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Kinetic modeling of methanol synthesis from renewable resources

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HIGHLIGHTS

• New kinetic models for methanol synthesis during chemical energy storage.

• The models are suitable for strongly fluctuating ratios of CO and CO2.

• Parameters are fitted to a large number of steady state and dynamic experiments using global optimization.

• Identifiability is critically discussed.

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ABSTRACT

(2)

(3)

In the present paper new detailed kinetic model for the methanol synthesis from H_2 , CO_2 and/or CO using a Cu/ZnO/Al₂O₃ catalyst is proposed. In contrast to most established models different active surface species for CO and CO₂ hydrogenation are taken into account. It is shown that changes in the relative amounts of these different surface species, which are related to changes in catalyst morphology, play an important role for the dynamic transient behavior. The model is therefore suitable for evaluating new applications in chemical energy storage, where strongly varying ratios of CO and CO₂ are of relevance. The model parameters were fitted to steady state and dynamic experimental data for varying CO/CO₂ feed ratios using global optimization. Identifiability is studied using the Profile-Likelihood method giving rise to a reduced kinetic model.

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1. Introduction

Methanol is an important basic chemical in the chemical industry (Fiedler et al., 2000). It can be used as starting material for paraffins, olefins or various organic chemicals like acetic anhydride and as fuel (Asinger, 1986). It is produced continuously in large amounts from synthesis gas using Cu/ZnO/Al₂O₃ catalysts. The reaction network comprises three main reactions, i.e. hydrogenation of CO and CO₂ as well as the water-gas shift reaction according to

 $CO + 2H_2 \rightleftharpoons CH_3OH \tag{1}$

 $CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$

 $CO_2 + H_2 \rightleftharpoons CO + H_2O.$

A very popular and widely known kinetic model was proposed by Graaf et al. (1986, 1988) in the 1980s assuming hydrogenation of CO as dominant path to synthesize methanol. But it is nowadays well accepted that under the reaction conditions employed in the chemical industry direct hydrogenation of CO is negligible (Bussche and Froment, 1996; Chinchen et al., 1987, 1990). Corresponding Langmuir-Hinshelwood kinetics were proposed by Bussche and Froment (1996) and further evaluated in a more recent review by Peter et al. (2012).

With the upcoming "energy revolution", methanol becomes, besides its relevance as C-1 industrial raw material, also an important energy carrier (Olah, 2004). Excess electrical wind or solar energy can be converted to hydrogen and react with CO and CO_2 to methanol for chemical energy storage. Typical sources for CO and CO_2 are biomass and waste streams with variable compositions (Larsen and Sønderberg, 2013; Martín, 2016; Raeuchle







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-	9	1

Nomen * β_i ΔG_i	reduced surface centers unknown parameter Gibbs free energy in J mol ⁻¹	K _i k _i m _{kat}	equilibrium constant rate constant mass of catalyst in kg
$\frac{V}{\frac{\gamma^*}{\gamma_0}}$	space velocity at norm conditions in mi*/min	p	pressure in bar
	relative surface contact free energy	p _i	partial pressure of component i in bar
	volume contraction	p _N	ambient pressure in bar
K	catalyst load in mol kg ⁻¹	q _{sat}	specific amount of surface centers mol kg ⁻¹
V _{i,j}	stoichiometric coefficient of component i in reaction j	R	gas constant in J mol ⁻¹ K ⁻¹
⊙	oxidized surface centers	R _{i,exp}	experimental reaction rate in mol $kg^{-1} s^{-1}$
⊗	active surface centers for hydrogen	r _i	modelled reaction rate in mol $kg^{-1} s^{-1}$
¢	fraction of reduced centers on the catalyst surface	T	temperature in K
$\stackrel{arphi}{ ilde{\mathcal{O}}}{}^k$	hold-up time in s	T_n	standard temperature in K
	surface coverage of species with variable ϕ	$y_{i,0}$	mole fraction of component i at input
$\widetilde{r}_i \\ \Theta^k \\ A, B$	advanced modelled reaction rate in mol kg ⁻¹ s ⁻¹	Y _{i,exp}	experimental mole fraction
	surface coverage of species k	Y _i	mole fraction of component i
	linearized Arrhenius parameter	Z	compressibility factor

et al., 2016; Olah, 2005). In the case of an energy deficit (e.g. no sun, no wind), methanol can be converted back to electrical energy. This will result in a more flexible use of electrical energy from renewable resources, especially in micro-grids. But in this case the methanol reactor may also face strongly varying ratios of CO to CO₂ in the feed resulting in more transient modes of operation, where established kinetics are insufficient. Changing requirements on the quality of kinetic models due to these new situations were recently summarized in Kalz et al. (2017). In particular, the fraction of active centers for CO and CO₂ hydrogenation and the related catalyst morphology change under transient conditions. Dynamic experiments by Muhler et al. (1994); Peter et al. (2012) showed interesting transient behavior, that was caused by a reversible conversion of the different active centers at the catalyst surface, according to Choi et al. (2001a,b) and Nakamura et al. (2003). Hence, a catalyst can become more active while facing a certain gas composition, which makes this aspect interesting for non stationary cases and is not taken into account by established kinetics. For this reason the main objective of this paper is to develop an extended reaction kinetic model, that is able to handle transient operating modes and a wide range of feed gas compositions. The paper is based on a comprehensive set of steady state and dynamic experiments, that are reported in the PhD thesis by Vollbrecht (2007) and starts with a detailed Langmuir-Hinshelwood model based on elementary reaction steps as proposed in the same thesis. The model is extended with a dynamic morphology model taking a variable amount of different active centers for each reaction into account. Parameters are fitted to steady state and dynamic experiments for varying ratios of CO to CO₂ using global optimization. Identifiability is critically discussed using the profile likelihood method leading to a simplified kinetic model, which fits the experimental data almost equally well and has improved structural identifiability.

2. Kinetics of methanol synthesis

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In the remainder, this paper focuses on methanol synthesis from H_2 , CO, and CO₂ over industrial Cu/ZnO/Al₂O₃ catalysts with pressure between 50–100 bar and temperatures between 473.15 and 573.15 K according to Eqs. (1)–(3). In this work the following model assumptions are made: The catalyst deactivation is neglected and no side reactions beyond Eqs. (1)–(3) are considered. The Modeling is based on the Langmuir-Hinshelwood mechanism and consists of three main steps: first adsorption at the surface, reaction at the surface and desorption from the surface. Therefore,

an important part of this mechanism is the availability of free active surface centers for the reaction. In the classical approach of Graaf et al. (1986, 1988) or Bussche and Froment (1996), a single type of active centers on the surface is assumed. In contrast to this, more recent studies have shown that different active centers are involved in the methanol synthesis (Choi et al., 2001a; Park et al., 2014a,b). In the remainder the following surface centers are considered:

- i: ⊙ for oxidized surface centers, also assumed as active center for CO-hydrogenation,
- ii: * for reduced surface centers, also assumed as active center for CO_2 -hydrogenation,
- iii: \otimes as active surface centers for heterolytic decomposition of hydrogen.

The corresponding relative amounts of free surface centers will be denoted below by Θ° for oxidized centers, Θ^* for reduced centers, and Θ° for hydrogen. Occupation of the center with component 'i' is indicated by the corresponding index. In a first step, constant total numbers of oxidized, reduced as well as hydrogen centers are assumed.

2.1. Detailed Langmuir-Hinshelwood kinetic model

Table 1

As a starting point the kinetic model suggested by Vollbrecht (2007) is considered. This model assumes a constant relative amount of centers for each species. The fraction of free surface centers changes with gas composition and their activity depends on the oxidation state of the catalyst surface. The kinetics is based on the elementary steps listed in Tables 1–3. Therein, rate determining steps are labeled as **RDS**. The other steps are assumed to be much faster such that equilibrium can be assumed for them.

Elementary	reaction	steps	for	CO-hydrogenation	on	а	Cu/ZnO/Al ₂ O ₃	catalyst
(Vollbrecht,	2007).							

Elementary step	Quasi-equilibrium/velocity
$\begin{array}{l} CO+\odot\rightleftharpoons CO\odot\\ H_2+2\otimes\rightleftharpoons 2H\otimes\\ 3H\otimes +CO\odot\rightleftharpoons H_3CO\odot +3\otimes\\ H\otimes +H_3CO\odot\rightleftharpoons CH_3OH\odot +\otimes\\ CH_3OH\odot\rightleftharpoons CH_3OH +\odot \end{array}$	$\begin{aligned} \Theta_{\rm CO}^{\circ} &= K_{\rm CO} p_{\rm CO} \Theta^{\circ} \\ \Theta_{\rm H}^{\circ} &= K_{\rm H_2}^{1/2} p_{\rm H_2}^{1/2} \Theta^{\circ} \\ \Theta_{\rm H_3CO}^{\circ} &= K_{\rm A3} \Theta_{\rm H}^{\circ3} \Theta_{\rm CO}^{\circ} \Theta^{\circ^{-3}} \\ r_{\rm A4} &= k_{\rm A4}^{+} \Theta_{\rm H}^{\otimes} \Theta_{\rm H_3CO}^{\circ} - k_{\rm A4}^{-} \Theta_{\rm CH_3OH}^{\circ} \Theta^{\circ} \text{ (RDS)} \\ \Theta_{\rm CH_3OH}^{\circ} &= K_{\rm CH_3OH}^{\circ} \rho_{\rm CH_3OH}^{\circ} \Theta^{\circ} \end{aligned}$

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