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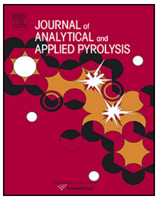

Experimental and modeling study of thermal and catalytic cracking of *n*-decane

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ABSTRACT

Catalytic cracking of *n*-decane over a platinum/lanthanum–alumina coated stainless steel tube is experimentally studied to obtain the product distributions and gas yield at a pressure of 1 atm and different temperatures 600, 650 and 700 °C. The results reveal that the higher the cracking temperature is, the higher the gas yield will be. A detailed micro-kinetic model for cracking of *n*-decane over a platinum/lanthanum–alumina catalyst is developed to simulate the gaseous product distribution and gas yield. In high temperature catalytic cracking systems, the interactions of gas-phase and surface reactions are very significant phenomena. Thus, the model contains a detailed gas-phase pyrolysis kinetic model along with a surface kinetic model for *n*-decane cracking over a platinum/alumina catalyst. The gas-phase pyrolysis kinetic model contains 304 species, 1104 reactions and the surface kinetic model contains 52 adsorbed chemical species and 218 reactions. The modeling results of the gaseous product distribution and gas yield are acceptable compared with experimental results. In order to evaluate the contribution of thermal cracking in catalytic cracking, simulation of thermal cracking of *n*-decane is performed by using the gas-phase pyrolysis kinetic model. The simulation results show that the contribution of thermal cracking in catalytic cracking is increasing with temperature increasing. This work provides insight at the molecular level for the kinetic process of *n*-decane cracking over a platinum/lanthanum–alumina catalyst.

1. Introduction

At high supersonic and hypersonic flight speeds, the temperature of the ram air taken on board is usually too high [1]. In order to solve this problem, endothermic hydrocarbon fuels on board are used as the primary coolant for thermal management, of which thermal and catalytic cracking of hydrocarbon fuels are common endothermic reactions for practical applications [1,2]. Heat sink capacity of hydrocarbon fuel plays an important role in the thermal management of supersonic and hypersonic vehicles, which is largely controlled by the ratio of olefins to *n*-paraffins produced during thermal or catalytic cracking [3]. Compared with thermal cracking, catalytic cracking generally can improve the heat sink capacity of endothermic hydrocarbon fuels. Thus, much attention has been paid to the catalytic cracking of endothermic hydrocarbon fuels [1–5].

The general catalysts for hydrocarbon cracking are zeolite catalysts, noble metal catalysts and so on. Owing to the high Brønsted acidity and shape selectivity, zeolites are used extensively for the cracking of alkanes to yield low-molecular-weight alkanes and alkenes in the processing of petroleum, and the involved mechanisms have been widely studied theoretically and experimentally [6–13]. Noble metals, such as Platinum (Pt), Palladium (Pd), and Rhodium (Rh) are used as catalysts in many heterogeneous catalytic reactions for its excellent activity, selectivity and stability [14]. Platinum, supported on Al_2O_3 or SiO_2, is one of the most valuable catalysts because of catalyzing a wide variety of hydrocarbon conversion reactions involving C—C and C—H bond activation and has been widely used in the catalytic cracking and reforming processes in industrial research [15–22].

A number of experimental studies have been performed on catalytic cracking of alkanes over Pt catalysts. Castaldi et al. [20] studied the cracking of JP-8 and JP-10 fuels over Pt/α-Al_2O_3 in a short contact-time reactor and found that the fuels can feasibly be converted to the desirable ethylene and hydrogen. Leylegian et al. [21,22] also used the short contact time reactor to investigate the cracking of logistical fuels (JP-7, JP-8, JP-10 and S-8) over a series

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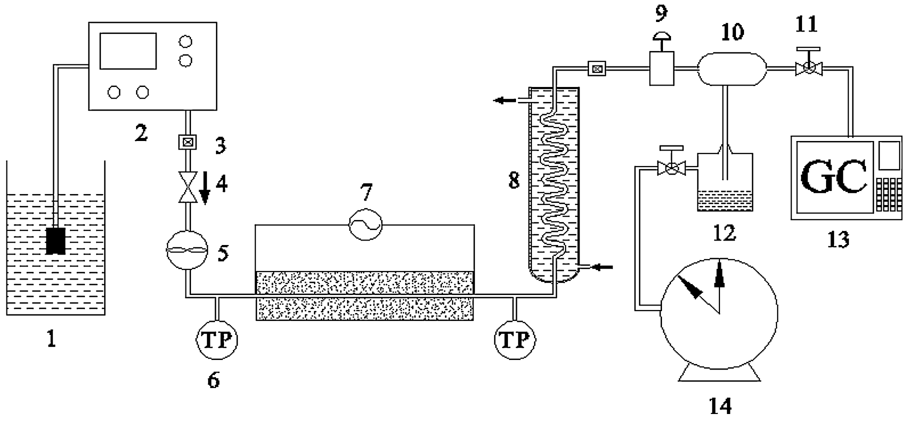

Fig. 1. Flow reactor device for catalytic cracking of *n*-decane.

of different catalysts (Pt/Al_2O_3, Rh/Al_2O_3 and zeolites) at pressures of 1–3 atm and 40–50 atm, temperatures of 650 and 750 °C. They concluded that the gaseous products shifted from hydrogen and ethylene formation at low pressures toward methane and ethane formation at high pressures. Brogan et al. [23] studied thermal and catalytic cracking of butane over Pt/Al_2O_3 and the product distribution identified by Raman spectroscopy showed that the catalytic cracking of butane yielded more methane and ethylene than those from thermal cracking.

Currently, extensive researches have been devoted to the modeling study of catalytic cracking of hydrocarbons over zeolite catalysts like HZSM-5 [3,6,9,13], such as the mechanistic modeling of the catalytic cracking of *n*-heptane [6], the micro-kinetic modeling of propane aromatization [9], the kinetic modeling of catalytic cracking of paraffinic surrogate [3] and so on. However, to our knowledge, the modeling study of catalytic cracking of hydrocarbons over Pt catalysts is still lacking. In order to understand the fundamental reaction mechanisms associated with hydrocarbon cracking reactions on Pt catalysts, first principle calculations are used widely, especially for low-molecular-weight hydrocarbons [24–31]. These research efforts provide insight at the molecular level for the chemistry involved in the catalytic cracking of linear hydrocarbons over Pt catalysts, which mainly focus on the elementary reaction dynamics over single-crystal metal surfaces. Actually, the catalysts used in catalytic process are more complex than single-crystal metal surfaces. Whereas, first principle calculations are of great help to construct a chemical kinetic model for catalytic cracking of alkanes over Pt catalysts to predict the product distribution [18].

A detailed mechanism for catalytic cracking of hydrocarbons usually contains a gas-phase reaction mechanism and a surface reaction mechanism, and this model has been widely adopted by previous studies [3,13,32]. As an approach, the surface reaction mechanism for catalytic cracking of alkanes over Pt catalysts can be extracted from the mechanism of catalytic partial oxidation of alkanes over Pt catalysts, and the gas-phase reaction mechanism can directly adopt the thermal cracking mechanism. Fortunately, detailed mechanisms for numerical simulation of catalytic partial oxidation of alkanes over Pt catalysts have been studied extensively, especially for catalytic partial oxidation of ethane [17,18]. Moreover, for most fuels, combustion is always accompanied by thermal cracking and the combustion mechanisms of hydrocarbon fuels are well studied [33–40]. Thus, the mechanism of thermal cracking is usually obtained from the combustion mechanism with oxygenic species and reactions being removed.

In the high temperature of catalytic cracking, thermal cracking usually occurs simultaneously [13]. The objective of this work is to investigate the mechanism of *n*-decane catalytic cracking over a platinum/lanthanum–alumina catalyst and evaluate the contribution of thermal cracking in the high temperature of catalytic cracking. The experiments are carried out in a stainless steel tube reactor with $Pt/La–Al_2O_3$ coated to obtain the product distribution and gas yield at 1 atm and different temperatures 600, 650 and 700 °C. A micro-kinetic model containing the gas-phase pyrolysis kinetic model along with a surface kinetic model is developed. The gas-phase pyrolysis kinetic model is used to predict the gas yield for thermal cracking, which is based on the core mechanism (C_0–C_4) [41,42]. Based on the mechanisms consist of elementary-like reactions, numerical studies are performed to predict the gaseous product distribution and gas yield for catalytic cracking using Chemkin-pro [43]. The present work provides insight into the chemistry involved in the cracking of *n*-decane over a $Pt/La–Al_2O_3$ catalyst at atmospheric pressure, which is significant for the further study under supercritical conditions.

2. Experimental methods

Alumina is prepared by peptizing method as described below. First, pseudo boehmite powder is dissolved in deionized water and $La(NO_3)_3$ solution, and then the sol (PH 4.5–5.5) is induced by addition of HNO_3 solution. The resulting sol is aged for 3 h and then added the polyethylene glycol (PEG) solution, dried at 100 °C and calcined for 4 h at 600 °C to produce the support materials $La–Al_2O_3$.

The Pt-loaded catalyst supported on $La–Al_2O_3$ is prepared by the method of incipient wetness impregnation using aqueous solution of chloroplatinic acid (the platinum loading corresponds to 0.7 wt%). The impregnated support is calcined in air at a temperature of 500 °C for 2 h and dried to obtain powered $Pt/La–Al_2O_3$ catalyst. The catalyst powder is subsequently ball-milled with deionized water and additive (La_2O_3), and then coated on the stainless steel tube (SS304) with an internal diameter of 0.2 cm and a length of 70 cm, following which the coated tube is dried at 110 °C and calcined for 2 h at 500 °C.

The cracking experiments are conducted in SS304 $Pt/La–Al_2O_3$ coated tube reactors at temperatures 600, 650 and 700 °C. In the present work, the tube length of 0 cm is defined as the inlet and 70 cm is defined as the outlet. The temperatures 600, 650 and 700 °C are the outlet temperature of the fuel. The experimental apparatus is shown in Fig. 1. Detailed descriptions for experimental procedure can be found elsewhere [44,45], and only a brief description is given here. The reactor is heated by direct current power and the temperature is measured by *K*-type thermocouples. Firstly, the feed is pumped at a flow rate of 90 ml/min with a high-performance liquid chromatography (HPLC) pump. The products at the outlet of the reactor are first cooled in the condenser and then flowed into a gas-liquid separator. The gaseous products are analyzed by