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Formation of Alkali-Aluminosilicate Layers on Thermochemically Dealuminated Y Zeolites by Alkaline Leaching

Zeolite Y was steamed at 873 K for 7 h. This thermochemical treatment increases the Si/Al ratio of the zeolite framework from 2.4 to 3.8 under the formation of non-framework aluminium species. Successive leaching in 0.25 M KOH at 353 K for 24 h decreases the Si/Al ratio of the zeolite to 2.6 due to the formation of a X-ray amorphous potassium aluminosilicate surface layer.

Keywords: zeolite, dealumination, realumination, alkaline leaching

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1. Introduction

It has been reported earlier that the hydrothermal stability of surface aluminated high-siliceous zeolites is increased by a protective surface layer of alkali aluminosilicate (LUTZ 1993). The basic zeolites were obtained by direct synthesis or by Al/Si substitution (DAY-S). Here the aluminosilicate surface layer could be created by externally offered solution of sodium aluminate and sodium silicate dissolved from the zeolite surface. In this context it was of actual interest whether zeolites dealuminated thermochemically in steam (DAY-T) could also be covered by a similar layer. In the following we show that alkali-aluminosilicate layers are invariably formed by the KOH leaching of DAY-T.

2. Experimental

The ammonium modification of zeolite Y (maximum of crystal size distribution 1.5 μm) obtained by a threefold exchange of NaY zeolite in 0.1 M solution of NH_4Cl at 298 K was steamed in a shallow bed at 873 K for 7 h (DAY-T). 1g of the steamed material was leached in 100 ml of a 0.25 M KOH solution at 353 K for 24 h without, with moderate, and with intensive stirring, respectively (DAY-T_{alkaline}). DAY-T was acid leached in 10^{-1} M solution of HCl up to a constant pH value = 3 (DAY-T_{acid}).

The products were characterized by ^{29}Si MAS NMR (at 79.48 MHz on a Bruker MSL 400 spectrometer) and by X-ray powder diffraction (Stoe Stadi-P in transmission mode, $\text{Cu K}\alpha$ radiation using silicon as external standard). Additionally, the samples were investigated by the Molybdate method (THILO).

For the Molybdate analysis 5 mg of the sample were hydrolysed in 100 ml of a 10^{-2} M HCl solution at 273 K. By this procedure the -Si-O-Al- bonds split immediately. The silicate building units set free are stable under these conditions. In the second step the silicate building units are degraded in presence of 2 ml of a 10% solution of molybdic acid. Since the

molybdic acid only reacts with monomeric silicate units, the formation of the yellow β -dodecamolybdate silicic acid complex in dependence with time is a measure of the degradation of the building units and thus a criterion of their structure. The formation is spectroscopically followed at a wavelength of 600 nm.

3. Results and discussion

It is known that zeolite Y is dealuminated by thermochemical treatment in steam (DAY-T) under formation of non-framework aluminium species (MC DANIEL). These are removable by an acid treatment without change of the framework structure (LOHSE 1978). Therefore, identical ^{29}Si MAS NMR signals and XRD pattern are obtained for DAY-T_{acid} and DAY-T. The NMR spectra of alkaline leached samples (DAY-T_{alkaline}) resemble however the spectrum of the parent Y zeolite more than that of DAY-T. The XRD pattern of these samples show a loss of crystallinity (Figs. 1 and 2).

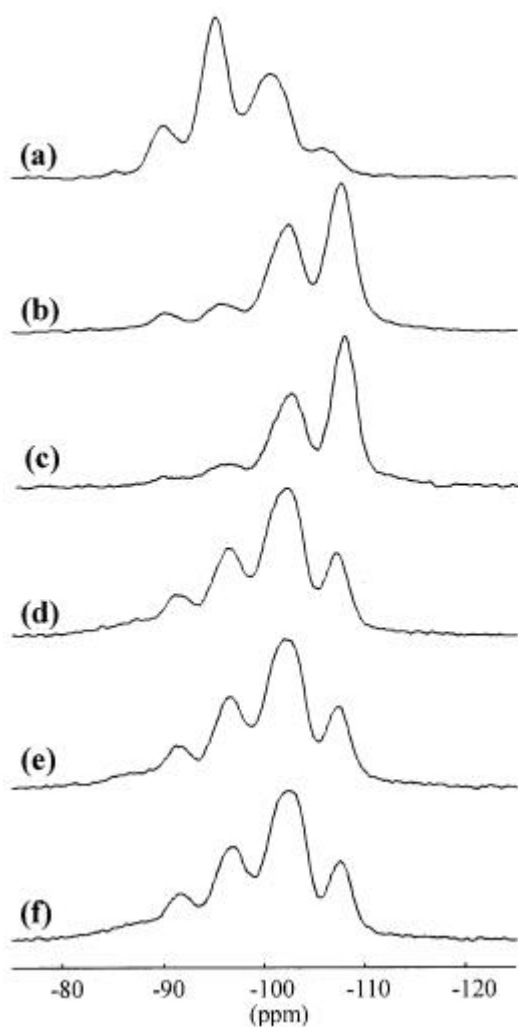


Fig. 1: ^{29}Si MAS NMR spectra of the hydrated zeolites Y (a), DAY-T (b), the acid treated DAY-T_{acid} (c), and the alkaline leached DAY-T_{alkaline} samples without (d), with moderate (e), and with intensive stirring (f)

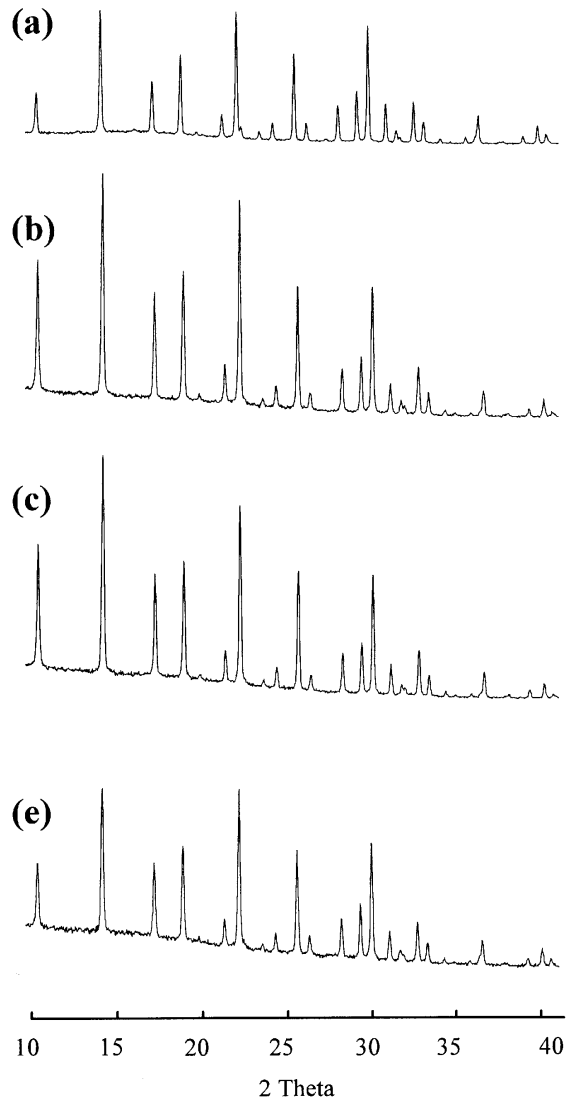


Fig. 2: X-ray diffraction pattern of the hydrated zeolites Y (a), DAY-T (b), the acid treated sample DAY-T_{acid} (c), and the alkaline leached DAY-T_{alkaline} sample with moderate stirring (e)

The lattice constants are increased and the Si/Al ratios determined by the empirical relation (Rüscher 2000, a)

$$x = 0.526 a (\text{\AA}) - 12.680 \quad \text{with Si/Al} = (1/x) - 1 \quad (1)$$

decreases from 3.8 to 2.6 (Tab. 1).

These results are in close agreement with experiments reported by Hamdan et al. of similarly treated zeolites. The authors have suggested a reinsertion of the non-framework aluminium into the zeolite framework. However, a different explanation should be considered on the basis of our earlier results (LUTZ 1988, 2000).

Wet chemical analysis of the current samples has shown the same Si/Al ratio of 2.4 of DAY-T and the parent zeolite indicating that no matter has left the bulk sample. Acid

leaching resolved the whole amount of non-framework aluminium from DAY-T which has been determined to contain 17 $[\text{AlO}_2]$ units with respect to the pseudo-elementary cell $\text{Me}_{56/n}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]$. No change of the lattice constant and thus of the Si/Al ratio of the framework of DAY-T_{acid} occurred (Tab. 1).

Tab. 1: Lattice constants of the hydrated zeolites Y (a), DAY-T (b), the acid treated DAY-T_{acid} (c), and the alkaline leached samples DAY-T_{alkaline} without (d), with moderate (e), and with intensive stirring (f)

sample	type	lattice constant/Å	Si/Al ratio*
(a)	Y	24.733 (6)	2.4
(b)	DAY-T	24.503 (1)	3.8
(c)	DAY-T _{acid}	24.511 (3)	3.8
(d)	DAY-T _{alkaline}	24.640 (1)	2.6
(e)	DAY-T _{alkaline}	24.633 (2)	2.6
(f)	DAY-T _{alkaline}	24.631 (2)	2.6

*calculated according to equation (1)

In our KOH leaching experiment on DAY-T carried out here at 353 K the 17 $[\text{AlO}_2]$ units were found again. 2 units were held from the alkaline solution. 15 units contributed to the newly formed non-framework material detected by the Molybdate measurements as potassium aluminosilicate (Tab. 2).

Tab. 2: Chemical composition of zeolite DAY-T_{alkaline} and of the alkaline solution calculated from results of Molybdate measurements and wet chemical analysis (composition of the parent zeolite Y: $\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]$)

Chemical composition (DAY-T _{alkaline})		
	AlO_2	SiO_2
zeolite framework	39 [#]	101
non-framework material	15	19
alkaline solution	2	16

[#]calculated from Si/Al ratio

Compared with the framework of DAY-T_{alkaline} with a Si/Al ratio of 2.6, the potassium aluminosilicate with Si/Al = 1.3 contains significantly more aluminium and thus shorter silicate units (maximum Si/Al ratio = 1). Therefore, the alkaline leaching of DAY-T causes a significant loss of framework silicon of about 25% in total or 35 units of $[\text{SiO}_2]$ as given in the balance in Tab. 2. Wet chemical analysis show that 16 $[\text{SiO}_2]$ units of the desilicated units are found in the solution while 19 units remain in the solid as non-framework material. This result shows that instead of an Al reinsertion the desilication of the DAY framework has to be considered as the main explanation also for the observation of the increased lattice constant and the changes in the ^{29}Si MAS NMR signals. It may be noted that the desilication observed here for the leaching at 353 K is somewhat increased compared to the effect observed at room temperature leaching (LUTZ 2000).

Our results also indicate that a steaming of NH_4Y evokes a Si/Al gradient from the surface to the centre of the crystal with higher Al concentrations in the inner part the non-framework aluminium not taken into account. The strongly dealuminated part consists mainly of $\text{Q}^4(0\text{Al})$ groups because of an annealing of the zeolite framework under the hydrothermal conditions of dealumination (LOHSE 1981). Nevertheless the present Q^3 groups ($(\text{HO})\text{Si}(\text{OSi}\equiv)_3$ - -102 ppm) and Q^2 groups ($(\text{HO})_2\text{Si}(\text{OSi}\equiv)_2$ - -92 ppm) superimpose the $\text{Q}^4(3\text{-1Al})$ ^{29}Si MAS NMR signals of DAY-T (LUTZ 2000) why the Si/Al ratio from NMR data (4.4) is determined higher than that of the XRD analysis (3.8).

Since the alkaline solubility of aluminosilicates increases with rising Si/Al ratio (Iler) the stronger dealuminated and partially disturbed part of the crystal (outer sphere) is preferentially dissolved after dissolution of the non-framework aluminium. Both, the silicate and aluminate ions form the non-framework aluminosilicate which precipitates onto the residual DAY-T_{alkaline} crystal. Electron micrographs support this assumption in so far as they show no significantly changed particle diameters. Only an increasing roughness of the particle surface from NaY to DAY-T and DAY-T_{alkaline} is visible. Any recrystallisation with formation of new crystalline phases typically for a treatment of zeolites at 353 K in solutions of sodium hydroxide (Barrer) can be excluded. However, the raised base line of the X-ray pattern of the KOH leached samples indicates the presence of the amorphous materials discussed above. The stirring does not influence the state of the samples (Fig. 2). This observation agrees with results for series of samples steamed at 773 K, 873 K, and 973 K which were alkaline leached (RÜSCHER 2000, b).

Conclusion

Our results demonstrate the generation of X-ray amorphous aluminosilicate phases in steamed and subsequently alkaline leached DAY-T_{alkaline} zeolites in close analogy to the alumination of high-siliceous zeolites. The aluminosilicate is formed from aluminate and silicate ions generated by dissolution of non-framework aluminium and of framework silicon. However, the alkaline treatment of steamed Y zeolites is rather an unsuitable way of increasing the hydrothermal stability since too much "protective layer" (25% non-framework aluminosilicate instead of 3% in aluminated high-siliceous zeolite (LUTZ 1993)) is formed and since the properties of the dealuminated framework, especially the Si/Al ratio, are too strongly changed by the desilication effect. Reduced amounts of aluminosilicate are expected by reducing the leaching temperature and the KOH concentration. Corresponding experiments are about to come.

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