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Coverage Effects in CO Dissociation on Metallic Cobalt Nanoparticles

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ABSTRACT: The active site of CO dissociation on a cobalt nanoparticle, relevant to the Fischer−Tropsch reaction, can be computed directly using density functional theory. We investigate how the activation barrier for direct CO dissociation depends on CO coverage for step-edge and terrace cobalt sites. Whereas on terrace sites increasing coverage results in a substantial increase of the direct CO dissociation barrier, we find that this barrier is nearly independent of CO coverage for the step-edge sites on corrugated surfaces. A detailed electronic analysis shows that this difference is due to the flexibility of the adsorbed layer, minimizing Pauli repulsion during the carbon−oxygen bond dissociation reaction on the step-edge site. We constructed a simple first-principles microkinetic model that not only reproduces experimentally observed rates but also shows how migration of carbon species between step-edge and terrace sites contributes to methane formation.

KEYWORDS: Fischer−Tropsch synthesis, DFT, microkinetic modeling, lateral interactions, activation energy

INTRODUCTION

The design of heterogeneous catalysts from first principles remains passionately sought after. This formidable task hinges on fundamental understanding of catalytic action through molecular insight into the chain of elementary reaction steps proceeding on the surface of heterogeneous catalysts. The three paradigmatic laws of catalysis were formulated by Berzelius, Ostwald, and Sabatier.¹ Of these, Sabatier’s principle is most helpful for predicting the composition of optimum catalysts. Sabatier postulated that reaction complexes formed between the catalyst and the reactant should be neither too strong nor too weak. With the advent of modern quantum-chemical methods and increased computational power, this led to the formulation of scaling laws that link catalyst composition to performance.²⁻⁵ The state of the art in computational catalysis is to explore the potential energy surface between reactants and products using density functional theory. Using Eyring’s transition state theory,⁶ these data can be used to make predictions about conversion rates and product distribution by, for instance, microkinetics simulations.⁷,⁸ Such simulations are usually based on the assumption of a Langmuir surface characterized by one type of sites.⁹ There are, however, many instances in heterogeneous catalysis that warrant an alternative Taylorian view of surface reactivity.¹⁰

That is to say that catalysis occurs by uniquely active sites that are sometimes present only in very small numbers. Important examples are the hydrogenation of dinitrogen to ammonia (Haber−Bosch process) and the hydrogenation of carbon monoxide to liquid hydrocarbons (Fischer−Tropsch process). It remains unclear if and how low-reactive sites influence the ongoing catalytic reaction. While the importance of stepped sites is well-accepted for the dissociation of dinitrogen,¹¹ there remains considerable debate about the nature of active sites for carbon monoxide dissociation, which is an essential step in Fischer−Tropsch (FT) synthesis. A key aspect of this ongoing discussion is the role of lateral interactions on the usually crowded surfaces. In particular, in the context of FT synthesis, high CO coverages encountered at reaction conditions are expected to substantially raise the barrier of CO dissociation.¹²,¹³ This would favor alternative pathways for CO dissociation and chain growth in the FT synthesis process.

Gas-to-liquid processes are gaining in importance as natural gas is increasingly used for the production of clean transportation fuels and chemicals in the Fischer−Tropsch (FT) process.¹⁴−¹⁷ It is of significant fundamental and practical interest to understand the molecular details underlying FT
synthesis catalyzed by metal nanoparticles. CO dissociation is a crucial elementary reaction step within the FT mechanism. Depending on catalyst choice and reaction conditions, the CO dissociation step can contribute to the degree of rate control in various amounts. A prerequisite for obtaining long-chain hydrocarbons is a high supply rate of C\(_1\) monomers. A common view is that low-barrier CO dissociation requires step-edge sites, which can explain the experimentally observed strong structure sensitivity of the FT reaction. Optimum FT catalysts comprise Co nanoparticles with a size of \(\sim 6\) nm, because smaller particles cannot accommodate a sufficient amount of step-edge sites. Typical activation barriers for direct CO dissociation computed by density functional theory (DFT) are in the range of \(100-150\) kJ/mol for most stepped Co surfaces. Lower barriers are reported for Ru surfaces. These values should be contrasted with barriers higher than \(200\) kJ/mol for direct dissociation of CO on close-packed surfaces. H-assisted CO dissociation pathways have also been explored. Although barriers for C–O bond cleavage in adsorbed HCO, H\(_2\)CO, and HCOH intermediates are lower than that for adsorbed CO, these hydrogenated surface intermediates are typically much less stable. Therefore, overall barriers for H-assisted CO dissociation are usually higher than those for direct CO dissociation on step-edge sites. For example, Filot et al. found a direct CO dissociation barrier of \(173\) kJ/mol on Rh(211), while the overall barriers via HCO and COH are 263 and 275 kJ/mol, respectively. Shetty et al. reported an overall barrier for HCO dissociation on Ru(112\(\bar{1}\)) of \(120\) kJ/mol, whereas the direct CO scission is only \(65\) kJ/mol on the same site. Liu et al. concluded that face-centered cubic (FCC) cobalt catalysts and hexagonal close-packed (HPC) cobalt terraces prefer the H-assisted route (\(125\) kJ/mol on Co(110)), while corrugated HCP cobalt catalysts have remarkably higher intrinsic activity via a preferred direct dissociation route (\(103\) kJ/mol on Co(1121)).

Although all these studies suggest a FT mechanism dominated by direct CO dissociation, significant changes in...
reaction kinetics can be expected due to carbon-induced deactivation and lateral interactions from high surface coverage. As both effects could block facile pathways for direct CO dissociation, the mechanism is expected to shift to an H-assisted mechanism. CO-scrambling experiments, however, contradict this. CO-scrambling rates on a cobalt FT catalyst were found to be fast, even without hydrogen. Moreover, it has been demonstrated that carbon deposition on a cobalt FT catalyst occurs mainly on terrace surfaces, and, at low concentrations, it does not affect FT activity. This implies that C atoms generated on step-edge sites are involved in chain-growth reactions and, therefore, do not block the step-edge sites.

Both experimental surface science data and DFT modeling of CO adsorption show that the CO saturation coverage for the Co(0001) surface is about 7/12 ML. Experimental steady-state isotopic transient kinetic analysis (SSTKA) data show that the CO coverage is between 0.4 and 0.6 ML under model FT conditions, in good agreement with extrapolated surface science data. On the other hand, Loveless et al. used DFT modeling to demonstrate that a higher than 1 ML CO coverage is possible on a cluster of 201 Ru atoms. These authors showed that the CO dissociation barrier on a (1105) step-edge site with a CO coverage of 1.07 ML is close to 150 kJ/mol, much higher than the barrier on a Ru(112̅1) step-edge at low coverage. Thus, a high coverage might lead to an increased CO dissociation barrier. Neurock, Iglesia, and co-workers alternatively emphasized the role of H- and also H2O-promoted pathways for CO dissociation on the terrace surfaces that dominate nanoparticles. A critique on these works mentions that the high coverage computed to be possible on a Ru201 cluster is mainly caused by expansion and restructuring of the relatively small cluster. In addition to this, we computed the activation barrier for CO dissociation on the Co(1105) surface at low coverage (see the Supporting Information). The computed value of 151 kJ/mol obtained at low coverage is also high, suggesting that the particular step-edge geometry used in the work of Neurock and Iglesia is not very favorable for CO dissociation. High CO coverages are expected to destabilize adsorbed hydrogen, which might lower the barrier for HCO formation. If this effect can significantly reduce the overall barrier for HCO dissociation on step-edges, then this pathway can compete with direct CO scission. Whether this happens depends on the amount of destabilization of the formed HCO. Su et al. considered the effect of a 7/12 ML CO coverage on the FT mechanism on Co(0001) and found that steric hindrance contributes to additional repulsive interactions on HCO compared to CO. From this data we deduce that the combined effect is a relatively constant overall barrier for HCO formation and dissociation. The question that remains then is whether the direct CO dissociation over highly active step-edges also maintains a low barrier at expected coverages of ~0.6 ML.

RESULTS AND DISCUSSION

Because systematic computational data of coverage-dependent CO dissociation are lacking, we made a detailed comparison of this aspect for the low-reactive Co(0001) and high-reactive stepped Co(1121) surfaces using DFT (see the Supporting Information for computational details). While the Co(0001) surface is planar, the Co(1121) surface contains a two-dimensional array of step-edge sites composed of a reactive pocket consisting of 5 cobalt atoms (Figure 1a, top left, Bc-site following the notation of Van Hardeveld and Hartog). We first determined stable CO configurations as a function of total CO coverage (Figures S1–S3). We find that CO preferentially adsors in 3-fold hollow sites. This is in contrast to the top-adsorption mode that is commonly observed in experiments. However, the computed difference in site preference is small, i.e., top-adsorbed CO is only 1 kJ/mol less stable at a 1/3 ML CO coverage on Co(0001). Overbinding and the incorrect site-preference prediction for CO have been frequently reported for GGA functionals like the PBE functional used here. Although applying hybrid functionals like B3LYP or methods like RPA can in principle improve these results, the small differences observed in this study do not warrant the additional computational expenditure. The same holds for predicting the exact influence of lateral interactions. While there are various flavors of DFT functionals available, there is no universal one that can guarantee a highly accurate description of subtle coverage effects. Therefore, we first compared the overall changes in adsorption energies as a function of coverage. As expected, higher CO coverage leads to a lower average CO adsorption energy, which is in line with both experimental findings and theoretical studies using different DFT functionals. Importantly, we find that the saturation coverage is ~0.6 ML for both surfaces. Notably, the differential CO adsorption energies for these surfaces show similar trends with CO coverage. Figure 1 shows the transition state for direct CO dissociation on the Co(1121) surface at a low 0.07 ML coverage. We compared direct and H-assisted CO dissociation pathways at this coverage (Figure S4) and found that direct CO dissociation is the preferred pathway on this surface, in line with the work of Liu et al. CO migrates from its most stable adsorption site to the B site, where it is less stable by only 17 kJ/mol. From this state, dissociation can occur with a barrier of 83 kJ/mol. The overall activation barrier for C–O bond dissociation is thus only 100 kJ/mol, which is sufficiently low to maintain a high rate of monomer formation.

Aiming at a deeper insight into this dissociation reaction, we also computed reaction energy diagrams at higher CO coverages (0.30, 0.44, and 0.59 ML). The transition states at higher CO coverage are similar to those computed at 0.07 ML coverage (Figure 1b). The same holds for the reaction pathways for CO dissociation on the close-packed Co(0001) surface (Figure 1c). Parts d and e of Figure 1 show the potential energy diagrams as a function of the C–O distance, which is used here as the reaction coordinate. The reaction shifts from exothermic at low CO coverage to endothermic at high CO coverage, which is due to the stronger lateral interactions of the adsorbed C and O atoms compared to adsorbed CO at higher coverage. An important finding is that the CO dissociation barrier on the Co(1121) surface does not appreciably change with CO coverage. The variation of the activation barriers is within 14 kJ/mol and remains below 100 kJ/mol (Table S5). Figure 1e shows that the activation barrier for the Co(0001) surface increases from 225 kJ/mol at a coverage of 0.11 ML to 269 kJ/mol at a coverage of 0.67 ML. The energy profiles in Figure 1 are relative to the electronic energy of the local initial state. This means that an additional reorientation may be necessary from the most stable adsorption configuration. This is mostly the case for the Co(1121) surface, as a properly located vacancy is needed, and the dissociating CO molecule is for most coverages more stable with the carbon atom in a 3-fold adsorption site (Figure S6).
The energetic differences between these configurations are small compared to the dissociation barrier. This indicates that the computed site preference only has a small influence on the overall barrier. More importantly, the barriers referenced to the most stable adsorption configurations have the same coverage dependence as those referenced to the local initial states. Thus, whereas on a terrace Co surface a higher CO coverage leads to the expected increase of the activation barrier for CO dissociation, this reaction is hardly affected by CO coadsorbates on the step-edge site.

We analyzed the origin of these differences in more detail by studying the electronic structure along the dissociation pathway. Repulsive interactions due to coadsorbates can originate from through-space electron–electron repulsion with the dissociating CO molecule and from a decreased reactivity of surface metal atoms due to metal valence electron sharing between the dissociating molecule and coadsorbates. We addressed the latter aspect by computing bond orders along the reaction coordinate during dissociation using the recently introduced DDEC6 atomic population analysis, which allows accurate charge partitioning to assign net atomic charges. Figure 2 shows the bond orders of the dissociating CO molecule and the Co–O bonds, along the reaction coordinate. It can be seen that the C–O bond order starts around 2.0 on the Co(0001) surface, while the C–O bond on Co(1121) is already elongated and starts at 1.5 (bond order in free CO is 2.5). The bond orders then decrease to a value close to zero in the final state. Strikingly, the changes in the C–O bond order do not depend on the CO coverage. Similarly, we find that the Co–O bond orders increase in a very similar manner for the two investigated surfaces along the reaction coordinate. Only at the highest CO coverage, the Co–O bond order is slightly lower in comparison to lower coverage. From these trends, we can infer that the sharing of valence electrons of the Co surface atoms involved in binding the C and O atoms is not strongly affected by CO coadsorbates and, therefore, cannot account for the stronger CO coverage dependence of CO dissociation on the Co(0001) surface.

To better understand the way through-space electron–electron repulsion from CO coadsorbates affects the activation barrier, we aimed for analyzing the Hartree potential along the reaction coordinate of C–O bond dissociation. The Hartree potential \( V_{\text{Hartree}} \) is defined as the electrostatic potential resulting from the electron charge density. This potential is repulsive, and larger values relate to regions of stronger Coulombic repulsion. In the VASP implementation of DFT, the Hartree potential cannot be separated from the attractive electron–ion potential \( V_{\text{ion}} \). The combined potential is negative, wherein values closer to zero relate to regions less favorable for inserting electron density of nearby atoms. Accordingly, we sampled the combined Hartree and electron–ion potential \( V_{\text{Hartree}} + V_{\text{ion}} \) hereafter called \( V_{\text{electrostatic}} \) on a sphere with 0.75 Å radius positioned concentric to the O atom of the dissociating CO molecule. We first focus on the differences for the two surfaces before discussing the coverage effects. Figure 3 shows that \( V_{\text{electrostatic}} \) increases for all reaction pathways considered during the stretching of the C–O bond. This increase is mainly due to the decreasing electron–ion attraction when the C–O bond is elongated. Notably, there is a very steep increase of the electrostatic potential along the reaction coordinate for the Co(0001) surface, which corresponds to the bending of the CO molecule toward the surface. Comparison of the two cases shows—as habitually assumed—that the energy needed to bend the adsorbed CO molecule makes up a large part of the CO dissociation barrier difference between terrace and stepped surfaces. In the \( \beta_3 \) site on the Co(1121) surface, the CO molecule is already preactivated. After the transition state, \( V_{\text{electrostatic}} \) becomes more negative for the Co(0001) surface, whereas there is a plateau for the Co(1121) surface. Inspection of the C–O bond-dissociation pathways shows that the decrease is due to migration of the O atom from 2-fold adsorption toward the final 3-fold adsorption site. The plateau for the Co(1121) surface corresponds to the migration of the O atom over the bridge site from one side of the step to the other side before the energy is lowered by movement into the 3-fold adsorption site. The final C–O bond distance after dissociation is longer for the Co(1121) surface because of the different geometry of the step-edge.

Next, we consider the effect of coadsorbates. The findings above imply that the changes in the electrostatic potential brought about by coadsorbates should be predominantly the result of variations in the electron–electron repulsion. Figure 3 shows then that the electron–electron repulsion for CO dissociation on Co(0001) is significantly stronger at a high CO.

Figure 2. Bond orders determined by a DDEC6 atomic population analysis for CO dissociation on Co(1121) and Co(0001) at low and high coverage. The filled symbols in panel (a) represent the bond orders between the dissociating carbon–oxygen pair, and the open symbols represent the cumulative bond order of the dissociating oxygen atom with the three cobalt atoms to which the oxygen binds to in the final state. The locations of the two transition states are also indicated. Panels (b) and (c) show the individual bond orders and atom–atom distances at low coverage for the transition state on Co(0001) and Co(1121), respectively. The cobalt atoms accommodating the oxygen atom are shown with smaller spheres for improved clarity.

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coverage. The corresponding data for Co(1121) surprisingly show that the electron–electron repulsion at higher coverage is not increased due to coadsorbates. These very different trends can well explain why CO bond dissociation is nearly unaffected by CO coadsorbates at the step-edge site. Analyzing the geometries along the reaction pathway, the possibility of CO coadsorbates to reorient at the step-edge site stands out over the rigid configuration of the adsorbed layer observed for the Co(0001) terrace at high CO coverage. The reorientation of the adsorbed layer at the step-edge site results in nearly similar electrostatic potentials at low and high CO coverage, both for the initial and the transition state. On Co(0001), this only holds for the final state. The reason is that in this case the oxygen atom obtained by CO dissociation is significantly closer to the surface than the oxygen atoms of the coadsorbed CO. Another possible effect is that the CO coadsorbates withdraw electron density from the two cobalt atoms at the top of the step-edge site, resulting in a larger cobalt–carbon distance. This distance is 2.47 Å at low coverage and increases to 2.58 Å at high coverage, which can explain the reduced energy for the O atom to cross the bridged site.

Encouraged by these insights, we determined the reaction energetics of relevant elementary reaction steps for the FT reaction on the Co(1121) and Co(0001) surfaces and used these data as input to microkinetics simulations (Tables S1 and S2). The simulations were carried out under conditions relevant to FT synthesis (H2/CO = 2, 473–553 K, 1 bar). We considered three different cases, namely, simulations for either the Co(0001) or the Co(1121) surface and simulations using a combination of these two surfaces in which we set the Co(0001)/Co(1121) ratio to 10. The site ratio is a conservative estimate of the abundance of step-edge sites at the optimum size of cobalt nanoparticles for FT synthesis.24 In the simulations involving the two cobalt surfaces, migration of C and CHx species (x = 1–3) from the step-edge site to the terrace was taken into account.

Clearly, the high barrier for CO bond dissociation on Co(0001) results in a very low CO conversion rate (turnover frequency at 493 K, TOF493K = 10−8 s−1), and the main product is methane (selectivity >99%). The CO conversion rate for the Co(1121) surface is much higher. The predicted TOF at 493 K is 0.01 s−1, which is in good agreement with surface cobalt atom normalized experimental data.25 The product distribution (Figure 4a) is also consistent with experimental data. The chain-growth probability is 0.81, and a low C2-selectivity is predicted. The methane selectivity is relatively low, indicating that the strong binding of C intermediates at step-edge sites suppresses methanation. The analysis of the product distribution over the isolated Co(0001) is not shown in Figure 4, because the corresponding rate is negligible and only methane is formed. Interestingly, when the two surfaces are coupled through migration of surface C and CHx species, we observe that the methane selectivity increases, while the chain growth probability decreases to 0.79. Analysis of the reaction network shows that these changes are predominantly due to the migration of CH3 species from the step-edge to the terrace surface. This migration also affects the apparent activation energy (Figure 4c), which is consistent with the experimental findings reported in Figure 1 in the work of Chen et al.19 In that study, the apparent activation energy based only on the TOF of CH4 (Figure 1b) is >100 kJ/mol, whereas the activation energy based on the total CO conversion ranges from 57 to 74 kJ/mol (Figure 1a). This indicates that the apparent activation energy will increase for...
systems with higher CH₄ selectivity. Without migration of CH₄ species, carbon species accumulate on the Co(1121) surface and termination reactions become more rate-controlling. The poisoning by hydrocarbon species is expected to increase at higher temperatures, which is in line with the stronger temperature dependency of the apparent activation energy and the higher hydrogen reaction orders for the Co(1121) case (Figure 4d). Yates and Satterfield reported apparent activation energies of 93–103 kJ/mol for a wide range of studied conditions. Our model predictions are in good agreement with these findings as well as the experimentally observed negative reaction order in CO. An important point here is that the negative CO reaction order does not imply that a CO needs to desorb every time that a dissociation event occurs. This would be the case for a fully covered surface, for which the reaction order with respect to CO has to be –1. The less negative reaction order in CO observed here can be explained by a changing number of empty sites as a function of CO partial pressure. Under realistic conditions there will be empty sites available for direct CO dissociation. With increasing CO partial pressure, more CO will adsorb at the expense of empty sites. Although a steep increase in CO coverage is counteracted by an increase in lateral repulsions, the relative decrease in the number of free sites is expected to be more significant. Thus, the reaction rate will decrease, explaining the negative reaction order in CO. As in most studies, the work of Yates and Satterfield indicates a hydrogen reaction order not higher than unity, while our microkinetic model exceeds this value. We surmise that this inconsistency is caused by an overestimation in our microkinetic model of hydrocarbons buildup on the step-edge surface, possibly because we neglect the effect of lateral interactions on termination reactions. A relative stabilization of hydrogenated species over coadsorbed hydrogen would promote these steps and would be a topic for further investigation into the promotion of hydrogen-assisted mechanisms of CO scission. Furthermore, although we corrected for the small change in the adsorption heat between C₂ and C₃ hydrocarbons, we did not yet correct in detail the hydrogenation and coupling steps of these species. Nevertheless, the relatively simple model provided here can already explain a wide range of experimental kinetic data for cobalt catalysts and can well explain recent experimental findings of lowered methane selectivity upon selective poisoning of the cobalt terrace surface.

CONCLUSIONS

DFT-computed reaction barriers reveal that step-edge sites remain highly active for direct CO dissociation at the high CO coverages relevant to practical FT synthesis. On the contrary, the further reduced rate of direct CO scission on terrace sites suggests that the much slower dissociation on those sites will proceed through a hydrogen-assisted pathway. We investigated the electronic structure along the direct CO dissociation pathway on step-edge and terrace cobalt surfaces. We find that the sharing of valence electrons of the cobalt surface atoms involved in binding the C and O atoms is not strongly affected by CO coadsorbrates and, therefore, cannot account for the differences in CO coverage dependence. A deep analysis of the electronic structure around the dissociating oxygen atom reveals significant differences of the electrostatic potential on the oxygen atom of the dissociating CO molecule between the two surfaces. The higher flexibility of the adsorbed CO layer on the corrugated stepped surface weakens lateral interactions and explains the lower dissociation barrier compared to the terrace surface that has a more rigid CO adsorbed layer. By integrating these barriers in a microkinetic model of FT synthesis, we not only show that experimentally observed rates can be reproduced but also can appreciate how migration of CH₄ species between step-edge and terrace sites can explain high rates of methane formation.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscatal.9b01967.

Computational methods, elementary reaction steps, and adsorption energies (PDF)

Movies of the electrostatic potential along the CO dissociation pathway. Movie 1 (MP4) Movie 2 (MP4) Movie 3 (MP4) Movie 4 (MP4)

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Notes

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