

含镓ZSM-5分子筛的制备及其在甲醇芳构化反应中的催化性能

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Synthesis of gallium-containing ZSM-5 molecular sieves and their catalytic performance in methanol aromatization

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摘要 用三种不同方法(水热合成法、浸渍法、离子交换法)制备了含Ga的ZSM-5分子筛,采用XRD、SEM、FT-IR、NH₃-TPD、ICP、XPS和氮吸附等多种技术对其进行了表征,并考察了硅源、Ga含量和Ga的存在状态等对该分子筛结构、酸性及其在甲醇芳构化反应中催化性能的影响。结果表明,硅源种类(硅溶胶、白炭黑、正硅酸乙酯)显著影响分子筛的形貌、晶粒粒径大小及杂原子Ga的存在状态,进而决定其在甲醇制芳烃反应中的芳构化催化活性和稳定性。分子筛中Ga物种主要有骨架Ga、骨架外表面游离态(与分子筛无相互作用)的Ga₂O₃以及与分子筛有相互作用的非骨架Ga三种不同的存在状态。骨架Ga物种以四配位形式存在,提供酸性位点;非骨架Ga作为芳构化活性中心,主要起脱氢芳构化作用。适量的非骨架Ga中心与酸中心协调匹配能有效促进芳烃产物的生成。

关键词: 甲醇芳构化 ZSM-5分子筛 硅源 Ga物种 Ga含量

Abstract: Gallium species were introduced into ZSM-5 molecular sieves through three different measures, i.e. hydrothermal synthesis, impregnation, and ion exchange. The gallium-containing ZSM-5 molecular sieves were characterized by XRD, SEM, FT-IR, NH₃-TPD, ICP, XPS and N₂ sorption. The effects of silica source and the content and state of gallium species on their structure, acid property, and catalytic performance in the aromatization of methanol were investigated. The results indicated that the silica source (silica white, tetraethyl orthosilicate, and silica sol) exhibits significant effects on the crystal size and the state of gallium species, and thus influences the catalytic activity and stability of the gallium-containing ZSM-5 molecular sieves in methanol aromatization considerably. There are three kinds of gallium species, i.e. framework Ga, Ga₂O₃ species on the crystal surface, and non-framework Ga species with strong interaction with the framework oxygen. The framework gallium species in the tetrahedral structure offers the acidic sites of the molecular sieves, while the non-framework gallium acts as the active sites for methanol aromatization. The proper amounts of non-framework gallium species matched with the acid sites can promote the formation of aromatics.

Key words: methanol aromatization ZSM-5 molecular sieves silica source Ga species Ga content

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