

## On the Road for Clean Energy: Computational Study of Catalysts for Fischer–Tropsch Reactions

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**Abstract:** Results from density functional theory calculations indicate that the CO molecule bonds strongly at a top site on Co(113). In nanocluster models, the DFT–predicted energy cost is large relative to the thermal energy available to the adsorbates; thus, hindering mass transport. We show the energy cost to hydrogenate CO varies as the composition of the nanocluster is manipulated. Thus, more detailed kinetic studies, taking into account the effect of CO coverage and varying the core–shell composition, are likely to reduce the energy costs.

**Keywords:** density functional theory, transition state theory, catalysts, Fischer–Tropsch, CO adsorption energy, carbon monoxide

### 1. Introduction

Due to the high dependence on fossil fuels, Fischer–Tropsch synthesis (FTS) process is attractive for the production of clean fuels. In general, FTS transforms CO and H<sub>2</sub> into long–chain liquid hydrocarbons [1]. The complex chemistry of FTS is not fully understood, despite being an established industrial technology since 1926 [2]. Moreover, FTS involves complex reactions involving many surface intermediates and reaction steps [3]. Hydrocarbon formation proceeds in the following sequence: chain initiator generation; chain growth or propagation and chain growth termination or desorption [4]. Central to the FTS process is the identity of the chain initiator. Despite the experimental and theoretical work, several mechanistic details for FTS process remain unclear and unpredictable. Thus, FTS mechanism elucidation requires detailed atomic studies of the hydrocarbon formation sequence. Moreover, in FTS, the reaction kinetics can improve with a suitable catalyst. Commonly used catalysts for the FTS process are 3–*d* transition metals such as Co, Fe, and Ru. Recently, Rochana and co–workers analyzed the electronic properties associated with CO adsorption on FeCo catalysts. They determined that the preferred adsorption site for CO at FeCo alloys differ from the preferred adsorption site at pristine Fe and Co metals, implying that alloying Fe with Co changes the properties of the pure metal and ultimately affects the CO adsorption energy. Indeed, bimetallic catalysts or stepped catalysts are attractive because they have different catalytic properties than either of the parent metals or flat surfaces. In order to implement the FTS process at a large– scale, two fundamental issues need to be addressed : I) Identification of intermediate species and identification of preferred reaction pathways II) Identification of preferred sites (i.e. Stepped surfaces, nanocluster surfaces) for catalytic reactions. In this work, promising stepped–surface catalysts and alloyed nanocluster

catalysts based on Co, Ni, and Fe are studied using electronic structure methods. The ultimate goal is to provide insights into the design of novel catalyst that will alleviate energy and environmental issues in the medium and long term.

## 2. Methodology

In this work, a stepped Co (113) five-layer thick slab was studied with the standard density functional theory (DFT) [5] method as applied in the CASTEP [6, 7] code of the Materials Studio 6.0 suite. The five-layer Co slab was optimized using a DFT-plane wave basis set in the generalized gradient approximation (GGA) as defined by Perdew, Burke and Ernzerhof [8], for the exchange–correlation energy calculations and a revised version of this functional for calculation of chemisorption energies.. The core electron's potential was described with ultrasoft pseudopotentials (USPP) [9] to avoid the computational cost of a large plane wave basis set. The irreducible Brillouin zone (IBZ) was integrated at the gamma point. Moreover, a vacuum gap equal to a seven-layer slab was added normal to the surface to allow a smooth decay of the wave function at this region. Results for atomic relaxations were checked for convergence with respect to the energy cutoff (340 eV). Furthermore, all atomic relaxations were performed at constant volume by using the quasi-Newton minimization method as applied in the Broyden, Fletcher, Goldfarb, and Shannon (BFGS) algorithm, which is appropriate for large molecular systems [10]. This electronic minimization technique was performed iteratively to achieve self-consistent convergence in conjunction with the charge density mixing method by Pulay [11]. It is important to note, zero-point energy (ZPE) corrections are not reported. All transition-state calculations were performed with Kohn–Sham DFT using the DMol3 module [12] with DNP basis set [13]. The transition-state calculations were performed using the synchronous transit methods as implemented by the DMol3 module. In addition, DMol3 uses the quadratic–nudged elastic band (NEB) method for minimum energy path calculations. Moreover, harmonic vibrational frequency analysis was carried to confirm first-order saddle points and to obtain thermodynamic functions (i.e. Gibbs Free energy, Entropy), as well.

## 3. Results

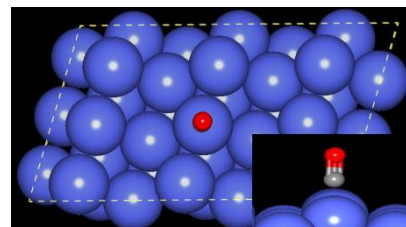
### 3.1. CO Adsorption on Stepped Cobalt Surfaces

Crystalline Co was used as an input material to create a (113) stepped–surface. A  $3 \times 3$  unit cell was constructed to model the surface. Each surface model consists of five-layer slabs and seven equivalent layers for the vacuum space. The structure of the Co atoms in the top two layers were allowed to relax to their ground state structure, whereas the atoms of the bottom layers were fixed in their cartesian positions, to simulate bulk material. Three adsorption sites were studied : CO (C–gray, O–red) on Top of a Co atom (Figure 1), CO on a hollow site and a bridge–stepped site, as well. The chemisorption energy  $E_{\text{chem}}$  was calculated as follows :

$$E_{\text{chem}} = E_{\text{system}} - (E_{\text{slab}} + E_{\text{CO}}) \quad [\text{Eq.1}]$$

where the total energies of the CO–catalyst system, of the clean surface, and of the free CO molecule in the gas phase are represented by  $E_{\text{system}}$ ,  $E_{\text{slab}}$  and  $E_{\text{CO}}$ , respectively. Thus, negative values indicate stable adsorption. To obtain the energy of the CO molecule, geometry optimization was conducted on a CO molecule placed in the middle of a 1 nanometer box. The computed binding energy of the on–top–CO configuration was found to be -

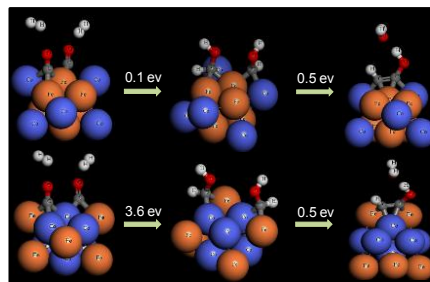
4.788 eV using the PBE functional and -1.465 eV with the RPBE functional [14] (which is close to values reported in the literature). Hence, the CO was found to bind more strongly with the top site (Figure 1). Indeed, the RPBE functional is expected to be more accurate than other functionals such as PBE in calculating binding energy [15]. Finally, The Co–C bond length reduces considerably from 1.98 Å (initial bond length) to 1.75 Å (relaxed bond length), while the O–C length increases to 1.176 Å (from its initial value of 1.13 Å), which is in accordance with other computational studies based on CO–surface models. Thus, based on the elongated bond length, it is safe to conclude that CO readily dissociates at this surface site.



**Figure 1.** Configuration of CO with a triple bond adsorbed on Top position of Co (113) slab. (Co atoms in blue, C in gray, and O in red).

### 3.2. Energy Cost for Reactions of Fischer–Tropsch at Core–Shell Nanoclusters

DFT calculations have been carried out to study FTS mechanism via oxygenates on core–shell *MX* (*M*: Co, Fe; *X*:Fe, Ru, Ni) nanoclusters. Here, *M* represents the core elements and *X* represent the shell elements. This mechanism produces formyl (HCO), which is considered to be a possible intermediate in FT chemistry [16]. As a first step, consideration was given to the core–shell nanoclusters composed of Co and Fe at the  $\text{Co}_6(\text{Fe}_6)$  and  $\text{Fe}_6(\text{Co}_6)$  combination. The energy cost to hydrogenate two CO molecules (docked at the nanocluster surface) to generate CHO–CHOH and CH–COH groups was calculated (Figure 2). The first hydrogenation energy cost for  $\text{Co}_6(\text{Fe}_6)$  is rather low at 0.1 eV. Note, however, that the hydrogenation energy cost for  $\text{Fe}_6(\text{Co}_6)$  is high at 3.6 eV. Similarly, the second hydrogenation step for  $\text{Co}_6(\text{Fe}_6)$  has a low energy cost of 0.5 eV. In parallel, the second hydrogenation step for  $\text{Fe}_6(\text{Co}_6)$  has an energy cost of 0.5 eV. Next, the feasibility of a  $\text{Co}_{10}\text{Ni}_4$  nanocluster (Figure 3) to produce a low energy cost for the first and second hydrogenation steps, was evaluated. The proposed hydrogenation steps bear similarity with steps discussed for CoFe and FeCo nanoclusters. The energy cost for the first step, 1.17 eV, is even higher than the cost that results from the  $\text{Co}_6(\text{Fe}_6)$  model. However, this cost is less than the cost when using a  $\text{Fe}_6(\text{Co}_6)$  nanocluster. On the other hand, the value for the second step is considerably higher (2.57 eV) than the value reported in the previous section (0.5 eV). The high energy cost in this model can be attributed to the strong surface bonds the reactant (CO) forms by solely bonding with Co atoms. Hence, we hypothesize that, at low CO coverages, the formation of Formyl intermediates in these clusters seems unlikely.



**Figure 2.** Forward energy cost for the dissociation of  $\text{H}_2$  on CO-covered  $\text{Co}_6(\text{Fe}_6)$  top row and  $\text{Fe}_6(\text{Co}_6)$ -bottom row nanoclusters. (Fe atoms in orange, Co atoms in blue, C atoms in gray, H atoms in white and O atoms in red).

## 4. Conclusion

A reaction mechanism starting with CO insertion and then followed by hydrogenation to generate formyl chains is studied as a possible mechanism for FTS over Co and Co–based catalysts. DFT calculations on a model Co(113) surface indicate that the CO molecule bonds strongly at a top site (placed above a Co surface atom). C–O

bond dissociation is a key step in the FTS mechanism. Hydrogenation can weaken the C–O bond and generate an intermediate (HCO). However, in  $\text{Co}_{10}\text{Fe}_4$  and  $\text{Co}_{10}\text{Ni}_4$  models, the DFT–predicted energy cost is large relative to the thermal energy available to the adsorbates; thus, hindering diffusion. On the other hand, as shown in the results, the energy cost to hydrogenate CO varies as the composition of the nanocluster is tweaked. In this sense,  $\text{Co}_6(\text{Fe}_6)$  shows the most promising result with energy costs as low as 0.1 eV. Thus, more detailed kinetic studies, taking into account the effect of CO coverage and varying the core–shell composition, are likely to reduce the energy costs.

## **5. Acknowledgments**

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