

Development of a complete kinetic model for the Fischer-Tropsch Synthesis over Co/Al₂O₃ catalysts

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Introduction

The Fischer-Tropsch synthesis (FTS) is a catalytic process that converts CO and H₂ into a mixture of linear gaseous, liquid and solid hydrocarbons. This synthesis has received considerable attention in recent years by both the industrial and academic world as a way of exploiting the huge natural gas reserves located in remote areas, leading to high-grade fuels. Concerning the kinetics of the reaction, two different approaches to the development of FTS kinetic models are available in the literature. In the first one a rate law for reactants conversion (often an empiric power law) and a product distribution model (like Anderson-Schulz-Flory, ASF) are developed separately. This is theoretically justified only if it can be assumed that the reaction products do not affect or participate in the monomer formation mechanism. In the second, more sound approach, all the mechanistic steps which consume CO and H₂ and lead to the final products are considered jointly. A major shortcoming of the publications implementing this approach so far, however, is the introduction of more or less empirical parameters, such as the chain growth probability (α), in order to describe the hydrocarbon distribution. In our Labs a more fundamental approach is under development. Mostly based on chemical enrichment experiments [1] we have first defined a detailed FTS mechanism explaining the synthesis of each product through the evolution of reaction intermediates and adsorbed species. Then, appropriate rate laws have been attributed to each elementary step and the resulting kinetic scheme has been fitted to a comprehensive set of FTS runs.

Materials and Methods

The kinetic measurements were carried out in a fully automated experimental set-up, comprising a fixed bed reactor loaded with 2g of a Co/Al₂O₃ state-of-art catalyst in powder form to prevent diffusional limitations. The catalyst preparation was carried out via aqueous incipient wetness impregnation of a commercial alumina support [2]. Experimental conditions were varied as follows: P=8-25bar, T=220-235°C, H₂/CO feed ratio=1.8-2.7mol/mol, GHSV=4000-7000cm³(STP)/h/g_{cat}.

Results and Discussion

The developed reaction scheme and related kinetic rate equations are shown in Table 1. After parameter optimization, the developed model could accurately predict the observed hydrocarbon product distribution up to n=49, as illustrated e.g. by a typical model fit in Figure 1(a). The model captured the typical deviations of the product distribution from the ASF model, namely the methane high selectivity, the low selectivity to C₂ species and the change of the slope with growing carbon number. Notably, with a single set of rate parameter estimates the model could also correctly describe the effects of all the investigated process

conditions on both CO conversion and product distribution: Figures 1(b) and 1(c) show e.g. the model predictions for the effects of the H₂/CO feed ratio. Further work is presently ongoing in order to make a more detailed description of the data, including also oxygenated species.

Table 1. Proposed FTS kinetic scheme

$H_2 + 2^* \rightarrow 2H^*$	$r_{H_2} = k_{H_2} \cdot P_{H_2} \cdot \theta^{*2} \cdot \theta_{H^*}^{-1}$
$CO + ^* \rightarrow CO^*$ $CO^* + ^* \rightarrow C^* + O^*$	$r_{M1} = k_{M1} \cdot P_{CO} \cdot \theta$
$C^* + H^* \rightarrow CH^* + ^*$ $CH^* + H^* \rightarrow CH_2^* + ^*$	$r_{M2} = k_{M2} \cdot \theta_{C^*} \cdot \theta_{H^*}$
$O^* + H^* \rightarrow OH^* + ^*$	$r_{W1} = k_{W1} \cdot \theta_{O^*} \cdot \theta_{H^*}$
$OH^* + H^* \rightarrow H_2O + 2^*$	$r_{W2} = k_{W2} \cdot \theta_{OH^*} \cdot \theta_{H^*}$
$CH_2^* + H^* \rightarrow CH_3^* + ^*$	$r_{IN} = k_{IN} \cdot \theta_{CH_2^*} \cdot \theta_{H^*}$
$CH_3^* + H^* \rightarrow CH_4 + 2^*$	$r_{CH4} = k_{CH4} \cdot \theta_{CH_3^*} \cdot \theta_{H^*}$
$R_n^* + CH_2^* \rightarrow R_{n+1}^* + ^*$	$r_{G,n} = k_{G,n} \cdot \theta_{R_n^*} \cdot \theta_{CH_2^*}$
$R_n^* + H^* \rightarrow P_n + 2^*$	$r_{P,n} = k_{P,n} \cdot \theta_{R_n^*} \cdot \theta_{H^*}$
$R_n^* \leftrightarrow O_n + H^*$	$r_{O,n} = k_{O_n,dx} \cdot \theta_{R_n^*} - k_{O_n,sx} \cdot X_{O_n} \cdot \theta_{H^*}$
$R_2^* \leftrightarrow O_2 + H^*$	$r_{O,2} = k_{O_2,dx} \cdot \theta_{R_2^*} - k_{O_2,sx} \cdot X_{O_2} \cdot \theta_{H^*}$

Significance

A complete kinetic model for a Co-based FTS catalyst is derived, on the basis of the carbide theory and of the CH₂ insertion alkyl mechanism. For the range of industrially relevant conditions, the developed model could accurately predict both the observed CO conversion and the products distribution up to n=49, in terms of total hydrocarbons, n-paraffins and α -olefins. Accordingly it can be applied to identify optimized process conditions which are suitable to grant the desired conversion with the requested products distribution.

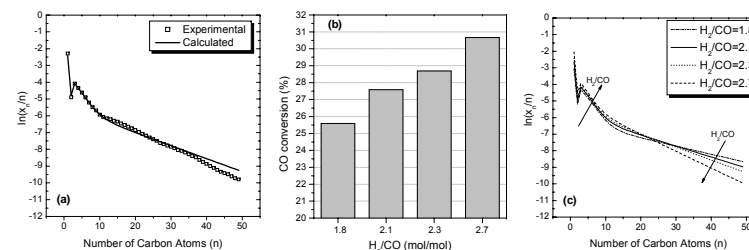


Figure 1. (a) Typical model fit of HC selectivities (T=230°C, P=20bar, H₂/CO=2.3mol/mol, GHSV=5000cm³(STP)/h/g_{cat}); Simulation of H₂/CO effects (b) on CO conversion and (c) on total hydrocarbon selectivities (T=230°C, P=20bar, GHSV=5000cm³(STP)/h/g_{cat}).

References

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