Journal of Catalysis 325 (2015) 9–18

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Methane, formaldehyde and methanol formation pathways from carbon monoxide and hydrogen on the (001) surface of the iron carbide χ-Fe_5C_2

M. Olus Ozbek [a,b,1], J.W. (Hans) Niemantsverdriet [a,b,*]

[a] Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands
[b] Syngaschem BV, Nuenen, The Netherlands

ARTICLE INFO

Article history:
Received 22 July 2014
Revised 12 January 2015
Accepted 20 January 2015
Available online 6 March 2015

Keywords:
DFT
Fischer–Tropsch
CO hydrogenation
Carbon monoxide
Methane
Methanol
Fe_5C_2
Hägg carbide

ABSTRACT

Formation of $CH_x(O)$ monomers and C_1 products (CH_4, CH_2O, and CH_3OH) on C-terminated χ-$Fe_5C_2(001)$ (Hägg carbide) surfaces of different carbon contents was investigated using periodic DFT simulations. Methane (CH_4) as well as monomer (CH_x) formation follows a Mars–van Krevelen-like cycle starting with the hydrogenation of surface carbidic carbon, which is regenerated by subsequent CO dissociation, while oxygen is removed as H_2O. In cases where surface carbon is readily available, the apparent barrier for CH_4 formation was found to be ~95 kJ/mol. However, different rate-determining steps show that different propagation mechanisms may be possible for actual chain growth, depending on the carbon content of the surface. Hydrogen addition to CO forms formyl (HCO), which is a precursor for both H-assisted CO activation and oxygenate formation. Further hydrogenation of HCO yields adsorbed formaldehyde and methoxy, rather than hydroxymethyl (HCOH) that would give C–O bond splitting. Full hydrogenation to gas-phase methanol faces a high barrier, suggesting that CH_xO species may be involved in higher oxygenate formation in a full Fischer–Tropsch mechanism or that the C–O bond does not break until the CHO fragment has been incorporated in a C_2 species, a route for which precedents are available in the literature.

1. Introduction

Fischer–Tropsch synthesis (FTS) enables the production of clean transportation fuels and chemicals from virtually any source of carbon, such as natural gas, shale gas, coal, or biomass. In the process, synthesis gas, ($CO + H_2$) obtained from these resources, is converted into hydrocarbons and oxygenated products using transition metal catalysts such as iron, cobalt, and ruthenium [1].

When iron is used in the industrial application, catalyst activation is achieved by reducing the iron oxide phase either in hydrogen or in synthesis gas [2–4]. The latter converts the catalyst into iron carbides. Among the mixture of carbide and oxide phases [5–8] present under process conditions, the Hägg carbide (χ-Fe_5C_2) is generally regarded as the active phase for FTS [2,5,6,9–18], although other phases such as ε-$Fe_{2.2}C$ or θ-Fe_3C may exhibit activity as well [9]. Mechanistic studies on CO hydrogenation and FTS on metallic iron surfaces are available in the literature [4,14,19–29], but studies on the catalytic properties of iron carbides in FTS are scarce, we refer to de Smit and Weckhuysen [13] for a recent review and to other literature [3,5,8–11,13,15,24,30–36].

In order for a surface to exhibit Fischer–Tropsch activity, it needs to enable C–O bond breaking, either before or following reaction with hydrogen. For CO dissociation, the activation barrier depends strongly on the catalyst surface [19–22,37,38] and particularly on its structure [6,8,21–24,39]. Hydrogen addition to surface carbon forms CH_2, which is the monomer for chain propagation in the carbene mechanism proposed by Fischer and Tropsch [25,26,40].

On the other hand, in cases where the CO bond cannot be broken directly, (partial) hydrogenation of CO can occur, as in the case of hydroxyl-carbene [41] and CO-insertion [42] mechanisms. Such reaction steps are likely to be involved in the formation of oxygenated products in iron-catalyzed FTS through the growth of CH_xO intermediates, similar as in the carbene mechanism. Indeed, metals such as copper or palladium with limited reactivity toward CO are known to produce methanol selectively [43].

* Corresponding author at: Laboratory for Physical Chemistry of Surfaces, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands. Fax: +31 40 245 5054.
E-mail addresses: m.o.ozbek@yeditepe.edu.tr (M.O. Ozbek), J.W.Niemantsverdriet@tue.nl (J.W. (Hans) Niemantsverdriet).
[1] Present address: Department of Chemical Engineering, Yeditepe University, İstanbul, Turkey.

http://dx.doi.org/10.1016/j.jcat.2015.01.018
0021-9517/

The present paper is part of a series in which we investigate the FTS mechanism on iron carbide surfaces by computational modeling. Starting point is the question how an iron carbide surface, which is "passivated" compared to a clean metal surface due to structural carbon (C*), can exhibit sufficient reactivity to activate the CO molecule. To address this problem rigorously, we use the carbon-rich χ-$Fe_5C_2(001)_{-0.05}$ surface [7], which has one carbidic carbon, denoted as C*, per two iron atoms (θ_{C*} = 0.5 ML) and investigate how removal of C* from this surface affects its reactivity in CO hydrogenation reactions.

The previous study [39] concerned the elementary reactions of CO and H_2 on the χ-$Fe_5C_2(001)_{-0.05}$ surfaces with different C* ontents. The results showed that the perfect (non-vacant) χ-$Fe_5C_2(001)_{-0.05}$ surface is not expected to be a successful FT catalyst as it cannot activate CO. However, C* hydrogenation to form CH is a feasible reaction. In this way, the carbide surface develops vacancies and increases its reactivity. On such a C*-vacant surface, both CO dissociation to C* + O and hydrogenation to HCO are possible. Upon consumption of all C*, the surface is Fe terminated and shows metallic-like properties, where the only feasible reaction is the dissociation of CO to regenerate C* and thus the carbidic surface. Thus, through the consumption and regeneration of C*, the active surface shows dynamic behavior, similarly as in the case of the Mars–van Krevelen (MvK) mechanism [44].

Furthermore, in cases where HCO forms, no energetically feasible route for C–O bond breaking could be found, suggesting that this intermediate may play a key role in production of oxygenated products.

Purpose of this paper was to explore hydrogenation routes of surface carbidic carbon (C*), the products of CO dissociation, and the HCO intermediate, on the χ-$Fe_5C_2(001)_{-0.05}$ iron carbide surfaces of different carbon contents. These reactions show the routes and feasible pathways for the CH_x and CH_xO monomers that produce the hydrocarbon and oxygenate products as proposed in the carbene mechanism. We have chosen the C_1 products CH_4, CH_2O, and CH_3OH as the end point. Although CH_4 is an undesired product in FTS, understanding the selectivity trends for CH_4 formation and chain growth is essential. We will consider chain growth reactions to longer hydrocarbons in the next and final paper of the series.

2. Computational details

Periodic DFT computations were performed using the VASP package [45,46], with plane-wave basis sets and RPBE functionals [47–49]. The cutoff energy used was 400 eV. Necessary dipole corrections due to the asymmetric usage of slabs were included in the computations. All the results presented are the output of spin-polarized computations that were obtained by relaxing the structures until the net force acting on the ions was <0.015 eV/Å. The reaction paths were generated using the climbing image nudged elastic band (CI-NEB) method [50].

A C-terminated χ-$Fe_5C_2(001)$ surface was used as the starting point for representing the (dynamical) active catalyst surface. The p(1×1) surface model (slab) contains 20 Fe and 8 C atoms and is 10.3 Å in height. The vacuum height separating the periodic slabs is 12 Å. In the computations, 10 Fe and 4 C bottom atoms were kept fixed, where all the remaining atoms were relaxed. The *k*-point sampling was generated by the Monkhorst–Pack procedure with a ($4 \times 4 \times 1$) mesh. The total energies of gas-phase molecules were calculated using a single *k*-point (gamma point), where the periodic molecules were separated with a minimum of 10 Å vacuum distances.

The vibrational frequencies of ground and transition states were computed by calculating the Hessian matrix based on a finite difference approach where the individual atoms were displaced with a step size of 0.02 Å along each Cartesian coordinate. During the frequency computations, symmetry was excluded explicitly. The frequencies of the surface ions were excluded based on the frozen phonon approximation. The transition states were verified by a single imaginary frequency along the reaction coordinate.

The relative energies were calculated with respect to $CO_{(g)}$ and $H_{2(g)}$ ($E_{DFT} = E_{system} - (E_{CO(g)} + nE_{H2(g)} + E_{\chi\text{-}Fe5C2})$). Zero-point energy (ZPE) corrections were calculated using the harmonic approximation and the positive modes of the vibrational data ($E_{ZPC} = \Sigma h\nu_i/2$), and included in all the energies reported herein ($E = E_{DFT} + E_{ZPC}$).

3. Results and discussion

Fig. 1 shows the χ-$Fe_5C_2(001)_{-0.05}$ surface at different C* contents, as they were used in our previous study on CO and H_2 activation [39]. We repeat the main findings here. Depending on the surface carbon (C*) concentration, different reaction paths are available for CO and H_2 [39]. On the perfect surface (θ_{C*} = 0.5 ML), C* hydrogenation is the most feasible path. On the C*-free surface (θ_{C*} = 0.00 ML), owing to the complete Fe termination, the surface favors direct CO splitting, which regenerates the C* and the carbide surface. In the intermediate phases with C*-vacancies (θ_{C*} = 0.25 ML), H addition to both C* and CO is possible, along with direct CO dissociation. Following these two directions for CO activation, we have further explored the formation of CH_x and CH_xO intermediates/monomers up to C_1 compounds (CH_4 and CH_3OH) starting from C* and CO to gain insight in the selectivity between desired and undesired products. The details of CH_4 formation, where C* is readily available, and similarly CH_3OH formation, where HCO formation is possible, are presented below.

3.1. CH_4 formation

When surface carbidic carbon (C*) is available, its hydrogenation is a feasible route, especially on the perfect (non-vacant) χ-$Fe_5C_2(001)_{-0.05}$ surface [11,39]. Here, we simulate the hydrogen addition to C*, which is a facile reaction on the non-vacant (θ_{C*} = 0.5 ML) and C*-vacant (θ_{C*} = 0.25 ML) surfaces of χ-$Fe_5C_2(001)_{-0.05}$. Fig. 2 shows the relative energies of the intermediates and transition states along the methanation path on non-vacant (perfect) and C*-vacant χ-$Fe_5C_2(001)_{-0.05}$ in a MvK-like cycle. The respective geometries can be seen in Figs. 3 and 4 (a larger set of figures is available in Supporting Information). The three major stages in Fig. 2 are as follows: (i) the formation of CH_4 through the hydrogenation of the surface carbon that leaves a C*-vacancy, (ii) adsorption of CO on top of a Fe atom and its dissociation to regenerate the surface carbon in the C*-vacancy, and (iii) formation of H_2O through the hydrogenation of oxygen. As CH_4 and H_2O adsorption are weak, these products desorb upon formation.

CH_4 formation on the perfect surface is exothermic by 43 kJ/mol with respect to the gas-phase reactants. As Fig. 2 and Table 1 show, the highest barrier (E_a = 93 kJ/mol) for methanation is faced for the CH_2 hydrogenation step, similar to the situation on Fe(100) [28,29,51]. This suggests that this step may be important in determining the selectivity between the desired chain growth (i.e., CH_x addition) and undesired methanation, as we address in a forthcoming paper on C_2 hydrocarbons. Indeed, a CH_2 coupling route appears feasible compared to CH_2 hydrogenation, which supports this point.

On the C*-vacant surface, as Fig. 2 and Table 1 show, CH_4 formation is exothermic by 67 kJ/mol. Furthermore, compared to the perfect surface, CH formation does not compete with H_2 desorption. On this surface, the most difficult step is the hydrogenation of CH to CH_2, with an activation barrier of 55 kJ/mol.