Hierarchically Structured-catalyst for Vapor Phase Beckmann Rearrangement: Effective Desilication of Silicalite-1

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Introduction

In the vapor-phase Beckmann rearrangement of cyclohexanone oxime to ε-caprolactam, nest silanols in the vicinity of the external surface of silicalite-1 has been proposed as active sites for this reaction [1,2]. Key issues are thus to develop a catalyst with a large external surface area and to facilitate the transport of oxime in the catalyst particles. Treatment of zeolite in an alkaline solution resulted in desilication from zeolite framework, accompanied with mesopore formation [3]. Here we report a simple preparation method of hierarchically-structured silicalite-1 catalyst by treating parent silicalite-1 with alkaline media. The catalysts developed in this study showed high catalytic activities for the Beckmann rearrangement.

Materials and Methods

Silicalite-1 was synthesized from a hydrogel with the composition was TEOS: TPABr: 0.5NaOH: 200H_2O. The hydrogel was crystallized for 20 min at 473 K in a microwave oven. As-made silicalite-1 was calcined at 793 K for 2 h in air. Post-treatment of silicalite-1 was performed in tetramethylammonium hydroxide (TMAOH), NH_3 and NaOH aqueous solutions. Silicalite-1 weighing 2.0 g was dispersed in 100 cm^3 of each solution and vigorously stirred at 333 K for 5 h. The initial *pH* of solution was 12.7. The residual alkali source remaining in silicalite-1 was removed by treating the sample with a 0.1 mol L^{-1} of HCl aq four times. The vapor phase Beckmann reaggrangement of cyclohenanone oxime was performed in a plug flow reactor with a fixed bed of catalyst at WHSV=8 h^{-1} and 753 K for 5 h. The weight ratio of methanol/oxime in feed was 1.8, and the flow rate of N_2 carrier was 4.2 L h^{-1}.

Results and Discussion

The XRD measurements showed that the structure of silicalite-1 was kept after each alkali treatment. The amount of silicon removed by the alkaline treatment depended on the kind of alkali source: the fractions of Si removed after 5 h of treatment using TMAOH, NH_3 *aq.* and NaOH were 7.6, 14.3 and 22.2 wt%, respectively. FE-SEM and TEM observations showed that the NaOH-treated sample possessed nanocrystals (ca. 20 nm) and open-porous structure, as typically shown in Fig. 1. Figure 2 shows the N_2 adsorption isotherms for parent and alkali-treated samples. As shown in Fig. 2, the NaOHaq treatment resulted in the appearance of a broadened large hysteresis, indicating development of mesoporous network without any damage of microporous channels. Namely, a hierarchically-structured porous system was effectively developed. While the NH_3aq-treated sample similarly formed mesopores, the TMAOHaq treatment was not effective for developing mesopores. The FT-IR spectra for NaOH- and NH_3-treated silicalite-1 had broad absorption between 3200-3600 cm^{-1}, which is attributed to nest silanols.

Alkali-treated samples were tested for vapor phase Beckmann rearrangement. Fig. 3 shows that catalytic activity and life were greatly improved by the alkaline treatment, and NaOHaq treatment of silicalite-1 was the most effective. In conclusion, hierarchical structure developed by alkali treatment would provide effective diffusion pathways in silicalite-1 and increase the amount of nest silanols in the vicinity of surface.

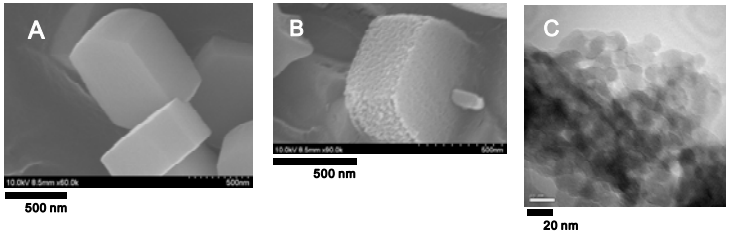

Figure 1. A, a typical FE-SEM view of parent silicalite-1; B, a typical FE-SEM view of NaOHaq treated-silicalite-1; C, a typical TEM view of NaOHaq treated-silicalite-1.

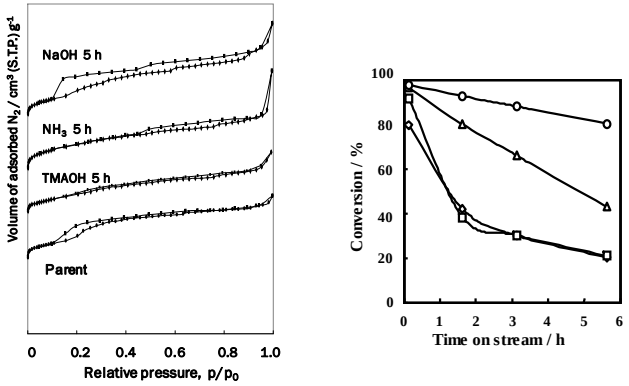

Figure 2. Nitrogen isotherms for parent and alkali-treated silicalite-1.
Figure 3. Results of catalytic tests at WHSV = 8 h^{-1} and 753 K. Catalysts: rhombus, parent; square, TMAOHaq-treated; triangle, NH_3aq-treated; circle, NaOHaq-treated.

References

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