

The effect of Hubbard correction on the structural model of manganese promoters*

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In the pursuit of a net zero economy, research and technology have steered towards producing alternative fuels to efficiently reduce net CO₂ emissions. One such sustainable approach is Power-to-Liquids utilising Fischer-Tropsch (FT) synthesis [1,2]. Cobalt-based catalysts are favoured 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]. Extensive research has gone into designing Co-based FT catalysts that direct the reaction towards forming desired products, with a high C₅₊ selectivity and low selectivity of by-products such as methane and CO₂. One effective method involves the addition of small amounts of manganese to the catalyst formulation, enhancing activity at high conversion and shifting the product selectivity towards C₅₊ hydrocarbons [5]. It has been shown that manganese may promote CO dissociation, however the mechanism underlying this promotional effect is unclear [6].

Hence, in recent years, density functional theory (DFT), has been employed to gain theoretical understanding of the promotional effect of manganese oxides on the cobalt surface [7-9]. To ensure that DFT is utilised effectively to model the manganese oxides that stimulate experimental findings, it is essential to explore its iterations. One approach being the use of Hubbard (U) correction [10], which applies an on-site potential to single element within a system. This has shown to improve the spin magnetic moment and orbital polarization which is postulated to enhance the accuracy of the description of the system, especially for 3d transition metals [11,12]. In this study, to determine if the employment of DFT+U better describes the Mn-Co system in regards to CO absorption, both spin-polarised DFT calculations, with and without Hubbard correction are performed for the modelling of different Mn_xO_y complexes on Co(111) surfaces. For the DFT + U calculation, an on-site potential (LDAUU) of 6 eV was applied to the Mn atoms. These results will illustrate that despite the additional computational hours required for DFT+U calculations, that applying an on-site potential to manganese can play an integral role in the accuracy of the description Mn-Co system. This is shown in the difference in the electronic energy and in adsorption energy on CO across the systems.

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