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CHEMICAL REACTIONS IN CHROMATOGRAPHIC COLUMNS

DEHYDROGENATION OF ETHANE OVER CADMIUM-EXCHANGED ZEOLITE 4A

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SUMMARY

Pulsed-flow techniques were used to detect considerable differences in the heats of adsorption of ethane and ethylene on various cadmium-exchanged zeolites 4A at temperatures up to 500 °C. Higher values (about 10.0 kcal/mole) were observed for ethylene than for ethane (5.0 kcal/mole) at 300–400 °C. Experimental verification is provided pertaining to the dehydrogenation of ethane in a gas chromatographic reactor. By appropriate choice of the reaction conditions, conversions up to 80% per pass could easily be obtained at temperatures (400–500 °C) at which the thermodynamic equilibrium for a diluted ethane stream ($p_{C_2^+} = 0.01$–$0.1\ p_{tot.}$) would not permit more than 25%.

INTRODUCTION

The development of gas chromatography as an analytical technique was accompanied by the use of chromatographic columns as chemical reactors[1–8], allowing applications such as the determination of adsorption isotherms under reaction conditions and the attainment of non-equilibrium conversions for reversible reactions in which products are separated.

This paper offers an example of both applications. We investigated cadmium-exchanged zeolites, which are known for their ability to separate alkanes from alkenes at temperatures up to 500 °C. The large separation effects reported for *n*-hexane *versus* *n*-hexene[9] prompted us to measure the adsorptive capacities of these 4A-type zeolites for the pair ethane–ethylene. The same adsorbents were used in pulsed-flow dehydrogenation of ethane to measure the non-equilibrium conversions for the reaction $C_2H_6 \rightleftharpoons C_2H_4 + H_2$ by taking direct advantage of differences in the adsorption capacities of the reactant (ethane) and the products (ethylene and hydrogen). The effects of the weight of catalyst, flow-rate, pulse size and frequency of the feed component were studied in single-pulse experiments; the effect of repetitive pulses was also considered.

EXPERIMENTAL

Sample preparation

Powdered CECA K_1 (4 Å) zeolites (nominal composition: $Na_2O \cdot Al_2O_3 \cdot 2SiO_2$), containing about 20% of a clay binder, were used in two different sample preparation procedures for ion-exchanged materials (mode A and B).

Mode A. A 103-g amount (dry basis) of the original zeolite was contacted with an aqueous solution of $CdCl_2 \cdot 2.5H_2O$ for 4 h at 65 °C. The solution compositions are listed in Table I. Unless otherwise indicated, the treatment was repeated three times with a fresh solution. After the final exchange, the material was washed repeatedly with distilled water (usually 5 l) until no chloride was detectable in the filtrate. The solid was then dried at 120 °C for 16 h and activated at 400 °C for 16 h.

TABLE I

PREPARATION OF CADMIUM-EXCHANGED ZEOLITES 4A

Sample	*Mode of preparation*	*Exchanging solution (M)*	*Time of exchange (h)*	*No. of treatments*	*Na exchanged in zeolite (%, dry basis)*
Cd-2	A	0.525	4	3	91.5
Cd-3	B	0.0025	21	–	93.0
Cd-5	A	0.190	4	1	55.0
Cd-6	A	0.290	4	1	58.0
Cd-7	A	0.700	4	3	78.0

Mode B. Dosed volumes of an aqueous solution of $CdCl_2 \cdot 2.5H_2O$ were recirculated at 70 °C through 40 g of the zeolite placed inside a column (I.D. 2 cm) by means of a peristaltic pump (delivery rate 20 l/h) for 21 h as indicated in Table I. After washing, the treatment followed mode A.

Heats of adsorption

Heats of adsorption (ΔH) were measured in a chromatographic unit consisting of a pulse injection system placed in series with a packed column containing the exchanged zeolite and a thermal conductivity cell. Helium was used as a carrier gas at flow-rates (F) varying from 15 to 40 cm³ (S.T.P.)/min. A six-port Carlo Erba injection valve was employed to inject dosed volumes of the hydrocarbon (usually 1 cm³) in admixture with non-adsorbable nitrogen. The differences in the emergence times of the hydrocarbon and nitrogen were equal to the retention time of the hydrocarbon (t_R^{obs}) through the packed section of the column. From the measured retention times *versus* $1/T$ (T = absolute temperature), ΔH values were calculated by means of the equations[9]

$$\log t_R^{corr} = C - \frac{\Delta H}{2.303\,R} \cdot \frac{1}{T} \qquad (1)$$

where

$$t_R^{\mathrm{corr}} = t_R^{\mathrm{obs}} \cdot \frac{T}{298}\left[\frac{3}{2} \cdot \frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right] \tag{2}$$

and P_i and P_o are the pressure at the column inlet and outlet, respectively. All measurements were carried out using U-shaped all-glass columns (I.D. 4 mm) packed with different amounts of zeolites (42–65 mesh), as indicated in Table II. Prior to the pulse, the zeolite was flushed with dry helium at a flow-rate of 25 cm^3/min for 2 h at 500 °C in order to remove adsorbed water.

Catalytic activity

The apparatus consisted of a modified version of the system used for adsorption measurements: columns of different lengths (30–150 cm) were enclosed inside a fluidized-solids sand-bath which ensured temperature control to within ± 3 °C. Helium or nitrogen was used as the carrier gas and the hydrocarbon was injected at evenly spaced intervals; pulse volumes of the hydrocarbon were varied from 0.2 to 5 cm^3. After passing through the reactor, the pulse product was analyzed by an F & M Model 500 gas chromatograph with a silica gel column.

RESULTS

Heats of adsorption

Heats of adsorption for various specimens are given in Table II; corrected pulse retention times (t_R^{cor}) for Cd-2 are plotted in Fig. 1. The pulse retention times of ethylene greatly exceed those of ethane, the difference still being appreciable even at temperatures as high as 400–500 °C. Accordingly, $\Delta H_{C_2^-}$ are higher than $\Delta H_{C_2^+}$ values showing little variation with the amount of zeolite packing (Table II). Instead, the ΔH values appear to depend upon temperature and the extent of sodium exchange; the heat of adsorption of ethylene increases with higher exchange values and varies from 6.8 kcal/mole for the original zeolite (K$_1$) to 11.0 kcal/mole for Cd-2 and Cd-3

TABLE II

HEATS OF ADSORPTION OF ETHANE ($\Delta H_{C_2^+}$) AND OF ETHYLENE (ΔH_{C^-}) OVER VARIOUS CADMIUM-EXCHANGED ZEOLITES

Sample	*Flow-rate (cm³/min)*	*W (g)*	*Temperature range (°C)*	$\Delta H_{C_2^-}$* *(kcal/mole)*	$\Delta H_{C_2^+}$** *(kcal/mole)*	*Na exchanged in zeolite (%)*
K$_1$	25	21.5	215–440	6.8	0	0
Cd-2	25	20–40	330–400	11.0	5.0	91.5
Cd-2	25	20–40	400–520	10.1	—	91.5
Cd-3	25	24	330–400	11.5	5.5	93.0
Cd-3	25	24	400–520	8.5	—	93.0
Cd-5	25	32.4	340–400	10.2	4.9	55.0
Cd-5	25	32.4	400–500	7.6	—	55.0
Cd-6	25	30–40	250–420	9.8	5.7	58.0
Cd-7	15–40	16.5	315–500	11.0	5.3	78.0

* Energy standard deviation 0 5 kcal/mole.

** Energy standard deviation 0.3 kcal/mole.

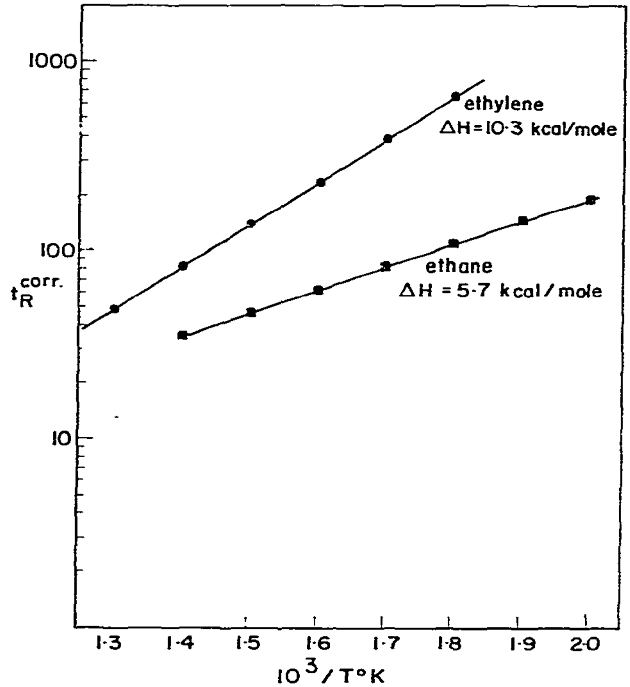

Fig. 1. Corrected pulse retention times on Cd-2 zeolite as a function of temperature ($W = 31$ g; $L = 150$ cm; I.D. = 6 mm; $F = 25$ cm^3 (S.T.P.)/min; pulse volume = 1 cm^3).

(90% exchange). With ethane, the original zeolite shows almost no adsorption, in contrast to cadmium exchanged zeolites for which $\Delta H_{C_2^+} = 5.0$ kcal/mole is calculated, irrespective of the extent of exchange. It is still noteworthy that at temperatures above 400 °C all cadmium-exchanged zeolites cease to adsorb ethane; for Cd-2 $\Delta H_{C_2^-} = 10.1$ and $\Delta H_{C_2^+} \approx 0$ kcal/mole. Consequently, differences with respect to ethylene become more pronounced at these temperature, thus confirming a unique characteristic of the cadmium zeolites, as noted earlier[9].

Catalytic activity

Owing to its higher degree of exchange, Cd-2 was preferred in catalytic activity experiments. The results for single- and repetitive-pulse experiments are illustrated here in terms of the variables considered.

The effect of pulse size is shown in Fig. 2 for runs at 400–500 °C using a 150-cm reactor packed with 28 g of 42–65-mesh Cd-2 catalyst, operated with a carrier gas flow-rate of 25 cm^3/min. Clearly, the fraction of ethane converted is almost independent of the pulse size, at least for the range from 0.2 to 5 cm^3. Differences arising when the sequence of pulses was reversed, *i.e.*, high pulse sizes first (Fig. 2, broken line at 450 °C) were ascribed to coking. Although no attempt was made to define kinetic parameters, the linear responses and symmetrical shapes of the concentration pulses at the exit, at all levels of injected pulses, suggest a first-order reaction[10,11].

Provided that columns with identical diameters are being used, the effects of

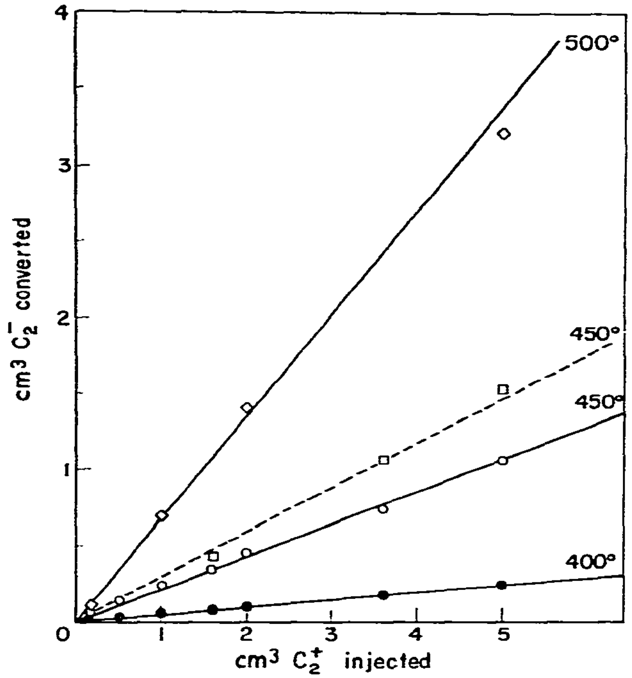

Fig. 2. Effect of pulse size of ethane on conversion on Cd-2 zeolite at various temperatures ($W = 28$ g; $L = 150$ cm; I.D. = 6 mm; $F = 25$ cm^3 (S.T.P.)/min).

the catalyst weight, *W*, and reactor length, *L*, are the same, namely an increasing conversion with increasing *W* or *L*, with departures from linearity only at the highest values of *W* or *L* (Table III).

The effect of throughput is shown in Fig. 3 for runs at temperatures from 400 to 500 °C; the pulse volumes were 0.5 cm^3, injected into a 150-cm column operated with a flow-rate of 25 cm^3/min. Considerable variations during the first pulses over a fresh catalyst are noticeable: product analysis shows that ethane is partly cracked to methane (Fig. 3). After 5–10 pulses, the catalyst reaches a steady state and little further change in the product distribution occurs. On the basis of the steady-state values of conversions to ethylene, the Arrhenius activation energy was found to be 28.2 kcal/mole (Fig. 4).

TABLE III

EFFECT OF CATALYST WEIGHT ON CONVERSION

Flow-rate of helium, 25 cm^3/min; pulse size, 0.5 cm^3.

W (*g*)	*Temperature* (*°C*)	t_c (*sec*)	*Conversion to ethane* (*%*)	*Selectivity towards ethylene* (*%*)	*N* (*mole/mole*)
18.7	500	43	58	95	50
28.0	500	64	70	94	50
38.0	500	87	90	87	50
28.0	450	56	27	100	50
38.0	450	76	32.5	92	50

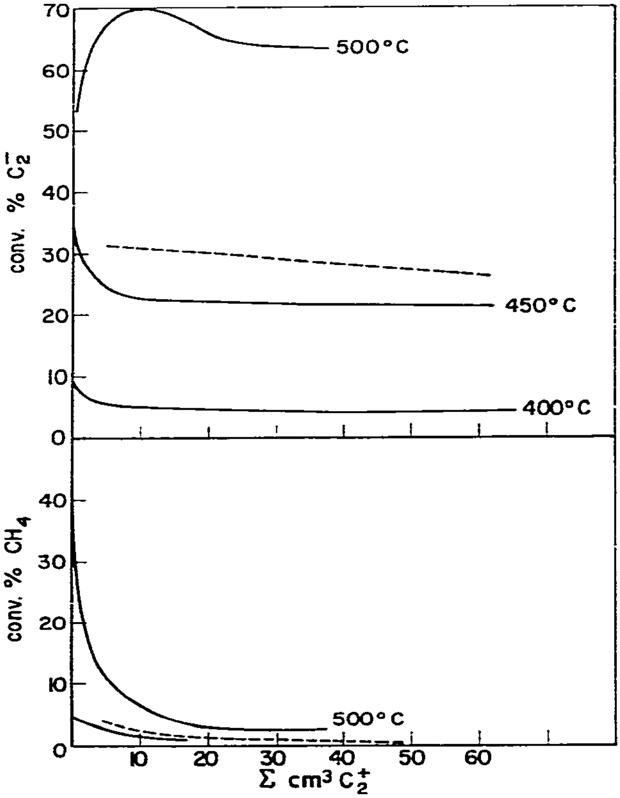

Fig. 3. Effect of throughput on conversion (pulse volume = 0.5 cm³; other conditions as in Fig. 2).

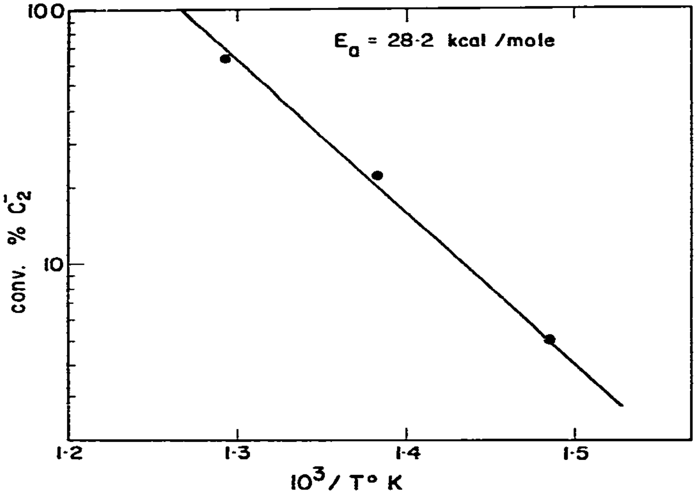

Fig. 4. Temperature dependence of conversion to ethylene (conditions as in Fig. 3).

The effect of flow-rate is illustrated in Table IV in terms of contact times, t_c (ratio of the catalyst volume to flow-rate of the carrier gas). Table IV also gives Δt values, defined as the excess time (with respect to less adsorbable ethane) a pulse of ethylene spends travelling through a column of packed zeolite.

TABLE IV

EFFECT OF FLOW-RATE ON CONVERSION

Reactor length, 150 cm; pulse volume, 0.5 cm^3 (ethane).

Flow-rate of carrier gas [cm^3 (S.T.P.)/min]	*Temperature (°C)*	t_c *(sec)*	Δt *(sec)*	*N (mole/mole)*	*Conversion of ethane (%)*
50	450	38	41	68.5	17.7
30	450	51	52	52.0	21.4
25	450	56	55	46.0	22.0
15	450	83	87	43.5	28.0
25	500	64	20	18.3	64.0

The results in Table IV suggest that only kinetic factors (adsorption, reaction and desorption) are rate controlling under the given conditions and that the extent of reaction is not equilibrium limited. We can compare the observed conversions with those expected from equilibrium for a diluted stream of ethane. Following the procedure outlined by Matsen *et al.*[3], the degree of dilution of ethane, N, is given by

$$N = \frac{Ft}{S} \tag{3}$$

where N = moles of carrier gas per mole of ethane, F cm^3/min = carrier gas flow-rate in at 25 °C and 1 atm, t min = time between pulses and S cm^3 = ethane sample size at 25 °C. Theoretical conversions for any given value of N and t can be derived from the equilibrium constants in ref. 12. The values reported in Figs. 5 and 6 were obtained for temperatures of 450 and 500 °C, respectively. Comparison with experimentally determined conversions proves that the reaction is not equilibrium controlled. Actually, the experimental conversions are always higher than those at equilibrium, the degree of improvement depending upon the reaction conditions. The influence of parameters such as pulse size (Figs. 2 and 3), carrier gas flow-rate (Table IV) and slug frequency (Table V) are depicted in Figs. 5 and 6.

The results of repetitive-pulse experiments (Table V) show only a minor effect on the conversions. In terms of productivity, improvements over the theoretical values are greatest when the time elapsed between pulses is increased. Obviously, the effect ceases for $\Delta t > t$, that is, when two consecutive pulses overlap. When $t \geqslant \Delta t$, the improvement is much higher than in conventional operations. As an example, consider the results obtained at 500 °C (Table IV): with t = 20 sec and pulse sizes of 5 cm^3, a conversion level of 64% would allow a productivity in the order of 10 cm^3/min of ethylene. With the same dilution but in flow operations, the expected productivity would be only of the order of 2 cm^3/min of ethylene; in addition, much more carrier gas would be needed as a diluent in a flow system in order to attain similar conversion levels.

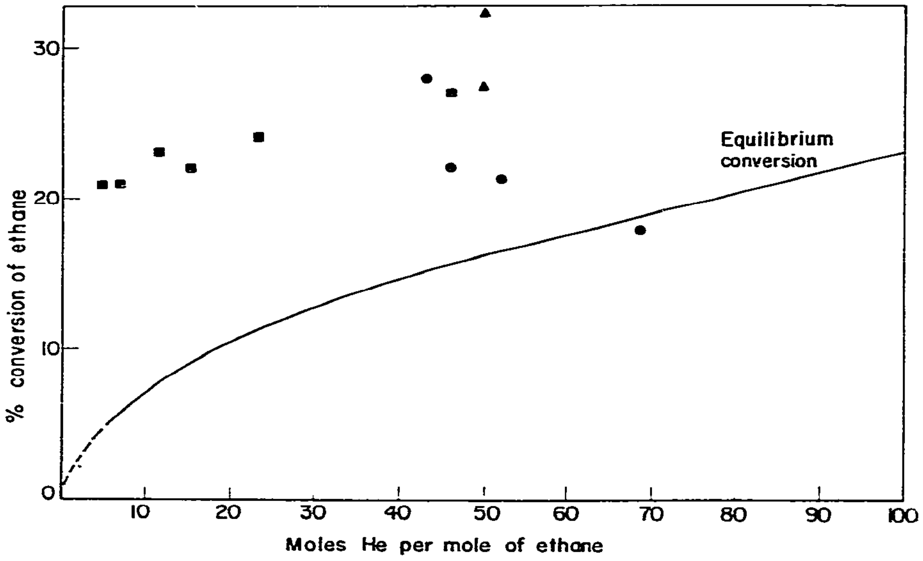

Fig. 5. Equilibrium conversions and repetitive-pulse conversions at 450 °C ($K_p/P = 5 \cdot 10^{-4}$ atm^{-1}; K_p = equilibrium constant of the dehydrogenation, P = total pressure). ▲, values from Table III; ●, values from Table IV; ■, values from Fig. 2.

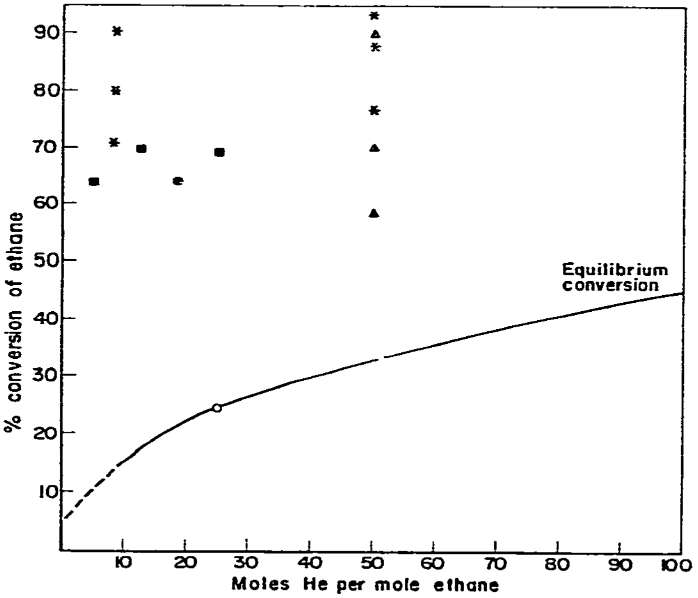

Fig. 6. Equilibrium conversions and repetitive-pulse conversions at 500 °C($K_p/P = 2.5 \cdot 10^{-3}$atm^{-1}). ▲, ●, ■ as in Fig. 5; *, see Table V; ○, CdO/SiO$_2$.

TABLE V

EFFECT OF REPETITIVE-PULSE EXPERIMENTS

Runs at 500 °C; pulse volume, 1 cm^3; flow-rate of helium, 25 cm^3 (S.T.P.)/min.

Pulse frequency (sec^{-1})	t_c *(sec)*	*Number of slugs*	*Conversion of ethane (%)*	*Selectivity towards ethylene (%)*	*N (mole/mole)*
20	86	1–10	94	94	50
20	86	11–25	88.6	92	50
20	86	26–40	76.8	94	50
120	86	1–10	90.5	86	8.2
120	86	11–25	79.5	92	8.2
120	86	26–80	71.0	92	8.2

DISCUSSION

The scope of this paper is limited to considerations concerning the catalytic dehydrogenation reaction of ethane. The differences in heats of adsorption for the ethane–ethylene system over cadmium-exchanged zeolites at temperatures up to 500 °C made it worthwhile investigating this reaction, known to be equilibrium limited. The results described show that conversions beyond thermodynamic equilibrium can be achieved under chromatographic conditions. Factors that optimize productivity are large sample sizes, low flow-rates and control of the pulse frequency, avoiding undesired interaction between successive pulses. On the basis of *a priori* information on the adsorption characteristics of the solid with respect to reactant (ethane) and product (ethylene), it has been possible to select operating conditions for maximal conversions. This is a highly desirable criterion in studies of reactions in chromatographic columns and it does not seem to have been exploited in previous work[2–6]. It appears that the observed improvement over equilibrium is not a matter of the active element, Cd^{2+} (compare the value of CdO/SiO_2 in Fig. 6), but rather the particular characteristics of the cadmium-exchanged zeolites, and hence their adsorption characteristics.

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