Microkinetic Model of Carbon Hydrogenation on Fe Catalyst

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Introduction

Reaction kinetics and mechanisms of Fischer Tropsch synthesis (FTS) have been studied extensively, and substantial work has focused on unraveling the elementary steps [1]. Substantial recent theoretical work has focused on the energetics and kinetics of elementary steps in FTS on single-crystal Fe. However, reliable data describing energetics and kinetics of the most basic steps, e.g., carbon hydrogenation on promoted and unpromoted polycrystalline Fe surfaces are yet needed for the development of commercially-relevant microkinetic models. Our work focuses generally on development of a microkinetic model for Fe-catalyzed FTS and more specifically in this presentation on the energetics and kinetics of hydrogenation of surface carbon on polycrystalline Fe.

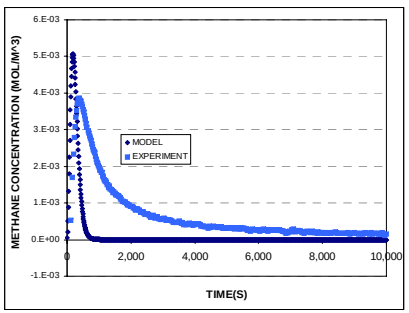
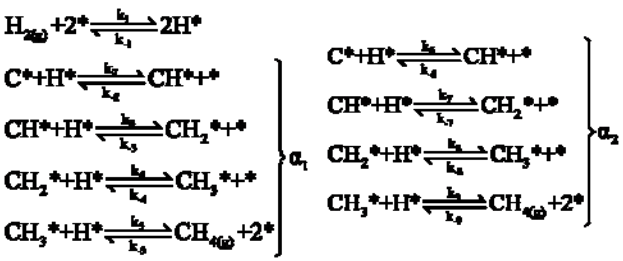


Figure 1. Methane concentration profile during hydrogenation of carbonaceous species at 175°C on 99% Fe catalyst fitted with a one-carbon-site model.

Table 1. Elementary steps for two-carbon site carbene mechanism



Materials and Methods

A 99% Fe/1% Al_2O_3 catalyst was prepared by co-precipitating Fe and Al oxides from a solution of Fe and Al nitrates with NH_4OH. The catalyst was reduced in 10% H_2 at 500°C following which the reactor temperature was lowered to 125, 150, 175, or 200°C, and FTS or CO dissociation was carried out for about 10 min at the specified temperature and 1 atm pressure. Following FTS reaction or CO dissociation, the reactor was purged with He to remove gas phase species while maintaining the same temperature. After purging, H_2 gas was added to the inlet stream to the reactor while the concentration of CH_4 produced was monitored using a UTI quadrupole mass analyzer. The concentration profile for H_2 was determined from the reaction stoichiometry.

Various elementary reaction mechanisms were postulated and tested to see how well they model the data. Model construction and data fitting involved (1) writing out the unsteady-state mass balance equations for gas phase and surface species according to each of the postulated mechanisms, (2) discreetizing the space variables in the partial differential equations describing the unsteady state mass balances for gas phase species assuming plug flow into a uniform grid, (3) integrating the resulting set of differential equations using DVODE, and (4) regressing kinetic parameters using DODRPACK (an orthogonal distance regression routine).

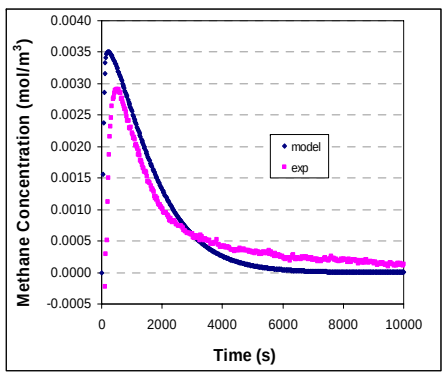


Figure 2. Methane concentration profile during hydrogenation of carbonaceous species at 175°C on 99% Fe catalyst fitted with a two-carbon model.

Results and Discussion

Figures 1,2 and 3 show the results of the measured methane concentration (at 175°C) as a function of time and those predicted with the different models, while Tables 1 and 2 show the various sequence of elementary steps in each model.

During the modeling process, several mechanisms were investigated. However, a mechanism consisting of a blend of carbene and CO-insertion mechanisms yielded the best fit.

We are currently analyzing data obtained at 150°C and 200°C respectively. It is hoped that from Arrhenius plots of the estimated rate constants, we will be able to estimate the pre-exponential factors and activation energies for each elementary step in the mechanism.

Table 2. Sequence of elementary steps for the carbene blended with CO insertion mechanism

$$H_2 + 2s \leftrightarrow 2H - s$$
$$CHO - s + H - s \leftrightarrow CH_2O - s + s$$
$$H - s + C - s \leftrightarrow CH - s + s$$
$$H - s + CH - s \leftrightarrow CH_2 - s + s$$
$$H - s + CH_2 - s \leftrightarrow CH_3 - s + s$$
$$H - s + CH_3 - s \leftrightarrow CH_4(g) + 2s$$
$$CHO - s + CH_3 - s \leftrightarrow CH_3CHO(g) + 2s$$
$$HO - s + H - s \leftrightarrow H_2O(g) + 2s$$
$$O - s + H - s \leftrightarrow OH - s + s$$
$$CH_2O - s + H - s \leftrightarrow CH_3O - s + s$$
$$CH_3O - s + H - s \leftrightarrow CH_3 - s + OH - s$$
$$CO - s + s \leftrightarrow C - s + O - s$$
$$CO - s + OH - s \leftrightarrow CO_2(g) + H - s + s$$

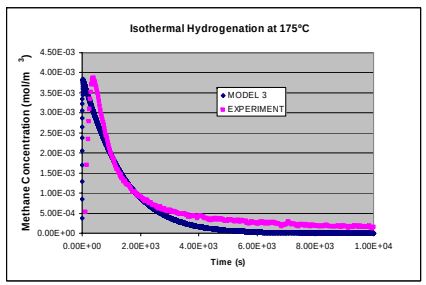


Figure 3. Methane concentration profile during hydrogenation of carbonaceous species at 175°C on 99% Fe catalyst fitted with carbene blended with CO insertion model.

References

[1] C.H. Bartholomew, R.J. Farrauto, Fundamentals of Industrial Catalytic Processes, Second edition, Wiley-Interscience, 2006.