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高岭土的低聚态化处理及其应用——沸石与硅铝气
凝胶的合成及表征

Depolymerization and application of kaolin —— Synthesis
and characterization of zeolites and silica - alumina aerogel
from kaolin

王 景 泉

指导教师姓名: 宓锦校 教授

专业 名称: 材料学

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**Depolymerization and application of kaolin —— Synthesis
and characterization of zeolites and silica - alumina aerogel**



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Fulfillment of the Requirement for the Doctor Degree of
Philosophy

By

Wang Jing-quan

Directed by Prof. **Mi Jin-Xiao**

**Department of Materials Science and Engineering, College
of Materials, Xiamen University**

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摘要

所谓高岭土是一种以高岭石族粘土矿物为主的非金属矿产，它广泛应用于造纸、陶瓷、耐火材料、医药、化工，尤其是石油化工等领域。高岭石是地表最常见的粘土矿物之一，其理想化学式为 $\text{Al}_2[\text{Si}_2\text{O}_5](\text{OH})_4$ ，晶体结构是由铝氧二八面体层(O)和硅氧四面体层(T)按 TO1:1 排列而成，因氧、硅、铝的丰度位于地壳的前三位，因此是廉价合成铝硅酸盐沸石的理想矿物原料。但是晶态的高岭石具有极高的化学稳定性，无法直接用于沸石合成。所以传统的生产工艺在高岭土精矿用于合成沸石之前必须经 700~900 °C 高温煅烧，将其转化为无定形的偏高岭土，以消除高岭土的化学稳定性。但是煅烧工艺需要消耗大量燃料，能耗高、污染重，与低碳经济和绿色环保的趋势背道而驰。此外，高岭土精矿中所残存的杂质矿物，如石英和云母，会严重影响沸石的产品质量。本文旨在开发一种新的高岭土活化新工艺，对高岭土进行低聚化处理，将高岭土转化为不依赖于原料的活性硅铝低聚态物质，并应用于合成沸石等铝硅酸盐产品。

从本质上讲，煅烧活化高岭土是将高岭石中六配位的 Al^{VI} 部分歧化反应为五配位 Al^{V} 和四配位的 Al^{IV} 。 Al^{V} 和 Al^{IV} 具有更高的反应活性， Al^{V} 和 Al^{IV} 可以通过 H^+ 的攻击断裂 Al-O-Si 键转化为高活性 Al^{IV} 并脱离原聚集态。本论文发明了一种低温（160~240 °C）碱热活化处理方法，可将高岭石中 Al^{VI} 全部转化为 Al^{IV} ，再进行酸性解聚，并通过对处理条件(体系浓度、温度和时间等)的优化，得到低聚态的高岭土酸解液，并以此为原料合成了各种沸石分子筛。通过 XRD、NMR 等分析表征手段对高岭土的解聚机理进行了深入的探讨。利用该方法合成沸石分子筛无需煅烧活化高岭土，大大降低了能耗，并可以去除高岭土内的石英和云母或将其转化为合成原料。此外，该方法获得的产品较传统煅烧方法具有均一的粒径和形貌，更高的白度和离子交换能力。

当高 Si/Al 比时，由于铝氧四面体 $[\text{AlO}_4]$ 被硅氧四面体 $[\text{SiO}_4]$ 紧密包围，高稳定性的硅氧四面体 $[\text{SiO}_4]$ 阻止了 H^+ 对 Al^{IV} 的攻击，最终导致后续酸性解聚反应的失败。本论文对上述低温（160~240 °C）碱热活化处理工艺又进行了进一步优化，不仅可将高岭石中 Al^{VI} 全部转化为 Al^{IV} ，同时还可避免四配位的铝氧四面体 $[\text{AlO}_4]$

被硅氧四面体[SiO₄]紧密包围，即避免不溶硅铝酸盐在活化过程中出现，解决了对高岭土和石英共存体系低聚化处理中的关键问题。在此基础上通过优化探索实验条件分别合成了纳米级的Y型沸石、丝光沸石、ZSM-5沸石和SAPO-34沸石等产品，为最终实现高岭土原矿直接合成沸石提供了实验基础。

上述高岭土低聚化处理关键性问题的解决，为克服硅、铝组分对来源的依赖，将高岭土应用于具有高附加值的领域提供了可能，本文首次以高岭土为原料成功合成出硅铝气凝胶。硅铝气凝胶材料具有极低的密度和超高的比表面积，是典型的多孔材料，极佳的催化剂载体和保温材料。高岭土成分与硅铝气凝胶成分相似但是却无法作为硅铝气凝胶的合成原料。高岭土经过煅烧后，其中高岭石的晶体结构虽然被破坏，但是其中的氧化硅和氧化铝依然保持高聚态，只有激烈矿化条件才能完成硅铝的解离和重排。而高岭土酸解液中的硅铝元素以低聚态的形式存在，这样就可以适用于制备合成条件温和的功能材料。所以，本研究首次提供了一种利用廉价高岭土替代昂贵化学试剂为原料合成氧化硅/氧化铝气凝胶的方法。将碱热活化高岭土经盐酸解理得高岭土酸解液，将其老化成胶，经溶剂置换得到醇凝胶，经改性，骨架强化，常压干燥得到氧化硅/氧化铝气凝胶。

关键词: 高岭土、低聚化处理、沸石分子筛、硅铝气凝胶

Abstract

Kaolin is non-metallic minerals of clay mineral and its main component is kaolinite, which are widely used in papermaking, ceramics, refractories, pharmaceutical, chemical, petrochemical and other fields. Kaolinite possesses a 1:1 layer structure constructed of $[\text{AlO}_6]$ octahedral and $[\text{SiO}_4]$ tetrahedral sheets, which is the preferable natural material for its low cost and wide availability for synthesizing aluminosilicate zeolites. However, crystalline kaolinite has high chemical inertness, and cannot be utilized for synthesizing zeolites directly. So prior to application for the synthesis of zeolites, kaolinite has to be calcined at high temperatures (700 ~ 900 °C) to reduce its chemical resistance by converting to amorphous metakaolin. Moreover, the calcined metakaolin from natural kaolin inherently contains impurity minerals, e.g. quartz and muscovite that adversely affect the qualities of zeolites products.

During calcination conversion of kaolin to metakaolin the hexa-coordinated Al^{VI} in the former disproportionate to form mixed tetra-coordinated Al^{IV} and penta-coordinated Al^{V} , which are soluble in acid solutions. During the depolymerization of aluminosilicates containing tetra-coordinated Al^{IV} , Al^{3+} is released by breaking Al–O–Si bonds after H^+ ion attacking. Low temperature hydrothermal alkaline activation (160 ~ 240 °C) were employed in this paper to turn Al^{VI} into Al^{IV} completely. Through optimizing series of acid depolymerization conditions, the depolymerized kaolin was utilized to synthesize various zeolites as raw materials. The primary advantage of this route is that the impurity minerals such as muscovite and quartz in the kaolin raw material can be eliminated or transformed to the chemical components of the target products. In addition, the zeolite A product from this new route has more uniform particle sizes and morphologies, higher brightness, and enhanced cation-exchange capacity than its counterpart from the conventional calcination technique.

When the system possesses a high Si/Al, the $[\text{AlO}_4]$ tetrahedron is tightly trapped

among $[\text{SiO}_4]$ tetrahedra, the stable $[\text{SiO}_4]$ tetrahedra would prevent the tetra-coordinated Al^{IV} being attacked by H^+ ions during the depolymerization processes. The addition of quartz in this system must aggravate this situation, so the main challenge for depolymerization of kaolin and quartz is to avoid the formation of acid-insoluble aluminosilicates during the activation process. On this basis, after exploring and optimizing experimental parameters, nanoscale Y-type zeolite, mordenite, zeolite ZSM-5 and zeolite SAPO-34 were synthesized and providing a foundation for synthetic zeolite from kaolin ore immediately.

Depolymerization of kaolin solved the key issues to overcome the dependence of silicon and aluminum component on raw materials resources and make it possible for kaolin to be applied to of a high value-added field. This is the first successful synthesis of a silica-alumina feedstock gas gel. Silica-alumina aerogel material owns an extremely low density and high specific surface area, which is a typical porous material, excellent catalyst carrier and thermal insulation material. The composition of kaolin is similar to the silica-alumina aerogel but kaolin can't be utilized as synthetic raw material for silica-alumina aerogel. After calcined, the crystal structure of kaolin is damaged, but the silica and alumina are still high polymerization, so the cleavage and rearrangement of silica and alumina are only occurred in fierce mineralization conditions. And the silica and alumina in acid kaolin solution are lowly polymerization, so it can be applied to produc functional materials in mild synthetic conditions. Therefore, our work firstly opens a new way for the synthesis of silica-alumina aerogel, using low-cost natural kaolin in comparison with the conventional technique with expensive chemical reagents. Hydrothermal alkali activated kaolin was dissolving and cleavage in acid solution, then aging to hydrogel, after solvent replacement, alcogel was obtained, silica-alumina aerogel obtained finally by modification, skeleton reinforcement and atmospheric drying.

Key words: Kaolin; Zeolite; Silica-alumina aerogel

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