

KINETICS OF *n*-HEPTANE DESORPTION FROM PELLETIZED ZEOLITE 5A

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ABSTRACT

Kinetic parameters for the desorption of normal heptane from pelletized zeolite 5A have been obtained by temperature-programmed desorption. The desorption spectra present two main peaks, which can be fitted quantitatively assuming four different binding states and neglecting readsorption.

INTRODUCTION

One of the major industrial applications of zeolites is in the area of adsorption processes. In these processes zeolite adsorbents (also called molecular sieves) are mainly used in fixed-bed operation. Thus, the adsorbent must have a reasonable size to avoid an excessive pressure drop. Synthetic zeolites produced in a fine powder have to be formed into pellets with a clay binder. Key factors determining the performance of adsorption separation processes are adsorptive capacity and selectivity, adsorption–desorption rate and the mechanical resistance of the pellets.

Normal paraffins are separated commercially from a mixture of branched hydrocarbons of the same chain length using a molecular sieve with an effective pore diameter of about 5 Å in pellets of size 0.0625 in or smaller. Because of its pore size, the molecular sieve adsorbs only the normal paraffin, while the branched isomers remain in the liquid phase. The adsorbed normal paraffin is later displaced from the bed using hydrogen or some other suitable displacing agent.

The overall production rate of *n*-paraffin separation processes is generally controlled by the rate of *n*-paraffin desorption [1]. However, few studies of

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the desorption of *n*-paraffins from 5A zeolites are available in the literature. In the present work, we studied the desorption kinetics of normal heptane from pelletized 5A zeolite. The sorption of normal heptane on 5A zeolite has been studied by other authors [2,3]. Diffusion coefficients and equilibrium constants have been reported, but we know of no published studies of the desorption kinetics. We obtained thermal desorption spectra for normal heptane for a number of heating rates. From these spectra we were able to determine kinetic parameters (activation energies and pre-exponential factors) for each of the observed binding states.

EXPERIMENTAL

Thermal desorption spectra were obtained gravimetrically using a Cahn 2000 recording electrobalance interfaced with an IBM-XT computer for data gathering and analysis.

Fresh samples of Linde 5A zeolites (0.0625 in pellets) were activated by heating under a dry argon purge. About 3 g of zeolite were placed in a glass vial and heated at 400 K for 1 h, then at 600 K for 3 h. After cooling to room temperature, the activated sample was saturated with normal heptane (Carlo Erba, 99.5%) by the addition of a few ml of the hydrocarbon to the vial. The sample was left submerged in liquid normal heptane for several hours before the desorption experiment was performed. No increase in the amount of hydrocarbon adsorbed could be observed after the sample had been kept in normal heptane for more than 2 h.

Approximately 25 mg of zeolite was subjected to programmed heating from ambient temperature to about 750 K in a glass bucket hanging from the weighing arm of the recording electrobalance. Argon gas, purified by passage through CaCl_2 and molecular sieve beds, flowed downwards with a superficial velocity of 350 cm s^{-1} . We had previously observed that desorption rates were independent of carrier gas flow rate for argon superficial velocities larger than 300 cm s^{-1} . Temperatures were programmed to vary linearly with time at rates in the range $45\text{--}440 \text{ K h}^{-1}$. A chromel–alumel thermocouple placed a few mm from the glass bucket was used to measure sample temperatures. The effect of temperature on the measured sample weight owing to carrier gas density and viscosity changes was assessed by running blanks with an empty glass bucket. Before the heating program was begun, sieve samples were left under argon gas flow until all excess hydrocarbon was evaporated and constant weight was obtained.

About 1500 sample weight vs. time data points were recorded at equal time intervals and fitted with several polynomials of order five. These polynomials were differentiated with respect to time to obtain the plots shown in Fig. 1.

RESULTS AND DISCUSSION

The rate of desorption of normal heptane from 5A zeolite pellets vs. sample temperature is shown in Fig. 1. Two distinct desorption peaks are evident, indicating that our zeolite samples present at least two sites for the adsorption of normal heptane. However, the broad second peak should correspond to several binding states separated by relatively small differences in binding energy.

The temperature at the peak maximum T_M increases with the heating rate β . It has been shown that, for first-order desorption, plots of $\ln T_M^2$ vs. $1/T_M$ should yield straight lines [4]. The activation energy for desorption and the pre-exponential factor can be determined from the slope and intercept of the straight lines. However, because of peak overlapping, this simple treatment could not be used with our results. Instead, we fitted the desorption spectra, solving the mass balance equations for adsorbed n -heptane:

$$\frac{dm_T}{dt} = \sum_{i=1}^4 \frac{dm_i}{dt} = r_d \quad (1a)$$

$$r_d = \sum_{i=1}^4 r_{di} = \sum_{i=1}^4 A_i \exp(-E_i/RT) m_i \quad (1b)$$

$$\frac{dT}{dt} = \beta \quad (1c)$$

with initial conditions

$$m_i = m_{0i}, \quad T = 300 \text{ K} \quad (2)$$

where m_T is the mass of normal heptane adsorbed per unit mass of dry

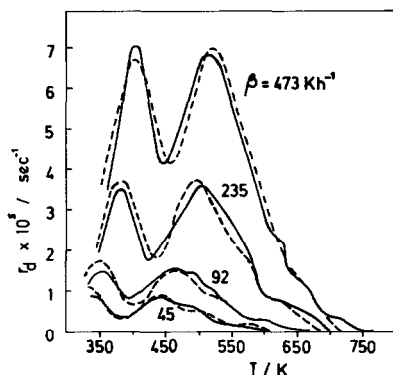


Fig. 1. Rate of normal heptane desorption r_d from pelletized Linde 5A zeolite vs. temperature for the heating rates β indicated. Dashed curves were calculated from eqn. (1) with parameters from Table 1.

TABLE 1

Kinetic parameters for normal heptane desorption from Linde 5A zeolite

| Desorption peak | A_d (s^{-1}) | E/R (K) | m_{0i} |
|-----------------|-----------------------|--------------|----------|
| I | 42 | 3800 | 0.043 |
| II | 490 | 6150 | 0.043 |
| III | 3410 | 8000 | 0.025 |
| IV | 79200 | 11000 | 0.009 |

zeolite, and r_d is the rate of normal heptane desorption. Curves calculated from eqns. (1) and (2) with parameters from Table 1 are shown in Fig. 1.

We should note that as the values of activation energy for desorption increase, the pre-exponential factors also increase, so that the product of the latter and the exponential factor does not vary much. This compensation effect has been observed frequently in kinetic and thermodynamic data for systematic variations in catalysts, reactions or solvents [5]. We may qualitatively explain the compensation effect in the data from Table 1 from the work by Gorte [6], who has observed that small pre-exponential factors for desorption from porous media should be obtained when readsorption is important. Molecules desorbing at low temperature should have a greater chance to readsorb than those desorbing at high temperature. Thus, the pre-exponential factors for desorption from sites with low binding energies should be smaller than those corresponding to sites with higher binding energies.

CONCLUSION

Our temperature-programmed desorption spectra for normal heptane adsorbed on commercial 5A zeolite pellets can be quantitatively fitted with a simple first-order kinetic model with four different binding states. A single desorption rate expression fits desorption spectra for temperatures varying between room temperature and 750 K and heating rates over an order of magnitude.

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