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多级孔道沸石分子筛的 合成、表征及催化应用

*Hierarchical Zeolite: Synthesis,
Characterization
and Catalytic Application*

方云明◇著



大连理工大学出版社 Dalian University of Technology Press

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序

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在我校研究生院的积极支持和配合下,出版社精心策划和编辑出版的“大连理工大学学术文库”即将付梓面市,该套丛书也获得了大连市政府的重点资助。第一批出版的是获得“全国百优博士论文”称号的6篇博士论文。这6篇论文体现了化工、土木、计算力学等几个专业的学术培养成果,有学术创新,反映出我校近几年博士生培养的水平。

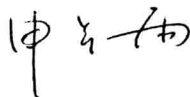
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博士生是我们国家学术发展最重要的力量,在某种程度上代表了国家学术发展的未来。因此,这套丛书的出版必然会有助于孵化我校未来的学术精英,有效推动我校学术队伍的快速成长,意义极其深远。

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大连理工大学校长



2013年10月

摘 要

多级孔道沸石分子筛是指具有额外介孔或大孔孔道的沸石分子筛,它同时具有沸石分子筛及介孔材料的优点,具有很高的酸性、水热稳定性及多级孔道结构,被学术界和工业界公认为是潜在的下一代催化材料,有望在重油裂化、大分子催化及精细化工等领域中发挥重要作用。它的合成、表征及催化应用是近十年来催化材料领域的研究热点。尽管已经开展了大量的探索性研究工作,但该方向仍未得到系统深入的研究,依然存在着诸多未解决的关键问题:如在理论层面,多级孔道沸石分子筛中介孔的形成机理及第二模板的作用仍不清楚;在合成技术层面,目前多级孔道沸石分子筛的合成成本过高,产品中介孔结构的可控性及介孔有序性较差;在催化研究层面,反应类型有待拓宽,同时迫切需要明确介孔对催化反应性能提升的具体机制等。

针对上述若干关键问题,书中发展了硬模板、软模板及无第二模板存在条件下的多级孔道沸石分子筛合成路线,详细研究了沸石分子筛在相应条件下的晶化过程,深入认识不同合成路线所蕴含的共同点,提出了多级孔道沸石分子筛晶化机理及介孔形成机理,同时考察了典型材料的催化性能。书中主要研究内容及结论如下:

1. 炭材料为第二模板合成多级孔道沸石分子筛:沸石晶化和介孔形成机理探讨

以纳米炭材料为硬模板的纳米复制路线是合成多级孔道沸石分子筛研究最为深入的方法。本书首先采用不同结构的纳米炭材料(炭气凝胶、炭黑及有序介孔炭材料 CMK-1 和 CMK-3)作为第二模板进行多级孔道纯硅 MFI 结构沸石分子筛的合成,并对最终产品和中间产物进行了详细的结构表征,考察炭材料结构对沸石

合成过程的影响。

结果表明,炭材料的存在很大程度上改变了沸石分子筛的晶化过程和最终产品。在所研究的4种炭材料中,以CMK-1为模板仅获得了有序的无定形二氧化硅,未能形成沸石结构;以CMK-3和炭黑为模板则合成了含无序介孔的纳米沸石团聚体,但介孔结构与模板结构并不具有对应关系;而以炭气凝胶为模板所合成的产品为含有晶体内介孔的沸石分子筛,介孔结构与炭材料模板结构具有良好的对应关系。对晶化过程的研究表明,除CMK-1以外,其他3种炭材料为模板均经历了无定形介孔二氧化硅的生成及溶解、纳米MFI沸石的形成及团聚重结晶等过程。

上述实验现象证实了炭材料的存在及结构很大程度上改变了沸石的晶化过程(成核速率、晶体生长速率及两者的比值)。一方面,炭材料的存在使沸石的成核和生长均受到了一定限制,在以CMK-1为模板时由于其介孔尺寸小于MFI沸石成核所需的2.8 nm,使沸石的成核被完全限制;另一方面,在可以成核的前提条件下,由于炭材料对沸石成核速率和晶体生长速率影响的不同,改变了成核速率与晶体生长速率比,导致了纳米沸石的大量生成,及纳米沸石在不同炭材料为模板时的不同团聚方式(模板内或模板外,有无后续营养及重结晶驱动力),决定了最终多级孔道沸石分子筛的类型。因此,在多级孔道沸石分子筛的合成中,炭材料最重要的作用是改变了沸石的晶化动力学,只有在特定的条件下才起到了造孔剂的作用。

书中进一步以具有不同炭纳米粒子尺寸的炭气凝胶为模板合成了晶体内介孔尺寸在10~100 nm内可控的沸石分子筛,并将沸石类型推广到ZSM-5、TS-1、BETA等。

本部分的研究工作阐明了炭材料为模板时多级孔道沸石分子筛的晶化和介孔形成机理及炭材料的作用,为后续研究工作奠定了理论基础,同时也得到介孔结构可控的多级孔道沸石分子筛,为进一步阐明介孔对催化性能影响提供基础。

2. 介孔形成机理的应用及进一步凝练:合成有序介孔沸石及无第二模板多级孔道沸石分子筛合成路线研究

合成有序介孔沸石是科学家长期努力的方向,也依然是多孔催化材料合成领域最具挑战性的课题之一。要合成有序介孔沸石,必须克服合成过程中介孔材料与沸石在合成条件上的竞争以及尺寸小于介孔孔壁的沸石纳米粒子的稳定和组装这两大关键难题。

书中尝试采用了在 SBA-15 中合成 CMK-5 后进行重结晶以及常规长链烷基阳离子表面活性剂及其硅烷化类似物混合物为模板两种方法进行有序介孔沸石的合成,通过控制 CMK-5 炭层厚度和两种表面活性剂的比例调节沸石晶化过程的受限制程度。结果表明,在适宜的条件下,两种方法均可成功合成有序介孔沸石,所得有序介孔沸石具有很好的水热稳定性,产品经过 120 h 沸水处理及在水蒸气条件下 850 °C 焙烧 4 h 后仍能保持所有的结构特征。晶化过程的研究表明,两种合成路线中有序介孔沸石的形成均经历了无定形有序介孔二氧化硅的生成、初始二氧化硅相的溶解、沸石的成核及晶化等过程。成功合成的关键是在合成过程中对沸石的生长进行一定的限制,使沸石分子筛成核、生长与介孔相生长保持匹配。这也是最先报道的通过实验证明有序介孔沸石存在的方法。另一方面,所合成的有序介孔沸石的介孔范围是炭材料模板法难以合成的小介孔尺寸,可望在一些催化反应中发挥重要作用。

针对书中所发现的第二模板可能并不是多级孔道沸石分子筛合成的必需条件,以及在以噻吩类含硫模型化合物的催化氧化反应为例证明具有介孔的纳米沸石团聚体确实具有比常规沸石更好的催化性能的基础上,采用极浓体系及添加成核促进剂的方式调控 ZSM-12 和 ZSM-5 的晶化动力学,成功地在没有第二模板存在的条件下通过纳米沸石的原位自组装配合成了相应的纳米沸石团聚体。这一研究结果使多级孔道沸石分子筛的合成成本有望降低到与常规沸石相当甚至更低的水平,克服多级孔道沸石分子筛大规

模应用的最大障碍。

综合硬模板、软模板及无第二模板存在条件下的晶化过程可以发现,多级孔道沸石分子筛经历了基于颗粒团聚的沸石生长机理,是沸石的晶化过程在特定的条件下终止而生成的动力学控制产物,而介孔的形成并不一定需要第二模板的参与。这一结论揭示了多级孔道沸石分子筛的晶化和介孔形成机理,可为以后的研究工作提供相应的理论指导。

3. 多级孔道沸石分子筛的催化作用:2-甲基萘选择甲基化

多级孔道沸石分子筛已被证明在大分子催化裂化等受扩散限制的反应中具有比常规沸石分子筛更好的催化性能。书中以 2-甲基萘选择甲基化合成 2,6-二甲基萘反应为例,证明多级孔道沸石分子筛在改善扩散性能的同时,还能保持其择形性。

在 2-甲基萘选择甲基化反应中,2,6-二甲基萘相对于 2,7-二甲基萘的选择生成以及 2,6-二甲基萘选择性与 2-甲基萘转化率之间的矛盾是需要克服的两个主要困难。书中首先采用量子化学计算纠正了广泛认同的 2,6-二甲基萘是所有二甲基萘分子中尺寸最小的异构体的观点,揭示了 2,6-二甲基萘相对于 2,7-二甲基萘的选择性难以提高的原因:尽管从本征的化学反应性上看 2,6-二甲基萘比 2,7-二甲基萘更有利于生成,但 2,6-二甲基萘的分子尺寸要略大于 2,7-二甲基萘。因此沸石分子筛的择形作用必须控制在合适程度,也即避免 α 位取代的发生。以此为指导研究了 Zr 同晶取代的 ZSM-5 作为这一催化体系的催化剂,取得良好效果。

书中进一步以有序介孔 ZSM-5 沸石(OMZ-1)为母体经 Zr 同晶取代后作为这一催化反应的催化剂,结果表明有序介孔 ZSM-5 沸石为母体的催化剂可获得目前文献中报道的 ZSM-5 系列沸石中最高的 2,6-二甲基萘的收率(18%),远高于常规 ZSM-5(5%)。这一结果证明了本书的设想,有望采用多级孔道沸石分子筛克服一系列择形催化反应中转化率与选择性间的矛盾。

Abstract

Hierarchical zeolite, novel zeolite with additional mesopore system besides the common micropore system, has advantages of zeolite (high thermal, hydrothermal stability and ordered microposity) and ordered mesoporous materials (large mesopore structure) simultaneity. The novel structure features make it highly desirable in catalysis and adsorption, especially in bulk molecule processes such as heavy oil catalytic cracking and fine chemical synthesis. A lot of exploring research works on the synthesis, characterization and catalytic performance of hierarchical zeolite have been carried out in the past decades. However, a systematic and deep investigation is highly needed to bring hierarchical zeolite into practical applications since there are a lot of unsolved fundamental and technical questions in the synthesis and application of hierarchical zeolite such as crystallization and mesopore formation mechanism, control of mesopore structure and cost effective synthesis of hierarchical zeolite.

In this book, in order to overcome above mentioned questions in hierarchical zeolite synthesis, a systematic research work on this topic was carried out. Hierarchical zeolite synthesis methods based on hard and soft secondary template as well as without secondary template were successfully developed, crystallization process in these synthesis methods were carefully analyzed to understand the crystallization and mesopore formation mechanism

of hierarchical zeolite, catalytic performance of typical materials was also investigated. The major contributions of this work are as following:

1. Hierarchical zeolite synthesized with carbon nanomaterial as template; the primary understanding of zeolite crystallization and mesopore formation mechanism

Nanocasting method with carbon nanomaterial as hard template is the most discussed method in literatures, hence this method was used as the starting point in the present work. Various carbon materials with different structure properties (carbon aerogel, carbon black and ordered mesoporous carbon material CMK-1 and CMK-3) were used as secondary template for hierarchical zeolite synthesis. The final product and materials obtained with different crystallization time were carefully characterized to understand the influence of carbon template structure on zeolite crystallization.

The results indicate that the structure of carbon materials has large influence on zeolite crystallization and the structure of zeolite product can be controlled by varying structure of carbon template. Zeolite can only be synthesized when the pore size of carbon template was large enough to allow the nucleation of zeolite, when CMK-1 was used as secondary template, only ordered mesoporous amorphous silica was obtained. Zeolite with intracrystalline mesopore system can be synthesized with ambient drying carbon aerogel as template without any control on crystallization conditions. The structure of so called mesoporous zeolite single crystal successfully cast the nanostructure of carbon aerogel template. By changing the structure of carbon aerogel through controlling the catalyst concentration during synthesis,

zeolites with tunable intracrystalline nanoporosity over larger range (10 nm-100 nm) were successfully synthesized. Hierarchical ZSM-5, TS-1 and BETA zeolite can also be synthesized. With carbon material as template, mesoporous aggregate of zeolite nanocrystals is often formed as product or intermediate phase for mesoporous zeolite single crystal synthesis, determining on the structure of carbon template, the structure of zeolite nanocrystals has no obvious relationship with carbon template.

Based on above experimental results, it can be summarized that the general effect of carbon material during zeolite synthesis was to affect the crystallization kinetics such as nucleation rate, crystal growth rate and the ratio of them, and not always act as pore former for hierarchical zeolite synthesis. A secondary template such as carbon template is not strictly needed in the synthesis of mesoporous aggregate of zeolite nanocrystals. These findings are the guideline of the following research work.

2. Application and further refine of zeolite crystallization and mesopore formation mechanism; synthesis of ordered mesoporous zeolite and secondary template free synthesis of hierarchical zeolite

Synthesis of ordered mesoporous zeolite was an objective of scientists in this area for long time, but is still one of the most challenge projects in porous materials synthesis area. Two challenges, the competitive formation of zeolite and mesoporous materials as well as the stabilization and assemble of zeolite nanocrystals with size can be accommodated in the wall of ordered mesoporous materials, must be solved.

Two methods, recrystallization of SBA-15 filled with in-situ formed CMK-5 and zeolite synthesis with mixture of common

cationic surfactant and its silylated analogue as secondary template, have been tried in this part. The confine degree of zeolite synthesis was carefully adjusted by controlling the carbon thickness of CMK-5 and the molar ratio between common cationic surfactant and its silylated analogue. Ordered mesoporous zeolite was successfully synthesized in both methods under certain conditions. As-synthesized ordered mesoporous zeolites with both two methods have very high thermal and hydrothermal stability, which are stable after treatment in steam at 850 °C for 4 h or refluxing in boiling water for 120 h. Carefully monitor of the crystallization process of ordered mesoporous zeolite indicated that the formation process of ordered mesoporous zeolite in the two synthesis methods was very similar, which is, the formation and dissolving of initial amorphous mesopore phase, zeolite nucleation and the formation of ordered mesoporous zeolite. In both synthesis routes, the confine effect of secondary template on zeolite growth is needed and should be controlled in a certain degree. Ordered mesoporous zeolite can only be synthesized when a good match between zeolite growth kinetic and ordered mesopore structure formation is reached. This is the first time that a real ordered mesoporous zeolite was synthesized and reported. Inspired by the discovery that secondary template was possibly not strictly needed for the hierarchical zeolite synthesis in the first part, synthesis of hierarchical zeolite without secondary template was also tried in this part. We first proved that mesoporous zeolite aggregate actually show better performance in bulky molecular containing reaction, for instance, catalytic oxidative desulfurization. Hierarchical TS-1 synthesized with CMK-3 as template show improved catalytic performance for

Abstract

thiophene removing compared with common TS-1 and was able to catalytic oxidation remove of large sulfur containing molecular such as DBT. Then mesoporous aggregate of ZSM-12 nanocrystals and ZSM-5 nanocrystals with single crystal like morphology were successfully synthesized without secondary template through in-situ assemble of zeolite nanocrystals under supersaturated solution and the existence of nucleation promoter, respectively. This synthesis route allow the synthesis cost of hierarchical zeolite lower down to a level similar or even cheaper than common zeolite thus possibly overcome the major hindrance of large scale application of hierarchical zeolite.

It was found that hierarchical zeolite generally crystallized through a nanoparticles based aggregation formation mechanism after carefully comparing the formation process of mesoporous zeolite in different routes. Hierarchical zeolite was generally kinetically favored product at the given condition and secondary template is not a prerequisite for hierarchical zeolite synthesis. A general crystallization map of hierarchical zeolite was given in chapter 6. This result can be used as guideline for the future hierarchical zeolite synthesis.

3. Catalytic application of hierarchical zeolite: selective methylation of 2-methylnaphthalene with methanol

Hierarchical zeolite has been found to show better catalytic performance in diffusion limited reactions such as large molecular cracking. In this part, selective methylation of 2-methylnaphthalene with methanol was selected as model reaction to demonstrate that hierarchical zeolite can retain its shape-selectivity together with improved diffusion properties.

In this reaction, selective formation of 2,6-DMN other than

2,7-DMN and the contradiction between 2,6-DMN selectivity and 2-MN conversion are the two main difficulties. Density functional theory was first used in this part to correct a general consideration that 2,6-DMN is the smallest isomer in all DMN isomers and disclose the root of difficulty in the improvement of ratio between 2,6-DMN and 2,7-DMN: though 2,6-DMN is intrinsic chemical reactivity more favored product than 2,7-DMN, it is slightly bulkier than 2,7-DMN. We thus point out that only synergistic effect of proper zeolite pore size and weak acid can result in high 2,6-DMN selectivity. Zr modified ZSM-5 with good catalytic performance was developed according to above principles.

Ordered mesoporous ZSM-5, after modified with Zr, was used as catalyst for this reaction. Ordered mesoporous ZSM-5 (OMZ-1) based catalyst show better catalytic performance on this reaction than ZSM-5 based catalyst concerning on 2-MN conversion, 2,6-DMN/2,7-DMN ratio and catalyst stability. Highest 2,6-DMN yield (18%) up to date was obtained over Zr/ordered mesoporous ZSM-5 (OMZ-1) as catalyst, which is much higher than ZSM-5 based catalyst (5%). This result proved that hierarchical zeolite can combine efficient mass transfer together with shape-selectivity, thus have potential to apply in other shape-selective catalytic reactions.