

Kinetic Desorption Study of Chemisorbed Alkene Molecules on H-Mordenite

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Kinetic desorption mechanism of chemisorbed alkene molecules in synthetic zeolites was investigated. First order kinetics was established with an activation energy for desorption equal to 25 ± 2 kcal/mole for the most stable *n*-hexene isomer—2,3 dimethyl-2-butene diffuse out of the H-mordenite in the temperature range of -75 – 50°C . The boundary layer theory was used to calculate the surface coverage and the depth of the layer in which the electron donated by alkene molecule should be delocalized. The orders of magnitude are reasonable in agreement with other published work on semiconductor solids.

INTRODUCTION

In petroleum industries, particular interest has been attached to the rate of migration of large hydrocarbon molecules into the zeolite, especially of *n*-paraffin and *n*-olefin (1). The pore aperture of the zeolite usually will regulate the diffusion rate of the molecule into intracrystalline voids. Once the molecules are inside the pore structure, various chemical transformations can take place by reaction with the acidic sites.

In general, the diffusion coefficients for desorption are many times smaller than those for sorption because sorption is strongly exothermic and desorption endothermic, so that sorption heats the zeolite crystal framework and surrounding molecules to facilitate further diffusion, while desorption cools the zeolite locally to decrease the rate of desorption. Apart from concentration dependence, the rate of uptake or desorption depended strongly upon the length of the diffusant molecule and were influenced by particle size of the zeolites (2).

Inside the intracrystalline voids where

the reaction is taking place, the effects of electronic charge transfer between molecule and zeolite on chemisorption and catalysis has been analyzed by Weisz (3). By use of semiconductor analogy, he developed a boundary layer theory to derive various relationships for the extent, heat, and rates of chemisorption and other consequences with respect to catalysis. Although an attempt has been made to illustrate the detailed physical processes in order to examine the meaning of "heterogeneity" and "active center" in cases of molecule-zeolite type of chemisorption, actual experimental data were not presented.

Recently we have firmly established the physical presence of electronic charge transfer between alkene molecule and H-mordenite (4). In order to analyze its physical implication and the mechanistic nature of boundary layer model, we have studied the temperature dependence on the amount of chemisorption. To avoid any complication due to chemical change of the ionized molecules, we have chosen the most thermodynamic stable *n*-hexene is-

omer-2,3-dimethyl-2-butene to measure the rate of desorption and to obtain the activation energy of desorption.

EXPERIMENTAL

The synthetic zeolite, H-zeolon, obtained from the Norton Company, was used in this study. Its main components are 73% SiO₂, 9.8% Al₂O₃ and the zeolite contains straight elliptical channels with major and minor axes of 7.0 Å and 5.8 Å. These main channels are connected by smaller side channels with a diameter of 3.8 Å.

The preparation of the sample has been given in a previous paper (5). A vacuum line system with mercury diffusion pump and absolute pressure gauge attached to sample tube by a flexible copper connector was used for kinetic desorption studies.

ESR spectra at various stages were obtained with a Varian 4502 X-band spectrometer with 100 KHz field modulation. Low temperature measurements were achieved with commercial temperature accessories. The spin concentration measurements were standardized with Varian pitch sample.

RESULTS AND DISCUSSION

The results of temperature dependence study with a sealed stationary liquid sample of 2,3-dimethyl-2-butene on zeolite is shown in Fig. 1, with corrections for usual ESR signal changes with temperature. The amount of chemisorbable molecules was found to be temperature dependent based on the formation of an electric boundary layer. However, the experimental data cannot be fitted by an exponential curve.

First order kinetic decay curve was found for the desorption study at various temperatures. A typical curve at constant pressure is shown in Fig. 2. Consequently, the activation energy of desorption $E_0 + Q$ was obtained from Fig. 3 to be equal to 25 ± 2 kcal/mole. The measured ionized alkene concentration on zeolite surface is

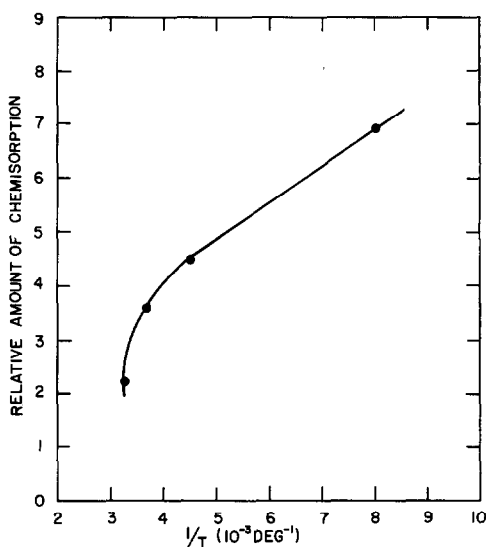


FIG. 1. Temperature dependence studies on the concentration of chemisorbed 2,3-dimethyl-2-butene on H-zeolon.

approximately 8×10^{18} spins/g at room temperature.

From these data, it is instructive to use the boundary layer model and express the maximum number of chemisorbable molecules per unit area N_0 within the zeolite of dielectric constant ϵ

$$N_0 \cong 10^3 (\epsilon E_0 n_D)^{1/2}, \quad (1)$$

where E_0 is the heat of chemisorption or surface potential which develops as a re-

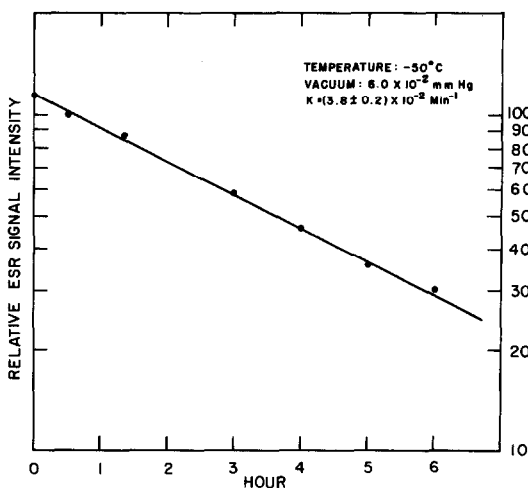


FIG. 2. Kinetic desorption rate of 2,3-dimethyl-2-butene chemisorbed on H-zeolon.

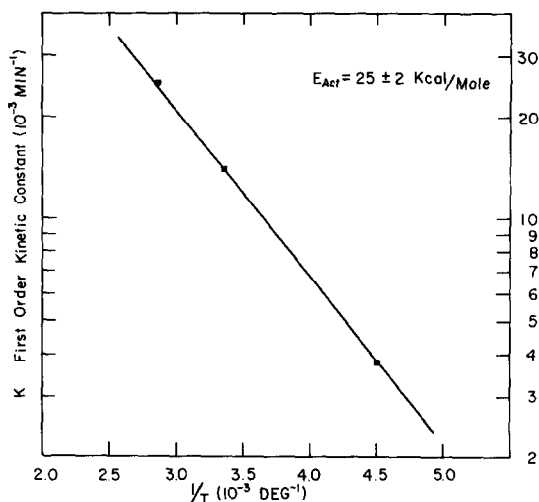


FIG. 3. Activation Energy ($E + Q$) for desorption of 2,3-dimethyl-2-butene on H-zeolon.

sult of electron-transfer between the molecule and zeolite surface. It is close to 1.1 eV calculated from the activation energy of desorption with the assumption of small Q value. With the measured spin concentration $n_D = 8 \times 10^{18}$ spins/g and a reasonable dielectric constant $\epsilon = 4$ (6). Inserting these values of E_0 , ϵ and n_D into Eq. (1) yields $N_0 = 6 \times 10^{12}$ sites/cm². Using the Van der Waals radii for the 2,3-dimethyl-2-butene, a surface area of 25\AA^2 is covered by this molecule. Thus, we found that the ion radicals occupied approximately 1.5% of the total surface area, which is reasonable to expect low surface coverage for the strongly chemisorbed species. Furthermore, the observed proton hyperfine splitting of this ionized species on H-zeolon is 7.2% higher than those measured in liquid phase (7), which is consistent with strong electrostatic field existing within the pore structure. The strength of this electrostatic interaction is measurable as demonstrated in this work.

To examine another aspect of the boundary layer model, we calculated the finite penetration depth D over which the space charge density is supposed to be uniformly distributed and equal to the density of ionized molecules n_D ,

$$D = 10^3 (\epsilon E_0 / n_D). \quad (2)$$

Using the same experimental data we obtained $D = 200\text{\AA}$, which is approximately the radius of the delocalized electron donated by molecules. The inability to detect the ESR signal from the delocalized electron at the present temperature range may be explainable in terms of very short relaxation time and large delocalization radius. Since the boundary layer model is based upon the physical concept of continuous medium, it is not unexpected that these calculated parameters are in reasonable agreement with other works on semiconductor solids (8).

In conclusion, we have explained our experimental results in terms of boundary layer model. It illustrates the cooperation of magnetic resonance techniques with other adsorption methods that can give meaningful parameters about the physical process of chemisorption.

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