

程序升温条件下甲醇转化反应及流化床催化剂 SAPO-34 的积碳

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摘要 在流化床反应条件下进行了 SAPO-34 催化的甲醇转化的程序升温反应, 并分析了不同反应温度阶段的积碳产物. 结合对反应流出物的检测结果和热分析及质谱联用分析确定的积碳物种变化, 解释了程序升温反应过程中甲醇转化特殊的变化趋势. 在程序升温甲醇转化的积碳产物中, 除芳烃外, 还有一种饱和的多环烷烃积碳物种, 它的生成影响了烃池活性中心的形成并引起甲醇转化在低温反应阶段的失活. 甲基取代苯和甲基取代金刚烷是低温条件下 SAPO-34 催化的甲醇转化产生的主要积碳产物, 它们在升温过程中会向甲基取代萘以及稠环芳烃转变. 积碳物种的演变对应了甲醇转化在起始反应阶段 (300~325 °C) 的反应活性升高和此后 (325~350 °C) 的失活以及在更高温度阶段 (350~400 °C) 活性的恢复. 在反应性能评价和积碳分析基础上, 首次提出了一种与金刚烷类积碳物种生成相关的低温甲醇转化的失活机理.

关键词: 甲醇转化 积碳 程序升温反应 烃池机理 失活 金刚烷类化合物

Abstract: Temperature-programmed methanol conversion was performed in a microscale fluidized-bed reactor and the deposited coke species formed during the reaction at different temperature ranges was analyzed. By combining effluent detection and measurements of confined coke species evolution with thermal analysis and GC/MS, a particular phenomenon that appeared in the methanol conversion was explained. Among the coke products, besides aromatic coke species, a new kind of coke compounds, multi-ringed alkanes, mainly composed of methyladamantane hydrocarbons were found in the low temperature range. The generation and accommodation of these adamantane hydrocarbons on the SAPO-34 catalyst suppressed the successive formation of hydrocarbon pool species, polymethylbenzenes, as the reaction center of methanol conversion, and caused the low activity of the SAPO-34 catalyst at low reaction temperature. In the temperature range of 300 - 350 °C, methylbenzenes and methyladamantanes were the main coke materials and they were transformed to methyl-naphthalenes and polycyclic aromatics at higher temperature. The evolution of the confined coke compounds corresponded to the initial reactivity enhancement of the catalyst at 300 - 325 °C, the lowered activity at 325 - 350 °C, and recovered methanol conversion at 350 - 400 °C. Based on the coke analysis and catalytic performance tests, a new deactivation mechanism was proposed for the methanol conversion with the consideration of the abundant formation of adamantane hydrocarbons as the confined materials at low temperature.

Keywords: methanol conversion, coke deposition, temperature-programmed reaction, hydrocarbon pool mechanism, deactivation, adamantane hydrocarbon

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