

Potential of a Loop Reactor for the Oxidation of Hydrocarbon Mixtures over a Cr_xO_3 Catalyst - Importance of the Reaction Kinetics

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Abstract

The reaction kinetics of the catalytic oxidation of carbon monoxide, ethylene and propylene were investigated in a broad temperature and concentration range applying a $\text{Cr}_x\text{O}_3 / \gamma\text{-Al}_2\text{O}_3$ catalyst. To improve the identifiability of the kinetic parameters the adsorption equilibrium constants of the Eley-Rideal reaction mechanism were estimated based on additional single gas adsorption measurements. Using these kinetic parameters within a reactor model a feasibility study of the Loop Reactor concept was performed and possible operation conditions were identified.

Keywords

Loop Reactor, Total Oxidation, Alkenes, Kinetic modeling, Model reduction, Parameter estimation

Introduction

The exhaust emission standards for industrial facilities, coal-fired power stations and automobiles were steadily increased in the last decades. Different attractive dynamic reactor concepts were introduced (Matros, 1996). One promising concept is the Loop Reactor (LR) (see Fig. 1) (Haynes and Caram, 1994; Sheintuch and Nekhamkina, 2005; Zahn, 2012). This system is suited to treat diluted waste gas streams, in which exothermic reaction fronts move through a reactor cascade in the gas flow direction. After passing a reactor segment, the feed position is shifted into flow direction. This periodic operation attempts to trap a self-sustained exothermic front and allows an auto-thermal operation. Thus, costs for thermal energy and additional units can be reduced. However, knowledge regarding processing industrially relevant gas mixtures is insufficient. First experimental results revealed very complex temperature profiles for the oxidation of mixtures of hydrocarbons characterized by different ignition temperatures (Zahn, 2012). To achieve successful quasi-stationary operation of the LR and understand the dynamics of such temperature fronts in order it is essential to quantify the reaction kinetics.

Kinetic Investigation

The postulated reaction network consider the total and partial oxidation reactions of the reactants ethylene (r_1 and r_2) and propylene (r_3 and r_4), respectively. Furthermore, formed carbon monoxide (r_5), can be complete oxidized (Fig. 2). Depending on the type of catalyst different reaction mechanisms are possible. At noble metal catalysts an

adsorption - desorption mechanism were often validated. That can be quantified using Langmuir-Hinshelwood-Hougen-Watson or Eley-Rideal (ER) mechanisms. At transition metal oxide catalysts, the catalyst works as an oxygen storage. The total oxidation consumes lattice, adsorbed and gas phase oxygen, respectively. Consequently, oxidation-reduction cycles take place (Mars and van Krevelen, 1954) (MvK). However, in many cases the real reaction mechanism remains unknown. In the literature different mechanisms of the total oxidation of short chain olefins and carbon monoxide at a Cr_xO_3 catalyst were discussed (Yao, 1973; Murzin and Salmi, 2005). In the present work, the oxidation reactions of the hydrocarbons were described via an ER mechanism, where the hydrocarbons are assumed to react directly from the gas phase with dissociated oxygen.

$$r_{jR} = \frac{k_{jR}(T) p_{jC} \sqrt{K_{O_2} \cdot p_{O_2}}}{\left(1 + \sqrt{K_{O_2} p_{O_2}} + K_{CO_2} p_{CO_2} + K_{CO} p_{CO} + K_{H_2O} p_{H_2O}\right)} \quad (1)$$

The carbon monoxide oxidation was described via MvK mechanism (Murzin and Salmi, 2005).

The adsorption constants in the kinetic expressions were typically estimated by kinetic measurements. The simultaneous estimation of the temperature dependencies of reaction and adsorption is difficult because of parameter correlations. To avoid this, a model reduction can be applied by subset selection methods (Fink et al., 2007; Kiedorf et al., 2014). Another approach applied in our work is to estimate independently the adsorption parameters by additionally measured adsorption equilibrium (Pöppken et al., 2000).

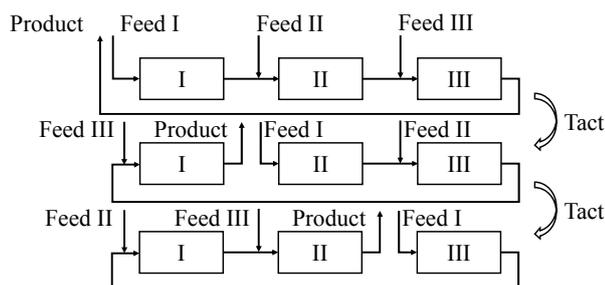


Figure 1: Schematic illustration of a loop reactor (LR) with an integrated Multi-Dosing concept

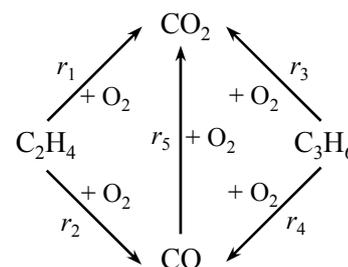


Figure 2: Reaction network for the total oxidation of carbon monoxide, ethylene and propylene

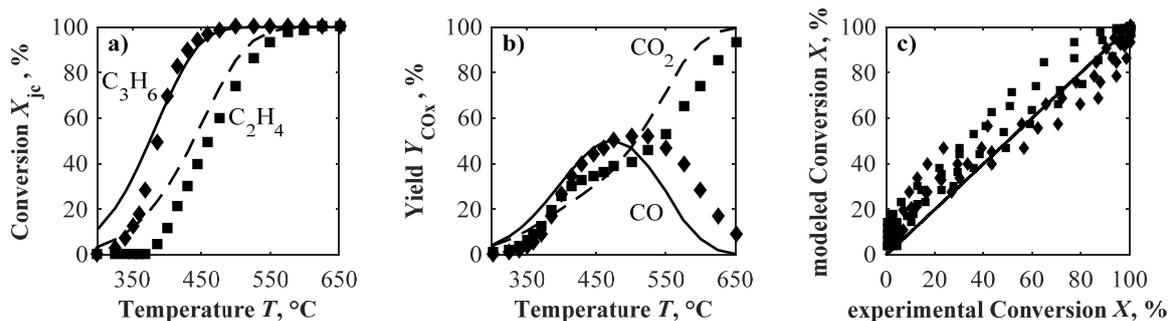


Figure 3: a-b: Experimental (symbols) and modeled (lines) steady state performance parameter (a: conversion of ethylene (square / dashed line) and propylene (diamond / solid line); b: yield of carbon monoxide (diamond / solid line) and yield of carbon dioxide (square / dashed line)) at $x_{O_2} = 20.9\%$ and $x_{C_3H_6} = x_{C_2H_4} = 0.50\%$ and c: parity plot of all measured and modeled ethylene (square) and propylene (diamond) conversions with a molar inlet feed range of $x_{C_2H_4} = 0.25-0.75\%$ and $x_{C_3H_6} = 0.25-0.75\%$ at $x_{O_2} = 20.9\%$

Thus, the significance of kinetic parameters can be increased. Independently measured single component adsorption isotherms of CO, CO₂ and O₂ were included in our kinetic modeling.

According to (Hu et al., 2011; Kiedorf et al., 2014) the complex total reaction network (Fig. 2) was subdivided in three different smaller sub-networks. Starting with investigations of the smallest sub-network of carbon monoxide oxidation ($r_1-r_4 = 0$) the complexity was increased to quantify finally the complete network ($r_1-r_5 \neq 0$). The intermediate steps include the ethylene sub-network ($r_3-r_4 = 0$) and the propylene sub-network ($r_1-r_2 = 0$). Figure 3 shows a validation of the kinetic model and parameter of the total reaction network within a PFTR-type of reactor model evaluating a large set of reactor runs.

Study of Application of the Loop Reactor

Applying the kinetic model subsequently a feasibility study of the potential of the LR concept was performed. Focus was on the maintainability of a quasi-stationary ignited state of the LR. One of the most important parameter to sustain this condition is the switching time. A dimensionless switching time γ was introduced (eq. 2) (Zahn, 2012).

$$\gamma = \frac{(\rho c_p)_g u_g \varepsilon}{(\rho c_p)_s L_R (1-\varepsilon)} t_{sw} \quad (2)$$

Figure 4 reveals modeled reactor temperatures for different switching times at an inlet feed mixture of carbon monoxide ($x_{CO} = 0.50\%$) and oxygen ($x_{O_2} = 20.9\%$). It can be observed that for successful operation only a small opera-

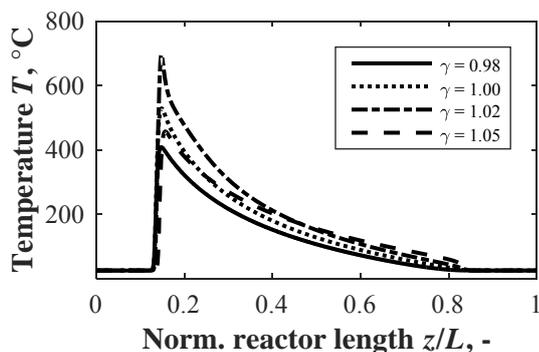


Figure 4: Temperature profile over normalized reactor length for different dimensionless switching times γ (eq. 2)

tion window is available. Possibilities to influence the moving thermal fronts in the reactor cascade and also the maximum temperature in the LR are to vary the residence time or the inlet concentrations of carbon monoxide and the hydrocarbons.

Multicomponent gas feed mixtures result in complex thermal fronts and different quasi-stationary operation conditions. For this reason also, diverse dosing concepts of the reactants were analyzed to limit the maximum temperatures and to improve the process stability.

Finally, experimental results validation of the predicted temperature and concentration profiles is owing.

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