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COMPARING CO DISSOCIATION PATHWAYS ON THE VARIOUS IRON SURFACES AS Fe(100) AND Fe(110)

M.R. Elahifard

Faculty of Engineering, Ayatollah Khatami Boulevard, P.O.Box:184, Ardakan University, Ardakan, Iran.

Email: mrelahifard@ardakan.ac.ir

Abstract: CO dissociation is generally seen as the first step in the mechanism of the Fischer-Tropsch process, which converts synthesis gas (CO and hydrogen) into hydrocarbons. Dissociation of an adsorbed CO may be direct, i.e. $\text{CO} \rightarrow \text{C} + \text{O}$ or assisted by adsorbed H-atoms, schematically indicated as $\text{H} + \text{CO} \leftrightarrow \text{HCO} \rightarrow \text{CH} + \text{O}$ or $\text{CO} + \text{H} \leftrightarrow \text{COH} \rightarrow \text{C} + \text{OH}$. In this paper we compare the energetics of these steps on the Fe(100) and Fe(110) surfaces on the basis of density functional theory (DFT) calculations and demonstrate that formation of HCO and subsequent dissociation to CH and O may at best compete with direct dissociation on open-packed Fe (100) surface. However, H-assisted dissociation is the preferred mechanism for the close-packed Fe (110) surface

1. INTRODUCTION

CO dissociation is addressed generally as a key step that is responsible for starting the F-T process. So, knowing the geometry of co-adsorbed H atom and CO molecule on the surface and the CO dissociation pathway are necessary to find out the detailed mechanism of the F-T reaction [1-5].

There are only 2 ways for CO dissociation on a surface including direct and H-assisted CO dissociation [6-8]. Although, several complexes of H and CO such as; HCO, COH, HCOH, H_2CO ,... may form on a surface in H-assisted process, but all of them obtain through HCO or COH formation as intermediates. Hence, comparing the HCO and COH formation processes with direct CO dissociation is initially enough to find the best alternative [9-11].

Although several transition metals showed catalytically active for the F-T synthesis, however, only iron and cobalt are considered to be of industrial significant [12]. Unlike cobalt, CO adsorption on the reactive iron surfaces release more energy and also CO dissociation has low barrier i.e. 0.7-1.2 eV that show the possibility of direct CO dissociation on these surfaces [8, 13].

The purpose of this paper is to compare the energetics of direct and H-assisted CO dissociation on the Fe(100) surface and compare it with these processes on the close-packed (110) surface. This question is relevant because first the bonding geometry of CO – in a tilted mode – differs from that on the (110) surface, where CO binds perpendicularly. Secondly, the Fe (100) is more reactive, causing the dissociation products C and O to bind stronger than on (110), hence providing a stronger driving force for the direct dissociation.

2. CALCULATION METHOD

Total energy calculations have been carried out with the Projector Augmented Wave (PAW) method as implemented in VASP [14-17]. Density-functional theory in the revised form of the Perdew-Burke-Ernzerhof exchange-correlation