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Synthesis and Catalytic Performance of Large Zeolite Y Crystals

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1. Introduction

Zeolites have gained an irreplaceable role as catalysts in the refining industry. With a production capacity of $625 \cdot 10^6$ t in 2004, the fluid catalytic cracking process (FCC) represents the second most important heterogeneously catalyzed process [1]. As an active component, the catalyst of this process contains zeolite H-Y. Since a high-molecular feed is used, a detailed knowledge of the diffusion behavior of the feed molecules within the pores of zeolite Y is of interest. For several types of diffusion measurements, it is favorable or even essential to apply zeolite crystals with several microns in size. However, until now, only small crystals of high-silica zeolite Y were accessible. The first synthesis of high-silica zeolite Y with crystals of ca. 3 µm has been reported by Delprato *et al.* [2] and was refined by Karim *et al.* [3]. Here, we present further efforts in the synthesis of larger crystals of zeolite Y. As a tool to detect different diffusion behavior in small and large crystals [4, 5], the cracking of 1,3,5-triisopropylbenzene over acidic forms of the prepared Y-type zeolites was investigated.

2. Experimental section

The synthesis of zeolite Y was carried out using the recipe described by Karim *et al.* [3]. The molar gel composition was 0.84 NaF : 2.4 Na_2O : 1.0 Al_2O_3 : 10 SiO_2: 1.0 15-crown-5 : 140 H_2O. The ageing period, the homogenization period directly after gel mixing and the synthesis temperature were varied systematically. The catalytic cracking of 1,3,5-triisopropylbenzene was carried out at ambient pressure in a flow-type apparatus with a fixed-bed reactor. Before activation, the samples were ammonium ion-exchanged to different degrees. The zeolite samples were labelled as follows: H,Na-Y-crystal size / µm-(n_{Si}/n_{Al}-ratio)-exchange degree / %. Nitrogen was used as a carrier gas and was loaded with 1,3,5-triisopropylbenzene ($p_{1,3,5\text{-triisopropylbenzene}} \approx 6$ Pa). Due to their high activity, the zeolite samples were diluted with silica gel to 2.2 wt.-% before pelletization. The temperature and the modified residence time amounted to 170 °C and ca. 150 $g \cdot h \cdot mol^{-1}$, respectively.

3. Results and discussion

The ageing period was proven to play an important role in the synthesis of zeolite Y in the presence of 15-crown-5. If the synthesis gel was homogenized for 2 h and the following ageing period was reduced from 24 h to 0 h, the crystal size increased concomitantly. While the crystals grown from a gel which was aged for 24 h had sizes in the range of 1 to 2 µm only, crystals with sizes up to 4.7 µm were obtained without

ageing (Figure 1). Even larger crystals with sizes up to 6.8 µm could be obtained by reducing the homogenization period to 30 min. However, these crystals were partly covered by overgrowth and the reproducibility of the synthesis turned out to be poor. In contrast, when the homogenization was further reduced to 5 min, no crystalline material was recovered. This demonstrates that 5 min are too short to form the required crystallization nuclei. Although a lower crystallization temperature would be expected to have a positive effect on the crystal size, a reduction by 10 °C only retarded the crystallization. No substantial increase in the crystal size was observed.

In the cracking of 1,3,5-triisopropylbenzene, higher conversions were observed for the zeolite samples containing the smaller crystals (Figure 2). This observation was independent of the ammonium ion exchange degree. At the low reaction temperature applied here, this effect is attributed to the larger external surface area of the smaller crystals rather than to the shorter diffusion pathways.

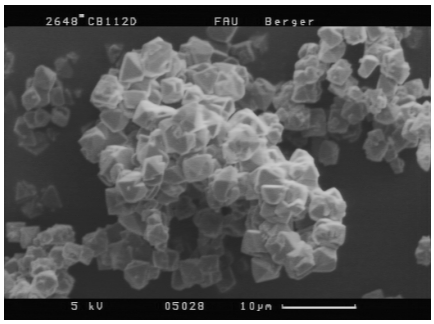

Figure 1: Crystals of zeolite Y obtained without ageing.

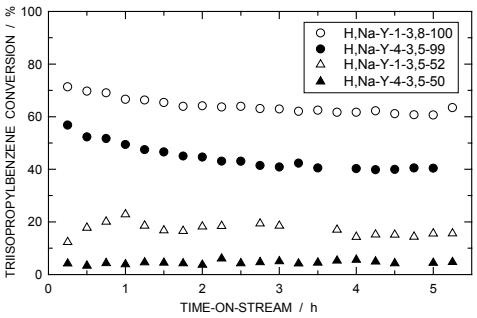

Figure 2: Catalytic conversion of 1,3,5-triisopropylbenzene over zeolite H,Na-Y.

4. Conclusion

The length of the ageing period is the most important parameter for the synthesis of larger crystals of zeolite Y in the presence of 15-crown-5. A minimum of crystallization nuclei is required to produce large and phase-pure products. Catalytic test reactions, *e.g.*, cracking of alkylaromatics, can be used as tools to distinguish between small and large crystals. However, the effects of intracrystalline diffusion and of reaction on the external surface have to be carefully differentiated.

References

[1] D. Nakamura, Oil Gas J. 102 (20. Dezember 2004) 46-53.
[2] F. Delprato, L. Delmotte, J.L. Guth, L. Huve, Zeolites 10 (1990) 546-552.
[3] K. Karim, J. Zhao, J. Dwyer, Micropor. Mater. 3 (1995) 695-698.
[4] S. Al-Khattaf, J.A. Atias, K. Jarosch, H. de Lasa, Chem. Eng. Sci. 57 (2002) 4909-4920.
[5] S. Al-Khattaf, H. de Lasa, Appl. Catal. A: General 226 (2002)139-153.