

学位論文の要旨

学位論文題目： Green synthesis process for catalytic zeolite materials

(ゼオライト触媒材料のグリーン合成)

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Zeolite was first discovered in 1756. Axel Fredrik Cronstedt, a Swedish mineralogist, found that a type of natural aluminate silicate ore will boil when burning, so it was named "zeolite" (Swedish zeolites). Zeolites can be divided into natural zeolite and artificial zeolite. More than 80 kinds of natural zeolite have been found all over the world, among which clinoptilolite, mordenite, chabazite, erionite, and analcime are the most common. Clinoptilolite and mordenite have been widely used. Zeolite minerals belong to different crystal systems, with most crystals appearing in fibrous, hairy, or columnar shapes. The general chemical formula of zeolite is: $A_m B_p O_{2p} \cdot n H_2 O$, the structural formula is $A_{(x/p)} [(AlO_2)_x (SiO_2)_y] \cdot n (H_2 O)$ where A is cations such as Ca, Na, K, Ba, Sr, B is Al and Si, p is the valence of cations, m is the number of cations, n is the number of water molecules, x is the number of Al atoms, y is the number of Si atoms, (y/x) is usually between 1 and 5, and (x+y) is the number of tetrahedrons in the unit cell.

Afterwards, people's research on zeolite continued to deepen. In 1932, McBain proposed the concept of "molecular sieve". A classic porous material that can screen substances at the molecular level. Up to now, there are over 200 artificially synthesized zeolites included in the zeolite data basement. Zeolite materials have good ion exchange properties, adsorption and separation properties, thermal stability, chemical reactivity, reversible dehydration, conductivity, etc. It is widely used in fields such as petrochemical, environmental, and gas separation. Zeolites are often used as catalytic carrier materials in the field of C1 chemistry. Because zeolites have unique acid centers that enable secondary reactions such as cracking, polymerization, and isomerization of products. At the same time, the selectivity effect of the pores in

zeolites can effectively screen the target product, which can regulate the selectivity of C1 products, thereby achieving the goal of high selectivity and high yield of products.

The development process of zeolite has been going on for a long time now. The commonly used methods of small-scale synthesis in laboratory include solvothermal method (hydrothermal method), dry gel method, ultrasonic synthesis and microwave synthesis. The commonly used large-scale method in industry is solvothermal method, which uses liquids such as water and ethanol as solvents to industrially synthesize zeolite under high temperature and pressure conditions. Although this method can achieve advantages such as good product dispersion and uniform morphology. The disadvantage is also obvious, as a large amount of alkaline wastewater is generated during the product purification process, and there is a potential explosion hazard during the production process due to high temperature and pressure. Therefore, how to produce zeolite materials in a green and safe manner is a hot research topic for many scientists.

We were inspired by Chongqing Hot Pot. Oil sealant above the liquid phase layer, which can isolate the external environment and reduce material exchange. In the chapter 1, we used the liquid sealant method to synthesize zeolite under atmospheric pressure. The results showed that LTA (NaA), MFI, FAU, and BEA zeolites could be successfully synthesized under atmospheric pressure conditions of 90-120 °C. Among them, we used NaA zeolite as a model to explore the conditions of crystallization temperature, crystallization time, type of liquid sealant solution, weight of liquid sealant solution, weight loss, and template in detail. The zeolite was characterized and analyzed by XRD, SEM, TEM, BET, NMR, and UV-Raman, and compared with the parameters of NaA zeolite synthesized by hydrothermal method. The results indicate that the optimal conditions for the synthesis of NaA zeolite are 120 °C and 4 hours.

Due to the severe limitations of temperature and test tube space caused by the liquid sealant method, in order to further optimize the process of synthesizing zeolite at atmospheric pressure, we focused on designing a reflux device that can synthesize zeolite at atmospheric pressure in chapter 2. We explore the synthesis conditions using NaA zeolite as a model. This device can use a reflux device to reduce liquid

evaporation and consumption while maintaining ambient pressure and high temperature. The original liquid sealant method for atmospheric pressure synthesis can only be used for small-scale static synthesis of zeolite in test tubes. As a comparison, the reflux synthesis device can perform large-scale dynamic synthesis. Under dynamic crystallization, the crystallization periods can be shortened, thereby reducing energy consumption.

Solvent-free synthesis method is a green synthesis process of zeolite. During the synthesis process, zeolite can be obtained through simple grinding of raw materials and high-temperature crystallization without adding any solvents. This method can reduce wastewater discharge due to the lack of solvent addition. In chapter 3, we take Silicalite-1 zeolite as an example and use a solvent-free method to rapidly synthesize submicron sized zeolites. We focused on exploring conditions such as crystallization temperature, crystallization time, and raw material ratio. The Silicalite-1 zeolite was characterized and analyzed by XRD, SEM, BET, and UV-Raman. The results indicate that the crystallization of Silicalite-1 zeolite can be successfully synthesized at 180 °C for 45 minutes. In addition, replacing the template with tetrabutylammonium hydroxide (TBAOH) and 1,6-hexanediamine can achieve rapid synthesis of Silicalite-2 and ZSM-22 zeolite, respectively. This process not only reduces the discharge of wastewater, but also greatly shortens the crystallization time, thereby reducing energy consumption.

【審査結果要旨】

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当学位審査委員会は本論文を詳細に審査し、かつ論文審査会を令和5年8月9日公開で開催し、その発表と質疑応答について審査した。その審査結果を下記のようにまとめる。

ゼオライトは多孔質固体酸触媒もしくは固体塩基触媒として工業的に広く使われている。その製造方法は高価な有機アミンなどのテンプレート剤と大量な水を使い、高温高压水熱合成条件下において、長時間を経て合成されることである。大規模均質合成が困難で、工業廃水も大量に出す。本研究はこれらの現行問題の解決を目指し、簡便かつ温和な快速無水合成方法を開発した。

本論文は緒言、第一章、第二章、第三章、まとめから構成される。緒言はゼオライト合成の最新動向に関する紹介である。

第一章はシリコンオイルなどのシール剤を生かし、常圧、90°C~120°C程度の温度で、LTA(NaA)、MFI、FAU、BETAなど各汎用ゼオライトの簡便製造方法を開発した。新方法の合成条件の最適化、得られた製品の性能に関する詳細な追跡・構造解析を行い、そのメカニズムを明らかにした。

第二章は第一章の結果を踏まえ、より大規模な製造方法として、上記ゼオライト合成設備に還流ユニットを投入した方法を開発した。実験的に最適な操業条件を定め、理論的にも解析し、このような流動的な還流装置を付加することで、合成試薬を節約でき、合成時間も大幅に短縮でき、コストの低い大規模ゼオライト合成方法を確立した。

第三章はゼオライトの無溶媒合成方法を報告した。Silicalite-1ゼオライトを代表例として、各試薬をメノウ乳鉢中混合し、すりつぶしてからオートクレーブに入れて無機合成を施した。得られたゼオライト製品は従来の古典合成法のものと同じ品質であった。各種分光解析で解明した結果、投入試薬に含まれる結晶水は従来法の仕込まれた水相と同じ役割を果たし、過剰な水の仕込みが不要になったと結論した。

最後に上記内容のまとめも記載してある。

上記の内容は国際学術専門誌に原著論文3報として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、無機化学、触媒化学諸分野において、学術的価値のある知見を与えたと判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。