OPTIMIZATION OF SYNTHESIS CONDITIONS FOR PSA ADSORBENTS

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ABSTRACT

Structured adsorbents in the form of supported thin zeolite films may represent a competitive alternative to traditional zeolite adsorbents used in PSA processes, due to the reduction of mass – and heat – transfer limitations typical of packed beds. Thin NaX films were grown by hydrothermal treatment using a clear solution on cordierite monoliths. Films grown by a multiple synthesis procedure were dense and uniform with a very small amount of sediments adjacent to the film, which may be an advantage in PSA applications. The CO₂ adsorption capacity and the pressure drop for the supported films were compared to those of a packed NaX bed. Although the adsorption capacity was 25 times lower, the pressure drop of the structured adsorbent was 100 times lower, indicating the potential advantage of structured adsorbents in PSA processes. Further investigations are needed in order to prove this hypothesis.

EXPERIMENTAL

Porous cordierite monoliths (400 cpsi, Corning) were used as structured substrates for the zeolite film growth. Growth of adsorbed 80 nm FAU seeds on the walls of the substrates was performed in a clear solution with molar composition of 80Na₂O:1Al₂O₃:9SiO₂:500H₂O, as described by Öhrman et al. (2004a) about the growth of thin ZSM-5 film on cordierite monoliths. The zeolite loading of the structured adsorbents was determined by the weight increase of the support before and after hydrothermal treatment. NaX (13X) molecular sieve zeolite beads (Qingdao JIT Corporation, Qingdao, China) with a diameter of 0.7 mm were used for comparison with the NaX film coated cordierite monoliths. The zeolite loading of the beads was determined by liquid N₂ adsorption as the ratio between the BET surface area of the sample and the reference crystals (Öhrman 2004b). SEM images were recorded on samples covered with a thin layer of gold (few nm) previously deposited by sputtering. The carbon dioxide adsorption capacity of the structured adsorbents and NaX beads was measured at 0° C by using a Micromeritics ASAP 2010 instrument. The pressure drop was measured as a function of air flow rates for the zeolite beads and the structured adsorbents in a single PSA column.

Figure 1. SEM top – view image of the NaX molecular sieve zeolite beads (a) and of the films grown on the cordierites support in one step of 6 h and 40 min (b) and 5 steps of 1 h and 20 min (c).

Figure 2 Cross – section image of the NaX film sample grown in one step of 6 h and 40 min (a) and in 5 steps of 1 h and 20 min on the 400 cpsi ceramic substrate (b).

Table 1. Sample characteristics.

Sample	Synthesis duration	Film thickness (mm)	Weight gain ($\frac{g_{\text{zeolite}}}{g_{\text{sample}}}$)	CO ₂ ads. capacity ($\frac{\text{mmol}}{g_{\text{sample}}}$)
NaX beads	---	---	0.83 ^a	4.7
Structured adsorbent	5 x 1h 20 min	1.5	0.036 ^b	0.19

^a From BET analysis.

^b From weight increase of the support after hydrothermal treatment.

RESULTS AND DISCUSSION

Figure 1 (a) shows the cross-sectional image of the NaX beads. It is possible to identify the typical octahedral shape of the NaX crystals. Figure 1 (b) shows the top-view image of the NaX film grown on the in one step of 6 h and 40 min. The film is not continuous and the NaX crystals look etched. Large sediments and hydroxysodalite (HS) crystals, probably originating from the combined effect of Al-leaching from the support and the thermodynamics of the system, were also observed. In order to minimize Al-leaching and sedimentation, a multiple step synthesis procedure was performed. Sediments and zeolite crystals other than NaX may be a disadvantage in PSA applications in terms of reduced separation performance. The synthesis duration of 6 h and 40 min was therefore divided in 5 steps of 1 h and 20 min. A top-view image of the film is shown in Figure 1 (c). The film is dense and the number, and size of the sediments adjacent to the film and HS crystals embedded in the zeolite coatings lowered compared to the film grown in one longer hydrothermal treatment.

Figures 2 (a, b) represent the cross-sectional images of the NaX film samples grown in one long hydrothermal treatment (a) and with the multiple step synthesis (b). The film thickness of the samples grown in 6 h and 40 min is lower (0.7 μm) than the one of the structured adsorbent grown in 5 steps (1.5 μm), although the weight gain of the two samples is of the same order of magnitude. This indicates that more sediments are deposited on the monolith after 6 h and 40 min, according to SEM observations.

Table 1 shows the sample characteristics of the NaX beads and structured adsorbent. The zeolite loading of the beads was 0.83 $\frac{g_{\text{zeolite}}}{g_{\text{sample}}}$, and was 23 times higher than the weight gain of the structured sample (0.036 $\frac{g_{\text{zeolite}}}{g_{\text{sample}}}$). This shows that the adsorption capacity of the structured sample should be about 23 times lower than the beads for any adsorption measurement, due to the lower amount of zeolite per gram sample of the former one.

Figure 3. CO₂ equilibrium isotherm measured at 0° C on the NaX beads and the structured adsorbent.

Figure 4. Pressure drop measured on the NaX beads and the structured adsorbent .

Figure 3 shows the carbon dioxide isotherms at 0° C of the beads and structured adsorbent. As expected, the CO adsorption capacity of the structured adsorbent is 25 times lower than the one measured for the NaX beads. High cell density monoliths will lead to increased zeolite loading.

The pressure drop was measured at different air volumetric flow rates in a single PSA column for the structured adsorbent and the beads, and the results are shown in Figure 4. The pressure drop measured in the packed bed is 100 times higher than for the structured adsorbent, although the volume of the packed bed and the monolith is the same. This suggests that there is considerable scope to increase the monolith cell density and therefore increase the zeolite loading while still maintaining a lower pressure drop than that of a packed bed.

The results of this work suggest the potential of structured adsorbents as competitive alternative to traditionally used packed beds in PSA processes. The adsorption capacity of the structured adsorbents may be increased by growing thicker NaX films on the cordierite monoliths or by using substrates with a higher cell density. In addition, heat – and mass – transport phenomena in the films should be investigated and PSA cycles evaluated to explore the poss

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