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Migration of butene isomers onto the acidic OH groups in small micropores of ferrierite

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Abstract

Kinetics on the adsorption of *n*-butene onto the acidic OH groups existing in the small pores of ferrierite (FER) were studied between 233 and 253 K by IR spectroscopy. The activation energies for the adsorption of 1-butene and *cis*-2-butene were estimated as 23.3 and 28.4 kJ mol^{-1}, while that of *trans*-2-butene was not obtained due to its rapid adsorption. The activation energy for adsorption was considered to have resulted from the diffusion of *n*-butene molecules into the small micropores of FER.

Keywords: Butene; Ferrierite; Zeolites

1. Introduction

Ferrierite zeolite (FER) has been found to be an excellent catalyst for the conversion of normal (*n*-)butene to isobutene owing to its small pore sizes which restrain the side reaction products via dimeric species [1,2]. The effect of pore sizes of zeolites on reactant and product molecules as well as intermediates is, therefore, regarded as of importance together with the strength of their acid sites. We have been studying the adsorption of small olefin molecules ($\leq C_4$) on the acidic OH groups in small pores of FER by low temperature FT-IR method in order to clarify the effect of the pore size on the size of adsorbing molecules. The energy barriers for adsorption of butene isomers on the acidic OH groups were qualitatively expected to be in the order as follows: isobutene $\gg$ *cis*-2-butene $>$ 1-butene $\gg$ *trans*-2-butene [3]. It was also inferred that the adsorption on the acid sites occurred via migration of olefin molecules from silanol groups on the external surface of FER [3]. Here, the quantitative interpretation of the previous study on the adsorption kinetics of butene isomers is shown.

2. Experimental

An IR disk of FER (Tosoh, $SiO_2/Al_2O_3 = 17.0$) was treated by O_2 at 773 K followed by evacuation and cooling to low temperatures. IR spectrum of FER after pretreatment is shown in Fig. 1(a), where silanol and the acidic OH groups were observed at 3750 and 3607 cm^{-1}, respectively. The amount of the acidic OH and silanol groups were measured by ethene and pyridine adsorption, respectively [4]. The interaction of the acidic OH groups was observed with ethene adsorption, while only the silanol groups was interacted with pyridine molecules. These results directly indicate that the acidic OH groups and the silanol groups

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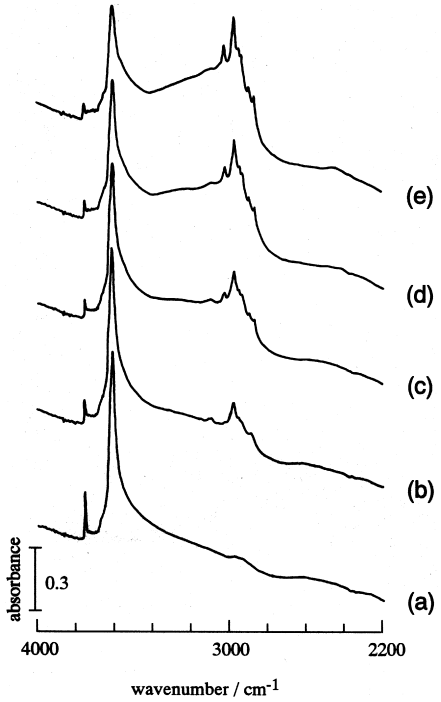
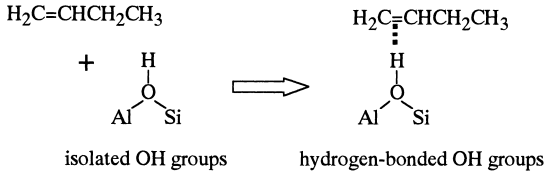


Fig. 1. Time course of IR spectra of 1-butene adsorbed FER at 253 K: (a) before adsorption; (b) after 1 min; (c) 10 min; (d) 30 min; (e) 60 min.

certainly exist in the pores and on the external surface of FER, respectively. Knowing the absorption coefficient of the acidic OH and silanol groups, the amounts of adsorption of butene on each site were estimated by the decrease of each band upon adsorption.

3. Results and discussion

A time course of spectral change during adsorption of 1-butene is shown in Fig. 1. The pretreated FER with an IR spectrum in Fig. 1(a) was exposed to Torr of 1-butene at 253 K. During the time course, the acidic OH groups decrease gradually, while silanol groups decreased immediately and kept unchanged for 60 min. When the system was evacuated at the same temperature, complete recovery of the isolated silanol groups was observed, indicating the equilibrium adsorption of 1-butene on silanol groups (not shown). On the other hand, the gradual decrease of the isolated acidic OH groups was accompanied by the appearance and increase of the broad hydrogen-bonded OH band centered at 3200 cm^{-1}. The CH stretching bands (3200–2800 cm^{-1}) due to 1-butene showed the same time course. These results indicate that the adsorption of 1-butene molecules onto the acidic OH groups gradually proceed at 253 K.



The dependence of the time course on the temperature is demonstrated in Fig. 2, where the rate of adsorption increased by increasing the temperature. When ethene or propene molecules were adsorbed, such a time course was not observed, but they immediately adsorbed on the acidic OH groups [3]. What is more, 1-butene adsorption on other zeolites which possess lager micropores did not result in such a time course [5,6]. Therefore, the adsorption of 1-butene on the acidic OH groups on FER is regarded as an activation process; an activation energy for 1-butene adsorption on the acidic OH groups exist. This is most probably due to the diffusion process of 1-butene molecules into the considerably small pores of FER.

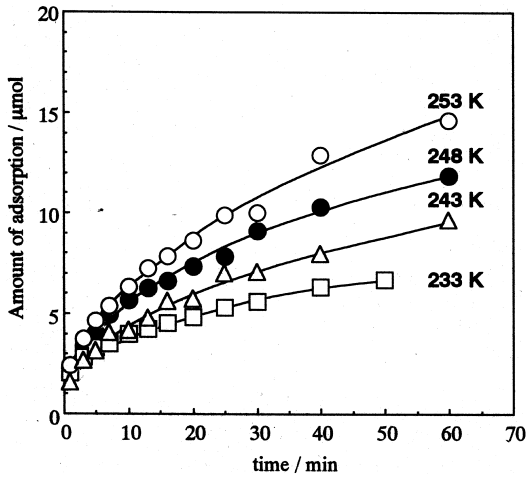


Fig. 2. Time course of the amount of 1-butene adsorbed on the acidic OH groups of FER at various temperatures.

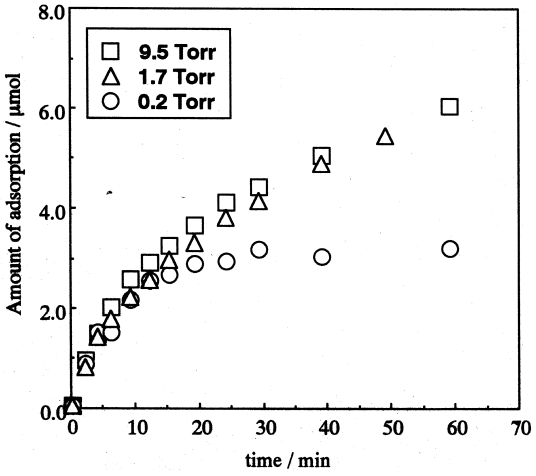


Fig. 3. Pressure dependence of the time course of 1-butene adsorption at various pressures at 253 K.

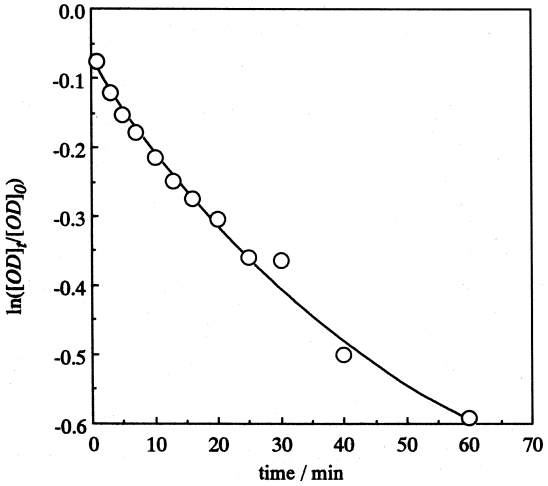


Fig. 4. The $-\ln([OH]_t/[OH]_0)$ versus *Nkt* plots for 1-butene adsorption on the acidic OH groups of FER, see text.

The migration of the adsorbed molecules to the stable adsorption sites is accounted for the rate determining steps on a flat surface, if the amount of adsorption is not limited by the pressure. The dependence of the rate of adsorption of the acidic OH groups on the pressure is shown in Fig. 3. Although the pressure was varied in almost three orders of magnitude, the initial rates of adsorption of 1-butene on the acidic OH groups were almost constant in an experimental error. The saturation of the amount of adsorption at 0.2 Torr after 15 min was due to the consumption of the gaseous molecules. Therefore, as long as the gaseous molecules are efficiently supplied (>ca. 1.0 Torr), the adsorption of 1-butene on the acidic OH groups is not restricted by the pressure. In general, the equation for the rate of adsorption is described as follows, assuming that the rate determining step is the two-dimensional migration:

$$\frac{\mathrm{d[OH]}}{\mathrm{d}t} = Nk[\mathrm{OH}] \tag{1}$$

where [OH], t and k represent the amount of the free acidic OH groups, time and the rate constant, respectively. N is a constant which indicates the amount of precursor 1-butene molecules for adsorption onto the acidic OH groups with a sufficient pressure (see Fig. 3). Eq. (1) leads to the following equation:

$$-\ln\left(\frac{[\mathrm{OH}]_t}{[\mathrm{OH}]_0}\right) = Nkt \tag{2}$$

where $[\mathrm{OH}]_t$ and $[\mathrm{OH}]_0$ indicate the amount of free acidic OH groups at the time equal to t and 0, respectively. The $-\ln([\mathrm{OH}]_t/[\mathrm{OH}]_0)$ versus *Nkt* plots shown in Fig. 4 is not a straight line, indicating that the rate determining step is not the migration on the two-dimensional surface. On the other hand, it is known that the rate of molecular diffusion into micropores is proportional to $t^{1/2}$ [7]:

$$-\frac{\mathrm{d[OH]}}{\mathrm{d}t} = Nkt^{1/2} \tag{3}$$

Here, the term $-(\mathrm{d[OH]}/\mathrm{d}t)$ corresponds to the rate of adsorption expressed by the rate of decrease of the free acidic OH groups. The time courses observed in Fig. 2 were re-plotted against $t^{1/2}$ in Fig. 5. The plots for 1-butene adsorption at all measured temperatures resulted in straight lines, and therefore, the adsorption of 1-butene is reasonably regarded as being restricted by diffusion of molecules into small micropores of FER. Using Eq. (3) the rate constants at various temperatures were obtained. The apparent activation energy for diffusion of 1-butene molecules onto the acidic OH groups in the micropores of FER was estimated as 23.3 kJ mol^{-1} through Arrhenius plots (Fig. 6). Similarly, the apparent activation energy for *cis*-2-butene diffusion was obtained as 28.4 kJ mol^{-1}, while that of *trans*-2-butene could not be estimated because of its rapid migration due to its smaller molecular size. The time courses of the

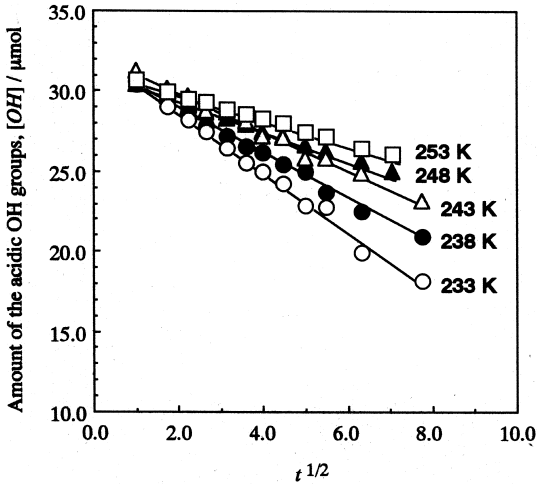


Fig. 5. The $-(d[OH]/dt)$ versus $t^{1/2}$ plots for 1-butene adsorption on the acidic OH groups of FER, see text.

amount of adsorption of 1-butene, *cis*-2-butene and *trans*-2-butene at 2.0 Torr and 253 K are compared in Fig. 7. The rapid adsorption of *trans*-2-butene onto the acidic OH groups in pores is perceived, while 1-butene and *cis*-2-butene reached the acid sites very slowly. The number of the acidic OH groups in the used IR

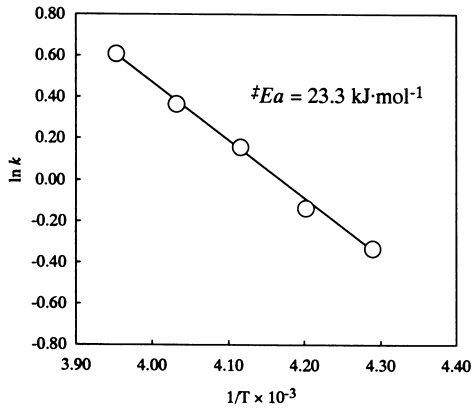


Fig. 6. Arrhenius plots for 1-butene adsorption on the acidic OH groups of FER.

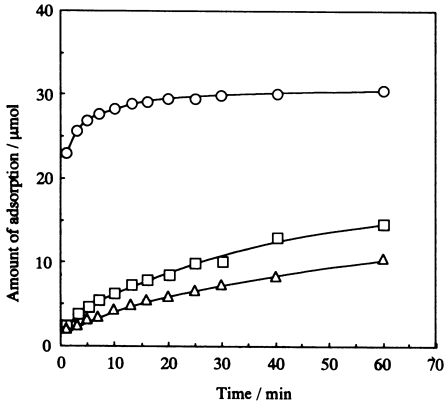


Fig. 7. Comparison of the rate of adsorption of 1-butene, *cis*-2-butene and *trans*-2-butene at 253 K.

disk of FER was quantified by ethene adsorption as 32.8 μmol [4] which is in good agreement with the saturation amount of adsorption of *trans*-2-butene in Fig. 7.

In summary, the difference in activation energy for migration into zeolitic pores for butene isomers reflected on the rate of adsorption on the acidic OH groups in the case of FER in the present experimental conditions. These experimental results will be an useful evidence also for MD simulations.

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