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Catalytic cracking of *n*-dodecane over HZSM-5 zeolite under supercritical conditions: Experiments and kinetics

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ABSTRACT

The catalytic cracking of *n*-dodecane over HZSM-5 zeolite catalyst was investigated at 400–450 °C under supercritical and subcritical pressures (0.1–4.0 MPa). The results show that both the activity of the catalyst and its stabilization towards deactivation decrease with increasing pressure, and the catalyst maintains substantially higher activity when feed rate exceeds 4.00 ml/min under supercritical conditions. A first-order Langmuir kinetic model with a novel decay function is developed for the supercritical catalytic cracking of hydrocarbon incorporating supercritical extraction effect on catalyst stability, which is satisfactory to describe the kinetic behaviors of catalytic cracking of supercritical *n*-dodecane. According to the estimated reaction rate and adsorption constant of *n*-dodecane on HZSM-5 at different temperature, the activation energy of 125.4 kJ/mol and adsorption heat 109.5 kJ/mol were calculated. An index of *CRSE* is proposed to define contribution ratio of supercritical extraction to the activity of the HZSM-5 catalyst in the developed kinetics model, and it is found that the *CRSE* increases with increasing hydrocarbon feed rates and decreasing catalytic activities, and reaches maximum value when the coke formation rate equals to the coke removal rate by supercritical hydrocarbon.

1. Introduction

As flight speeds of aircraft increase to supersonic and hypersonic regime, aerodynamic heat became such a crucial issue that jet fuels have to be utilized as the primary coolant, before injected into the combustion chamber, to remove waste heat from various aircraft subsystem and components, such as engine lubricating oil, environmental control system, electrical system, air frame, etc. (Edwards et al., 2006; Huang et al., 2002, 2004; Lang et al., 1995; Liu et al., 2008; Sicard et al., 2008; Sobel and Spadaccini, 1997; Wickham et al., 2008).

Generally, the liquid hydrocarbon fuels can offer the required cooling capacity (heat sink) by significant physical sensible heat as well as endothermic chemical reactions, such as thermal and catalytic cracking. In the cooling system of aircraft, the fuel is under high pressure (3.4–6.9 MPa) and high temperature (above 400 °C), corresponding to supercritical conditions of typical hydrocarbon fuels (Edwards and Zabarnick, 1993; Ervin et al., 1998). At such high temperature, the thermal cracking of hydrocarbons proceeds via a free radical chain mechanism. Yu and Eser (1997a, b, 1998a, b, 2000) investigated the thermal cracking of different type of model fuels, and reported the product distributions and corresponding kinetics. For example, in the thermal cracking of C_{10}–C_{14} *n*-alkanes the primary products were *n*-alkanes and 1-alkenes while the secondary products were *cis*- and *trans*-2-alkenes, normal and branched alkanes larger than the reactant. French researchers have also performed their program for scramjet thermal management through thermal cracking of model fuels (Daniau et al., 2005; Sicard et al., 2005). However, these investigations also show the following disadvantages of thermal cracking: (1) a significant conversion can only be obtained at high temperature due to the low cracking rate (e.g. 0.0453 h^{-1} for *n*-C_{12}) and high apparent activation energy (e.g. 251 kJ/mol for *n*-C_{12}) (Wickham et al., 2001); (2) maximum heat sink comes out at a specific conversion (e.g. 60% for *n*-hexadecane) since the selectivities of desired endothermic reactions change with conversion and cannot be controlled (Lander, 1971). Catalytic cracking of hydrocarbons fuels is another potential and attractive endothermic reaction for the cooling system of aircraft. Huang et al. (2002, 2004) performed the catalytic cracking of several jet fuels such as JP-7, JP-8+100 and JP-10 first in catalyst-coated tubes, and demonstrated that JP-7 and JP-8+100 cracking over inexpensive zeolite catalysts can provide substantial heat sink (3.41and 2.91 MJ/kg, respectively). Sobel and Spadaccini (1997) conducted the catalytic cracking of *n*-heptane and Norpar 12 fuels over inexpensive zeolite (SAPO-34 and SAPO-5) catalyst-coated tube reactor, and obtained high heat sink (approximate 3.93 MJ/kg) and attractive product selectivity

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(such as hydrogen, ethene and propene) with excellent combustion characteristics. Meng et al. (2010) prepared HZSM-5 zeolite coatings in stainless steel tubes by washcoating methods for the supercritical catalytic cracking of *n*-dodecane, and then investigated the effect of catalyst coating thickness on catalyst activity, deactivation of catalyst and adhesion strength. Sicard et al. (2008) compared the catalytic cracking of *n*-dodecane over HZSM-5 and HY zeolite with thermal cracking in a stirred batch reactor heated up to 425 °C under pressure up to 15 MPa, and found that at lower temperature (375–400 °C) the conversion was approximately one time higher for cracking over HZSM-5 catalyst than that for thermal cracking. Castaldi et al. (2006) showed that the cracking of JP-8 and JP-10 fuels over precious metal formulations (such as Pt/α-Al_2O_3) in a short contact-time reactor can feasibly convert the fuels to gaseous products, particularly the desirable ethene and hydrogen. Dardas and Moser studied the catalytic cracking of *n*-heptane over Y-type zeolite under supercritical and subcritical conditions, and observed the significant stabilization of the catalyst towards rapid deactivation even at relatively moderate pressure, which was explained by the extraction of coke by the superdense reaction fluid within the micro-pores of the catalyst (Dardas et al., 1996; Süer et al., 1996). In summary, the catalytic cracking of hydrocarbon fuels can provide substantial heat sink compared to thermal cracking. However, up until now all those works have not referred to the accurate kinetic model for catalytic cracking of the fuels, regardless of its importance in the design of active cooling structure and combustor using cracked fuels as power source.

Previously, much work have been done to develop kinetic models for catalytic cracking with various reaction mechanisms: simple kinetic model (Al-Sabawi and Lasa, 2009; Corma et al., 2004; Fierro et al., 2002), lumped kinetic model (Abul-Hamayel, 2003; Bollas et al., 2007; Chen et al., 2007; Delattre et al., 2001; Hagelberg et al., 2002; Meng et al., 2006; Quintana-Solo´rzano et al., 2008; Wang et al., 2005), and micro-kinetic model (Carabineiro et al., 2004; Dewachtere et al., 1999; Feng et al., 1993; Quintana-Solórzano et al., 2007; Sotelo-Boya´s and Froment, 2008; Surla et al., 2004). In addition, those kinetic models for catalytic cracking were generally attached with the catalyst deactivation due to such a rapid deactivation rate compared with the time scale of the process. As the first step of a series work towards developing an accurate kinetic model for catalytic cracking of hydrocarbons under supercritical conditions, an effort was made in this work to provide a simple kinetic model with a novel decay function incorporating the effect of supercritical extraction.

Early work showed that the kinetics of paraffin cracking under conditions favored by monomolecular cracking followed simple first-order kinetics (Wojciechowski, 1974). Haag et al. (1991) studied the catalytic cracking of hexane under limiting conditions, and showed that the kinetics of the two reaction mechanisms both follow a first-order rate law while in the intermediate regime the kinetics is quite complex. Kotrel et al. (2000) carried out the catalytic cracking of *n*-hexane over HZSM-5 and Hβ zeolites through *in situ* diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS), and elucidated the origin of the first-order kinetics under bimolecular conditions. However, those works did not consider the competing adsorption between the paraffin reactant and olefin products. Abbot and Wojciechowski (1987) first used the general Langmuir adsorption model to represent the competing adsorption into the catalytic cracking of *n*-paraffins on HY zeolite. Zhao et al. (1993) presented a chain mechanism model for the catalytic cracking of branched alkanes in the catalytic cracking of 2-methylpentane. Abbot and Wojciechowski further extended the adsorption kinetic model (Abbot and Wojciechowski, 1987) to a more complex one including a “bimolecular” or “chain” component of reaction, and pointed out that the simple one was sufficient for the catalytic cracking all linear alkanes (Groten and Wojciechowski, 1993). Corma and Ortega (2005) applied the Langmuir–Hinselwood adsorption model to the catalytic cracking of some pure hydrocarbons (an alkane, an alkene, a cycloalkane, and an aromatic), and determined the corresponding kinetic and adsorption parameters of reactants and products. However, the above mentioned researches were all conducted under ambient pressure condition, i.e., the effect of the supercritical reaction conditions was not taken into consideration.

For the supercritical reaction medium, the density and transport properties can be continuously pressure-tuned in the near-critical region to obtain unique fluid properties (e.g. gas-like transport properties, liquid-like solvent power and heat capacities) (Subramaniam, 2001), thus the catalyst activity maintenance due to the in situ extraction of coke compounds by the dense phase and effect of special diffusivity on the mass transport are the extensively discussed characteristic of supercritical catalytic reactions. The supercritical reaction media have been employed in isomerization of alkane (Bogdan et al., 2004) and olefin (Baptist-Nguyen and Subramaniam, 1992; Clark and Subramaniam, 1999; Ginosar and Subramaniam, 1995; Saim and Subramaniam, 1990, 1991; Subramaniam and McCoy, 1994; Subramaniam and McHugh, 1986; Tiltscher and Hofmann, 1987; Wang et al., 2009), Fischer-Tropsch synthesis (Lang et al., 1995; Subramaniam, 2001; Yokota and Fujimoto, 1991), disproportionation of ethylbenzene (Manos and Hofmann, 1991), transalkylation of diethylbenzene with benzene (Rodríguez et al., 2008), and regeneration of deactivated zeolite catalyst (Ginosar et al., 2004; Thompson et al., 2005). Generally, compared with conventional gas-phase processing, the supercritical catalysis may result in the following differences: (1) different product selectivity caused by change of reaction mechanism; (2) higher or lower reaction activity depending on the relative weight between coke extraction and transport limitation due to the dense phase reaction medium (Süer et al., 1997; Savage et al., 1995). Therefore, it is necessary to develop of a kinetic model for catalytic cracking under supercritical conditions considering the possible stabilization of catalyst deactivation and mechanism difference of catalytic cracking.

The objective of this work was to investigate the supercritical catalytic cracking of *n*-dodecane and to develop a simple kinetic model with a novel catalyst decay function incorporating the effect of supercritical extraction of coke precursor. The effect of operating pressure, temperature, catalyst loading and hydrocarbon flow rate on the catalytic cracking activity, catalyst decay and product selectivity, was also systematically studied. The kinetic parameters of developed model, such as activation energy and adsorption heat of *n*-dodecane on HZSM-5 zeolite under supercritical conditions, were regressed from the kinetic experimental data, and then used to simulate the contribution of supercritical extraction of coke precursor on the catalyst activity.

2. Experimental section

2.1. Materials

The *n*-dodecane (99%) from Sinopharm Chemical Reagent Co., Ltd. was used without further treatment, and its critical properties were listed in Table 1. Extruded HZSM-5 zeolite (Si/Al = 50) was obtained from Tianjin Nankai Catalyst Factory, China. Before the experiments, fresh catalyst was first crushed and sieved to 20–40 mesh, and then calcined at 500 °C for 4 h. The detailed properties of the HZSM-5 zeolite catalyst were listed in Table 2.