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Thermodynamic equilibrium distribution of light olefins in catalytic pyrolysis

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ABSTRACT

Catalytic pyrolysis is a promising technology to produce light olefins. Gibbs free-energy minimization method was used to study the thermodynamic equilibrium distribution of olefins in catalytic pyrolysis with Aspen Plus software. The result showed that olefin systems with different carbon numbers demonstrated a similar thermodynamic equilibrium distribution. The ethene equilibrium composition increased with increasing reaction temperature and decreased with increasing total hydrocarbon pressure. By contrast, the propene equilibrium composition reached a maximum of 40 wt% at 850–950 K under 0.1 MPa. Ethene yield and propene yield of thermodynamic equilibrium, catalytic pyrolysis and thermal pyrolysis were compared. The use of catalyst greatly increased the yields of ethene and propene, but the yields were still lower than the equilibrium data. Catalytic pyrolysis was carried out in the interaction zone where both catalytic conversion and thermal conversion were important. Propene yield was close to ethene yield at about 950 K from the thermodynamic view. Given the shape-selective effect of the catalyst on branched olefins with large carbon number, the equilibrium carbon number distribution of olefins possibly shifted from large carbon numbers to low carbon numbers, resulting in enhanced ethene and propene yields.

1. Introduction

Steam cracking and fluidized catalytic cracking (FCC) are conventional processes to produce light olefins such as ethene and propene through petroleum-dependent route [1,2]. Ethene and propene are obtained mainly from steam cracking with high reaction temperature and energy consumption. Light oils are the main products in FCC process, and the yields of ethene and propene are limited [3,4]. Meanwhile, there is a big gap between supply and demand in the market of fundamental chemical raw materials for ethene and propene. Catalytic pyrolysis of petroleum fractions can be used to produce ethene and propene, and it has recently been attracted great attention [5,6]. Catalytic pyrolysis inherits the advantages of steam cracking and FCC, and it can process various feedstocks ranging from light hydrocarbons to heavy oils [7–9]. Depending on feedstock properties and operating conditions, fixed bed or fluidized bed reactors are usually used in catalytic pyrolysis. Effective shape-selective catalyst is of the most importance in catalytic pyrolysis, and it can enhance cracking reaction of feedstocks and improve the yields of light olefins. ZSM-5 catalyst and its modification, as one of the representatives, has been studied widely and related researches have made great progress [7,10–12].

However, when it comes to the fundamental theoretical study of catalytic pyrolysis reactions, little attention has been payed to the thermodynamic equilibrium. It is reported that light olefin distributions are quite similar regardless of catalyst types and reaction conditions in catalytic naphtha cracking, indicating interconversion of light olefins occurs simultaneously together with naphtha cracking, and therefore, it is difficult to control the selectivity of ethene and propene in catalytic naphtha cracking [13]. One reason for this phenomenon is that the selectivity of ethene and propene was restricted by the thermodynamic equilibrium.

In the study of methanol to olefins (MTO), researchers have observed that the yields of light olefins will be restricted by thermodynamic conditions [14,15]. Catalyst has great influence on product distribution because of its shape selectivity, from the perspective of relationship among catalyst, product distribution and thermodynamics in catalytic pyrolysis. On the other hand, reasonable thermodynamic calculation system could be built according to the characteristics of product distribution. Finally, both the thermodynamic state of the product system and the effect of the

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Nomenclature

a_{il}	Number of atoms of the lth element in a mole of the ith species
b_l	Total moles of the lth element (mol)
G_t	Total Gibbs free energy of mixed system (kJ)
G_i^θ	Standard mole Gibbs free energy of component i (kJ/mol)
$\Delta G_{i,f}^\theta$	Standard mole generation Gibbs free energy of component i (kJ/mol)
n_i	Moles of component i (mol)
p	Total hydrocarbon pressure (Pa)
p^θ	Standard pressure (Pa)
T	Temperature (K)
Greek letters	
λ_i	Lagrange multiplier of the lth element
$\hat{\phi}_i$	Fugacity coefficient of component i

catalyst on product distribution can be evaluated. For example, when the yields of light olefins and conversion of feedstock are restricted in thermodynamics under certain operating conditions, catalyst development to improve yields of light olefins will be of no use. Here, it is more necessary to break the thermodynamic equilibrium via the adjustment of operating parameters. In brief, thermodynamic equilibrium is the limit of the system state. Studying thermodynamic equilibrium in catalytic pyrolysis has great practical significance in optimizing operating conditions and in pointing direction of catalyst development.

Stoichiometric and non-stoichiometric approaches are usually applied to thermodynamic equilibrium analysis [16]. Catalytic pyrolysis is a complex process, including such reactions as decomposition, polymerization, isomerization, hydrogen transfer, dehydrogenation, cyclization, aromatization and condensation [17]. Because of the complexity of the reaction system, non-stoichiometric approach, namely the Gibbs free energy minimization method, is more suitable. Tang et al. analyzed the thermodynamic characteristics of C7 hydrocarbons catalytic pyrolysis, and the results showed that the yields of propene and butene, but not the conversion of feedstock, were restricted by thermodynamic reaction conditions [18]. Compared with steam cracking, catalytic pyrolysis using molecular sieve catalysts could result in a different product distribution, but the yield of propene did not increase prominently. However, molecular sieve catalysts with shape selectivity could favor the yield of propene. Liu et al. investigated the thermodynamic equilibrium state of the C2–C5 olefins system with the Gibbs free energy minimization method, and the theoretical analysis was consistent to experimental study [19]. However, the thermodynamic equilibrium of catalytic pyrolysis reaction system are not deep and the systems being studied are simple. It is necessary to simplify the thermodynamic system reasonably due to the complexity of reaction process.

In this work, the thermodynamic equilibrium of olefin products distribution was studied using Gibbs free-energy minimization method with Aspen Plus software. The effects of reaction temperature and hydrocarbon pressure on equilibrium distribution of olefin systems were studied, the reaction performance of *n*-hexene catalytic pyrolysis and thermal pyrolysis was investigated, and then the function of both temperature and catalyst was analyzed. This research aims to provide theoretical guidance for light olefins production.

2. Thermodynamic equilibrium analysis method

2.1. Minimization of Gibbs free energy

Minimization of Gibbs free energy is a thermodynamic analysis method to study the thermodynamic state. According to the Gibbs criterion, chemical reaction is always in the direction of Gibbs free energy decrease spontaneously, then the system reaches a thermodynamic equilibrium state until $\Delta G = 0$. Therefore, the total Gibbs free energy of the system at certain temperature and pressure can be expressed by Eq. (1) [20,21].

$$G_t = \sum n_i \times \left[G_i^\theta + RTln\frac{p}{p^\theta} + RTln\hat{\phi}_i + RTln\frac{n_i}{\sum n_i} \right] \tag{1}$$

The fugacity coefficient in Eq. (1) is a parameter characterizing the deviation between the actual state and the ideal state. For the actual system, fugacity coefficient is related to equation of state (EOS) and mixing rule. For the ideal gaseous system, fugacity coefficient of a single pure component in a mixed system is equal to 1. According to the definition in thermodynamics, Gibbs free energy is a state function and its absolute value is unknown. When the standard for calculation is regulated, the specified value of Gibbs free energy can be obtained. Provided that Gibbs free energy of stable elementary substance is 0 in the standard state, mole Gibbs free energy of a pure compound at certain temperature should be standard Gibbs free energy change from the elementary substance to the compound at the same temperature, namely the standard generation Gibbs free energy of the compound $\Delta G_f{}^\theta$. Based on the above principle, minimization of total Gibbs free energy for the ideal system can be expressed by Eq. (2) [22].

$$\mathrm{min}G_t = \sum n_i \times \left[\Delta G_{i,f}^\theta + RTln\frac{p}{p^\theta} + RTln\frac{n_i}{\sum n_i} \right] \tag{2}$$

An optimization problem has been described in Eq. (2), in which the constraint is elemental balance. This problem can be also solved by Lagrange multipliers approach. The Lagrange function is performed as follows [23].

$$F = G_t + \sum_{l=1}^{L} \lambda_l \left(\sum_{i=1}^{N} a_{il} n_i - b_l \right) \tag{3}$$

The partial derivatives of Eq. (3) for every component n_i are set to 0 in order to get the extremum point.

$$\Delta G_{i,f}^\theta + RTln\frac{p}{p^\theta} + RTln\frac{n_i}{\sum n_i} + \sum_{l=1}^{L} \lambda_l a_{il} = 0 \tag{4}$$

Eq. (4) stands for $N + L$ equations, including unknown N component n_i and L Lagrange multipliers λ_l. It is obvious that the minimization of Gibbs free energy approach is in accord with Lagrange multipliers approach.

2.2. Thermodynamic equilibrium analysis in catalytic pyrolysis

Independent reactions occurring among components in catalytic pyrolysis are difficult to define, and it is difficult to study the thermodynamic equilibrium through chemical reactions. Minimization of Gibbs free energy method does not require to know the chemical reactions occurring among components, and the thermodynamic equilibrium can be analyzed if the components participating in the chemical reactions are specified according to product distribution. Cracking is the main reaction and light olefins are the main products in catalytic pyrolysis, so this study focuses on the thermodynamic equilibrium of light olefin products system. For example, in the catalytic pyrolysis of FCC naphtha for propene