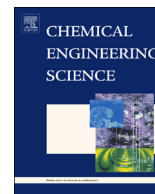




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A computationally simple technique for analyzing catalyst inhibition dynamics involving multiple competing inhibitors



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HIGHLIGHTS

- Develop a dynamic method for studying kinetics and catalyst characterization.
- Reduce governing partial differential equations to ordinary differential equations.
- A computationally efficient method for modeling and parameter estimation.
- Apply the method to deep hydrodesulfurization for production of clean fuels.

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ABSTRACT

In catalyst development a targeted reaction often is inhibited by strongly adsorbed species that are present in the feed. To develop means of mitigating the inhibition effect, it is important to gain a predictive understanding of the inhibition dynamics from modeling of transient response experiments. This approach can also be used for catalyst characterization and mechanistic kinetics studies. Accordingly, this work considers a general class of catalyst inhibition problems involving m competing inhibitors in fixed-bed reactors under non-equilibrium conditions. A mathematical model consisting of a system of $2m + 1$ nonlinear hyperbolic partial differential equations is reduced to that of $2m$ first-order ordinary differential equations. The result is an efficient method for discriminating rival models and extracting active site densities and adsorption-reaction rate constants from transient response data.

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1. Introduction

Catalyst inhibition and poisoning are commonplace in catalytic processes in the petroleum and chemical industries. In most cases the targeted reaction is severely inhibited by a small amount of species that are present in the feed. Such strongly adsorbed species occupy the majority of the active sites that are otherwise available to the main reactant. An essential step toward developing ways to mitigate catalyst inhibition is to gain a quantitative understanding of the inhibition dynamics and correlate the results with catalyst properties such as active site density and adsorptivity. One of the most direct ways of estimating active site density for highly disordered catalysts at realistic conditions is to conduct modeling and experimental studies under transient conditions (Ho and Nguyen, 2004). This entails tracking and modeling changes in catalyst behavior following an imposed perturbation

such as a sudden change in the inhibitor concentration in the feed. Berger et al. (2008) reviewed various dynamic methods for studying mechanistic kinetics and catalyst structure-activity relations.

Previously, we presented an analytical treatment of a class of catalyst inhibition problems in fixed-bed reactors involving only one inhibiting species (Ho and White, 2011). We found a solution that is loosely termed “exact” in that the governing nonlinear partial differential equations were reduced to quadratures. This leads to a computationally simple technique for parameter estimation and hence facilitates quantitative explanation and prediction. The technique was used to examine the inhibiting effects of 3-ethylcarbazole on the hydrodesulfurization (HDS) of 4,6-diethyl-dibenzothiophene over an unsupported CoMo metal sulfide and an $\text{Al}_2\text{O}_3\text{-SiO}_2$ -supported CoMo sulfide catalysts. Both catalysts are notoriously difficult to characterize by surface science techniques.

In this study we generalize the previous treatment to include an arbitrarily large number of inhibitors in a fixed-bed flow reactor. Problems of this type are quite common. Many supported metal bifunctional catalysts are inhibited by sulfur species, nitrogen species, and/or CO (Matsui et al., 2005). Petroleum fractions contain highly

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adsorptive organic nitrogen and metal (e.g., V and Ni) species which inhibit catalysts used in refining of heavy or residual oils. Hydrodenitrogenation (HDN) and hydrodemetallization are essential parts of oil refining.

Similar to our prior work (Ho and White, 2011), here we consider a catalyst inhibition problem in the context of organonitrogen inhibition on HDS catalysts. Specifically, the system considered has a total of m types of inhibiting nitrogen species. It is described by a model consisting of $2m + 1$ nonlinear hyperbolic partial differential equations. We show that the model can be reduced to a system of $2m$ first-order ordinary differential equations. The result is a simple, efficient procedure for discriminating rival models and determining model parameters. A two-inhibitor system taken from HDS of hydrocarbon oils is used as an illustrative example.

2. Modeling of inhibition dynamics

A word about the experimental procedures is in order before proceeding further. As detailed elsewhere (Ho and Nguyen, 2004), the HDS fixed-bed experiments are started with an organosulfur-containing feed without inhibitors. Once the catalyst levels out its activity after the initial transient (pre-inhibition steady state), the feed is switched over to one that contains m organonitrogen inhibitors in addition to the organosulfur species. The reactor effluents are intermittently analyzed until the catalyst levels out its activity again (post-inhibition steady state).

Let S and N_i ($i = 1, 2, \dots, m$) be the concentrations of sulfur and nitrogen atoms in the flowing stream, respectively. Also, let q_s and q_{ni} be the adsorbed sulfur and nitrogen atom concentrations on the catalyst, respectively. Denoting q_m as the catalyst's total chemisorption capacity, then $\theta_{ni} = q_{ni}/q_m$ is the fractional coverage of individual adsorbed nitrogen. For sulfur species, k_s , k'_s , and k_{HDS} are the adsorption rate constant, desorption rate constant, and surface HDS rate constant, respectively. Likewise, the corresponding rate constants for nitrogen species are k_{ni} , k'_{ni} , and k_{HDNi} .

The simplifying assumptions used in the model development were discussed previously (Ho and Nguyen, 2004). They are $k_{ni}N_{fi} \gg k'_{ni}$, $k_{HDNi} \gg k'_{ni}$, $k_{ni} \gg k_s$, $k_{si}S_{fi} \ll k_{HDS}$, and $q_s \ll q_{ni}$ for every i . These assumptions were justified in a more detailed study (Ho and Nguyen, 2006). It bears emphasizing that organonitrogen species are very sticky so the desorption is not fast enough (Sau et al., 2005) to fulfill the equilibrium requirement of the classical Langmuir–Hinshelwood theory. Essentially, what we do here is to use the highly adsorptive organonitrogen species as a sensitive chemical probe to “sample” the limited number of active sites *in situ*. Thus, q_m is a measure of the maximum site density. The transient response of the system after introducing the nitrogen inhibitor (time $t > 0$) is described by the following plug-flow reactor model.

(i) S mass balance in the fluid phase

$$v \frac{\partial S}{\partial z} + \varepsilon \frac{\partial S}{\partial t} + (1 - \varepsilon) \rho_p k_s q_m S \left(q_m - \sum_{j=1}^m q_{nj} \right) = 0 \quad (1)$$

(ii) N mass balance in the fluid phase ($i = 1, 2, 3, \dots, m$)

$$v \frac{\partial N_i}{\partial z} + \varepsilon \frac{\partial N_i}{\partial t} + (1 - \varepsilon) \rho_p k_{ni} N_i \left(q_m - \sum_{j=1}^m q_{nj} \right) = 0 \quad (2)$$

(iii) N mass balance in the solid phase

$$\frac{\partial q_{ni}}{\partial t} = k_{ni} N_i \left(q_m - \sum_{j=1}^m q_{nj} \right) - k_{HDNi} q_{ni} \quad (3)$$

Here ε , ρ_p , and v are bed void fraction, catalyst bulk density (in sulfided form), and the superficial fluid velocity based on empty reactor, respectively. The average fluid velocity in the interstices

between particles is v/ε . The symbols are defined in the Nomenclature if not stated otherwise.

The pre-inhibition steady state is characterized by the boundary conditions at $z=0$, which are $S=S_f$ and $N_i=N_{fi}$. At $t=0$ ($z \geq 0$), we have $N_i=q_{ni}=0$ and

$$v \frac{d\hat{S}}{dz} + (1 - \varepsilon) \rho_p k_s q_m \hat{S} = 0 \quad (4)$$

where $S=\hat{S}(z)$ at $t=0$. Integrating Eq. (4) yields $\hat{S}(z) = S_f \exp[-(1 - \varepsilon) \rho_p k_s q_m z / v]$.

The post-inhibition steady state is governed by the following equations.

$$v \frac{dS}{dz} = - \frac{(1 - \varepsilon) \rho_p k_s q_m S}{\left(1 + \sum_{j=1}^m k_{nj} N_j / k_{HDNi} \right)} \quad (5)$$

$$v \frac{dN_i}{dz} = - \frac{(1 - \varepsilon) \rho_p k_{ni} q_m N_i}{\left(1 + \sum_{j=1}^m k_{nj} N_j / k_{HDNi} \right)} \quad (6)$$

Eqs. (5) and (6) capture two characteristic features of the deep-HDS process: sulfur removal is predominantly controlled by nitrogen species (Ho and Markley, 2004) and nitrogen removal is governed by self-inhibition (Ho, 2010). The model has the following parameters: k_{HDNi} , k_{ni} , k_s and q_m . As discussed elsewhere (Ho and Nguyen, 2004), Eqs. (5) and (6) provide constraints for the parameter estimation problem to be discussed later.

We nondimensionize Eqs. (1)–(6) to identify system parameters representing the relative time scales of competing events in the bulk fluid phase and on the catalyst surface. Let $s=S/S_f$, $n_i=N_i/N_{fi}$, $\xi=z/L$, $\tau=t/(L\varepsilon/v)$, and $\theta_i=q_{ni}/q_m$, we obtain the following dimensionless parameters: $\eta=(1 - \varepsilon) \rho_p k_s q_m L / v$, $\mu_i=(1 - \varepsilon) \rho_p k_{ni} q_m L / v$, $\alpha_i=k_{ni} N_{fi} L \varepsilon / v$, and $\gamma_i=L\varepsilon k_{HDNi} / v$. The governing equations then become

$$\frac{\partial s}{\partial \xi} + \frac{\partial s}{\partial \tau} + \eta s (1 - \theta_1 - \dots - \theta_m) = 0 \quad (7)$$

$$\frac{\partial n_i}{\partial \xi} + \frac{\partial n_i}{\partial \tau} + \mu_i n_i (1 - \theta_1 - \theta_2 - \dots - \theta_m) = 0 \quad (8)$$

$$\frac{\partial \theta_i}{\partial \tau} = \alpha_i n_i (1 - \theta_1 - \theta_2 - \dots - \theta_m) - \gamma_i \theta_i \quad (9)$$

with the boundary conditions $s=n_i=1$ at $\xi=0$, $n_i=\theta_i=0$ at $\tau=0$, and $s=\exp(-\eta\xi)$ at $\tau=0$.

Eqs. (7)–(9) represent the general class of catalyst inhibition problems we wish to address here. The targeted reaction, represented by Eq. (7), is slaved to inhibitors whose behaviors are governed by Eqs. (8) and (9). During the breakthrough period, the catalyst bed is divided into two moving zones. The upstream zone is essentially saturated with organonitrogen, while the downstream zone has not seen organonitrogen yet, so n_i and θ_i are identically zero in this zone. In what follows we develop an analytical treatment to solve the above nonlinear partial differential equations.

3. Analytical treatment

Eqs. (7)–(9) can be simplified by changing the physical coordinates ξ and τ to the characteristic coordinates x and y (Aris and Amundson, 1973). Let $x=\xi$ and $y=\tau-\xi$, Eqs. (7)–(9) become

$$\frac{\partial s(x, y)}{\partial x} = -\eta s \left(1 - \sum_{j=1}^m \theta_j \right) \quad (10)$$

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