ABSTRACT

The excessive utilisation of fossil fuel for meeting global energy demand leads to dwindling crude reserves, which develops an urge for alternative fuel production to meet global energy demands. Fischer-Tropsch synthesis is a commercially available technology capable of producing a broad range of gaseous, liquid and solid phase hydrocarbons using syngas with an approximate $H_2/CO$ ratio in the range of 1.6-2. Fischer-Tropsch fuel has gained interest due to its better Internal-Combustion engine performance and NO$_x$ and SO$_x$ free emissions. The syngas used as a feedstock is generated from steam reforming of natural gas and gasification of coal, biomass, heavy petroleum residue and other carbonaceous waste. After removing contaminants, the cleaned syngas obtained has a low Ribblet ratio ($H_2/(2CO+3CO_2) <1$). In order to balance the Ribblet ratio, the additional energy-intense pretreatment units involving $H_2$ enrichment and $CO_2$ absorption are installed before the Fischer-Tropsch reactors. Currently, direct utilisation of syngas with low Ribblet as a feedstock has become an aspect of consideration. High carbon utilisation in the Fischer-Tropsch process will improve energy efficiency, reduce production costs, and enhance industrial sustainability. The enormous amount of $CO_2$ released during syngas generation and from the Fischer-Tropsch tail-gas is added back to the FT reactor.

The present study focuses on the catalytic conversion of low Ribblet ratio syngas over Fe-Co bimetallic catalysts supported on hierarHZSM-5. Hierarchical pore structure was developed on HZSM-5 with silica to alumina mole ratio 50 using the post-synthetic modification technique. The catalytic activity of synthesised catalysts was tested in a laboratory-scale fixed-bed reactor. Fe-Co bimetallic active metals were loaded on hierarHZSM-5 varying Fe-Co ratio with a constant total metal loading of 30% using the sonication process to increase active metal dispersion. The advantage of incorporating Fe metal into Co catalyst was evidenced through positive $CO_2$ conversion and higher selectivity to diesel range hydrocarbons. Mechanistic studies reveal that the inter-conversion of the oxide and the carbide phases of active metals during the Fischer-Tropsch reaction conditions is responsible for carbon dioxide formation. Synergistic effect of milder Bronsted acidity and hierarchial porous structure of Fe-Co bimetallic catalyst supported over hierarchical HZSM-5 resulted in enhanced syngas conversion towards high-quality C$_{10}$-C$_{20}$ range liquid synthetic fuel with stable catalytic activity for a longer time.
A series of 26 experiments were conducted using optimised Fe-2Co/hierarZSM-5 catalyst for understanding the influence of a particular parameter and the synergy arising due to the second-order interaction among these process parameters. The experimental results were fitted into an empirical regression model, and the second-order Taylor series with a coefficient of determination ($R^2$) closer to 0.99 was used to approximate the process response. The developed regression models were statistically and experimentally validated. C$_2$-C$_3$ olefins play an essential role in deciding the chain growth. Thus, the relationship between C$_2$ and C$_3$ hydrocarbons was experimentally investigated over various process parameters.

In this study, the catalytic activity and stability of auxiliary iron introduced in different proximities to Co$_3$O$_4$ spinel are compared under the identical Fischer-Tropsch conditions for a continuous 120 hours’ time-on-stream run. The spatial distance between different functionalities was monitored by various bulk and surface characterisations. A reconstructed partially inverse FeCo$_2$O$_4$ spinel with a closer and uniform iron and cobalt proximity shows superior catalytic performance with excellent stability ascribing to the interplay of cations having divalent and trivalent oxidation states in different geometric coordination. The cation substitution is found to tailor catalyst properties through modification in the preferential CO adsorption sites. The quantity and the nature of carbon deposited on the spent catalyst during optimal process conditions were also evaluated.

Further, the reaction mechanism and kinetics are investigated over the most promising catalyst. The combined transient IR and steady-state LHHW intrinsic kinetic model suggests formation of HCO/HCOO$^-$ intermediate species over Fe-Co sites. In order to derive a more reliable rate expression, simultaneous kinetics of Fischer-Tropsch and Water-Gas-Shift reactions are studied. The developed comprehensive reaction model postulates that the CO molecule adsorbed on FT active sites dissociates via a hydrogen assisted route and forms HCO intermediate species, and its subsequent reaction with atomic hydrogen (H*) initiates chain growth. The hydrogenation of surface formyl (HCO) is the Fischer-Tropsch rate-controlling step more relevant than the other proposed elementary reactions. Finally, a three-layer Back Propagation Neural Network was tested and trained to predict the relation of non-linearity among the five process variables and the consumption rate of CO and total syngas. A similar prediction trend of CO and total syngas consumption rate provides evidence for the applicability of machine learning in modelling the kinetics of a complex gas-solid reaction.