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吸热型碳氢燃料正癸烷热裂解机理、热沉及产物分布的理论研究

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Theoretical study on the mechanism, heat sink and product distribution for thermal decomposition of endothermic hydrocarbon fuel *n*-decane

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摘要 采用密度泛函理论(DFT)的B3LYP方法在6-311G(d,p)基组水平上对正癸烷裂解过程中涉及的反应物、产物及过渡态进行了几何构型优化和振动频率计算,运用B3LYP/aug-cc-pVTZ方法计算单点能并构建势能剖面图。利用TheRate程序包及Eckart校正模型计算了各反应速率常数k。采用统计热力学原理求得不同温度下的热容$C_{p,m}^{\theta}$及熵$S_{298 K}^{\theta}$,并通过设计等键反应获得了各物种的标准生成焓$\triangle_f H_{298 K}^{\theta}$。用Chemkin II程序模拟预测了产物分布,理论计算了热沉值,并讨论了温度、压力对产物分布和热沉的影响。结果表明,C-C键断裂过程是反应的初始步骤,且抽氢反应较β键断裂反应更易进行。裂解起始温度为500 ℃,反应主要发生在600~700 ℃,其主要产物为氢气、甲烷、乙烯、乙烷、丙烯和1,3-丁二烯,且产物分布随温度不同而变化。模拟计算获得正癸烷在温度600 ℃、压力2.5 MPa条件下的总热沉值为2.334 MJ/kg,对应的热裂解转化率为25.9%,该热沉值可以满足速率为5~6马赫数的飞行器的冷却要求。

关键词: 正癸烷   热裂解机理   速率常数   动力学模拟   热沉   产物分布

Abstract： The geometry optimizations and vibrational frequencies of reactions, products and transition states involved in pyrolysis of *n*-decane were performed using the hybrid method B3LYP with 6-311G (d,p) basis set based on density functional theory. The potential energy surfaces of *n*-decane were built by the B3LYP/aug-cc-pVTZ methods. The rate constants of all reactions with Eckart correction were calculated by the TheRate program package. The heat capacity and entropy ($C_{p,m}^{\theta}$ and $S_{298 K}^{\theta}$) at different temperatures were obtained by statistic thermodynamics. In order to calculate the standard formation enthalpy ($\triangle_f H_{298 K}^{\theta}$) for all species, isodesmic reactions were designed. The Chemkin II program was used to model the product distribution and heat sink. The effects of the temperature and pressure on the heat sink and product distribution were discussed. The results show that the C-C bond breaking process is the initial step of all reactions and H-abstraction reaction is easier to proceed than the β-scission reaction. The cracking initial temperature is 500 ℃ and the reactions mainly occur in the range of 600~700 ℃. The major products are hydrogen, methane, ethylene, ethane, propylene and 1,3-butadiene and the product distributions vary with temperatures. The total heat sink of *n*-decane is 2.334 MJ/kg at 600 ℃ and 2.5 MPa, with the conversions of 25.9%, which could meet the cooling requirement of aircrafts at 5~6 Mach number.

Key words: *n*-decane   mechanism of thermal decomposition   rate constant   kinetic modeling   heat sink   product distribution

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