

## 正辛烷热裂化和催化裂化生成甲烷反应机理

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### Mechanism of methane formation in thermal and catalytic cracking of *n*-octane

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**摘要** 采用脉冲微反装置, 在反应温度为550~650 °C, 低转化率(小于15%)下, 研究了正辛烷在石英砂和ZRP分子筛上的热裂化和催化裂化反应, 分析了甲烷的生成机理。结果表明, 正辛烷热裂化时, 乙烯、丙烯和正丁烯是初始产物, 甲烷由4种反应路径生成。当反应温度为600 °C时, 甲基自由基攻击碳链端部C-H键生成甲烷。中部C-H键脱氢形成的辛基自由基在端部C-C键断裂的活化能较高, 仅在高温下生成甲烷。正辛烷在ZRP分子筛上主要发生质子化裂化反应, 正构烷烃占有相当比重, 甲烷由质子化裂化步骤生成。热裂化与质子化裂化对甲烷贡献的对比可知, 当反应温度低于600 °C时, 甲烷由质子化裂化反应生成; 在高温下, 热裂化反应决定甲烷选择性。

**关键词:** 正辛烷 热裂化 催化裂化 甲烷 反应路径

**Abstract:** The thermal and catalytic cracking reactions of *n*-octane were carried out in a temperature range of 550~650 °C with low conversions ( $x < 15\%$ ) in a pulse micro-reactor over quartz and ZRP zeolite. Reaction mechanism of methane formation was analyzed. The results showed that ethylene, propylene and *n*-butylene were primary products and four paths contributed to methane formation in thermal cracking of *n*-octane. At 600 °C, dehydrogenation of terminal C-H bond in the chain attacked by methyl radical led to methane production. Due to higher activation energy of cleavage of terminal C-C bond in octyl radical formed via dehydrogenation of central C-C bond, only methane can form at higher temperature. Protolytic cracking was predominant with relatively remarkable yield of normal paraffin in catalytic cracking of *n*-octane over ZRP zeolite. Methane was produced by protolytic cracking route as well. By comparison of methane formation between thermal and protolytic cracking, it revealed that methane formed through protolytic cracking below 600 °C while thermal cracking dominated the selectivity of methane at higher reaction temperatures.

**Key words:** *n*-octane thermal cracking catalytic cracking methane reaction path

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