

Structure of the manganese promotor and adsorption of carbon monoxide on a cobalt surface: a DFT study

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The Fischer-Tropsch (FT) synthesis is the conversion of syngas (a mixture of CO + H₂) into various hydrocarbon chains which are further processed to produce valuable products such as diesel fuels, gasoline and lower olefins etc. [1,2]. Cobalt-based catalyst are well-known for their application in the commercial FT-process due to their high selectivity for long-chain hydrocarbons, low water-gas shift activity, and resistance towards oxidation with water [3,4]. The design of Co-based FT catalysts has been thoroughly researched and tuned the reaction towards the formation of the desirable products, with a high C₅+ selectivity and low selectivity of by-products such as methane and CO₂. One such way is via the addition of small amounts of manganese to the catalyst formulation, resulting in a higher activity at high conversion, a shift in the product selectivity towards the formation of these desirable products [5]. The mechanism underpinning the understanding of this promotional effect is however lacking [6].

Density functional theory (DFT) is a useful tool to obtain a theoretical understanding of catalysts [7]. Hence, in recent years, DFT has been implemented to study the promotional effect of manganese oxides on the cobalt surface. It has been shown that manganese may promote CO dissociation, although the strength of CO adsorption on unpromoted and Mn-promoted cobalt surfaces with various MnO_x structures has not been established unequivocally [8-10]. In this study, the effect of the presence of different MnO_x complexes on cobalt surfaces on the adsorption and dissociation of CO is studied using spin-polarised DFT calculations with the revised Perdew-Burke-Ernzerhof (RPBE) [11] exchange correlation functional. These results illustrate the importance of establishing a base model for Mn-Co system to effectively determine the role of manganese as a promotor.

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