Dealumination of Zeolite Beta using $(NH_4)_2SiF_6$ and $SiCl_4$

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Zeolite Beta can be dealuminated by treatment with either $(NH_4)_2SiF_6$ in aqueous suspension or $SiCl_4$ vapours in a high temperature reaction; under appropriate conditions, the material essentially retains its crystallinity.

Zeolite Beta is a large pore (12-membered ring) zeolite with a three-dimensionally interconnected channel system.[1—3] Although it can be synthesized from alumosilicate gels with Si/Al-ratios ranging from 5 to 100, it has been shown that the yield of crystalline product decreases drastically with increasing Si/Al-ratio.[4] Here, we report on an alternative method for obtaining zeolite Beta enriched in silicon, *viz.* post-synthesis dealumination using $(NH_4)_2SiF_6$ (after Breck and Skeels[5]) or $SiCl_4$ (after Beyer and Belenykaja[6]).

Zeolite Beta was synthesized according to a modified

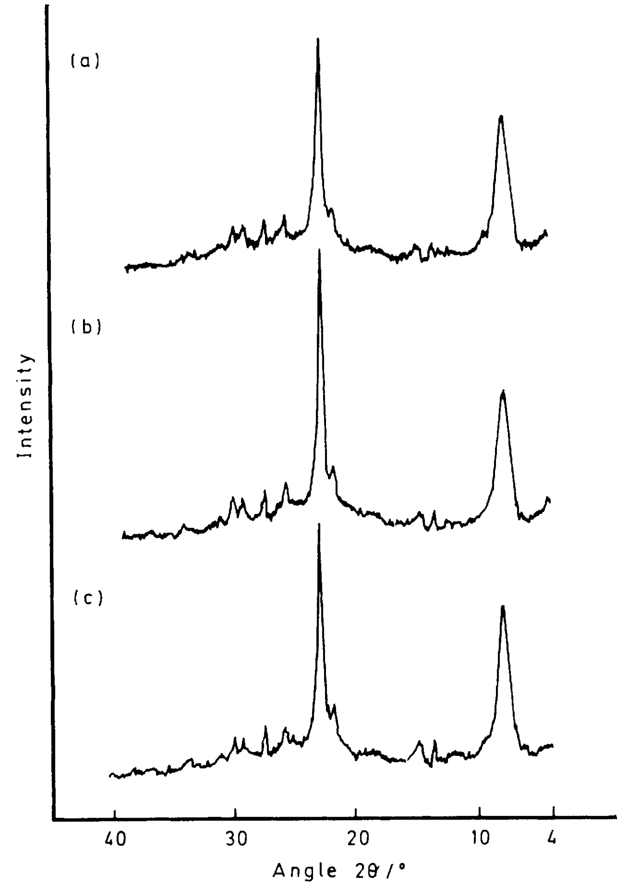

Figure 1. X-Ray powder patterns (Cu-K$_\alpha$ radiation) of parent and dealuminated samples of zeolite Beta; (a) NH$_4$-Beta, (b) NH$_4$-Beta/(NH$_4$)$_2$SiF$_6$, (c) NH$_4$-Beta/SiCl$_4$.

Figure 2. Lattice IR vibrations obtained by the KBr pellet technique; (a) NH$_4$-Beta, (b) NH$_4$-Beta/(NH$_4$)$_2$SiF$_6$, (c) NH$_4$-Beta/SiCl$_4$.

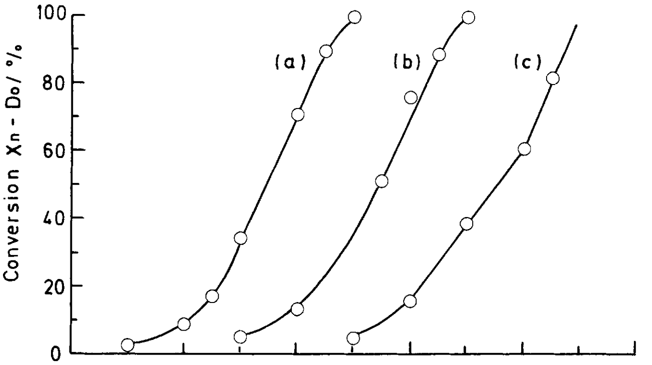

Figure 3. Catalytic activities of parent and dealuminated samples in the hydroconversion of n-dodecane (n-Do); $p_{\text{n-Do}} = 1.3$ kPa, $p_{H_2} \sim 100$ kPa, mass of dry catalyst (W) ~ 0.6 g, $W/F_{\text{n-Do}} = 250$ g h mol^{-1}; (a) 0.27 Pd/NH$_4$-Beta, (b) 0.27 Pd/NH$_4$-Beta/(NH$_4$)$_2$SiF$_6$, (c) 0.27 Pd/NH$_4$-Beta/SiCl$_4$.

method for the synthesis of zeolite ZSM-20.[7] After calcination in air for 16 h at 540 °C to remove the organic material occluded during the synthesis, zeolite Beta was ion exchanged under reflux with an aqueous solution of NH$_4$Cl (1 M). This parent sample (NH$_4$-Beta) was treated in two different ways. Firstly, NH$_4$-Beta (5 g) was suspended in an aqueous solution of ammonium acetate (50 ml, 10 M) at 75 °C. To this suspension, a precalculated amount of a solution of (NH$_4$)$_2$SiF$_6$ (0.75 M) in water (*e.g.*, 4.4 ml) was added dropwise (*ca.* 0.3 mmol Si min^{-1}). Afterwards, the reaction temperature was raised to 90 °C and kept there for *ca.* 16 h. This sample is denoted as NH$_4$-Beta/(NH$_4$)$_2$SiF$_6$. Secondly, the parent zeolite was treated for 2 h at 350 °C in a flow of dry nitrogen and then cooled to 250 °C. The stream of nitrogen was then saturated at room temperature with SiCl$_4$ vapour and the temperature of the zeolite bed was raised to a preselected temperature (*e.g.*, 450 °C). After 40 min at this temperature, the gas flow was switched to pure nitrogen for another 15 min, then the zeolite was cooled to room temp. and washed thoroughly with distilled water (NH$_4$-Beta/SiCl$_4$).

X-Ray powder patterns of the materials obtained by these two techniques are given in Figure 1, along with the pattern of the parent sample. Obviously, dealumination does not bring about any significant change in the crystallinity. This is also evidenced by IR spectroscopy (KBr pellet technique) in the region of lattice vibrations (Figure 2). Upon dealumination, the pattern remains essentially unchanged (note that the peak at *ca.* 1400 cm^{-1} is due to N–H vibrations which appear for the samples containing NH$_4{}^+$ cations, but not for the SiCl$_4$ sample heated at elevated temperature). Evaluation of temperature programmed desorption of ammonia gave the following Si/Al-ratios of the zeolites: NH$_4$-Beta, Si/Al = 13; NH$_4$-Beta/(NH$_4$)$_2$SiF$_6$, Si/Al = 16; NH$_4$-Beta/SiCl$_4$, Si/Al = 38. During the dealumination experiments using (NH$_4$)$_2$SiF$_6$, it has been generally observed that there seems to be a certain upper limit for the Si/Al ratio which can be obtained, *e.g.* around 20. If, for example, an amount of $(NH_4)_2SiF_6$ theoretically sufficient to remove 80% of the aluminium in the parent sample is added, zeolite Beta is dealuminated to only 12%. The existence of an upper limit for the degree of dealumination in the $(NH_4)_2SiF_6$-method has also been reported for zeolite Y,[8] however, it is not yet clear why such an upper limit exists.

The catalytic activities of the parent and the dealuminated samples of zeolite Beta were characterized in a flow-type fixed bed apparatus. n-Dodecane was converted in the presence of hydrogen over zeolite samples loaded with 0.27 wt.% of palladium. In such a system, an n-alkane isomerizes and, at elevated conversions, hydrocracks.[9] In Figure 3, the conversions of n-dodecane are plotted *vs.* the reaction temperature. With increasing Si/Al-ratio the catalytic activity decreases. This can, at least qualitatively, be understood in terms of the decreasing number of Brönsted acid sites while their strength is not significantly influenced in this range of Si/Al-ratios.

Further work is underway in our laboratories to optimize the dealumination procedures and to evaluate the properties of zeolite Beta enriched in silicon by post-synthesis modification.

Financial support by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and Max Buchner-Forschungsstiftung is gratefully acknowledged.

Received, 10th August 1989; Com. 9/03436F

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