



# Stability and effects of carbon-induced surface reconstructions in cobalt Fischer–Tropsch synthesis



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## ARTICLE INFO

### Article history:

Received 26 February 2016

Received in revised form 6 June 2016

Accepted 8 June 2016

Available online 11 June 2016

### Keywords:

Density functional calculations

Surface reconstruction

Carbon induced B5 site

Cobalt

Fischer–Tropsch

Carbon diffusion subsurface

## ABSTRACT

This computational study of carbon induced reconstruction of Co surfaces demonstrates that surface reconstruction is stable in the presence of a hydrogen at low coverage. These reconstructions can create new sites that allow for low activation energy CO dissociation. Carbon induced surface reconstruction of the edge of the FCC-Co(221) step surface will result in highly reactive step-edge sites. Such sites also provide a low activation energy for carbon to diffuse into the subsurface layer of cobalt.

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## 1. Introduction

Fischer–Tropsch (FT) synthesis is an integral part of the gas-to-liquids (GTL) process that has regained recent current interest [1,2], to exploit natural gas reserves for the production of liquid fuels. On a fundamental level substantial new insights on the molecular basis of the Fischer–Tropsch synthesis reaction has been obtained by the increasing amount of new molecular data from computational catalysis studies [2].

Of the many proposed mechanisms of the FT reaction, the carbide mechanism is currently the most widely accepted [3,4]. According to this mechanism the Fischer–Tropsch reaction is a polymerization reaction that occurs on the heterogeneous catalyst surface, in which a CH<sub>x</sub> species, generated by decomposition of CO, is inserted into the growing adsorbed hydrocarbon chain. The intrinsic rate of CO activation has to be fast compared to the methanation reaction, but should be slow compared with the rate of the chain growth reaction or chain growth termination [3,5]. Hence the activation of CO is one of the key elementary reactions that control the Fischer–Tropsch reaction.

Since surface terraces of catalytically active Fischer–Tropsch reactions have too high energy barriers for selective CO conversion, it has been proposed that step-edge sites, such as the so called B<sub>5</sub> sites are required for this reaction [6]. Recently it has been shown that Co can expose a number of step-type sites at meaningful concentrations on cobalt nanoparticles [7]. We will use the site reference nomenclature set out in that paper. The high reactivity of such sites has been computationally, as well as experimentally demonstrated for several of the Fischer–Tropsch active metals, such as Ru [8], Co [5,9] and Ni [10] catalyst. Alternative activation paths for intermediate activation energy dissociation of the C–O bond proceed through H activation of the CO molecule. However, such reactions also require step-edge sites to reduce the overall activation energy for CH<sub>x</sub> formation too the required level [11].

In FT catalysis catalyst deactivation [12,13] is undesired and large efforts are undertaken to mitigate this. One cause of deactivation is carbon deposits [14]. Recent work [15] shed some light on the nature of the specific deactivating carbon species. It is clear that some sort of polymeric carbon and maybe subsurface carbon, contribute to the deactivation. Surface reconstruction was postulated also a possible deactivation mechanism [16]. Surface reconstruction induced by strongly adsorbed reactive species can convert a dense surface into a more open one, when the surface has a high adsorbate coverage. The energy gain due to the adsorbate–metal interaction by reconstruction

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overcomes the difference in surface energies between the open surface and the more dense surface. We have previously [16] shown that carbon can induce surface reconstruction on Cobalt surfaces. This was also confirmed by Saeys et al. [17], who found that carbon can induce clock reconstruction at the step edges. Similar observations have been made by Weststrate [18] using a combination of XPS, STM and LEED.

This paper deals with various aspects of carbon induced surface reconstruction. Firstly we look at the stability of this reconstruction in the presence of coadsorbed hydrogen. Secondly we demonstrate the ability of carbon to alter the cobalt surface geometry to allow for carbon diffusion into the subsurface layer (see also [19]). Lastly we show that carbon induced surface reconstruction of the step edges of FCC-Co(221) can create  $B_5$ -A sites that are even more active for CO dissociation than the regular  $B_5$ -A sites as found at the step edge of FCC-Co(211).

## 2. Method and surface model

Density Functional Theory (DFT) calculations presented in this paper were performed with the VASP code [20–23] (Vienna *ab initio* Simulation Package). This code applies DFT to periodical systems, using plane waves and ultrasoft pseudopotentials (US-PP)[24,25]. The US-PP reduces significantly the number of plane waves needed by relaxing the norm conservation constraint on the pseudo

wave-function. The Kohn–Sham equations are solved self-consistently with an iterative matrix diagonalisation combined with a Broyden mixing [26] method for the charge density. The combination of these two techniques makes the code very efficient, especially for transition metal systems that present a complex band structure around the Fermi level. The forces acting on the atoms are calculated and can be used to relax the geometry of the system.

The functional from the generalized gradient approximation of Perdew and Wang PW91 [27] has been chosen because of its good description of chemical bond energies.

Plane waves are used as basis set and ultra soft pseudopotentials are replacing the core part of atoms. This allows a significant decrease of computational time. The number of *k*-points sample in the irreducible part of the Brillouin zone is important for the accurate integration of the properties computed in reciprocal space. The *k*-points sample is often calculated by the program using the Monkhorst–Pack [28] method using a given mesh. Within the finite temperature approach, forces are defined as the derivative of the generalized free energy.

Full optimization of the systems was carried out and no symmetry constraints were applied, except for the inversion center to assure the equality of the two surfaces of the slab. The cut-off energy for the calculations was set to 350 eV. Because of cobalt magnetic properties, open shell calculations were performed.

The calculations on the reconstructed surface was carried out in a  $14 \times 2$  unit cell to deal with the difference in lattice parameters

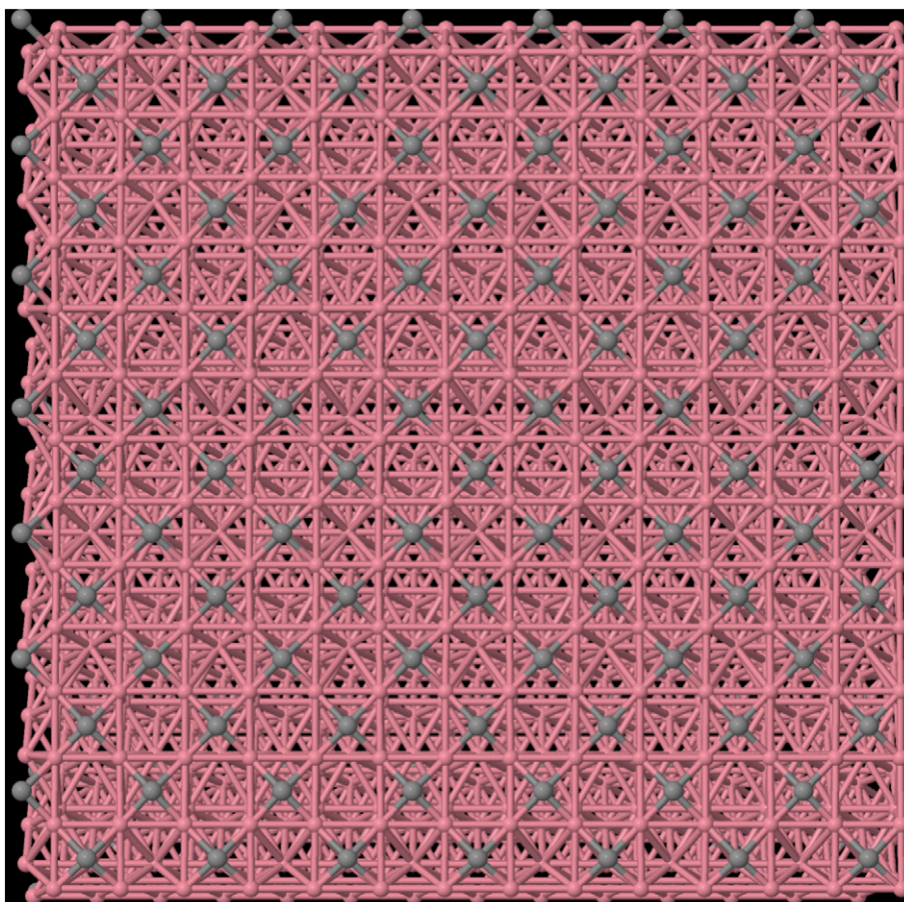


Fig. 1. Carbon induced (111) to (100) reconstruction. Co atoms are pink and C atoms are gray.

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