Effect of Magnetic States on the Reactivity of an FCC(111) Iron Surface

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ABSTRACT: We have carried out calculations to compare the catalytic activity of ferromagnetic (FM) and antiferromagnetic (AFM) states of the (111) surface of an FCC iron film by evaluating the reaction energy and activation barrier for the dissociation of H₂ and CO. The calculations were carried out using density functional theory and a meta-GGA approximation of the energy functional. The results show significant sensitivity to the magnetic state of the surface. We find that charge transfer upon adsorption is more efficient at the AFM2 surface. For H₂, this leads to barrierless dissociative adsorption on the AFM2 surface, while a molecular adsorbed state is metastable at the FM surface, separated by an activation energy of 0.35 eV from the dissociated state. CO adsorbs more strongly on the AFM2 surface, but the activation energy for dissociation is 0.27 eV lower on the FM surface mainly because the energy of the transition state is lower. The difference in reactivity is analyzed in terms of integrated density difference and spin-dependent projected density of states. It is concluded that empty, back-bonding orbitals of the reactants on the AFM surface are more favorable for CO dissociation than on the FM surface leading to a more facile CO dissociation. The results indicate that catalytic activity can be strongly affected by the application of a magnetic field when it can induce a change in the magnetic state of the catalyst.

1. INTRODUCTION

Chemical reactions are characterized by reorganization of electrons and nuclei. From a fundamental point of view, both charge and spin can affect such transitions and thereby be of chemical interest. Varying the charge state of a molecule has well-known and established effects on reactivity, whereas the effect of spin on reactivity has been explored less. Manipulation of spin states has been shown to lead to rearrangements of electrons and hence affect reaction rates, yields, and product distributions. For molecules and molecular solids, spin-crossover (SCO) between high- and low-spin structures as well as magnetic field effects (MFEs) on chemical reactivity have been observed. However, little is known about the effect of spin on heterogeneous catalysis at magnetic surfaces. An especially interesting topic is whether such reactions may be controlled by an external magnetic field. In principle, spin-crossover could be used to affect and even control the reactivity of catalytic surfaces by an external magnetic field.

The most studied SCO materials are octahedral organometallic compounds where a d₇–d₇ transition metal ion can adopt either a high (HS) or low-spin (LS) electronic arrangement depending on crystal field splitting. Obviously, the ligand and oxidation states of the metal are the key factors in determining the spin state. If the two states have comparable energy, a transition between HS and LS states may be triggered by external stimuli, such as light, pressure, magnetic field, or temperature. The spin-transition can lead to large geometric and electronic changes enabling spin-state controlled chemistry.

If several SCO molecules are brought in contact to form either 1D, 2D, or 3D structures, short and long-range interactions between the monomers can affect the overall response of the system to external perturbations. These interactions can lead to the formation of various ferromagnetic, antiferromagnetic, or noncollinear magnetic structures which can be influenced by external perturbations. While keeping the temperature and pressure constant, an external magnetic field provides a natural way to access different magnetic states.

The MFEs on reactivity have so far mainly focused on reaction kinetics, while the effect on thermodynamics has been considered to be negligible. The MFE on kinetics takes many forms, but the basic requirement is that the electronic wave function in the vicinity of the transition state exhibits some sort of discontinuity or diabaticity. As the total spin states of both reactants and products must be the same (in the absence of spin–orbit coupling), a reaction must follow spin selection rules. MFEs allow switching between spin-forbidden and spin-allowed pathways by altering time-dependent spin evolution. Thus, the key feature is to alter spin-selective competitive kinetics, which leads to different product distributions via a variety of pathways. Experimentally, MFEs have been found to have important consequences in various areas. Most straightforward is the identification of radical reactions affected by...
external magnetic fields, for example, radical enzymatic and organic reactions. Another important field is photochemistry where solid state and molecular MFEs have been identified.1–3,6,7

A magnetic field, \( H \), can have a significant thermodynamic effect on a reaction only if the field strength is high or the change in magnetization, \( M \), is large. This can be seen from the change in Helmholtz free energy related to MFE at constant temperature:

\[
dF_H = \mu_0 H \cdot dM
\]

For a heterogeneous system where a large change in magnetization occurs, the thermodynamic MFE could be significant already for a low applied field. An example of such a transition is an antiferromagnetic-to-ferromagnetic spin-crossover controlled by an external magnetic field. The spin-crossover leads to changes in the magnetization of the surface and thereby different orbital populations because of Pauli repulsion and exchange interaction between the electrons. This in turn can have a profound effect on charge transfer, donation/back-donation, Fermi-energy, d-band energy, and atomic structure, all of which are common reactivity descriptors in heterogeneous catalysis. As an example, Figure 1 shows how small alterations in the FCC iron lattice constant and magnetic state lead to large variations in the spin-dependent density of states (DOS).

A few experimental observations have been reported which illustrate the possibility of utilizing MFEs in the field of heterogeneous catalysis. In an early review from 1975, Atkins and Lambert6 questioned whether an actual proof of MFEs in heterogeneous catalysis had been realized at that time while emphasizing its technological importance. Much work has been done since then. Studies of CuO nanoparticles revealed that a weak magnetic field can cause a change from antiferromagnetic to ferromagnetic spin ordering and increase ammonia desorption by 50%.9,10 In the presence of a weak magnetic field, CO oxidation on nonmagnetic Pt catalysts supported on carbon coated magnetic Co particles was found to decrease by 10–14%.11 On lanthanide containing perovskite type structures, conversion of CO oxidation was shown to increase from 5% up to 25%.12 Also, the activation energy for NO reduction was found to reduce by 6 kJ/mol, leading to a 10% increase in conversion rate at 453 K in a 0.02 T magnetic field.13

A few computational studies have also demonstrated the effect of magnetic states on admolecule binding and dissociation. The adsorption energy of hydrogen on small Rh clusters was found to vary by 0.5 eV depending on spin-multiplicity.14 \( \text{N}_2\text{O} \) dissociation on small Rh clusters was found to depend on the spin multiplicity of the cluster as charge transfer is effective only for some of the magnetic states.15 Recently, a computational study showed that during CO dissociation on a \( \text{Fe}_3\text{O}_4 \) nanoparticle, the total magnetic moment changes from 42 to 40 or 38 \( \mu_B \) indicating diabaticity and the importance of multiple energy surfaces near the transition state. Furthermore, the dissociation barrier was lowered by 0.2 eV by optimizing the spin state.16 Thus far, however, theoretical studies have not addressed the basic mechanism by which magnetic fields change chemical reactivity in heterogeneous catalysis nor identified how reaction paths are affected by changes in the magnetic state of the surface.

In order to study spin state effects in heterogeneous catalysis, we have performed density functional theoretical calculations of the reactivity of an \( \text{FCC}(111) \) iron film in different magnetic states. It is well established that bulk FCC iron can exist in various magnetic configurations.17–20 Also, thin films of iron deposited on, e.g., copper,21–27 can be in either antiferromagnetic or ferromagnetic states. Stability of the different magnetic states depends strongly on lattice constant, film thickness, surface orientation, and the presence of adsorbates. Computations using DFT and GGA functionals have been shown to describe the magnetism of the bulk BCC iron28–30 and also thin film systems31,32 accurately. As iron is an important catalyst in the Fischer–Tropsch reaction for the production of hydrocarbons from a mixture of CO and \( \text{H}_2 \), the surface chemistry of these reactants has been studied in detail. The same reactants also form the basis of the water–gas shift reaction.33 Furthermore, \( \text{H}_2 \) dissociation is well understood and is sensitive to changes in charge state (electrode potential) of the catalyst, so it is interesting to see whether changes in spin states exhibit similar changes in reactivity. CO is not only an important reactant but also a common probe for surface chemistry. Our results show that SCO between different magnetic states in heterogeneous systems can be used to significantly affect charge transfer and reactivity. Furthermore, the changes in electronic structure and chemical bonding that occur when the magnetic state of the iron film changes are discussed.

2. METHODOLOGY

The calculations were carried out within the projector augmented-wave method as implemented in the GPAW software.29,30 The total energy calculations, as well as DOS and PDOS calculations, were carried out using a real-space grid. PDOS plots were computed using an all-electron wave function obtained from the PAW calculations. The calculations require a

Figure 1. Above: Density of states for FCC iron in ferromagnetic (FM) and double-layer antiferromagnetic (AFM2) states at the minimum energy lattice constants (see Figure 2). Below: Comparison of spin dependent total density of states for high (3.575 Å)- and low-spin (3.55 Å) FCC iron crystals in FM state.
The choice of the exchange-correlation functional must be made with care as the magnetism and chemical properties of FCC iron are highly sensitive to even small changes in electronic and atomic structure. Thus, to study adsorption on Fe-FCC(111) surfaces, the magnetic, structural, and energetic properties must be reliably obtained. This presents a serious challenge for the commonly used GGA functionals that depend on the electron density and its gradient. For example, pure PBE is often used for studying heterogeneous catalysis. It gives rather accurate results on structure and total energy for a wide range of systems. By changing the exchange enhancement factor, other functionals such as revPBE, RPBE, and PBEsol have been constructed to improve the results for specific categories of systems. Both revPBE and RPBE give improved estimates of adsorption energy but make a compromise in structural factors and yield, e.g., too large lattice constants. PBEsol, however, gives improved estimates of structural properties but yields poor adsorption energy. This example illustrates a common feature of GGA functionals: not all properties can be accurately computed. A more flexible functional form includes also the Laplacian of the electron density, the so-called meta-GGAs. Since the meta-GGA functional form provides more flexibility, the compromises made by GGAs may be partly alleviated. We have used the revTPSS meta-GGA functional. It was designed as an all-purpose functional for both solid and molecular systems with reliable performance for adsorption energy without structural compromises. Also, a particularly important aspect for the present study, the magnetic moments and relative energy of magnetic structures in BCC Fe and FCC Ni, is well produced by revTPSS. The iron film was modeled with a slab of FCC atomic structure with a 3 × 3 × 5 unit cell periodically replicated in the x- and y-directions with an 8 Å vacuum in the z-direction. The two bottom layers were held fixed during geometry and spin optimization. Periodicity of the wave function was modeled using a 5 × 5 × 1 k-point sampling. Bulk properties were calculated using a 2 × 2 × 8 unit cell with 8 × 8 × 4 k-point sampling. Structure optimizations were carried out using the BFGS (Quasi-Newton) algorithm until forces dropped below 0.05 eV/Å. Dissociation pathways were calculated using the climbing image nudged elastic band method (CI-NEB). The concept of varying spring constants, as described in ref 41, was also applied. All the NEB paths were optimized using the FIRE algorithm, which is more stable than, e.g., BFGS. The convergence criterion for atomic forces was 0.2 eV/Å. Spin-polarization was included in all the calculations with an optimization of the magnetic moments.

The adsorption energy is defined as $E_{\text{ads}} = E_{\text{surf+mol}} - E_{\text{surf}} - E_{\text{mol}}$, so a more negative value means stronger binding. CO adsorption on ferro- and antiferromagnetic surfaces was also studied by computing the density difference defined as

$$\Delta \rho(x, y, z) = \rho_{\text{FeCO}} - \rho_{\text{Fe}} - \rho_{\text{CO}}$$

Figure 2. Left: Schematic illustrations of collinear antiferromagnetic (AFM1), bilayer-antiferromagnetic (AFM2), and ferromagnetic (FM) spin structures of FCC iron crystal where the c/a ratio is 2.5. Right: Relative energy and atomic magnetic moments of various spin structures as a function of the lattice constant.
When CO is aligned along the z-axis, integration of the density difference over the x and y axes gives the charge displacement along the CO axis

\[ \Delta q(z) = \int_{-\infty}^{\infty} dz' \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} dx dy \Delta \rho(x, y, z') \]  
(3)

For charge-neutral systems, \( \Delta q(\infty) \) should be zero. This function can be used to interpret and study the charge-transfer upon adsorption. According to the Blyholder model, CO adsorption is governed by bonding \( \Delta q(\infty) \) and backbonding effects from \( \Delta q(\infty) \) to \( \Delta q(\infty) \) interactions. As these effects are controlled by the orbital overlap, filling, and energies, each contribution can be affected by changing the spin state of the iron surface. As bonding contributions are characterized by positive and back-bonding by negative \( \Delta q(z) \) values, eq 3 can be used to analyze bonding/back-bonding effects. Furthermore, spin-polarized charge-transfer can be obtained when \( \Delta q(z) \) is evaluated from either \( \alpha \) or \( \beta \) spin-density difference instead of the total electron density difference. Charge-transfer was also studied by estimating atomic charges using the Bader scheme \(^{40}\) implemented with the grid approach. \(^{40}\)

3. RESULTS

3.1. Magnetic Structure of FCC Iron and the FCC(111) Surface. Iron crystals have many stable magnetic states with different spin structure and atomic magnetic moments. The relative stability of different spin structures and the magnetic moments are highly sensitive to the lattice constant and to the crystal structure. FCC is the most stable structure and is always ferromagnetic, whereas the FCC iron is higher in energy and exhibits various collinear and noncollinear spin structures depending on the lattice constant. \(^{17-20}\) The FCC iron becomes more stable than BCC at high temperature (\( \sim 1200 \) K) or can be grown as a thin film on FCC crystal surfaces (see Introduction and Discussion). This opens the possibility of tuning the magnetism of FCC iron films by choosing the substrate and thereby the lattice constant. Here, we focus on the three most stable collinear structures of FCC iron depicted in Figure 2 and their reactivity. Also, the energy and atomic magnetic moments are shown.

Figure 2 shows the large changes in stability of various magnetic states of an iron crystal with FCC structure as a function of the lattice constant. For a small lattice constant, the various collinear spin structures are almost equally stable and have small magnetic moments. Earlier studies have shown that a noncollinear magnetic state is lowest in energy when the lattice constant is below 3.5 Å. \(^{17-20}\) We thus focus on lattice constants beyond this value. Our results show that between 3.5 and 3.6 Å, AFM2 is the lowest energy state of the collinear FCC iron. At about 3.6 Å, the FM structure becomes the most stable. The increased stability of the ferromagnetic state is associated with an abrupt change from a low-spin to a high-spin state. As a general feature, the magnetic moments of all of the structures studied increase as the lattice constant is increased. As shown in Figure 1, the electronic density of states (DOS) of FCC iron also changes significantly as the lattice constant is changed. These results are in good qualitative agreement with earlier studies on the magnetism of FCC iron, but denser k-point sampling is required to achieve closer, quantitative agreement. Here, the main objective is to qualitatively study how different spin states can affect heterogeneous catalysis and high quantitative accuracy for each structure is not needed.

To study the effect spin states can have on the reactivity of iron, we chose to study the close-packed Fe-FCC(111) surface slab with a lattice constant of 3.575 Å. This lattice constant corresponds to the AFM2 bulk structure, but the FM state is only 0.07 eV/atom higher in energy. This lattice constant was chosen as most of the experimental examples on MFES in heterogeneous reactions (see Introduction) were made on antiferromagnetic nanoparticles. Thorough computational \(^{26,27}\) studies have shown that the double-layered antiferromagnetic structure is the most stable spin-structure of 4 to 10 ML thick Fe films on copper. Also, the transition from AFM2 to FM can be achieved by applying an external magnetic field, whereas changing from ferromagnetic to antiferromagnetic structure is experimentally more difficult. At this value of the lattice constant, the changes in magnetization are large when going from AFM2 to FM so that thermodynamic changes given by eq 1 can also be significant. The larger the changes in magnetization are, the more pronounced is the thermodynamic effect.

The structural and magnetic properties of Fe-FCC(111) slabs in AFM2 and FM magnetic states at a lattice constant of 3.575 Å are given in Table 1. It can be seen that the FM state

<table>
<thead>
<tr>
<th>Layer</th>
<th>AFM2</th>
<th>FM</th>
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<tbody>
<tr>
<td>mag. mom.</td>
<td>2.69</td>
<td>2.78</td>
</tr>
<tr>
<td>relaxation</td>
<td>−0.39</td>
<td>−1.98</td>
</tr>
</tbody>
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Table 1. Magnetic Moments (\( \mu_b \)) and Surface Reactivity (% of Clean AFM2 and FM Slabs with a Lattice Constant of 3.575 Å in the Surface Plane

The projected DOS (PDOS) on the d-orbitals, which is shown in Figure 3, can give valuable information about reactivity. The well-known d-band model describes how the center and width of the d-band energy obtained from the PDOSs can be used to understand trends in catalytic activity. \(^{49-51}\) According to this model, a higher d-band center and decreasing width are indications of stronger bonding of admolecules. Both the total PDOS and contributions from each d-type orbital change when switching between FM and AFM2 states. Also, the d-band energy center and width of both up- and down-spin components differ between the AFM2 and FM structures. The d-bands of AFM2 are slightly narrower for both spin channels, whereas the d-band centers of FM lie closer to the Fermi-energy. However, AFM2 has a significant “shoulder” in the PDOS around 1.5 eV. The PDOS is the first indication that a change in the spin state (by an external magnetic field) may be used to control orbital occupation and energy, the key

the top-site and dissociates spontaneously. The dissociation energy is \(-2.28\) eV compared to that of \(H_2\) in gas phase and that of the clean AFM2 surface. However, on the FM surface \(H_2\) is molecularly adsorbed, and a stable Kubas complex has been formed. In the Kubas complex, the \(H-H\) bond is elongated to \(0.85\) Å from \(0.74\) Å in the gas phase. The molecular adsorption and atomic adsorption energies are \(-0.51\) eV and \(-1.04\) eV compared to those of the gas-phase \(H_2\) and clean FM surface, respectively. The energy barrier for \(H_2\) dissociation going from the molecularly adsorbed state to the H-adatom state on FM is \(0.35\) eV, which shows that the Kubas complex is quite stable on the FM surface and may have a significant effect on hydrogen desorption from the FM iron surface (see also the Discussion section). Furthermore, these results show that \(H_2\) dissociation is much more facile on the AFM2 than on the FM surface.

To understand the difference between FM and AFM2 toward \(H_2\) dissociation, atomic charges and density difference integrals of eq 3 were computed for the dissociated states. On both surfaces, each hydrogen adatom is positively charged by \(+0.4\) e. It is concluded that the total charge transfer between the dissociated hydrogen and the two surfaces remains unchanged when the spin structure is changed. The density difference integrals presented in Figure 6 show how the density is reorganized upon bond formation between the surface and dissociated \(H_2\). From this figure, it is readily visible that on the AFM2 surface the accumulation of charge between Fe and H (peak at \(\sim 17\) Å) is greater than that on the FM surface. Furthermore, both spin channels donate electrons when the bond is formed on AFM2. On the FM surface, however, electrons are donated only from the \(\beta\) channel, whereas \(\alpha\) electrons do not participate in charge transfer from the surface to hydrogen adatoms. As a result, less charge is accumulated between the surface and hydrogen adatoms leading to weaker bonding. In the dissociated state, the magnetic moment of the Fe atom, which is in between the hydrogen adatoms, decreases from 2.69 to 2.43 \(\mu_B\) on AFM2 and from 2.78 to 2.56 \(\mu_B\) on FM. The larger decrease in magnetic moments on AFM2 is attributed to stronger charge donation to hydrogen from both spin channels.

### 3.3. Magnetic State Effects on the Stability and Reactivity of CO Admolecules

Adsorption and dissociation of CO are common probe reactions in surface chemistry and are important in, e.g., Fischer–Tropsch and water–gas shift chemistry on iron.\(^{53,54}\) On BCC iron surfaces, CO is molecularly adsorbed in an upright fashion with carbon closer to the surface. Depending on the surface structure, nanoparticle size, and lattice-constant, either top- or hollow sites are the favorable adsorption sites.\(^{56}\) Below, we analyze how the spin structure of FM and AFM2 affects CO adsorption and dissociation on the FCC(111) iron surface.

CO adsorption on all relevant sites was studied for both FM and AFM2 slabs. The adsorption energy values are given in Table 2 where it can be seen that top-sites are the most favorable adsorption sites on both surfaces. Adsorption on AFM2 is slightly stronger than that on FM. During adsorption on top- and hcp/fcc sites, the C–O bond is elongated from the gas-phase value of 1.14 Å to 1.17 or 1.19 Å, respectively, on both surfaces. Also, the atomic charges of carbon and oxygen in the adsorption complex are e\(^{-}\) compared to those on the gas phase. As a result, less charge is accumulated between the surface and carbon atom, leading to weaker bonding. In the dissociated state, the magnetic moment of the Fe atom, which is in between the carbon atoms, decreases from 2.78 to 2.56 \(\mu_B\) on FM and from 2.78 to 2.56 \(\mu_B\) on AFM2. The larger decrease in magnetic moments on AFM2 is attributed to stronger charge donation to oxygen from both spin channels.

### Conclusion

The current study sheds light on the effect of Fe magnetic moments on CO adsorption and dissociation as well as molecular H adsorption on Fe(111). Both the adsorption and dissociation energies are significantly affected by Fe magnetic state, indicating the importance of spin structure in understanding reactivity. The findings provide valuable insights for the development of iron-based catalysts for hydrogen storage and CO conversion processes.
interesting to note the two donation mechanisms are highly
dependent on spin polarization: back-donation is due to the
changes in spin-up density, whereas donation is reflected in
spin-down density differences. For top-site adsorption, the
magnetic moment of the underlying iron atom decreased from
2.69 to 1.21 μB on AFM2 and from 2.78 to 1.60 μB on FM. This
observation is in line with the larger charge transfer on AFM2

Figure 5. Energy along optimal paths for H₂ adsorption on FM and AFM2 surfaces. The local minimum for the H₂ admolecule on the FM surface was found from minimum energy path calculation and corresponds to a Kubas complex (H–H bond length 0.85 Å). At the transition state for dissociation, the H–H bond length is 0.95 Å. On the AFM2 surface, dissociation is barrierless, and an admole is not formed. (Note: The clean AFM2 slab is 0.033 eV/atom higher in energy than the FM slab. For the crystal, AFM2 is 0.03 eV/atom lower in energy than FM.)

Figure 6. Density difference integrals for H-adatoms on FM and AFM2 (111) surfaces of the FCC iron. The horizontal axis is the distance along the surface z-direction, and the vertical axis is the integral of the charge difference.

Table 2. CO Adsorption Energy on the FCC(111) Surface of Fe in FM and AFM2 States (in eV)

<table>
<thead>
<tr>
<th></th>
<th>top</th>
<th>HCP</th>
<th>FCC</th>
</tr>
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<tbody>
<tr>
<td>FM</td>
<td>−2.15</td>
<td>−1.72</td>
<td>−1.73</td>
</tr>
<tr>
<td>AFM2</td>
<td>−2.31</td>
<td>−1.90</td>
<td>−1.61</td>
</tr>
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surface. Thus, the spin structure may be used to affect the degree of charge transfer in the case of CO adsorption.

The orbital interactions between CO and the two Fe-FCC(111) surfaces may be investigated further by projecting the Kohn–Sham states (KS) on frontier orbitals of CO in a top adsorption site and the nearest iron atom. The former yields three molecular orbital density of states (molDOS), whereas the latter gives PDOS broken down into specific atomic orbital symmetries. The equations are as follows:

\[
\text{molDOS: } \rho_n(\epsilon) = \sum_l \langle \psi_l^{\text{KS}} \rangle \langle \psi_l^{\text{CO}} \rangle \delta(\epsilon - \epsilon_n)
\]

\[
\text{PDOS: } \rho_n^s(\epsilon) = \sum_l \langle \phi_l^i \rangle \langle \psi_l^{\text{CO}} \rangle \delta(\epsilon - \epsilon_n)
\]

where \(\psi_l^{\text{CO}}\) are the KS states of the adsorption complex, \(\psi_l^{\text{CO}}\) is one of the frontier orbitals in CO, and \(\phi_l^i\) is the \(i\)th atomic orbital of atom \(a\). The DOSs represent hybridized orbitals in the adsorption complex. As can be seen from eq 4, both the molDOS and PDOS have peaks at the same values of the orbital energy, \(\epsilon_n\), and the height of these peaks corresponds to the overlap of the integrals. Thus, the peaks with the same energy correspond to the same hybrid orbital. From the DOSs in Figure 8, one can infer to which d-orbital a frontier orbital is coupled.

From Figure 8, it can be seen that the HOMO of CO, the \(5\)-\(\pi\) is mainly coupled to the \(d_{z^2}\) orbital in all cases, which is in line with the Blyholder model. Both bonding (around \(-9.8\) eV) and antibonding (\(-8\) to \(-6\) eV) parts of \(5\)-\(\pi\) lie almost completely below the Fermi-level in the down-spin channel (Figure 8B and D), whereas the up-spin channels (Figure 8A and C) have also some empty states. Also the \(5\)-\(\pi\)-molDOS are rather similar for both spin states, and it may be concluded that the \(5\)-\(\pi\)-d\(_{z^2}\) interaction cannot explain reaction differences between the FM and AFM2 states.

Interactions between the surface and the two LUMO orbitals of CO can mainly be attributed to \(2\pi^* - d_{xy}\) contributions. For this interaction, both up-spin channels (Figure 8A and C) and the down-spin channels (Figure 8B and D) have similar peak positions and heights below the Fermi-level. However, the largest difference between the two magnetic states is the larger amount of empty \(2\pi^*\) states above the Fermi-level at \(0\) eV for FM. As these states remain empty during CO adsorption, they are unimportant for adsorption of the energy, but as shown in a previous article,\(^{16}\) they can play a key role in the dissociation process. On FM, the empty \(2\pi^*\) states have more overlap with the metal and can accept electrons from the surface allowing electron flow to the antibonding \(2\pi^*\)-orbital during dissociation. This may be classified as a back-donation effect, but note that these states are empty in the adsorption complex. Thus, they do not contribute to charge transfer or back-bonding during adsorption but become important in the transition state for CO dissociation.

To study the difference in reactivity, minimum energy paths for CO dissociation starting from top-sites were computed. During the reaction, the carbon atom moves to a 4-fold coordinated HCP-type site, while the oxygen atom moves to an adjacent HCP site. On the FM and AFM2 surfaces, the barrier for CO dissociation is calculated to be 1.40 and 1.67 eV, respectively. The calculated reaction energy is \(-0.17\) eV and \(-0.16\) eV, respectively. Viewing this in light of adsorption energy and charge transfer, it is interesting to notice that stronger charge transfer on AFM2 increases the stability of the adsorption complex and makes it more difficult to dissociate the molecule. However, the energy at the saddle point is \(-0.75\) and \(-0.64\) eV on FM and AFM2 surfaces, respectively, with respect to gas phase CO. This means that the transition state for CO dissociation is lower in energy on the FM surface even though the reaction energy is independent of the magnetic state of the surface. This may be explained by the amount of available empty \(2\pi^*\) states above the Fermi-level, as discussed above.

![Figure 7. Charge density difference integrals (eq 3) for CO adsorption on top sites of FM and AFM2 surfaces. The horizontal axis gives the distance along the surface's z-direction, and the vertical axis gives the integral of charge difference.](image-url)
4. DISCUSSION

As presented in the Results section, changing the magnetic state of the FCC iron provides a way to modify band structure, orbital population, and d-band characteristics. These findings alone suggest that the reactivity of iron is sensitive to its spin-structure and that magnetism is an important aspect for understanding the reactivity of iron surfaces. From Figures 6 and 7, it becomes evident that charge transfer between the surface and admolecules can be affected by changes in spin state. Depending on the reaction, the increased charge transfer may lead to either stabilization or destabilization of the reactants. Also, activation energy is sensitive to the magnetic state of the iron catalyst. Thus, the effect of the spin-state on reactivity could be useful for modifying rates and thermodynamics of a reaction with the possibility of controlling yield and selectivity.

As an example, we have considered the chemistry of CO and H₂, which are reactants in iron catalyzed Fischer–Tropsch synthesis (FTS) and the water–gas shift (WGS) reaction. As several reaction pathways for these reactions are feasible, selective stabilization of certain surface complexes of carbon, hydrogen, and iron could help in controlling yield and the selectivity of these industrially important reactions. Controlling surface reactivity by switching between different magnetic
structures could be realized, e.g., by application of an external magnetic field.

Even though FCC iron is seldom found and used in catalysis, several iron containing systems with interesting magnetic properties can be realized. First, iron thin films may be grown on various substrates with different lattice constants and crystal structure.27,56 These films can have various magnetic states23−27,59 similar to the ones considered in this article. In addition to collinear (anti)ferromagnetic states, noncollinear23−20,24 states may have unexpected effect on reactivity. Also, the low Curie temperature of thin films (around 220−300 K for Fe on FCC copper,25 for example) can result in the formation of a paramagnetic state at rather low temperature. These disordered states are expected to have average adsorption/reactivity properties of the different, ordered spin structures.

Second, depending on size, geometry, and the synthesis method, both pure and bimetallic nanoparticles with various magnetic properties can be synthesized.60 Small, gas-phase iron nanoparticles are icosahedral and have antiferromagnetic spin-structure,61 and icosahedral iron particles up to 13 nm have been synthesized,61 while bulk and nanoparticles of BCC iron are ferromagnetic.62 Alloying of iron nanoparticles with other metals can also be used to tune magnetic properties. Iron—platinum nanoparticles, especially, have varying magnetic properties; antiferromagnetic FePt particles are characterized by large coercivity63 or superparamagnetism,64 whereas FCC-structured FePt is antiferromagnetic with high Curie temperature.65

Oxides are a third class of iron compounds whose catalytic activity could be manipulated by a magnetic field. Several iron oxides present in FTS and WGS are antiferromagnetic or have Fe(II) in octahedral coordination28,55 both of which have plausible structures for magnetically controlled reactivity.5 Here, magnetism rises from metal ions with atomically localized unpaired electrons rather than the band magnetism in metals. Despite the different origin of magnetism in metals and oxides, changes in the magnetic structure change electronic structure in both materials enabling magnetic control of reactivity.

The above discussion gives an indication of the various magnetic properties that are present in iron containing systems. As changes in magnetic structure are intimately coupled to electronic and even geometric properties, access to different magnetic states allows modifications in the chemical reactivity of surfaces of iron-based catalysts. The various spin-states can be accessed in several ways, but applied external magnetic fields provide a natural way of controlling the spin-structure of a magnetic system, and MFEs on reactivity should be visible in several iron-based catalysts. If changes in magnetization are large, both thermodynamic and kinetic MFEs are possible. However, experimental realization of these effects requires careful consideration in the choice of reaction and system.

From the results described above, one can think of various experiments for realizing the effect of a magnetic field on the adsorption or desorption of hydrogen from the surface of a Fe—FCC(111) thin film. Since the binding energy of the adatoms is quite different depending on the magnetic state, a temperature-programmed desorption (TPD) experiment66 should give different results depending on the magnetic state of the slab. Figure 9 shows simulated spectra using the calculated H2 desorption energy and the Redhead equation as follows:67

\[ \tau_f = -\frac{d\theta(T)}{dT} = \frac{k_b \beta^* \exp\left(-\frac{E_d}{k_b T}\right)}{\beta_H} \]

where \( k_b = 10^{13} \text{s}^{-1} \) is the temperature-independent frequency factor, \( \beta_H = 0.6 \text{ K/s} \) is the heating rate, \( k_b \) is the Boltzmann factor, and \( E_d \) is the desorption energy from the dissociated state (2.28 eV for AFM2 and 1.04 eV for FM). \( n = 2 \) is the reaction order for the H2 desorption reaction, \( 2H_2^* \rightarrow H_2(g) + 2^* \). The prediction is that H2 is desorbed around 380 K from the FM surface and around 790 K from the AFM2 surface, a clear difference.

**Figure 9.** Simulated TPD curves for H2 desorption from an Fe-FCC(111) film in AFM2 and FM states. The upper panel gives the surface coverage as a function of temperature, while the lower one shows the desorption rate as a function of temperature.
Another possibility is to use a thick enough film that the AFM2 state is lower in energy but prepare the iron film initially in the FM state by using an external magnetic field. If the temperature is not too high, the H₂ molecules will then adsorb in a Kubas complex and will not climb the 0.35 eV barrier to the dissociated state. Then, as the magnetic field is turned off and the system switches to the AFM2 state, spontaneous dissociation of the H₂ molecules should occur (unless coercivity is too large). A third option is to keep the temperature fixed and adsorb H₂ on the surface of a film in the AFM2 magnetic state, which binds hydrogen atoms more strongly. Then, use a magnetic field to switch to the FM state and observe hydrogen desorption.

5. CONCLUSIONS

This article presents a computational study of the effect magnetic states can have on the reactivity of an iron surface. More specifically, the reactivity of antiferromagnetic (AFM2) and ferromagnetic (FM) FCC(111) iron slabs have been compared using DFT calculations at the meta-GGA level. The results show that spin-structure can strongly affect orbital occupation of the surface and especially charge-transfer between the catalyst surface and the adsorbate. It is shown that H₂ and CO adsorption and dissociation are modified by changes in spin-structure. In both cases, charge transfer on AFM2 is greater than that on FM. Interestingly, H₂ dissociation occurs more readily on AFM2, whereas CO dissociation is more facile on the FM surface, which is explained by the presence of empty 2p* states. The calculations show that the reactivity of the surface can be affected significantly by changing the magnetic state. These findings suggest that several important reactions utilizing H₂ and CO as reactants, including Fischer-Tropsch synthesis and the water-gas shift reaction on magnetic iron catalysts, may be sensitive to the spin-state of the catalyst. As the magnetic state can be changed by applying external perturbations, including magnetic field, these considerations point to ways of modifying the thermodynamics and kinetics of heterogeneous catalyzed reactions.

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Notes
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The Journal of Physical Chemistry C


