I. Shape Selectivity of Small-pore Molecular Sieves for the Methanol-to-Olefins Reaction
And
II. Synthesis and Topotactic Transformation of Germanosilicate CIT-13

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ABSTRACT

This thesis presents research results from two projects involving molecular sieves. These investigations concern their synthesis, characterization and use as heterogeneous catalysis

In part I, the shape selectivity in the methanol-to-olefins (MTO) reaction is studied, and a new molecular sieve structure – MTO reaction selectivity relationship is developed. 17 zeolites and 13 phosphate-based molecular sieves having 14 selected cage-type/small-pore topologies (CHA, AFX, SFW, LEV, ERI, DDR, AEI, RTH, ITE, SAV, LTA, RHO, KFI, and UFI) are synthesized. The MTO reaction is performed using these catalysts at the same reaction conditions.

The reaction results lead to the conclusion that the molecular sieve cage topology is the most important structural factor that primarily determines the olefin product distribution. For example, AEI and CHA are synthesized with four different elemental compositions (zeolite, SAPO, CoAPO, MgAPO). Regardless of differences in elemental compositions, very similar product distribution patterns are observed in each of the isostructural groups of molecular sieves. Additionally, other isostructural pairs of SAPOs and zeolites show similar product distributions.

The reaction results from 14 topologies are grouped into four categories. Category I consists of CHA, AFX, SFW, and other GME-related topologies. Catalysts having these topologies show ethylene-to-propylene ratios close to one. Category II is a group of ERI and LEV which generate more ethylene than propylene. Category III is a group of DDR, AEI, RTH, ITE, and SAV which shows propylene selectivities higher than those of ethylene. Category IV is a group of LTA, RHO, KFI, and UFI which possess LTA-cages. These types of catalysts give high butylene selectivities.

The concept of cage-defining ring and its size is introduced as a reliable geometric indicator on the basis of a hypothetical ellipsoid cage model. The cage-defining ring size can be easily calculated from crystallographic information which is available online. A strong correlation is found between the cage-defining ring sizes and the four categories of reaction behavior.

In part II, an extra-large-pore germanosilicate molecular sieve CIT-13 with 14- and 10-ring pores is synthesized using monoquaternary, methylbenzylimidazolium-derivative OSDAs, and the synthesis conditions are optimized. Fluoride-free synthetic pathways for pure germanosilicate CIT-13 and isomorphous aluminum substitution in synthesis of aluminogermanosilicate CIT-13 are also described. The nature of disorder in the arrangement within CIT-13 framework is discussed, and its physicochemical properties compared to a UTL-type germanosilicate IM-12.

A comprehensive network of topotactic transformation and postsynthetic modification pathways starting from germanosilicate CIT-13 (Ge-CIT-13) is described. The moisture-mediated transformation of Ge-CIT-13 into another extra-large-pore CFI-type germanosilicate (Ge-CIT-5) is discovered, and the role of sorbed water in the transformation kinetics studied. The resultant Ge-CIT-5 is the first germanosilicate molecular sieve having a CFI topology, and the corresponding transformation is also the first inter-germanosilicate transformation occurring at room temperature. The microporosity of Ge-CIT-5 matched well with the reference pure-silica CIT-5 synthesized using the sparteine-type OSDA.

The acid-delamination processes of Ge-CIT-13 and Ge-CIT-5 are investigated. Ge-CIT-13 can be transformed into two new frameworks, CIT-14 with 12- and 8-ring pores and CIT-15 with 10-ring pores, on the basis of an ADOR-type topotactic transformation. The inverse sigma transformation of Ge-CIT-13 directly into CIT-14 is also firstly described. The conventional acid-delamination of Ge-CIT-13 does not yield Ge-CIT-5. However, the CIT-15-type material is obtained via the base-delamination pathway from Ge-CIT-5. The postsynthetic alumination of Ge-CIT-13 and Ge-CIT-5 is also achievable.

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