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研究課題名（和文）Emulsion-Based Continuous Flow Synthesis of Zeolites

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研究成果の概要（和文）：ゼオライトは化学・石油化学プロセスにおいて高い産業的価値をもつ材料であり、その合成技術の創出は極めて重要である。本研究ではエマルジョン法に基づくゼオライトの流通合成に着目した。エマルジョン法の採用により合成中の急速な粘度上昇による沈殿の問題を解決し、ゼオライトの連続流通合成が容易になった。この方針に基づき流通合成装置を設計・組立し、ERI、CHA、ベータ型などのゼオライトの流通合成を実現した。得られたERIゼオライトはNH₃-SCRにおいて高い触媒性能を示した。さらに、メタンの部分酸化反応においても本研究のERIゼオライトは147 μmol/g-zeoliteもの高いメタノール収量を実現した。

研究成果の学術的意義や社会的意義

Zeolites play a critical role in achieving the sustainable development goals. This research created an advanced synthesis route that is expected to greatly reduce the production costs of zeolites. This research also developed new applications of zeolites for emission control and methane utilization.

研究成果の概要（英文）：Innovating synthesis techniques for zeolites is of high importance considering their industrial values in chemical and petrochemical processes. This project focused on developing an emulsion-based, continuous flow synthesis of zeolites. This synthesis strategy solved the precipitation issue caused by sharp viscosity increase and thus facilitated the continuous flow synthesis of zeolites. This research designed and fabricated a continuous-flow system to fulfill this objective and led to the emulsion-based, continuous flow synthesis of several zeolites including ERI, CHA and beta. This research studied the performances of the ERI zeolite in the NH₃-SCR of NO_x and the partial oxidation of methane to methanol. With an optimal Cu/Al ratio of 0.2, the ERI zeolite proved to be a high-performing NH₃-SCR catalyst that matched the benchmark catalyst Cu-CHA. In addition, the ERI zeolite led to a methanol yield of 147 μmol/g-zeolite, proving its potential in this challenging reaction.

研究分野：functional porous materials

キーワード：zeolites continuous flow heterogeneous catalysts emission control methane utilization emulsion

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1. 研究開始当初の背景

Annual consumption of zeolites is expected to increase because of newly commercialized applications such as ammonia selective catalytic reduction (NH₃-SCR) of NO_x. The synthesis of such materials has been typically realized via long-time hydrothermal treatment conducted in batch reactors, which suffers from drawbacks such as frequently start-up and shut-down operations and low energy efficiency. Continuous flow synthesis is considered as a promising alternative for large scale production of zeolites because it can overcome drawbacks of the batch process. Due to the involvement of solid reactants and products, however, the continuous flow synthesis often limited by precipitation and blockage problems (**Figure 1**). The continuous flow synthesis becomes particularly challenging in the cases where a synthesis precursor forms a highly viscous and cohesive gel upon heating. Emulsion is a heterogeneous mixture where an immiscible liquid is dispersed in another liquid to form droplets through the addition of surfactants. This feature offers a unique opportunity to overcome the precipitation issues occurring in the continuous flow process as the sharp viscosity increase can be avoided and the products can easily flow out of the reactor in forms of suspension. In addition, the surfactants can considerably influence the local reaction environment, opening up windows for tuning product properties. Thus, the emulsion-based, continuous flow synthesis is an opportunity to address the challenges in efficient synthesis of zeolites as well as to tailor the properties such as structure, morphology and composition.

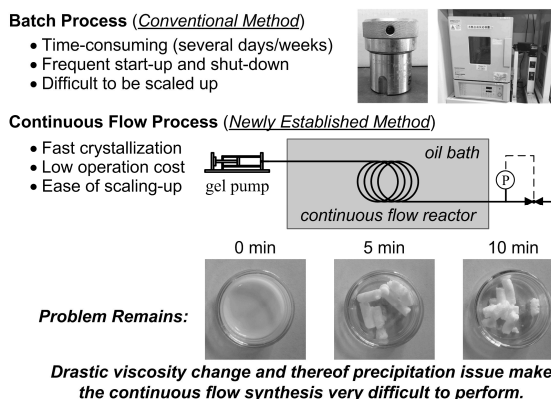


Figure 1. Research background. Comparison of batch process and continuous flow process for the synthesis of zeolites. **Key issue:** Viscosity change and precipitation hinder the establishment of a generalized continuous flow synthesis.

2. 研究の目的

This research aimed to establish an emulsion-based, continuous flow synthesis of zeolites. The research objective pursued a methodology of reactor design, with which the emulsion-based, continuous flow synthesis of different types of zeolites can be realized. In addition, this research also pursued fundamental understandings into the crystallization behavior occurring in the emulsion-based, continuous flow synthesis and the catalytic performance of the zeolites in the applications of NH₃-SCR and methane partial oxidation.

3. 研究の方法

The research approach included the two aspects. First of all, the research focused on the design of synthesis reactor and consequently the establishment of the emulsion-based, continuous flow synthesis of representative zeolites. Secondly, the research centered on exploring the catalytic performance of the zeolites, in particular ERI zeolite, in reactions such as NH₃-SCR and methane partial oxidation.

4. 研究成果

1. The establishment of the emulsion-based, continuous flow synthesis

Figure 2A presents the schematic layout of the continuous flow system, which consisted of a HPLC pump as the emulsion feeder, a coiled stainless steel tube as the continuous flow reactor, an aluminum block heater and other auxiliary elements such as back-pressure regulator. The emulsion-based, continuous flow synthesis of ERI zeolite with span 80 as the

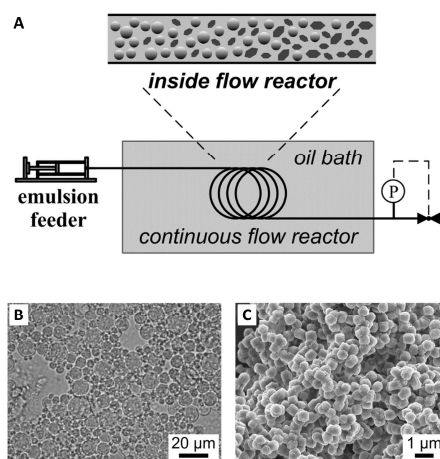


Figure 2. Emulsion-based, continuous flow synthesis of zeolites. **A.** Scheme of the synthesis concept and the key apparatus. **B.** Optical microscopic photograph of the emulsion containing the synthesis gel (in forms of droplets). **C.** Erionite synthesized for 7 min in the continuous flow reactor.

surfactant was attempted. The well-blended W/O emulsion was injected into a Teflon-lined continuous flow reactor using the HPLC pump. The solid products were successfully collected because the W/O emulsion provided a segmented flow (**Figure 2B**) so that the obtained ERI zeolite could flow out of the apparatus, avoiding the blockage of the reactor during the synthesis. The ERI product was confirmed to be fully crystalline after a synthesis of 7 min at 240 °C, as demonstrated by the SEM image (**Figure 2C**). A stable hydrodynamic condition is evidenced by the pressure profiles. In contrast, without emulsion, the pressure drastically increased when precipitation and clogging problem occurred during the synthesis.

To demonstrate that the emulsion-based, continuous flow synthesis can be applied to the synthesis of other types of zeolites as well, the syntheses of *BEA and SSZ-13 zeolite (CHA) were attempted. Similar to the case of ERI, a stable hydrodynamic condition was maintained throughout the continuous flow synthesis of *BEA and SSZ-13.

2. The exploration of the ERI zeolite in NH₃-SCR and methane partial oxidation

The ERI zeolite prepared from the emulsion-based, continuous flow synthesis proved to be highly crystalline. Therefore, further efforts were devoted to explore the catalytic performance of the ERI zeolite. As a small-pore zeolite, the ERI zeolite synthesized in the ultrafast route possessed a high hydrothermal stability, making it potential to be developed into an NH₃-SCR catalyst. We then researched the copper-ion-exchanged ERI zeolites with different copper loadings (**Figure 3A**). It was verified that the fast-synthesized ERI zeolite, after being ion-exchanged to the copper form (denoted as fast-synthesized Cu-ERI), exhibited an unprecedented high performance in NH₃-SCR.

Considering that the study on the hydrothermal stability of the ERI zeolites in the previous reports was insufficient and the behavior of copper species in ERI zeolite remained unclear, we thus investigated the effect of copper loading on the hydrothermal stability and the NH₃-SCR activity. Four fast-synthesized Cu-ERI catalysts with different Cu/Al ratios were prepared, including 0.11, 0.20, 0.30 and 0.41. The results indicated that the copper species sitting at different locations exhibit variant hydrothermal stability and NH₃-SCR activity, suggesting the importance of the interplay between the copper species and the zeolite host. Different copper locations in the ERI zeolite were proposed based on various characterizations, which were found to exert distinctively different interactions with the zeolite host, leading to varied hydrothermal stability and NO_x conversion (**Figure 3A**). With an optimal Cu/Al ratio of 0.20, the fast-synthesized Cu-ERI zeolite could withstand severe hydrothermal aging at 850 °C for 5 h and still exhibited a high NH₃-SCR activity (**Figure 3B**). Despite the presence of residual potassium cations, with the optimal Cu/Al ratio of 0.20, the fast-synthesized Cu-ERI achieved hydrothermal stability as well as NH₃-SCR activity that was comparable to the benchmark catalyst Cu-SSZ-13 (**Figure 3C**).

The partial oxidation of methane to methanol (MtM) is highly desirable but extremely challenging due to the higher chemical reactivity of methanol than methane. Copper-ion-exchanged zeolites have emerged as a promising class of materials for the stepwise conversion of methane to methanol. In the conventional protocol, copper zeolites are activated with oxygen at temperature above 450 °C and subsequently the system is cooled down to a lower temperature (ca. 200 °C) in the reaction to minimize the over oxidation. The repeated heating and cooling cycles involved in this conventional approach are significant barriers. In this research, we discovered that the Cu-ERI zeolite can achieve an unprecedented methanol yield even in an isothermal chemical looping.

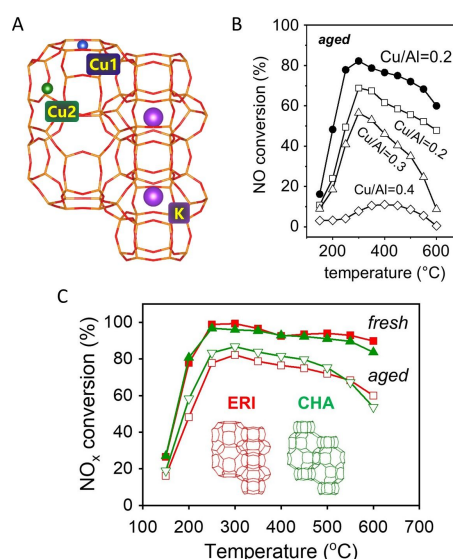


Figure 3. The catalytic performance of the Cu-ERI zeolite in NH₃-SCR. **A.** Scheme of the proposed copper locations in the fast-synthesized Cu-ERI zeolite. **B.** NH₃-SCR activity of aged fast-synthesized Cu-ERI with different copper loadings. Hydrothermal aging condition: 800 °C × 5 h with 10 % steam. **C.** Comparison of the NH₃-SCR activities of the fresh and the aged fast-synthesized Cu-ERI and Cu-SSZ-13.

We employed *in situ* Fourier transform infrared (FTIR) spectroscopy to study the surface species formed after the reaction of methane over activated Cu-ERI materials and to understand the effect of the reaction temperature, which is supposed to significantly affect selectivity and thus impact the methanol yield. FTIR could help us to identify the methoxy species and the formate species formed over the Cu-ERI zeolite after the reaction with methane; and thus, from the FTIR results, we were able to estimate the selectivity. From the temperature-dependent observations of product formation, the optimal temperature regime for the operations of Cu-ERI in direct methane conversion to methanol was determined to be around 300 °C, which is 100 °C

higher than that generally reported for other types of zeolites (**Figure 4A**). The attainment of high selectivity at this higher temperature might be ascribed to the strong stabilization of methoxy species by Brønsted acid sites, which could prevent further oxidation of methoxy species to carbon monoxide, formate, and carbon dioxide. Furthermore, the confinement within the small-pore structure could possibly exert a positive effect, particularly on C–H bond cleavage toward methanol formation, and thus on the stabilization of methoxy species while disfavoring overoxidation. With an optimized copper loading and under elevated methane partial pressure, Cu-ERI led to a methanol yield of as high as 147 μmol/g-zeolite at 30 bar of methane under conventional conditions. Thanks to its high activity and selectivity at 300 °C, an equivalently high methanol yield was achieved by means of the isothermal procedure with both oxygen activation and reaction with methane carried out at 300 °C. These results rendered the Cu-ERI zeolite to outperform other types of copper-containing-zeolites in the partial oxidation of methane to methanol in terms of isothermal chemical looping (**Figure 4B**).

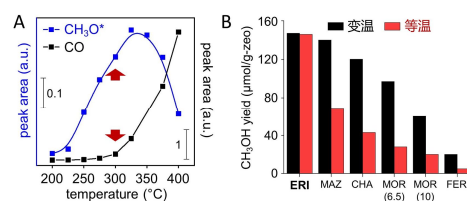


Figure 4. The performance of the Cu-ERI zeolite in the partial oxidation of methane to methanol. **A.** Comparison of the relative intensity of the bands of methoxy species and formate species formed after the reaction with methane at different temperatures. **B.** Comparison of the performances of different zeolites.

5. 主な発表論文等

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〔図書〕 計0件

〔産業財産権〕

〔その他〕

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6. 研究組織

氏名 (ローマ字氏名) (研究者番号)	所属研究機関・部局・職 (機関番号)	備考

7. 科研費を使用して開催した国際研究集会

〔国際研究集会〕 計0件

8. 本研究に関連して実施した国際共同研究の実施状況

共同研究相手国	相手方研究機関