Chemical Reaction Engineering-Beyond the Fundamentals
L.K. Doraiswamy and D. Uner
MODULE 2.1
COMPLEX REACTION ANALYSIS

OBJECTIVE

After the completion of this module, you will be able to

- Differentiate between multiple and multistep complex reactions
- Articulate the selectivity and yield concepts
- Select the type of ideal reactor to run complex reactions with improved selectivity

READING ASSIGNMENT

Read pages 33-59 of Chapter 2 D&U.

DERIVE

All of the equations in the assigned section.

COMPUTE

1. Methane partial oxidation reaction is a widely investigated industrial reaction. In the table below you will find a set of reactions taking place in a catalytic reactor(Enger, B.C., Lodeng, R., Holmen, A., Appl. Catal. A.- Gen. 346 (2008) 1-27).
    a. Set up a reaction matrix and determine if all the reactions are independent.
    b. In the article, short contact time reactors are particularly emphasized. Discuss the benefits of keeping the contact time short for the methane partial oxidation reaction.
    c. Write down the expressions for the hydrogen and CO selectivity.
    d. Write down an expression for carbon selectivity. Discuss the relevance of the carbon deposition on this catalyst and coke formation in a FCC (fluidized catalytic cracking) catalyst.
    e. List all of the products. For each one, discuss whether a CSTR, a PFR or a combination would be beneficial for improved selectivity. What particular information do you need to decide?

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$	(1)
$CH_4 + 0.5O_2 \rightarrow CO + 2H_2$	(2)
$CH_4 + O_2 \rightarrow CO_2 + 2H_2$	(3)
$CO + H_2O \rightleftharpoons CO_2 + H_2$	(4)
$CH_4 + H_2O \rightleftharpoons CO + 3H_2$	(5)
$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2$	(6)
$CO + H_2 \rightleftharpoons C + H_2O$	(7)
$CH_4 \rightleftharpoons C + 4H_2$	(8)
$2CO \rightleftharpoons CO_2 + C$	(9)
$CO + 0.5O_2 \rightarrow CO_2$	(10)
$H_2 + 0.5O_2 \rightarrow H_2O$	(11)

2. Catani et al. (Catani, R.; Centi, G.; Trifiro, F.; Graselli, R.K., Ind. Eng. Chem.Res. 31 (1992)107) Have reported a reaction network for the ammoxidation of propane over V-Sb-Al mixed oxides. The reaction network and the individual steps are given below. Determine if all the reactions in this network are independent.

direct formation of products from propane

$$C_3H_8 + \tfrac{1}{2}O_2 \rightarrow C_3H_6 + H_2O \quad (2)$$

$$C_3H_8 + 2O_2 + NH_3 \rightarrow C_3H_3N + 4H_2O \quad (3)$$

$$C_3H_8 + 4O_2 \rightarrow 2CO + CO_2 + 4H_2O \quad (4)$$

$$C_3H_8 + 3O_2 + NH_3 \rightarrow C_2H_3N + 4H_2O + CO_2 \quad (5)$$

$$C_3H_8 + \tfrac{7}{2}O_2 + 3NH_3 \rightarrow 3HCN + 7H_2O \quad (6)$$

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \quad (7)$$

secondary reaction products from intermediates

$$C_3H_6 + \tfrac{3}{2}O_2 + NH_3 \rightarrow C_3H_3N + 3H_2O \quad (8)$$

$$C_3H_6 + \tfrac{5}{2}O_2 + NH_3 \rightarrow C_2H_3N + 3H_2O + CO_2 \quad (9)$$

$$C_3H_6 + 3O_2 + 3NH_3 \rightarrow 3HCN + 6H_2O \quad (10)$$

$$C_3H_6 + \tfrac{7}{2}O_2 \rightarrow 2CO + CO_2 + 3H_2O \quad (11)$$

$$C_3H_3N + \tfrac{7}{2}O_2 + NH_3 \rightarrow 2CO + CO_2 + 3H_2O + N_2 \quad (12)$$

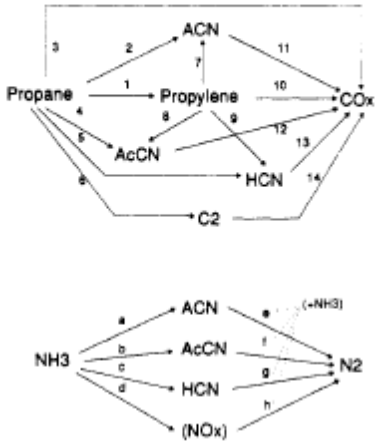
$$C_2H_3N + 3O_2 + NH_3 \rightarrow CO + CO_2 + 3H_2O + N_2 \quad (13)$$

$$HCN + 2O_2 + NH_3 \rightarrow CO_2 + 3H_2O + N_2 \quad (14)$$

$$C_2H_4 + \tfrac{5}{2}O_2 \rightarrow CO + CO_2 + 2H_2O \quad (15)$$

$$\tfrac{3}{2}O_2 + 2NH_3 \rightarrow N_2 + 3H_2O \quad (16)$$

Scheme I. Kinetic Reaction Network in Propane Ammoxidation on V–Sb–Al Based Catalysts: (a) Reaction Pattern of Propane Depletion; (b) Reaction Pattern of Ammonia Depletion



3. *Attempt this problem if you feel comfortable with the surface reactions and surface reaction mechanisms. A thorough study of chapter 5 would be beneficial otherwise.*
   Hickmann and Schmidt (AIChE 39 (1993) 1164) have published a detailed surface mechanism for the methane partial oxidation reaction. Go over the reaction mechanism and the derivations. Reproduce the results presented in the article.

4. Selectivity of chemical reactions depends also on reactor operational parameters such as mixing. Find and review the article by Bourne (Org. Proc. Res. Dev. 7 (2003) 471-508) for a nice selection of liquid phase complex reactions whose selectivity are influenced by the rate and sequence of mixing. The concepts introduced in this article will prepare you for Chapter 3.

BRAINSTORMING

- Find at least 3 industrially relevant complex multiple reaction schemes

- Find at least 3 industrially relevant complex multistep reaction schemes