

Deciphering the relationship between formal oxidation state and Bader charge of manganese oxides in manganese promoted cobalt-catalysts*

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The Power-to-Liquids process utilising the Fischer-Tropsch (FT) synthesis is a sustainable method to produce alternative fuels, which can efficiently reduce CO₂ emissions and aiding the shift towards a net zero economy [1,2]. Cobalt-based catalysts are favoured in the commercial FT-process as they exhibit high selectivity for long-chain hydrocarbons, minimal water-gas shift activity, and resistance to oxidation in the presence of water [3,4]. The design of Co-based FT catalysts has been extensively studied and steered towards producing desired products, with a high C₅₊ selectivity and low selectivity of by-products such as methane and CO₂. The addition of small amounts of manganese to the catalyst formulation results in a higher activity, and a shift in the product selectivity towards the formation of the desirable long chain hydrocarbon products [5]. However, the mechanism inherent to the understanding of this promotional effect is unclear [6].

In recent years, density functional theory (DFT) has been applied to gain theoretical understanding of the promotional effect of manganese oxides on the cobalt surface [7-12]. These DFT studies have explored the influence of various manganese structures such as metallic manganese (Mn) [7], MnO [8-11], and O-Mn-O [12] on different cobalt surfaces. There is an apparent gap between theoretical data to experimental is apparent. For instance, surface science indicates that divalent manganese is present in the catalyst under reaction conditions, but DFT calculates only partial charges. [13]. Resolving the relationship between these charge definitions is crucial for aligning DFT studies with experimental methods like X-ray Photoelectron Spectroscopy (XPS) for oxidation state determination. In this study, the relationship between manganese oxides with known formal oxidation states were modelled and DFT calculations were performed to obtain the Bader charge.

Manganese oxides in both their gaseous and bulk crystalline structures were evaluated. The calculated Bader charge for bulk crystalline structures were higher than that of the gaseous structures of the same formal oxidation state e.g. MnO₂ had a charge that was + 0.463 higher than of the MnO₂(s). The relationship between formal oxidation state and Bader charge for all the manganese structures fall on a single curve when correcting the formal charge with the experienced charge using the Madelungs constant. The obtained relationship is however not linear but is fitted with than a hyperbolic function. These results illustrate the importance of establishing relationship between the rationalization for charge between DFT and experimental studies for manganese as this will contribute to effectively determining the role of manganese as a promotor.

[1] Drünert, S, Neuling, U, Zitscher, T and Kaltschmitt, M. *Applied Energy*, 2022, **277**, 115578.

[2] Cabrera, E and de Sousa, J.M.M, *Energies*, 2022, **15**, 2240

[3] Adeleke, A.A, Liu, X, Lu, X, Moyo, M and Hildebrandt, D. *Rev Chem Eng.*, 2020, **36**, 437-457.

[4] Gholami, Z, Tišler, Z and Rubáš, V. *Catalysis Review*, 2021, **63**, 512-595.

[5] Morales, F, de Smit, E, de Groot, F.M, Visser, T and Weckhuysen, B.M. *Journal of Catalysis*, 2007, **246**, 91-99.

[6] Johnson, G.R, Werner, S. and Bell, A.T. *ACS Catalysis*, 2015, **5**, 5888-5903.

[7] Pedersen, E.Ø, Svernum, I.-H and Blekkan, E.A. *Journal of Catalysis*, 2018, **361**, 23-32.

[8] Zhang, M, Chi, S, Huang, H and Yu, Y. *Applied Surface Science*, 2021, **567**, 150854.

[9] Gupta, S.S, Shenai, P.M, Meeuwissen, J et al. *The Journal of Physical Chemistry C*, 2021, **125**, 21390-21401.

[10] Gençoğlu, M. *Masters dissertation*, İzmir Institute of Technology, İzmir, Turkey, 2019, p. 91.

[11] Doorslaer, M.V. *Masters dissertation*, Ghent University, Ghent, Belgium 2017.

[12] Tucker, C.L., Ragoo, Y., Mathe, S et al. *Journal of Catalysis.*, **411** (2022) 97

[13] Kishore, M.R, Okamoto, H, Patra, L et al. *Phys Chem Chem Phys* **18** (2016) 27885-27896.