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# Kinetic analysis of *n*-tridecane desorption from type 5A zeolites

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## Abstract

Kinetic parameters for desorption of *n*-tridecane adsorbed on commercial 5A zeolite pellets have been measured. Pre-exponential factors, activation energies, and the populations of each binding state are reported. The results can be quantitatively fitted with a first order desorption rate equation and three different desorption zones could be determined. The possible existence of a compensation effect is qualitatively discussed. Desorption rates for powder and pellets are compared and the influence of initial coverage of pelletized zeolite on population and maximum temperature is presented.

*Keywords:* Desorption; *n*-Paraffins; Temperature-programmed desorption; *n*-Tridecane; Zeolites, type-5A

## 1. Introduction

There is a considerable economic incentive for the separation of medium molecular weight ($C_{10}$–$C_{18}$) linear paraffins from mixtures with branched chain and cyclic isomers, since normal paraffins are extensively used as feedstock in the manufacture of detergents and plasticizers while branched paraffins are the main component of unleaded gasoline. The difference in relative volatility between linear, branched, and cyclic isomers is small so that such a separation cannot be simply achieved by distillation. Instead, it can be efficiently achieved by selective adsorption on synthetic zeolites. Several commercial processes for *n*-paraffin separation on zeolite adsorbents have been developed over the past two decades [1]. Key factors determining the

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performance of these processes are the rate of diffusion of the normal paraffins in the zeolite and their rate of desorption.

Results reported here are part of an ongoing program aimed at studying the desorption kinetics of normal paraffins from pelletized 5A zeolites. In this work, we discuss the desorption kinetics of normal tridecane from pelletized Linde 5A zeolite. Although the overall rate of such separation processes is generally controlled by the rate of *n*-paraffin desorption [2], the desorption of higher hydrocarbons has received little attention in the literature. Vavlitis et al. [3] measured diffusivities of several normal paraffins while Jasra and Bhat [4] presented a thermogravimetric study of normal paraffins in the range from $C_8$ to $C_{18}$. However, these authors reported only one thermogram for each paraffin investigated and made no attempt to determine kinetic parameters.

In temperature-programmed desorption (TPD) experiments, desorption is taken to occur from the sample under a carrier gas stream. For carrier gas flow rates high enough, it is possible to avoid accumulation of the adsorbate at the sample surface. Experimentally, the carrier-gas flow rate is increased until the shape of the TPD spectra and the peak temperature are unaffected by a further increase. Under this condition, however, we cannot assume that readsorption is unimportant since flow out of the sample consists in a diffusion process. It is considered, then, that the solid contains different adsorption sites with specific binding energies and that as it is heated species desorb with different rates from each type of site and are occasionally readsorbed by the surface.

In this paper we report thermal desorption spectra for *n*-tridecane for a number of heating rates and for two different initial coverages from pelletized 5A zeolite. From these spectra we were able to extract kinetic parameters (activation energy and pre-exponential factors) for each of the observed binding states.

## 2. Experimental

Commercially manufactured Linde 5A zeolite was obtained in the form of 1/16” pellets. Scanning electron micrographs of the zeolite showed crystal sizes varying between 1.5 and 3.5 microns. No attempt was made to determine the crystal size distribution. The ratio Si/Al was 1.05 for the zeolite crystals, as measured by energy-dispersive X-ray analysis. Temperature programmed desorption (TPD) spectra were obtained gravimetrically using a Cahn 2000 recording electrobalance interfaced with a computer for data acquisition and analysis. The fresh zeolite was first activated by heating under dry argon purge. A 3 g zeolite sample was placed in a glass vial and heated at 400 K for 1 h and then at 600 K for 5 h. After cooling to room temperature, a few $cm^3$ of *n*-tridecane (Carlo Erba, 99.9% pure) were added to the vial. Control experiments showed that no tridecane was taken up if adsorption is carried out at ambient temperature. Therefore, to achieve hydrocarbon adsorption the sample was left immersed in liquid normal tridecane and kept at 363 K for 3 h. The amount of paraffin used was greater than the volume required for saturation of the zeolite sample.

In a typical run, one pellet was placed in a glass bucket hanging from the weighing arm of the recording electrobalance [5,6]. Argon of ultra high purity was passed through the system at 110 $cm^3 \, min^{-1}$; previous experiments showed that desorption rates were independent of carrier-gas-flow rate for argon flows exceeding 90 $cm^3 \, min^{-1}$, thus allowing perfect reproducibility of the experimental data. Temperatures were programmed to vary linearly with time between room temperature and 700 K at rates in the range from 45 to 440 K $h^{-1}$ using an Omega CN3002 programmable process controller. A chromel–alumel thermocouple placed a few millimeters from the glass bucket was used to measure sample temperatures. The effect of temperature on the measured sample weight due to carrier gas density and viscosity changes was assessed by running blanks with an empty glass bucket. Before starting each TPD experiment, the molecular sieve samples were left under argon flow until the measured weight was constant, indicating that all the hydrocarbon adsorbed in the external surface had evaporated.

Thermal desorption spectra for lower initial coverages were also obtained. Experimentally, a decrease in the hydrocarbon coverage in zeolite 5A was achieved by starting with a pellet at saturation coverage. Before running the TPD experiment, the zeolite sample was heated to different temperatures in order to achieve varying degrees of hydrocarbon desorption. It was then left under argon flow until ambient temperature was reached.

For each run, about 1500 sample weight versus time data points were recorded at equal time intervals and fitted with several splined fifth-order polynomials (~13). These curves were then numerically differentiated with respect to time to obtain the TPD spectra.

## 3. Results and discussion

The rate of desorption of *n*-tridecane from 5A pelletized zeolite for different heating rates as a function of sample temperature is shown in Fig. 1. Two distinct desorption

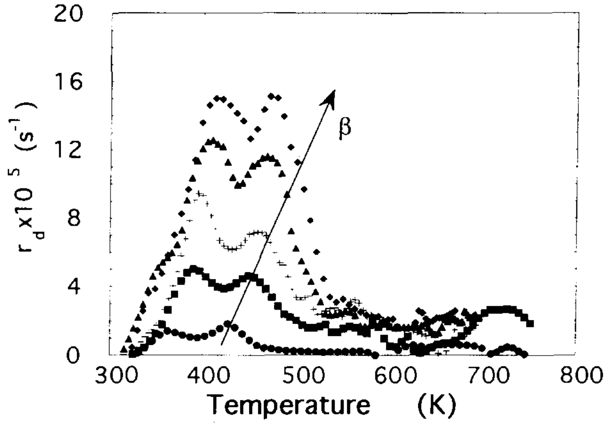

Fig. 1. Rate of *n*-tridecane desorption, $r_d$, from pelletized Linde 5A zeolite versus temperature for the heating rates 60, 300, 420, 480 and 600 K $h^{-1}$.

peaks are evident, indicating that this system contains at least two sites for the adsorption of *n*-tridecane. However, the broad second peak corresponds to two states, as we could conclude from fitting the TPD spectra.

Using different heating rates ($\beta$) the desorption peaks occur at different temperatures ($T_M$). For first order desorption, a plot of $2\ln T_M$-$\ln\beta$ versus $1/T_M$ should yield a straight line with slope and intercept equal to $E_d/R$ and $E_d/A_dR$, respectively [7]. Here $E_d$ is the activation energy, $A_d$ is the pre-exponential kinetic factor, and $R$ is the gas constant. This simple treatment has been extensively used in order to obtain the kinetic parameters. The usual application of this method suffers from a number of drawbacks. It fails to yield the population of each binding state, error bounds for the parameters obtained from a logarithmic plot are difficult to assess, and the peak maximum may be affected by peak overlapping. Instead, we fitted the spectra by solving the mass balance equations for adsorbed *n*-tridecane considering three binding states,

$$\frac{dm_T}{dt} = \sum_{i=1}^{3} \frac{dm_i}{dt} = r_d \tag{1}$$

$$r_d = \sum_{i=1}^{3} r_{di} = \sum_{i=1}^{3} m_i A_i \exp(-E_i/R\,T) \tag{2}$$

$$\frac{dT}{dt} = \beta, \tag{3}$$

with the initial conditions

$$m_i = m_{0i} \tag{4}$$

$$T = 300\ \mathrm{K}, \tag{5}$$

where $m_T$ is the total mass of *n*-tridecane adsorbed per unit mass of dry zeolite, $m_i$ is the mass adsorbed on binding site *i*, and $r_d$ is the desorption rate of *n*-tridecane.

By solving Eqs. (1) to (4) and fitting the numerical results with our experimental spectra we were able to calculate the parameters shown in Table 1. From the kinetic parameters listed in Table 1, it appears that a compensation effect exists, i.e., there is a linear relationship between the logarithm of the pre-exponential factor ($\ln A$) and the activation energy ($E$). This compensation effect has been observed frequently in kinetic and thermodynamic data [8]. It arises when $E$ and $A$ vary in concert so as to keep the product $A\exp(-E/RT)$ approximately constant at a certain temperature. This behavior cannot be predicted a priori and should not be assumed [9]. We may qualitatively

Table 1
Kinetic parameters for desorption of *n*-tridecane from Linde 5A zeolite pellets, obtained by applying Eqs. (1) to (4).

| Desorption peak | $E_d/R$/K | $A_d$/s$^{-1}$ | $m_{0i}$ |
|---|---|---|---|
| I | 5459 | 3225 | 0.051 |
| II | 7563 | 45380 | 0.056 |
| III | 10349 | 2122509 | 0.016 |

understand the compensation effect in the data from Table 1 by means of the analysis done by Gorte [10], who pointed out 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.

Fig. 2 shows the desorption of *n*-tridecane from powdered and also from pelletized Linde 5A zeolite for 240 K $h^{-1}$. From these data it can be seen that, when the adsorbent is in powder form, the peaks are narrower with higher maxima shifted to lower temperatures relative to the desorption peaks from the pelletized form. We found a very good fit to the powder experimental curves with a single pre-exponential factor of $3.67 \times 10^{10}$ $s^{-1}$ and with the same activation energies as those obtained for desorption from the pellets. Hence, there is no need to invoke a compensation effect as spectra can be fitted with the same pre-exponential factor, close to what is expected from the vibrational frequency of the adsorption bond. In particular, we conclude that the apparent compensation effect exhibited by the data in Table 1 should be regarded as a falsification of the kinetic parameters obtained when readsorption is important.

Fig. 3 depicts the rate of desorption of *n*-heptane, *n*-nonane, and *n*-tridecane for the same heating rate (473 K $h^{-1}$). Note that as the molecular weight of the adsorbed hydrocarbon increases, an increasingly intense peak appears at high temperature indicating that the higher hydrocarbons adsorb very strongly on type A zeolites. Clearly, the high temperature regime corresponds to cracking of the hydrocarbon and does not represent the desorption kinetic of the adsorbate from the zeolite. Therefore, no attempt was made to fit the third zone of the curve.

As can be seen from Fig. 3, several different zones of desorption appear in the spectra of hydrocarbon desorption from zeolite A. From the TPD curves of *n*-heptane and

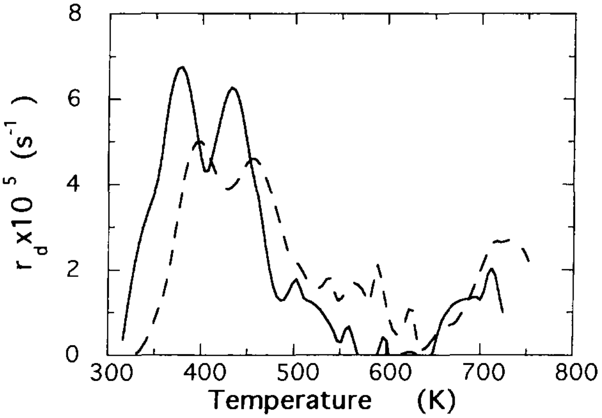

Fig. 2. Rate of *n*-tridecane desorption, $r_d$, from pelletized Linde 5A zeolite versus temperature. The dashed curve represents desorption from pellets and the continuous curve desorption from powdered zeolite for a heating rate of 240 K $h^{-1}$.

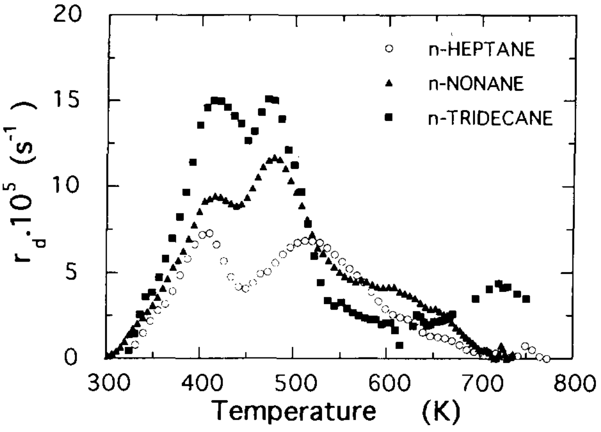

Fig. 3. Rate of desorption of *n*-heptane, *n*-nonane and *n*-tridecane, $r_d$, from pelletized Linde 5A zeolite versus temperature for a heating rate of 473 K $h^{-1}$.

*n*-nonane, we can conclude that two principal desorption peaks appear (zone I at 350–450 K and zone II at 450–600 K). However, for *n*-tridecane, a well differentiated third zone appears at higher temperatures (zone III above 600 K). This feature is more important as the molecular weight of the hydrocarbon increases for a given heating rate. It is important to note that the temperature ranges of these zones do not vary much with the chain length of the hydrocarbon. The first zone might be related to the desorption of the hydrocarbon remaining from the external surface of the crystal and from the intercrystalline spaces. The second, near 500 K, consists of two narrow peaks and represents the desorption from the internal surface. The third zone, which appears at temperatures above 600 K, is only present for higher hydrocarbons. The peaks at zones II and III may be related with the different geometrical localization of the hydrocarbon molecules adsorbed inside the cavity of the zeolite.

In Fig. 4, we show the experimental TPD spectra for *n*-tridecane desorption from pelletized zeolite A, for two different initial coverages and for a heating rate of 235 K $h^{-1}$. The curve with circles refers to maximum coverage (15 wt% of *n*-tridecane) and the curve with rhombi to a lower coverage (12.5 wt% of *n*-tridecane). The spectra are clearly different, with decreasing initial coverage, the population of phase II increases although the peak position does not change. As the temperature begins to increase,the phases are desorbed according to their energies. As one particular phase is desorbing, the higher energy phases, which have not yet been desorbed, are almost fully populated and thus readsorption into these phases is unlikely. In the spectra shown in Fig. 4, the situation appears to be different. At first, the temperature is increased until half of the population of phase I is desorbed, the sample is then cooled until ambient temperature is reached. While the sample is cooling down, molecules adsorbed in phase I can adopt the adsorption site corresponding to phase II, as can be noticed by the increasing population of this site with higher activation energy. It follows that attention must be paid to the complexity of the mechanism, to its development, and to its correct

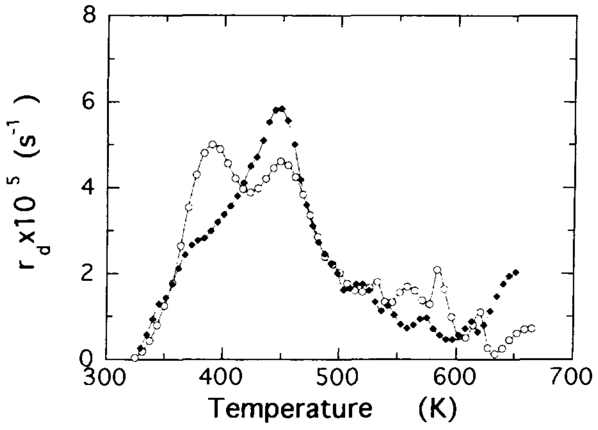

Fig. 4. Rate of *n*-tridecane desorption, $r_d$, from pelletized Linde 5A zeolite versus temperature at different initial coverages and for a heating rate of 235 K h$^{-1}$. The curve with circles represents the desorption at maximum coverage (15 wt% *n*-tridecane) and the curve with rhombi represents desorption for a lower coverage (12.5 wt% of *n*-tridecane).

interpretation from a mathematical point of view. The spectra shown in Fig. 4 represent a starting point for the study of TPD spectra at different initial coverages and will be the subject of future work.

## 4. Conclusions

We have measured desorption rates for normal tridecane adsorbed on commercial 5A zeolite pellets and the results are reported in standard rate units. The temperature-programmed desorption spectra for *n*-tridecane can be quantitatively fitted to a simple first order kinetic model independent of coverage with three different binding states. A single desorption rate expression fits desorption spectra for temperatures varying between room temperature and 650 K and for heating rates varying over an order of magnitude.

The population of the desorbing phases can be determined from the desorption spectra.These populations can be equated to the populations of the various adsorbed phases only if redistribution among the adsorbed phases does not occur during desorption.

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