Chapter 12
Kinetic Models for Complex Parallel–Consecutive Reactions Assessment of Reaction Network and Product Selectivity

Hamdy Farag
Kyushu University, Japan & Mansoura University, Egypt

Masahiro Kishida
Kyushu University, Japan

ABSTRACT

Kinetic models were developed to account for the partial contributions of intermediates in complex parallel–consecutive reactions. The models allow precise estimation of the apparent rate constants of all steps in such a reaction network. The hydrodesulfurization (HDS) of dibenzothiophene (DBT) over CoMo-based alumina and carbon catalysts, and over an unsupported molybdenum sulfide catalyst, were investigated in a batch reactor and used to represent this type of reaction. The HDS reactions proceeded through two parallel–consecutive reaction pathways, i.e., direct desulfurization (DDS) and hydrogenation (HYD), in which two main intermediates, namely biphenyl and partially hydrogenated DBT, were involved. Different selectivities in terms of yield fraction (percentage ratio of HYD/DDS) were observed for these catalysts. The results are discussed in the context of proposed HDS reaction networks. Use of these models enables more accurate assessment of differences among the performances of different catalysts.

1. INTRODUCTION

A reaction between molecules implies the breaking of existing bonds and/or the formation of new bonds. A catalyst is a substance that affects the rate or the direction of a chemical reaction, but is not consumed or altered during the process. This definition is, however, valid only theoretically in terms of chemistry, because the catalyst may undergo physical and sometimes chemical changes.) A catalyst therefore affects only the rate of a chemical reaction and not its equilibrium, i.e., a catalyst may increase or decrease the

reaction rate and it may influence the direction or the selectivity of a reaction, but it cannot change the ultimate thermodynamic equilibrium. Heterogeneous catalysis enables the development of large-scale continuous processes, whereas homogeneous catalysis is mainly used in fine chemicals manufacturing. Catalysis is mainly developed through advances in three areas: kinetics, synthesis, and characterization. Chemical kinetics is an important tool for studying catalytic reactions, and is concerned primarily with chemical changes and the energy and mass fluxes associated with them. Kinetics is simply the measurement and analysis of reaction rates. The rate of a chemical reaction is defined as

$$R = \frac{1}{v} \frac{dC}{dt}$$

where *V*, *C*, and *t* are the system volume, extent of reaction, and time, respectively.

Usually, integral methods based on integration of the reaction rate expressions and differential methods based on differentiation of experimental concentration versus time data are the techniques used to determine empirical reaction rate functions. The rate equations of simple reactions for which the concentrations of reactants, intermediates, and products depend on time can be solved analytically. However, for complex parallel–consecutive reactions, the rate expression becomes unmanageable and closed-form solutions cannot be easily obtained, especially for the time dependence of various species concentrations in the system. Parallel–consecutive reactions are dominant in complex petrochemical reactions (Vasudevan & Fierro, 1996; Whitehurst et al., 1998). There are also numerous chemical reactions that show this parallel–consecutive behavior; examples include HYD, oxidative dehydrogenation, hydrodesulfurization (HDS), and selective oxidation (Babich et al., 2003; Grabowski, 2006; Singh & Vannice, 2001). The term consecutive reactions refer to those reactions in which one or more of the products formed initially (primary product) undergoes a subsequent reaction to give another product. A secondary product may therefore be produced by various routes. In handling such reactions, it is necessary to deal with the problems of determining the orders and rate constants for each individual reaction. Many catalysts can stimulate one reaction with various activities and selectivities. Appropriate and reliable kinetic investigations are crucial for ranking catalysts in order of activities and selectivities. The product distribution as a function of contact time between catalyst and feed can help to identify the reaction network. The validity of the postulated reaction network is difficult to judge unless extensive kinetic studies are undertaken. Here, we focus on such reactions and discuss the key issues in selecting an appropriate reaction network by analyzing the reaction selectivities. The rate-law models described are valid for application to such reactions. Experimental results provide factual information on reactions. Although agreement between a rate law and the experimental data suggests that the proposed mechanism is valid, disagreement is enough to rule out the proposed mechanism. However, It should be noted that agreement between the predicted and measured kinetics is not always enough to assign a mechanism, unless the number of constants in the numerical rate formula is limited. Sophisticated reaction rate laws can be considered, but such rate laws usually include a high number of constants, which makes it difficult to identify certain mechanisms.

In this chapter, we provide some models to describe substrates that are transformed via parallel–consecutive reaction networks. We use the HDS of dibenzothiophene (DBT) as a representative reaction. Such aromatic sulfur-containing species accumulate mainly in high-boiling-point petroleum fractions such as middle distillate fuels (Mochida et al., 2003). These compounds have been proved to be the

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