DOS is projected onto the atomic N 2p state (red line). The surface d band DOS of metal atoms at the N adsorption sites are shown for comparison (blue line). The peaks of N 2p anti-bonding states are indicated by wide arrows. Dashed lines represent the Fermi level. As indicated by the gray shade, only states below the Fermi energy (which is the energy zero in all cases) are filled. (b) Scheme of the relations between the d-band center and the filling of the antibonding state of N.

spin up and spin down states as illustrated in Figure 4b−d for Co, Ni, and Fe. Since the dependence of the adsorption energy on the d-band center has a positive curvature, the adsorption energy on the spin polarized surface is higher (less bonding) than on the non-spin polarized surface in agreement with the full density functional theory (DFT) calculations (details in Figure S7). The trend that the spin effect varies in the order Fe > Co > Ni is well reproduced by the simple d-band model and even the absolute magnitude of the spin effect is quite well described.

The remaining question is what is the origin of the non-linear behavior in Figure 4a. We note first that the range of d

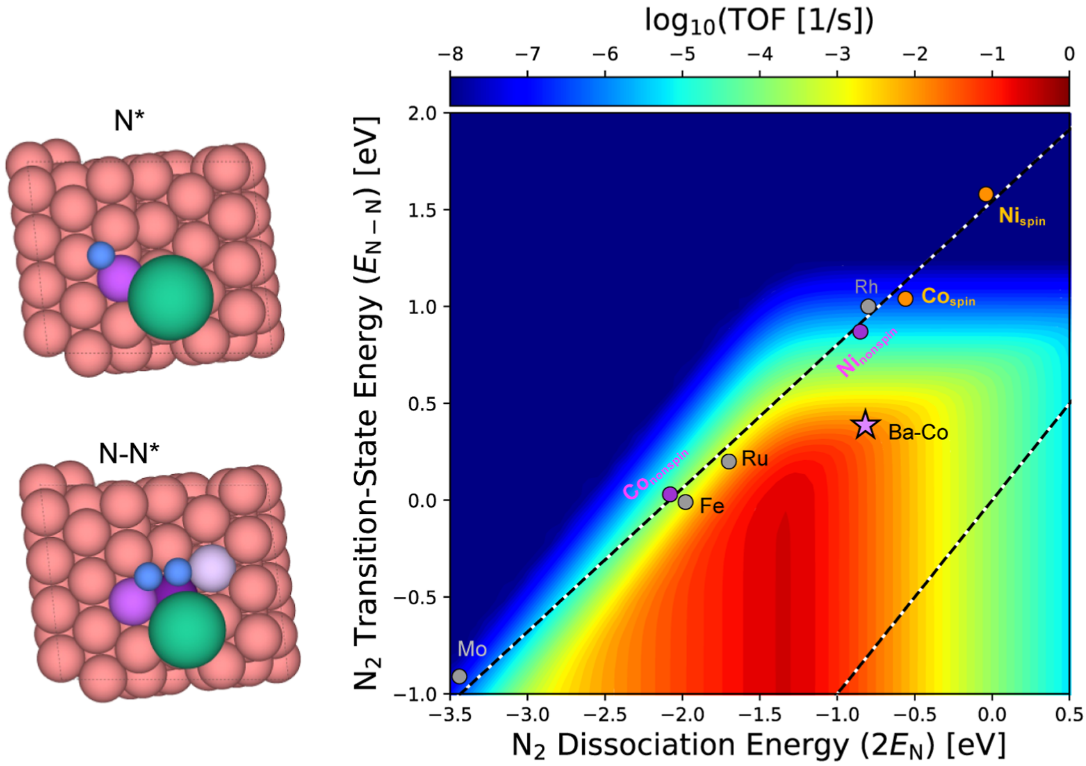


Figure 6. Spin effect promoted the activity of ammonia synthesis. Two-dimensional activity heatmap describing the steady-state time-of-flight to NH_3 as a function of N_2 transition-state energy (E_{N-N}) and N_2 dissociation energy ($2E_N$), computed at a temperature of 673 K, a stoichiometric ratio of H_2 to N_2 (3:1), a total pressure of 1 bar, corresponding to 0.2% of N_2 conversion respectively. Two scaling lines are shown (upper dashed black corresponding to stepped transition metal surfaces and lower dashed black line corresponding to the ideal limit). The left configurations show the adsorption structure of N* and N−N TS on Ba promoted Co catalyst, where metallic Ba is adsorbed on the Co(1015) surface. Pink, green, and blue spheres represent Co, Ba, and N atoms, respectively. The purple spheres around Ba means the degree of spin moment change, where the darker the purple color, the larger the spin moment drop. Note that, we only show the spin moment change on Co atoms at the adsorption site of N and N−N TS. Detailed spin moment change is shown in Figure S9.

band centers is quite large, spanning from the coinage metal Cu to the early transition metal V. In the mid-range, the variation of adsorption energy with ε_d is relatively linear, but two regions stand out, the highest and the lowest values of ε_d. Note that our point about the dependence being linear in the mid-range just reflects that any curve is well described by the first derivative in a narrow range and refers to the fact that most studies[24−27] of the d-band model have indeed considered a fairly narrow range of d band energies and hence found an approximately linear dependence. Qualitatively, the non-linear behavior can be understood as follows.

For the coinage metals, ε_d is so low that the d bands are completely full and the antibonding states formed between the adsorbate states and the d states are almost filled (Figure 5). This means that the ε_d dependence becomes weaker (when all d states are well below the Fermi level, all antibonding states are also well below the Fermi level and the d center dependence vanishes). For the highest values of ε_d corresponding to the early transition metals (like V), the d states are so high in energy that the antibonding adsorbate/d states become more and more empty, and again, the ε_d dependence gradually disappears. It is the latter effect that gives the curvature in Figures 4a and S3 that leads to the weaker adsorption on the spin polarized surfaces. Or to put it differently: the up-shift of the minority-spin (spin down) metal d states does not give as enough extra bonding to compensate for the weaker bonding due to the down-shift of the majority-spin (spin up) d states relative to the non-spin polarized case.

■ DISCUSSION

We note that surface spin states have been discussed extensively in connection with electrocatalysis.[28−30] For example, Cu doped NiFe-layered double hydroxides were suggested to be an excellent oxygen evolution reaction (OER) catalyst due to the regulation of Cu^{2+} to the spin states of the Fe^{3+} sites.[31] The addition of V into Co_3O_4 also shows superior performance for oxygen reduction reaction (ORR) compared to pure Co_3O_4, as a result of the Co^{2+} cations at the octahedral sites taking the lower spin state (with one e_g filled) than that in the pure Co_3O_4.[32] The influence of the spin polarization on ORR activity is explicitly reflected in the case of single atom catalysts, because the spin state of the metal center can be directly tuned by the coordination environment.[33,34] Similarly, for alkaline water electrolysis, the activity is significantly enhanced for $NiZnFe_4O_x$ oxide when a moderate magnetic field is applied to the anode.[35] The corresponding working mechanism of spin polarization on OER and ORR has been well studied by Shao-Horn et al.[36,37] and Gracia.[38,39] These effects are outside the scope of the present paper, which focusses only on transition metal surfaces, but they could very possibly be understood in the same general scheme.

The adsorption energy of key reaction intermediates to the catalyst surface has been widely used as a descriptor to capture trends in the activity of the catalyst with a volcano-type plot. For example, the adsorption energy of OH*/H*/N*/HCOO* has a strong correlation with the activities of the ORR,[40] the hydrogen evolution reaction (HER),[41] N_2 reduction,[42] and

CO_2 electro-reduction.[43] Consequently, a change in the adsorption energy of the descriptor will cause an alteration in the catalytic activity. According to Figures 1−3, the spin state of the metal surface has a significant impact on the adsorption energy of the adsorbate. The spin effect is therefore likely to control the reactivity of many reactions.

The spin effect provides a strategy to drive the activity of magnetic catalysts toward the tip of the volcano plot, by optimizing the binding energy between the reaction intermediates and the catalyst via tuning the surface spin state. As an example, consider the rate of ammonia synthesis on different stepped metal surfaces. The transition state energy for N_2 dissociation scales with the N adsorption energy, as shown in Figure 6. Here, we also include the rate of ammonia synthesis as a contour plot calculated in a mean field kinetic model[44] using the scaling relations found for all intermediates as a function of the N adsorption energy. It can be seen that Ru and Fe have the highest rates, whereas ground state magnetic Co has a considerably lower rate in agreement with experimental data.[10,45] If we could make non-spin-polarized Co, on the other hand, it should be comparable to Ru in ammonia synthesis activity according to the present model.

It is worth noting that the adsorption energy of various adsorbates is affected by the surface spin state to a varying degree, that is, some adsorbates are spin-sensitive while others are less so. The effect, for example, is up to 0.8 eV for N and quite small ~0.1 eV for H (Figures 1e and 2). It suggests that the spin effect over magnetic metal catalysts is evident for ammonia synthesis, while it is suggested to be marginal for HER.

The fact that the spin effect affects different adsorbates differently can be used to break the scaling relations, particularly for reactions that require two descriptors and in which the two descriptors behave differently in response to the surface spin state, such as C and O.[46] In addition, change in the surface spin of a magnetic surface due to another adsorbate (promoter) is not uniform and hence may affect, e.g., the N_2 dissociation transition state more than the final state N adsorption. This breaking of the pure metal scaling relation is what makes Ba promoted Co considerably better than un-promoted Fe or Ru for ammonia synthesis; see Figure 6. As shown in Figure S9, electrons will transfer from the Ba promoter to the Co surface and then set up an electrostatic effect. In addition, the spin moment of Co atoms that around the Ba promoter was also reduced and then induced a spin effect.

We suggest that there may be additional interesting opportunities in using the tuning of surface spin in catalyst design.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.2c06319.

> Detailed information about the computational methods, calculated adsorbates energies, and d-band centers for metals (PDF)

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Author Contributions

J.K.N conceived the project. A.C. performed DFT calculations and data analysis. J.K.N. provided additional theoretical analysis. A.C. and J.K.N wrote the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This project has received funding from Villum Fonden V-SUSTAIN (grant no. 9455).The authors thank Dr. Zhenbin Wang and Dr. Sudarshan Vijay (Technical University of Denmark) for their discussion and support on this work.

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