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A Kinetic Analysis of Steam Reforming of Ethane and Propane over a Ni/$MgAl_2O_4$ Catalyst.

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Highlights

- Kinetic high pressure investigations of steam reforming of ethane and propane is presented.
- Microkinetic analysis of steam reforming including methanation and water gas shift reaction.
- Carbon-carbon bond cleavage is the rate limiting step in ethane reforming.
- Cleavage of the first carbon-carbon bond is the rate limiting step in propane reforming.

1. Introduction

Generation of hydrogen and synthesis gas is an important process in the production of ammonia, methanol, refining of oil or synthesis of synthetic fuels [1]. The feedstocks usually range from natural gas to naphtha. Most plants process natural gas or naphtha in an adiabatic preconverter where higher hydrocarbons are equilibrated into a mixture of methane, carbon monoxide, carbon dioxide and hydrogen over a nickel based catalyst. Subsequently, the gas mixture is processed in conventional steam reformers such as tubular reformers and air-fired secondary reformers or autothermal reformers. Several reactions occur in the adiabatic preconverter; steam reforming of the higher hydrocarbons and methane, methanation and the water gas shift. An understanding of the mechanism and kinetics of these reactions are therefore of importance to realise the full potential of this process. Many detailed kinetic studies of steam reforming or partial oxidation including steam reforming of higher hydrocarbons over transition metals at atmospheric pressure have been published [2,3,4,5]. However, none of these studies address the kinetics at high pressure over a nickel based catalyst. To improve the understanding of the industrial process we have carried out experimental studies and kinetic modelling of steam reforming of ethane and propane at conditions relevant to the industrial adiabatic reformer.

2. Methods

Ethane and propane reforming was studied in a pressurized tubular flow reactor. Feed gases were supplied from high-purity gas cylinders and water was dosed by a Quizix pump and steam generated by evaporation. Water was condensed from the product gas and the dry gas was analyzed using a micro-GC. The catalyst was a pre-aged catalyst consisting of Ni supported on a $MgAl_2O_4$ carrier. To control the conversion level and assure isothermal conditions the catalyst was crushed, sieved and fractionized to particles from 0.125-0.3 mm and diluted with inert material. Ethane reforming was studied at pressures from 6 to 21 bar, in a temperature range from 425 to 475°C, and steam to carbon ratios from 1.5 to 7.5. Propane reforming was studied at 21 bar, in a temperature range from 425 to 475°C, and steam to carbon ratios from 2.6 to 8.

3. Results and discussion

Ethane reforming:

A mechanism consisting of 10 elementary steps are proposed consistent with previous studies of methane reforming over Ni [6] and DFT-calculations of C-C and C-H bond breaking [7]. The mechanism includes dissociative adsorption of ethane to adsorbed ethyl and hydrogen, splitting of ethyl by carbon-carbon bond cleavage and oxidation of adsorbed carbon. Three kinetic models were formulated assuming each of these three different steps being rate limiting (i.e., either ethane adsorption, carbon-carbon bond cleavage or

carbon oxidation). The analysis of the kinetic data clearly supports the assumption of carbon-carbon bond cleavage being rate limiting and describes the kinetic data very well (Figure 1) in contrast to the two other models. Furthermore, the adsorption enthalpies in the model are in agreement with adsorption enthalpies reported for Ni surfaces.

Propane reforming:

The analysis of propane reforming takes its starting point in the knowledge gained from the microkinetic analysis of ethane reforming. A mechanism is formulated based on 13 elementary steps. Propane adsorbs by abstraction of one hydrogen atom to adsorbed propyl and then by carbon-carbon cleavage dissociate to methyl and ethyl. Ethyl is then dissociated by carbon-carbon bond cleavage and adsorbed carbon is oxidized. Two models were formulated with either carbon-carbon bond cleavage of propyl or carbon-carbon bond cleavage of ethyl as rate limiting step. The model with cleavage of the first carbon-carbon bond was able to describe the kinetic data reasonably well (Figure 1) whereas the model with cleavage of the second carbon-carbon bond failed to describe the kinetic data.

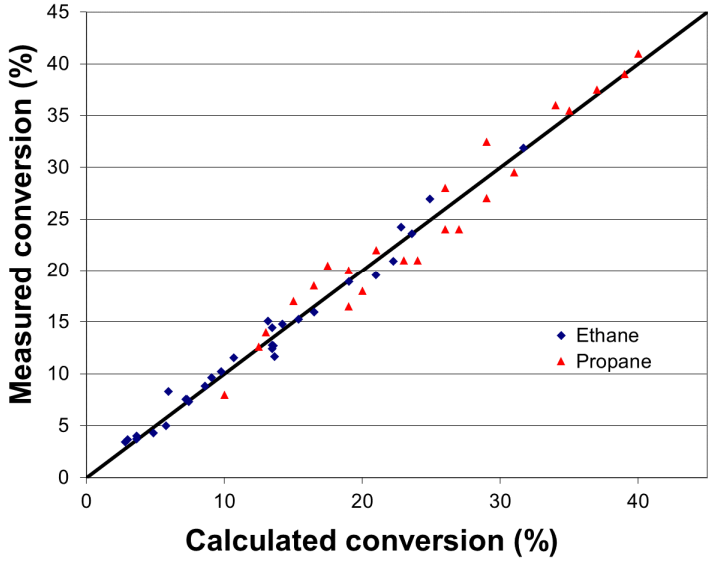

Figure 1. The ability of the kinetic models to describe ethane and propane steam reforming data.

4. Conclusions

A microkinetic analysis of steam reforming of ethane and propane at pressures up to 21 bar has been performed. Carbon-carbon bond cleavage of adsorbed ethyl is the rate limiting step in ethane reforming whereas carbon-carbon cleavage of adsorbed propyl is the rate limiting step in propane reforming.

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Keywords
Steam reforming; Ethane; Propane; Nickel.