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On the elucidation of mechanistic aspects during the oxidative dehydrogenation of ethane to ethylene on a mixed metal oxide (MoVTeNbO)

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Highlights

- A detailed kinetic model is developed following the pseudo state approach.
- The mechanism is based on elementary steps.
- Main reaction steps limiting the production of ethylene are identified.
- The kinetics is coupled to the model of an industrial wall-cooled packed bed reactor.
- Industrial reactor simulations allow for a better relation between the elementary reactions and heat transport phenomena.

1. Introduction

Ethylene oxidative dehydrogenation (ODH) appears to be a promising technology for producing ethylene [1]. This reaction, with the use of a suitable catalyst, can be selectively activated to ethylene at temperatures below 500 °C, consuming lower energy and producing lower carbon oxides than the conventional process thermal cracking of petroleum hydrocarbons to produce ethylene. The main challenges for designing a technology based on ethane ODH have been the design of the catalyst [1] and the design of the industrial reactor [1-3]. The development of a catalyst for ethane ODH has been the subject of study by several researchers worldwide [3]. In the actuality, the multimetallic catalyst MoVTeNbO, which achieves a conversion to ethane up to 60% and selectivity to ethylene up to 90% at temperatures below 500 °C is one of the materials that can be implemented in the petrochemical industry to produce ethylene via ODH [1]. The conceptual design of the industrial reactor for the ODH of ethane on a MoVTeNbO requires from a reliable kinetic model; nevertheless, models reported in literature, besides being macroscopic, have not described properly observations, essentially the production of carbon oxides.

The objective of this work is to develop a kinetic model for the ODH of ethane on a MoVTeNbO. The model is based on elementary reaction steps, which is aimed, on the one hand, to describe observations and, on the other side, to understand and identify limiting mechanistic steps on the catalytic surface of the catalyst. This kinetics is used to carry out the conceptual design of an industrial wall-cooled packed bed reactor.

2. Methods

The development of a kinetic model requires a systematic reaction engineering methodology that accounts for the design of experiments, the execution and analysis of these experiments and literature which leads to the proposal of the reaction scheme (Figure 1) and reaction mechanism, the translation of the mechanism to a model, and the determination of the kinetic parameters evaluating their confidence describing observations (Figure 2). It is worth stressing that the reaction mechanism is proposed using kinetic and catalytic observations, but also catalytic results and studies based on the density functional theory (DFT) reported in literature [5-7]. The model is developed applying the approximation of the pseudo steady state with the objective of identifying the reaction steps controlling the kinetics of the MoVTeNbO during the ODH of ethane to ethylene. The kinetic parameters in this model are determined by methods of statistical thermodynamics and theories based on molecular approximations such as the UBI-QEP method and Single Event Micro kinetic (SEMK) [5,6,8] and engineering approaches that are based on parameter estimation [9]. Finally, this kinetics is used to carry out the conceptual design of an industrial wall-cooled packed bed reactor.

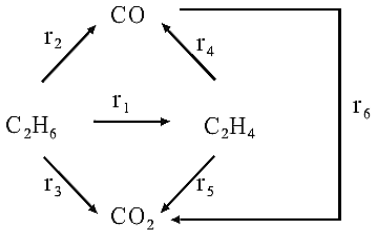

Figure 1: Reaction scheme of ODH from ethane to ethylene on a catalyst based on MoVTeNbO

3. Results and discussion

Figure 2 shows industrial reactor prediction once the kinetic model developed in couple to the reactor model. Simulations are obtained evaluating the developed kinetic model and that one already reported in the literature for the studied reaction-catalyst, showing the importance of the kinetics on the model prediction when the aims is to carry out the conceptual design of an industrial catalytic reactor.

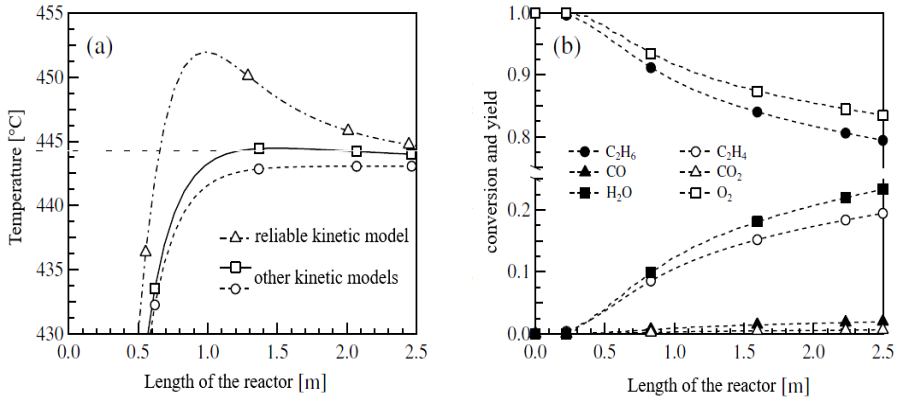

Figure 2. a) Temperature profiles, and b) conversion and yield profiles

4. Conclusions

The development of a kinetic model at the elementary level following the pseudo-state approach seems to be more reliable than the conventional macroscopic models reported in the literature for the studied reaction On the other hand, the coupling of this kinetic model to the reactor model allows to describe and relate the formation of hot spots with the formation of CO_2 and CO, which is completely related to the capability of the kinetic model accounting for their formation on the catalytic surface.

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Keywords

ethylene; kinetics; ODH