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DEALUMINATION OF NH_4NaY ZEOLITES THROUGH HYDROTHERMAL TREATMENT: KINETIC ORDER WITH RESPECT TO ALUMINIUM

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The dealumination of a NH_4NaY zeolite through hydrothermal treatment at 500 °C and 650 °C occurs apparently through a kinetic law of the second order with respect to aluminium. The kinetic order is actually equal to one when the hydrolyzable aluminium atoms only are taken into account i.e. those to which ammonium ions and not sodium ions are associated.

1. Introduction

Hydrothermal treatment of zeolites is the most commonly used method in the preparation of dealuminated samples. Moreover in the regenerator of a fluidized catalytic cracker unit the conditions are similar to those of the hydrothermal treatment and hence dealumination of the framework of the zeolitic component of the catalyst (USHY or REY) occurs during regeneration. Therefore the effect of the operating parameters (time, temperature, water pressure...) on the properties of zeolites must be determined quantitatively; and yet very few kinetic studies have been carried out. Recently it has been found that the dealumination of NH_4NaY zeolites was of the second order with respect to framework aluminium [1].

2. Experimental

The dealumination of a NH_4NaY zeolite ($(NH_4)_{48}Na_{14}Al_{62}$ $Si_{130}O_{384}$) by hydrothermal treatment at 500 °C and 650 °C was studied using a flow reaction as a function of time, the operating conditions being: partial pressures of water and of nitrogen 93 and 7 kPa respectively; flow rate of water equal to one gram per hour and per gram of catalyst. While the temperature was increasing to reach

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treatment temperature (5 to 10 minutes) the catalyst was under a flow of dry nitrogen. Water was introduced when the catalyst had reached the treatment temperature (time zero). All the samples obtained were characterized by X-ray diffraction, and the crystallinity C_{RX} and the unit cell parameter a_0 were determined according to ASTM methods D3906 and D3942. The number of aluminium per unit cell N_{Al} was deduced from a_0 by using the equation proposed by Breck and Flanigen [2].

3. Results and discussion

Irrespective of temperature, N_{Al} decreases rapidly during the first three hours, and subsequently, more slowly. Dealumination begins during the rise of the reactor temperature: N_{Al} passes from 62 before the rise in temperature to 51.5 at 650 °C and to 58 at 500 °C (fig. 1). A decrease in crystallinity of about 20% occurs, mainly during this period. Subsequently the crystallinity remains constant. The decrease in crystallinity is probably due to the absence of extraframework silicon on the NH_4NaY zeolite which could replace the aluminium extracted. As found by Martins et al. [1], a straight line is obtained for the period of

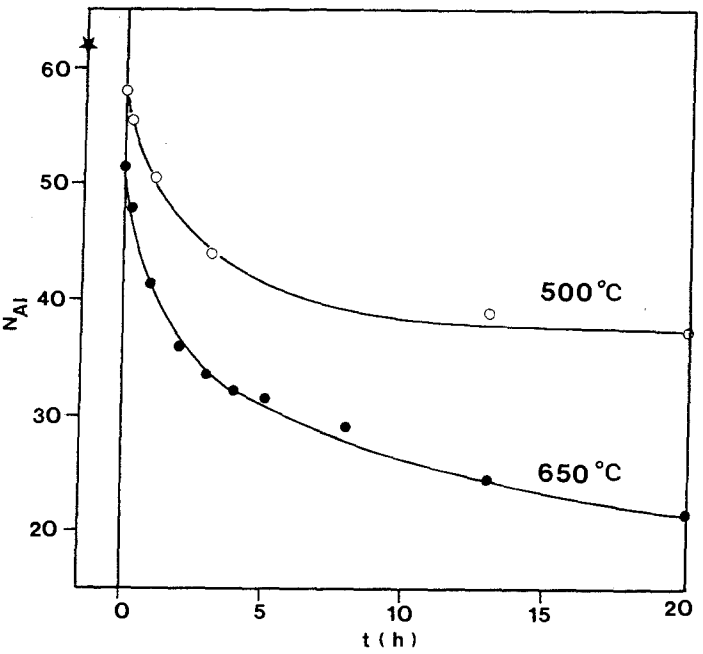

Fig. 1. Change in the number of framework aluminium atoms per unit cell N_{Al} as a function of time on stream t(h), * corresponds to NH_4NaY before hydrothermal treatment.

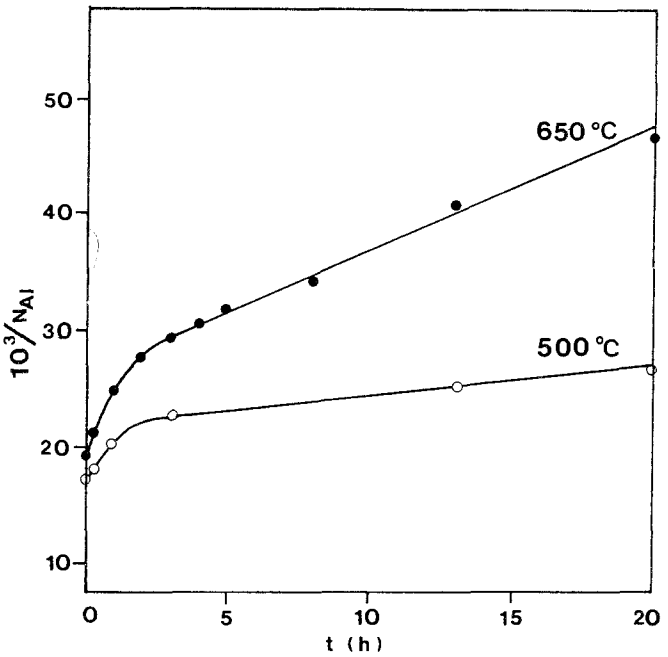

Fig. 2. Kinetic study of the dealumination of NH_4NaY through hydrothermal treatment. Checking of a second order equation rate. N_{Al} number of framework aluminum atoms per unit cell.

slow dealumination when plotting $1/N_{Al}$ as a function of time (fig. 2). Dealumination would therefore be of the second order with respect to aluminium:

$$\frac{-\mathrm{d}N_{Al}}{\mathrm{d}t} = kN_{Al}^2 \Rightarrow \frac{1}{N_{Al}} - \frac{1}{N_0} = kt$$

with k the rate coefficient of dealumination for given values of temperature and water pressure.

However this value of the kinetic order would imply an elimination of the aluminium atoms by pairs, whereas NMR studies show that aluminium atoms are extracted one by one [3]. Moreover this apparent second order was obtained by taking into account all the framework aluminium whereas it is well known that the aluminium atoms to which are associated sodium ions are very difficult to hydrolyze. Figure 3 shows that the kinetic order with respect to aluminium is actually equal to unity (both for the periods of rapid and slow dealumination) when the number of aluminium atoms considered is N_{Al}^* the number of hydrolyzable ones ($N_{Al}^* = N_{Al} - N_{Na}$ with N_{Na} the number of sodium per unit cell). This kinetic order value is not specific to the NH_4NaY sample used in this work. Indeed it was also obtained for the dealumination of a $USNH_4Y$ zeolite (unit cell formula $Na_{0.5}\ (NH_4)_{34.5}\ Al_{35}\ Si_{157}\ O_{384}$) by steaming at 650 °C [4]. In this case the number of sodium atoms per unit cell being very small, N_{Al}^* is practically equal to N_{Al}. Moreover an order equal to one can be deduced from the results

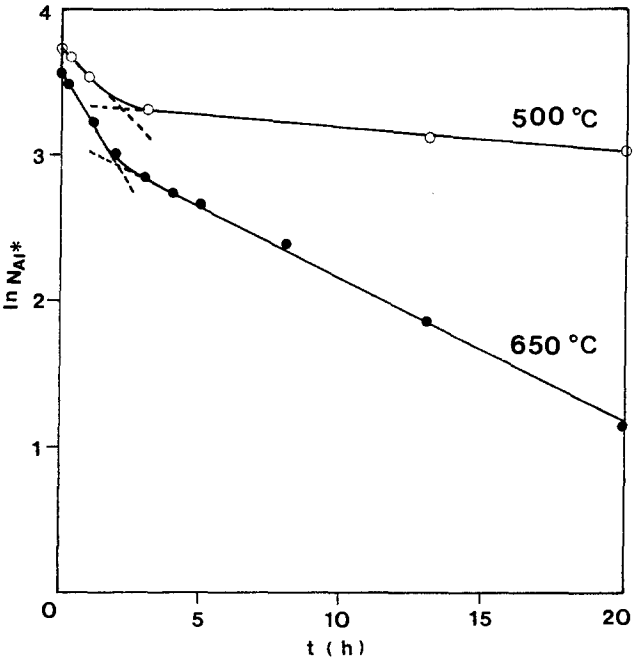

Fig. 3. Kinetic study of the dealumination of NH_4NaY through hydrothermal treatment. Checking of a first order equation rate. N_{Al}^*: number of hydrolyzable framework aluminium atoms per unit cell; t: time on stream (h).

published by Fleisch et al. [5] concerning the dealumination by steaming at 500 °C of a USHY zeolite with about 40 Al and 2.5 Na per unit cell. The results of a complete kinetic study of the dealumination of NH_4NaY zeolites through hydrothermal treatment will be reported elsewhere.

References

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