Investigating mechanisms of hydrocarbon formation from synthesis gas on Fe(100)

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Introduction

The Fischer-Tropsch Synthesis (FTS) produces liquid hydrocarbons from synthesis gas (CO and H_2) in the presence of a catalyst. According to the favoured mechanism of hydrocarbon formation [1], CO dissociatively adsorbs on the catalyst surface, generating surface carbon and surface oxygen. This has been reported previously [2,3]. Surface oxygen reacts with adsorbed hydrogen or CO and leaves the surface as water or CO_2.

Surface carbon is successively hydrogenated yielding CH, CH_2 and CH_3 surface species. If the hydrogenation runs to completion, methane is the by-product. However, under FTS conditions, the CH_x fragments propagate chain growth leading to the formation of heavier hydrocarbons.

Materials and Methods

All calculations are performed using VASP [4]. The Fe(100) surface has been modelled within the slab model approximation using a four-metal layer slab model representing a p(2x2) unit cell. Plane-waves with a kinetic energy below or equal to 400 eV have been included. The exchange-correlation energy and potential has been calculated within the generalised gradient approximation (GGA-PW91). The electron-ion interactions are described by optimised projector-augmented waves. A first order Methfessel-Paxton smearing function with a width of $\sigma \leq 0.1$ eV has been used. Calculations were spin-polarised. We put the adsorbate, at 0.25 ML coverage, on one side of the slab and allowed the top layer and adsorbate to relax. The relative positions of the metal atoms have been fixed initially as those in the bulk, with an optimised lattice parameter of 2.8313 Å (the experimental value is 2.8665 Å). The reciprocal space of the p(2x2)unit cell has been sampled with a (5x5x1) k-points grid.

Results and Discussion

We have used DFT to investigate CH_x (x=0-4) and C_2H_y (y=0-6) adsorption on the clean Fe(100) surface and derived potential energy surfaces (PES) for methane, acetylene, ethylene and ethane (Figure 1) formation by considering carbon-carbon (C-C) coupling and hydrogenation and reactions.

Carbon (C), methylidyne (CH) and ethynyl (CCH) are the most stable species when adsorbed at the four-fold hollow site. The carbon-carbon coupling reactions are generally endothermic. We propose four possible pathways towards the formation of ethane and ethylene. These comprise of a combination of C-C coupling and hydrogenation steps. $CHCH_3$ and CH_2CH_3 are important precursors towards C_2 products and possibly also towards further chain growth.

We will present optimised geometries of CH_x species and C_2H_y species, complete potential energy surfaces as well as the proposed pathways. Furthermore we will discuss the effect of zero-point energy (ZPE) correction on adsorption energies and activation energies. In methane, for example, the reaction energy doubles to +1.45 eV with ZPE. We find that it is an important effect and should be considered especially in hydrogen-containing species.

Significance

This work examines the possible pathways leading to various Fischer-Tropsch products, in terms of carbon-carbon coupling and hydrogenation reactions.

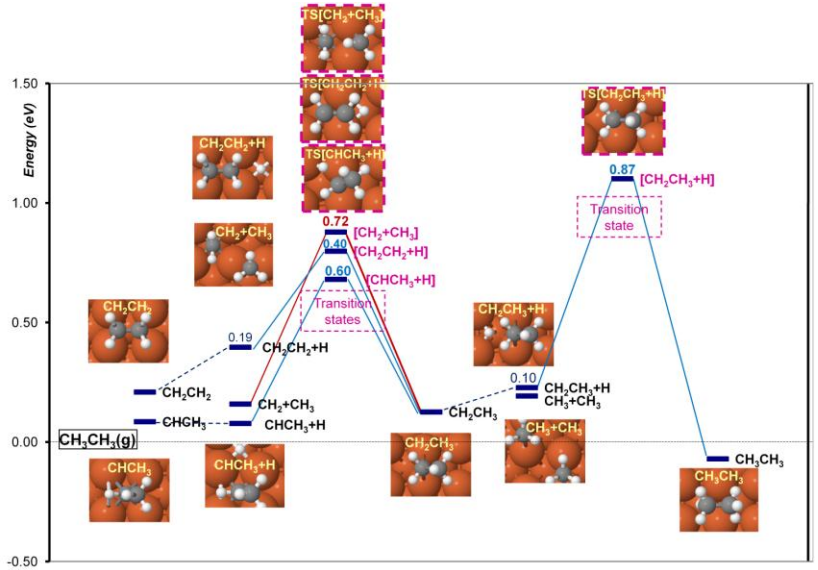

Figure 1. Potential energy surface (in electronvolts) for ethane formation on clean Fe(100). The reference is ethane in the gas phase and the clean slab.

References

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