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The Consequences of Steam Dilution in Catalytic Cracking

I. Effect of Steam Dilution on Reaction Rates and Activation Energy in 2-Methylpentane Cracking over USHY

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We have examined steam dilution in the cracking of 2-methylpentane on USHY at 400, 450, and 500°C. Steam appears to act as a more "intrusive" diluent than the diluents we have previously examined, i.e., N_2, H_2, CO_2, and CO. We find that at 400°C (and probably below this temperature), a small amount of H_2O has a strong promoting effect on the rate of the isomerization reaction which accompanies cracking. This effect is so strong at small dilution ratios that, rather than reducing the rate of overall conversion (by diluting the reactants), steam actually *increases* the overall conversion rate. However at 450°C and above, even low levels of steam dilution *reduce* the overall rate of conversion, as we might have expected. Due to this temperature dependence of the dilution effect, steam dilution reduces the apparent activation energy of the overall reaction, making the rate of the cracking reaction less sensitive to temperature changes in the presence of steam. Higher dilution ratios invariably reduce the rate of conversion with the result that at the low temperature there is a dilution ratio which yields a maximum rate. It is this maximum rate that is higher than the rate of the undiluted reaction. Here we present quantitative data on these effects and offer a possible interpretation of the mechanism behind it in order to provide a framework for the discussion and utilization of this interesting phenomenon.

INTRODUCTION

Recently we have reported on the effects of N_2, H_2, CO_2, and CO as diluents on the activity and selectivity of 2-methylpentane cracking over USHY zeolite (1, 2). We found that the inert diluents N_2 or H_2 reduce both the cracking and the decay rate of this reaction simply by diluting the reactant concentration. On the other hand, polar CO and polarizable CO_2 "passivate" both monomolecular and bimolecular reaction sites, thus reducing the rate of reaction even more than N_2 and H_2, both of which seem to act only by diluting the concentration of the feed. These investigations appear to indicate the existence of an electron donor–acceptor interaction between active sites and polar or polarizable diluent molecules, despite the obvious difficulty of adsorbing these molecules on the zeolite at reaction temperatures.

This raises interesting possibilities. If this type of interaction can be enhanced to yield commercial benefit, cracking reaction rates and selectivities may be controllable by the addition of appropriate diluents to the feed stream. The phenomenon is also potentially important since it throws new light on our understanding of the elementary events which take place on the catalyst surface during the catalytic cracking process.

In this connection we have examined the influence of the ubiquitous diluent: moisture. The influence of H_2O as a catalyst modifier in high temperature "steaming" of cracking catalysts has been widely studied (3–8). On the other hand, the influence of H_2O as a diluent on activity and selectivity during the catalytic cracking process has received little attention. In this work, we report on our observations when steam was added to the reactant stream. We present a detailed report of the resulting changes in activity and some of the effects on selectivity in 2-methylpentane cracking over USHY over the temperature range 400–500°C.

THEORY

The Catalytic Cracking Chain Mechanism

Our recent studies (9, 10) show that catalytic conversion of 2-methylpentane over USHY proceeds via a chain mechanism, consisting of three main reaction types:

1. chain *initiation* by the protolysis of C−C and C−H bonds in feed molecules on the lattice-resident Brønsted acid sites;
2. chain *propagation* by disproportionations between feed molecules and carbenium ions resident on the Brønsted bases on the lattice;
3. chain *termination* by the desorption of carbenium ions as olefins, leaving behind a proton to reconstitute the Brønsted site for further initiations.

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Other reactions accompanying the main chain processes include the rearrangement of carbenium ions leading to isomer production, β-cracking of carbenium ions leading to "excess" olefin production, and coke formation by the disproportionation reaction between adjacent carbenium ions.

The Kinetic Model

A kinetic model accounting for the chain mechanism in all paraffin cracking has been developed (9–11) and applied to a number of systems (11–14). The differential form of this rate expression is

$$\frac{dX}{d\tau} = \frac{A_1\left(\frac{1-X}{1+\varepsilon X}\right) + A_2\left(\frac{1-X}{1+\varepsilon X}\right)^2}{1 + B\left(\frac{1-X}{1+\varepsilon X}\right)}[1+Gt]^{-N}, \qquad [1]$$

where

X	is the instantaneous fractional conversion of reactant at time on stream t;
τ	is the space time;
G	is the deactivation rate constant;
N	is the decay exponent;
ε	is the volume expansion coefficient (calculated from selectivity data).

The constants A_1, A_2, and B are defined by the expressions

$$A_1 = \frac{\sum k_i K_A + \sum k_{jR} \sum K_j n_j [C_A]_0}{1 + \sum K_j n_j [C_A]_0}[SH]_0 \qquad [2]$$

$$A_2 = \frac{-\sum k_{jR} \sum K_j n_j [C_A]_0}{1 + \sum K_j n_j [C_A]_0}[SH]_0 \qquad [3]$$

$$B = \frac{\left(K_A - \sum K_j n_j\right)[C_A]_0}{1 + \sum K_j n_j [C_A]_0}, \qquad [4]$$

where

n_i	is a stoichiometric factor accounting for the number of ith product molecules formed from a feed molecule;
K_A	is the adsorption constant for the reactant;
K_j	is the adsorption constant of the jth product;
k_i	is the rate constant of the ith mode of monomolecular (initiation) reaction;
k_{jR}	is the rate constant for the carbenium ion $C_jH_{2j+1}S^+$ undergoing the Rth mode of bimolecular (propagation) reaction;
$[C_A]_0$	is the initial concentration of reactant.

The parameter A_1 is related to the sum of the rates of feed conversion occurring via both monomolecular (initiation) and bimolecular (propagation) processes. The parameter A_2 is related to the sum of the reaction rates of bimolecular processes alone. The parameter B reflects the relative values of the adsorption constants of reactant and products (11).

Reaction Rates

The rate of feed conversion by initiation reactions alone can be calculated from the values of A_1, A_2, and B (obtained by fitting the total rate data set), by noting that Eq. [1] under the condition $t = 0$, $X = 0$, gives

$$r_0 \equiv \left(\frac{dX}{d\tau}\right)_{t\to 0,\, X\to 0} = \frac{A_1 + A_2}{1+B} = \frac{\sum k_i K_A [SH]_0}{1 + K_A [C_A]_{0,0}}. \qquad [5]$$

The total rate of the feed conversion can be obtained from r_0 using the relationship:

$$r_{\text{tot}} = r_0\left(\frac{1}{\sum X_{0i}}\right), \qquad [6]$$

where X_{0i} is the probability of feed conversion via the ith path of protolysis (10) (i.e., by initiation).

In our notation $\sum X_{0i}$ is therefore the fraction of total conversion which proceeds via protolysis. This value is obtained from selectivity data, as we will show elsewhere.

Dilution Effect

It is convenient to define a dilution ratio β, as

$$\beta = \frac{\text{moles of a diluent}}{\text{moles of a reactant}}. \qquad [7]$$

Thus, the mole fraction of feed in the input stream is given by $1/(1+\beta)$ and the concentration of feed at dilution ratio β is given by

$$[C_A]_{0,\beta} = \frac{[C_A]_{0,0}}{1+\beta}, \qquad [8]$$

where $[C_A]_{0,0}$ is the initial concentration of pure feed (at $\beta = 0$).

As a result, the parameters A_1, A_2, and B are also functions of the dilution ratio β (2):

$$A_{1,\beta} = \frac{\sum k_i K_A (1+\beta) + \sum k_{jR} \sum K_j n_j [C_A]_{0,0}}{(1+\beta) + \sum K_j n_j [C_A]_{0,0}}[SH]_0 \qquad [9]$$

$$A_{2,\beta} = \frac{-\sum k_{jR} \sum K_j n_j [C_A]_{0,0}}{(1+\beta) + \sum K_j n_j [C_A]_{0,0}}[SH]_0 \qquad [10]$$

$$B_\beta = \frac{\left(K_A - \sum K_j n_j\right)[C_A]_{0,0}}{(1+\beta) + \sum K_j n_j [C_A]_{0,0}}, \qquad [11]$$

where $[C_A]_{0,0}$ is the initial concentration of pure feed and the initial rate of reaction (Eq. [5]) will be

$$r_\beta \equiv \left(\frac{dX}{d\tau_\beta}\right)_{\tau_\beta \to 0} = \left(\frac{A_{1,\beta} + A_{2,\beta}}{1 + B_\beta}\right) = \frac{(1+\beta)\sum k_i K_A[SH]_0}{1 + \beta + K_A[C_A]_{0,0}}. \quad [12]$$

Equation [12] shows that the initial rate at a dilution ratio β can be obtained from the parameters $A_{1,\beta}$, $A_{2,\beta}$, and B_β, obtained from fitting the full rate-data set at that dilution.

EXPERIMENTAL

The feedstock, 2-methylpentane (99+%) was obtained from Aldrich and used without further purification. The distilled water and feed at the desired ratio are pumped simultaneously into the reactor, vaporized, and mixed before the mixed stream contacts the catalyst bed.

HY zeolite was prepared from NaY (BDH Chemicals) by exchanging 10 times with 0.5 *M* NH_4NO_3 solution at 20°C for 24 h, drying at 110°C for 24 h and calcinating at 500°C for 2 h after each exchange. The final HY zeolite was then modified to give ultrastable HY (USHY) by steaming at 400°C for 24 h.

All experiments were performed in a fixed-bed plug-flow glass reactor. Details of the apparatus and methodology have been described previously (15). Before we carried out the main experimental runs using steam dilution, more than 25 replicate runs at a time on stream of ~725 s, with the H_2O/feed ratio of 0.73 at 500°C, were carried out to examine the stability of USHY at high temperature in the presence of steam as a diluent. The results in Fig. 1 show good stability under these conditions, and good reproducibility in our experimental results.

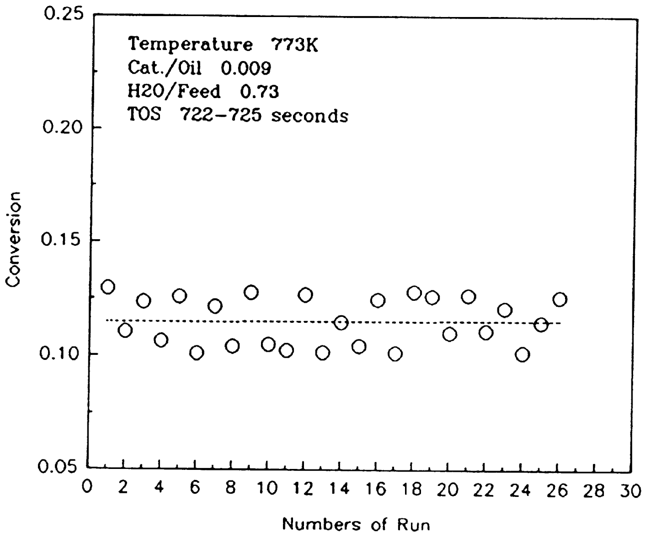

FIG. 1. Conversion of 2-methylpentane over USHY vs numbers of run: temperature, 500°C; Cat./Oil, 0.009; H_2O/feed, 0.73; TOS, 722–725 s.

All of the products were identified by GC/MS and analyzed using a Carle chromatograph (for gases) or a capillary chromatograph (for liquids).

RESULTS AND DISCUSSION

Conversion Curves

The various curves of cumulative conversion as a function of time on stream at different catalyst/feed ratios (0.01–0.1), diluent H_2O/feed ratios (0.07–1.46) and temperatures (400–500°C) are presented in Fig. 2. We see that the early slopes of these conversion curves increase with increasing catalyst/feed ratio or reaction temperature, indicating in a readily visible way that rising temperature and cat/oil ratio increase the initial rate of 2-methylpentane conversion on USHY. For each curve in these figures, a limiting conversion is approached at long time on stream, showing that deactivation involves two sites at a time and hence a decay exponent of $N = 1$ (16). This kinetic order suggests that the dominant form of site deactivation is the disproportionation of adjacent carbenium ions on the catalyst surface. The result of such an event is the formation of a gas phase paraffin leaving behind on the surface a di-ion attached to two sites. A species of this kind, if it is less active than normal carbenium ions, will deactivate two sites at a time; hence, the second order in site concentration in the deactivation behaviour.

The level of limiting conversion at a given catalyst/feed ratio increases with increasing temperature and decreases with increasing H_2O/feed ratio, also indicating that the addition of H_2O generally lowers the rate of feed conversion.

Kinetic Parameters

Optimum values of the parameters A_1, A_2, B, and G were determined by fitting the experimental conversion versus time-on-stream data using the established kinetic model (Eq. [1]), and are given in Table 1. An initial fitting showed that in all cases the value of the decay exponent N was close to one, and therefore N was fixed at 1.0 for the final fitting of the data (16).

From Table 1 we see that the values of A_1 increase with increasing temperature and decrease with added H_2O, and that the parameter A_2 is nontrivial in all cases, indicating that feed conversion by chain propagating processes is important in all cases.

In all cases the parameter B has a negative value near -1, indicating that there is strong preferential adsorption of the product species (11). The absolute value of the B parameter decreases with increasing dilution ratio, indicating that H_2O weakens the adsorption of products vis-à-vis the reactants (17).

As expected, the values of parameter G decrease with increasing H_2O dilution ratio, indicating a decrease of the decay rate in the presence of steam dilution.

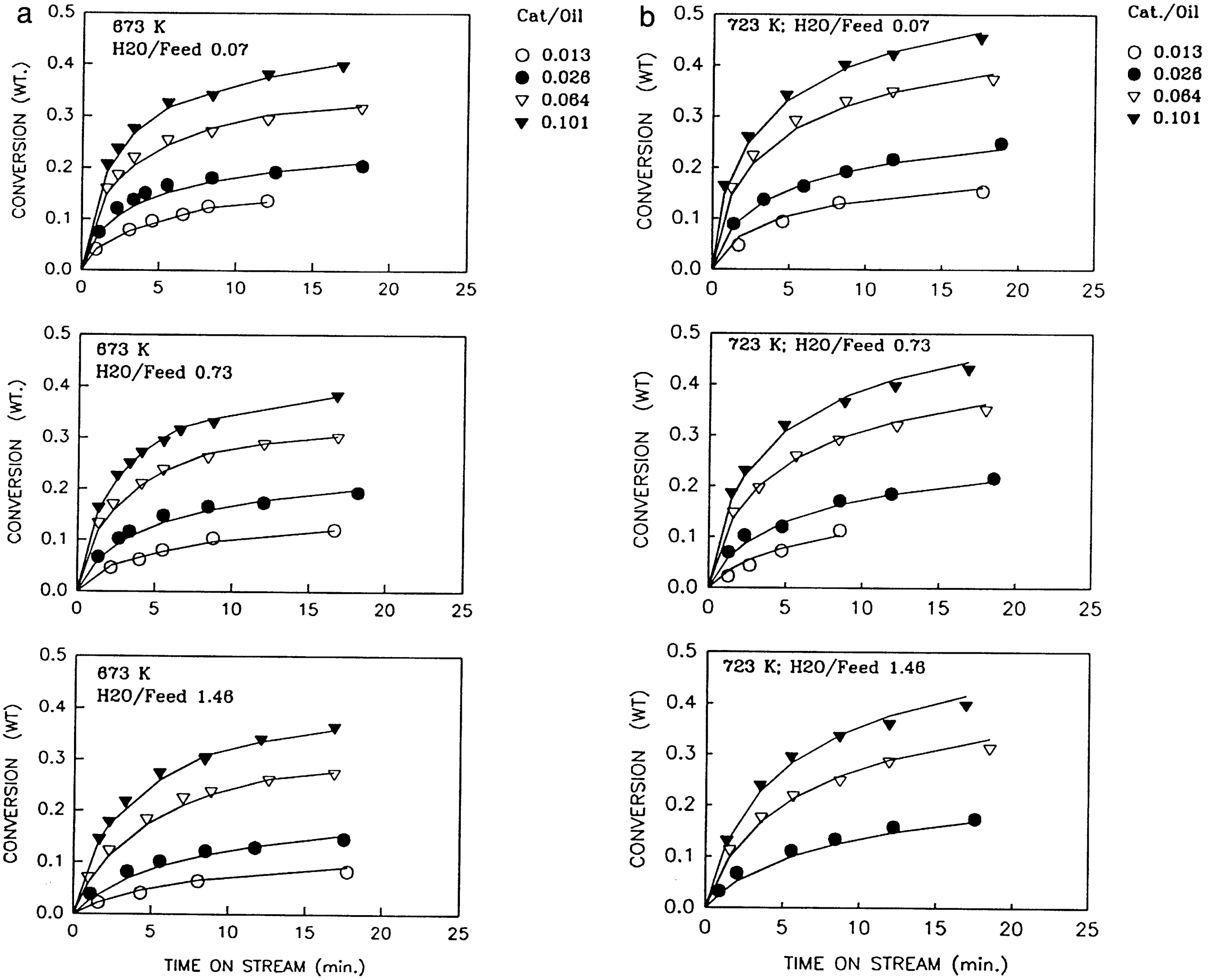

FIG. 2. Theoretical conversion curves and experimental points for 2-methylpentane cracking on USHY and with steam dilution: (a) 400°C; (b) 450°C; (c) 500°C.

A detailed discussion of the absolute value of each individual parameter is not warranted due to the strong correlation among them. We prefer to use the initial rates given in Eqs. [5] and [12], as these expressions involve all the kinetic parameters in one expression. Any correlations between parameters will tend to compensate in such a case, allowing us to interpret the effect of steam dilution on activity more credibly.

Reaction Rates

1. *Initiation rate.* Information about the rate of feed conversion by initiation reactions can be extracted from the values of parameters A_1, A_2, and B in Table 1 by using Eqs. [5] and [12]. The initiation rates of 2-methylpentane cracking on USHY at various temperatures and with steam dilution at various ratios have been calculated and are listed in Table 1. We find that the initiation rate increases with increasing temperature at all dilution ratios and decreases with increasing dilution ratio at all temperatures. At higher temperatures the addition of even a small amount of water causes a large drop in the initiation rate. For example, at 450 and 500°C this rate goes down by a factor of $\sim$2 when dilution of $\beta = 0.07$ is implemented. The rate of initiation continues to decrease with further increases in the dilution ratio, as shown in Table 1.

2. *Overall rate of the feed conversion.* According to the chain mechanism (10), feed can be converted not only by initiation processes, but also by propagation processes. The overall rates of 2-methylpentane conversion over USHY have been calculated by Eq. [6], and are presented in the last column in Table 1.

The total rate of the feed conversion increases with increasing temperature at all dilution ratios and decreases with increasing dilution ratio at 450 and 500°C. At 400°C,

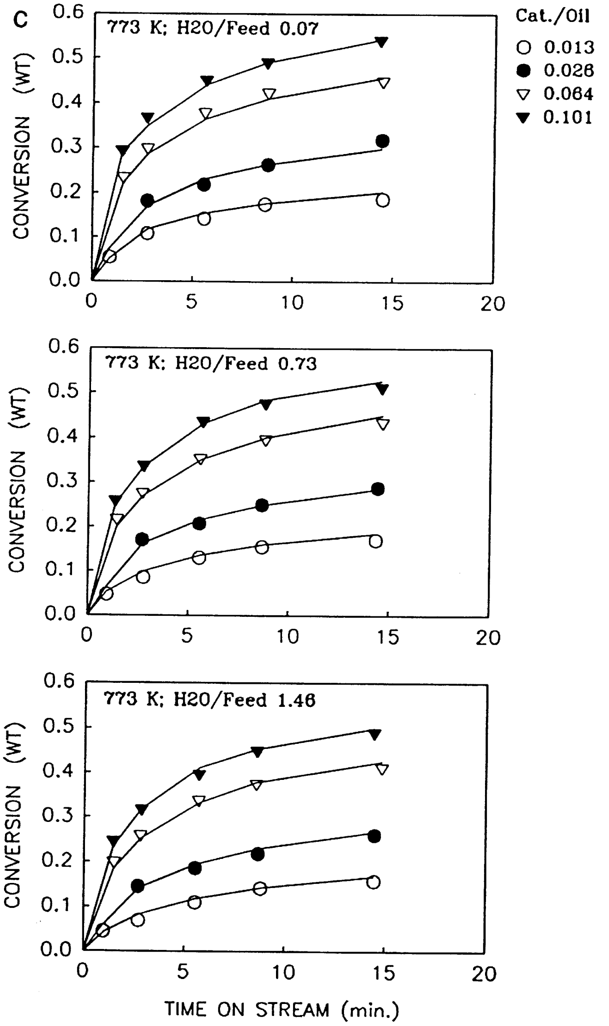

FIG. 2—*Continued*

however, this rate increases with the addition of a relatively small amount of steam ($\beta = 0.07$) and then decreases with further increases in steam dilution. This result shows that at the lowest temperatures, the addition of a small amount of H_2O encourages the conversion of feed via propagation processes only; initiation rates go down at all dilution ratios. It does this to an extent sufficient to more than compensate for the reduction in feed conversion due to the reduction in the rate of initiation, a fact documented in Table 1.

Activation Energy and Reaction Order

1. *Apparent activation energy of the overall reaction.* As we have seen in the previous discussion, the effect of an increase in temperature on 2-methylpentane cracking over USHY at all dilution ratios is an increase in reaction rate.

In a fully mechanistic interpretation, the "true" activation energies involved in the overall process are related to elementary reactions. In the present case, 2-methylpentane is converted to products via various simultaneous monomolecular and bimolecular processes and the total rate of feed consumption is given by

$$\begin{aligned} r_{\text{tot}} &= \sum r_{0i} + \sum r_{ij} \\ &= \left(\sum k_{0i}[SH] = \sum k_{ij}[I_j]\right)[C_A] \\ &= \left(\sum A_{0i}\theta^{-E_{0i}/RT}[SH] + \sum A_{ij}\theta^{-E_{ij}/RT}[I_j]\right)\frac{[C_A]_{\beta=0}}{1+\beta}, \end{aligned} \qquad [13]$$

where $[SH]$ is the concentration of unpoisoned and unoccupied acid sites; $[I_j]$ is the concentration of the ith carbenium ions.

A valid theoretical activation energy cannot be obtained by plotting the above total rate of conversion because the various elementary reactions involved have different activation energies and appear in the rate expression in the form of sums. As a result, we are reduced to using a phenomenological approach to the study of temperature effects on the overall reaction. Fortunately the plots of $\text{Ln}(r_{\text{tot}})$ vs $1/T$ shown in Fig. 3 do show an approximately linear relationship in the range of 673–773 K at each dilution ratio. This experimental observation allows us to correlate the rate data using the classical Arrhenius relationship:

$$\text{Ln}(r_{\text{tot}}) = \frac{a}{T} + b, \qquad [14]$$

where the slope a and intercept b are constants depending on the ratio β.

In view of this we can express the total rate as an empirical power function of the concentration and assume the empirical rate constant to be exponentially dependent on $1/T$, that is,

$$r_{\text{tot}} = k'[C_A]^n = A'\theta^{-E_\beta/RT}\left(\frac{[C_A]_{\beta=0}}{1+\beta}\right)^n \qquad [15]$$

or

$$\text{Ln}(r_{\text{tot}}) = -\frac{E_\beta}{RT} + \text{Ln}\,A' + n\,\text{Ln}[C_A]_{\beta=0} - n\,\text{Ln}(1+\beta). \qquad [16]$$

We call E_β the "apparent" activation energy at dilution ratio β and n the "apparent" reaction order. Values of E_β can be extracted from the slopes of plots in Fig. 3 and are shown in Table 2, where we see that

$$E_0 \approx 150 \text{ kJ/mol} \gg E_{0.07} \approx E_{0.73} \approx E_{1.46} \approx 84 \text{ kJ/mol}.$$

The observation that $E_0 \gg E_\beta$, suggests that the addition of a small amount of H_2O efficiently supresses some processes requiring a high activation energy and/or enhances other processes requiring a low activation energy. Regardless of the specific cause, the presence of steam obviously reduces the sensitivity of the reaction to temperature changes.

TABLE 1

Optimum Kinetic Parameters for 2-Methylpentane Cracking on USHY at 400, 450, and 500°C, and with Steam Dilution

Temp. (K)	β^b	$A_{1,\beta}{}^a$	$A_{2,\beta}{}^a$	$B_\beta{}^b$	G^a	ε^b	N^b	r_0	$r_{\text{tot}}{}^c$
673	0.00	0.267	−0.084	−0.902	0.262	0.309	1.0	1.87	6.30
	0.07	0.258	−0.080	−0.881	0.263	0.138	1.0	1.49	10.59
	0.73	0.246	−0.069	−0.862	0.253	0.096	1.0	1.28	7.89
	1.46	0.232	−0.053	−0.749	0.250	0.079	1.0	0.71	3.71
723	0.00	0.540	−0.146	−0.981	0.231	0.470	1.0	20.74	48.33
	0.07	0.449	−0.130	−0.967	0.214	0.280	1.0	9.67	34.40
	0.73	0.417	−0.107	−0.949	0.208	0.191	1.0	6.08	18.74
	1.46	0.398	−0.092	−0.917	0.191	0.147	1.0	3.68	10.29
773	0.00	1.015	−0.152	−0.995	0.301	0.760	1.0	172.60	258.03
	0.07	0.912	−0.121	−0.990	0.228	0.589	1.0	79.10	127.56
	0.73	0.835	−0.060	−0.983	0.217	0.371	1.0	45.59	71.60
	1.46	0.767	−0.040	−0.971	0.193	0.267	1.0	25.06	38.40

[a] A_1, A_2, and G have units of min^{-1}.

[b] B, N, β (see Eq. [7]) and ε (volume ratio) are dimensionless.

[c] All rates r_i have the formal units min^{-1}. These apply to Eq. [1], where X is the mole fraction while $\tau = bPt_f$. In calculating τ b is taken to be 1; P is the cat/oil weight ratio; and t_f is the catalyst time-on-stream.

2. *Apparent order of overall reaction*. Since the experimental data of $\text{Ln}(r_{\text{tot}})$ vs $1/T$ provide a good fit to Eq. [16], as shown in Fig. 3, the slopes a_β and intercepts b_β of the curves at various dilution ratios are extracted and presented in Table 2. This done, the observation that $E_{0.07} \approx E_{0.73} \approx E_{1.46}$ provides us with a method of evaluating the apparent reaction order n.

Comparing Eq. [14] with Eq. [16], the parameter b_β can be expressed by

$$b_\beta = \text{Ln } A'_\beta + n \text{ Ln}[C_A]_{\beta=0} - n \text{ Ln}(1+\beta). \qquad [17]$$

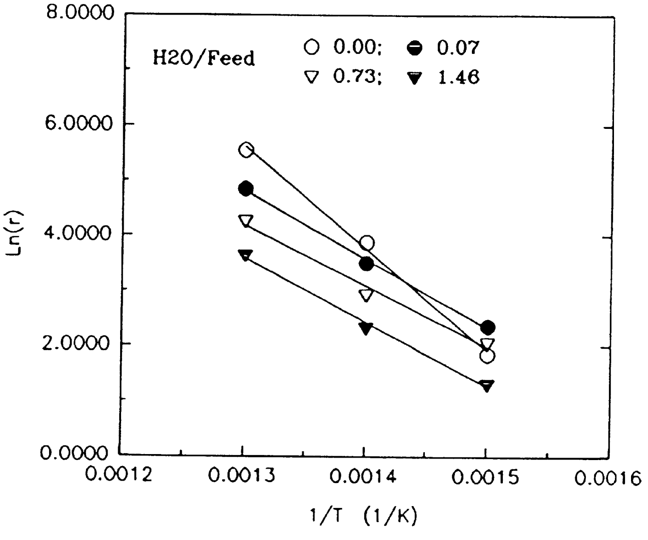

FIG. 3. Arrhenius plots of overall reaction in 2-methylpentane cracking on USHY and with steam dilution, H_2O/feed: ○, 0.00; ●, 0.07; ▽, 0.73; ▼, 1.46.

Using the data in Table 2, we have

$$b_0 = 29.73 = \text{Ln } A'_0 + n \text{ Ln}[C_A]_{\beta=0} \qquad [18a]$$

$$b_{0.07} = 18.33 = \text{Ln } A'_{0.07} + n \text{ Ln}[C_A]_{\beta=0} - n \text{ Ln}(1+0.07) \qquad [18b]$$

$$b_{0.73} = 17.41 = \text{Ln } A'_{0.73} + n \text{ Ln}[C_A]_{\beta=0} - n \text{ Ln}(1+0.73) \qquad [18c]$$

$$b_{1.46} = 16.74 = \text{Ln } A'_{1.46} + n \text{ Ln}[C_A]_{\beta=0} - n \text{ Ln}(1+1.46). \qquad [18d]$$

From plots of b_i versus the RHS of Eqs. [18] we can see that:

$$A'_0 \gg A'_{0.07} \approx A'_{0.73} \approx A'_{1.46}.$$

Assuming $A'_{0.07} = A'_{0.73} = A'_{1.46}$, we obtain

$$\text{from Eqs. [18b] and [18c]} \Rightarrow n = 1.92 \qquad [19a]$$

TABLE 2

Activation Energies and Intercepts of Arrhenius Plots in Fig. 3

H_2O/Feed (β)	$b_\beta{}^a$	E_β (kJ/mol)
0.00	29.73	150.93
0.07	18.33	84.23
0.73	17.41	83.13
1.46	16.74	85.20

[a] The b_i values have no units as they represent the sums of logarithms of various quantities in Eq. [17]. According to Eq. [15] the quantities whose logarithms are taken must be in compatible units for: A_i in concentration per unit time; C_{Ai} in corresponding units of concentration; β as defined by Eq. [7].

$$\text{from Eqs. [18b] and [18d]} \Rightarrow n = 1.91 \quad [19b]$$

$$\text{from Eqs. [18c] and [18d]} \Rightarrow n = 1.90. \quad [19c]$$

The average apparent reaction order n in the range of dilution ratio $\beta = 0.07$ to $\beta = 1.46$ is therefore 1.91.

Although we know that the conversion of 2-methylpentane on USHY consists of both monomolecular and bimolecular processes, we may conclude from the order of 1.91 that bimolecular processes are dominant in 2-methylpentane cracking on USHY. This indicates that the major part of conversion is due to bimolecular (propagation) reactions, which agrees with selectivity results (18), as we will show elsewhere.

The Effects of Various Diluents

By studying the effects of various diluents on 2-methylpentane cracking on USHY, the roles of diluents in hydrocarbon cracking become more understandable. We discuss the effects of various diluents on the rates of this reaction at 400°C where the most interesting phenomena take place.

1. *Conversion of feed.* Figure 4 shows the changes in the rate of overall feed conversion with dilution ratio at 400°C using various diluents. The changes clearly vary significantly from diluent to diluent. Dilution by N_2 and H_2 causes a slight decrease in the rate of overall conversion; CO causes a larger decrease; CO_2 falls in the middle. On the other hand, H_2O has a very different effect on the rate of conversion. As shown in Fig. 4, a small amount of steam ($\beta = 0.07$) causes a surprisingly large increase in the rate of conversion, which then declines sharply as the ratio is increased to 1.46.

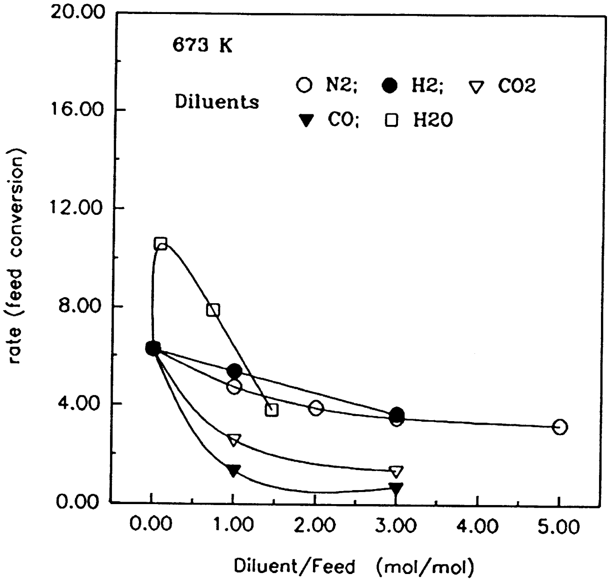

FIG. 4. Conversion rate of 2-methylpentane vs dilution ratio at 400°C, diluents: ○, N_2; ●, H_2; ▽, CO_2; ▼, CO; □, H_2O.

In earlier papers (1, 2), we concluded that the role of "inert" N_2 and H_2 is simple dilution of the feed concentration, which slows down the rates of feed conversion via both monomolecular and bimolecular reactions, with bimolecular reactions suffering the larger decrease. The roles of the more "active" CO_2 and CO also involve simple dilution plus some kind of "passivation" of the reaction sites. This causes an additional drop in the rate of feed conversion. Finally, the role of steam appears to involve simple dilution, plus a new effect, which at 400°C, and perhaps at lower temperatures, causes an *increase* in the rate of feed conversion at lower dilution ratios, as illustrated in Fig. 4.

2. *Formation of cracked products.* Cracked products in 2-methylpentane conversion over USHY include hydrogen, C_1–C_5 paraffins, and C_2–C_6 olefins. Figure 5 shows the effect of changing the dilution ratio on total rates of formation of both paraffinic products (including hydrogen) and olefinic products at 400°C, using different diluents. We see that increasing ratios of N_2 and H_2 dilution cause a slight decrease in the formation rates of both paraffinic and olefinic products, and that CO and CO_2 cause a larger decrease. The effect of steam dilution on the formation of olefins is similar to that of CO and CO_2 dilution. However, steam has a very different effect on the rate of formation of paraffins. As shown in Fig. 5, a small amount of steam (dilution ratio 0.07) causes a slight *increase* in the formation rate for paraffins, which then decreases as the dilution ratio increases from 0.07 to 1.46. In terms of the chain mechanism, paraffins are produced by both protolysis and propagation processes while, in the absence of β-cracking, olefins are produced by termination (desorption) processes only. We conclude that, besides simply diluting the feed concentration, CO and CO_2 also "passivate," that is, debilitate, the sites involved in bimolecular reactions. This causes a drop in the rates of desorption of carbenium ions. At the same times steam enhances certain disproportionation reactions.

3. *Formation of isomeric products.* Figure 5 shows the change in the rate of formation of feed isomers at 400°C using various diluents. We see that a small amount of steam causes a larger increase in the formation of isomers. This rate then decreases as the dilution ratio increases from 0.07 to 1.46. According to the chain mechanism, isomers of the feed are produced only in bimolecular (propagation) processes. We therefore conclude that a small amount of steam augments the ability of carbenium ions and, in particular, "parent" carbenium ions, to extract hydride ions from the feed molecules.

The role of steam can be explained as follows: steam dilution extends the surface residence times of ions and inhibits proton release (desorption) by weakening the Brønsted bases. The picture of the role of H_2O in this reaction which emerges from all this is as follows. Steam causes:

—a simple dilution of the feed concentration (as do N_2, H_2);

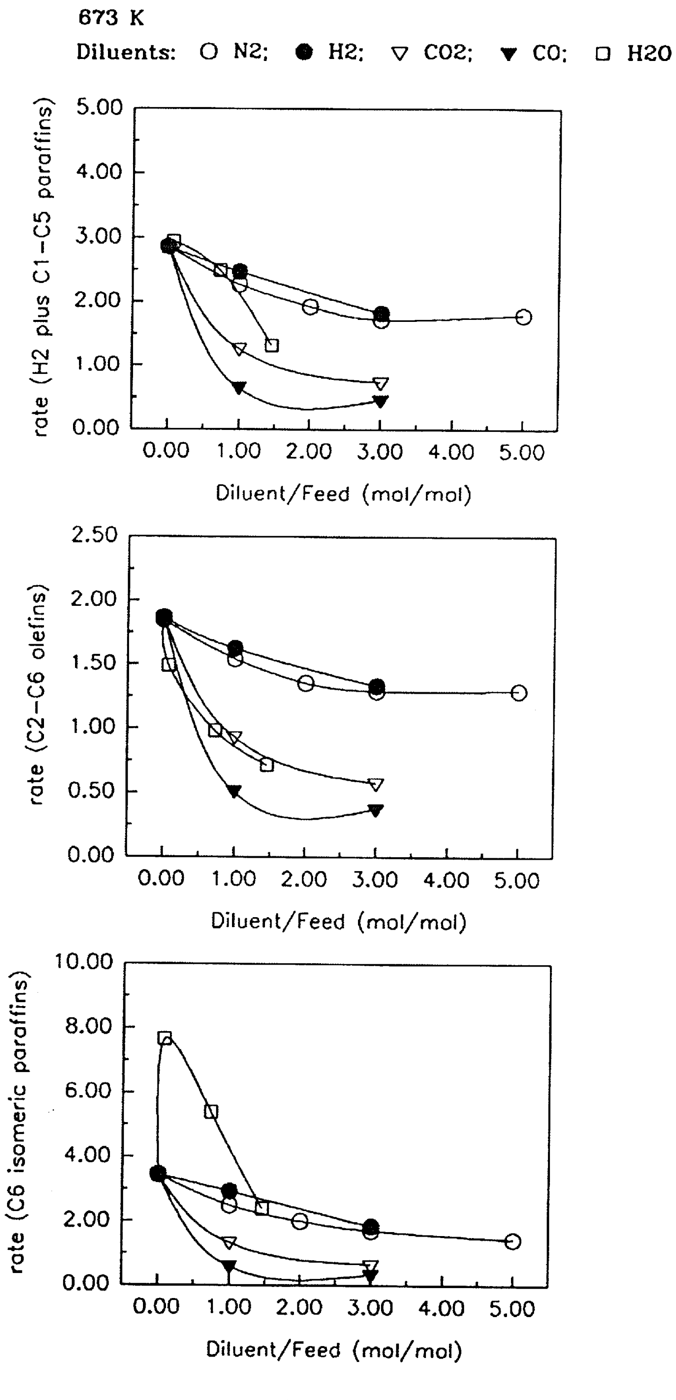

FIG. 5. Formation rates of products vs dilution ratio at 400°C, diluents: ○, N_2; ●, H_2; ∇, CO_2; ▼, CO; □, H_2O.

—passivation of the protolysis sites, like CO and CO_2;

—suppression of carbenium ion release from the Brønsted bases, thereby reducing the desorption of olefins and promoting bimolecular processes, isomerization in particular. It may well be that this effect is simply an exaggerated version of the "passivation" effect already noted with CO and CO_2.

CONCLUSIONS

An investigation of the influence of steam dilution on the activity in 2-methylpentane cracking over USHY zeolite at 400–500°C shows that:

—at 400°C, a small amount of H_2O *increases* the rates of isomerization and the rate of overall conversion for this feed;

—above this temperature, even low levels of steam dilution reduce all rates;

—steam reduces the apparent activation energy of feed conversion at all dilution ratios, making the rate of a steam-diluted reaction less sensitive to temperature changes.

In comparison with the effects of other diluents we have studied, the effects of steam dilution are more pronounced and potentially more important. Steam dilutes the concentration of the reactant just as N_2 and H_2 do; it passivates the sites of the initiation reaction like CO and CO_2; but it also promotes isomerization at low temperatures and relatively low steam dilutions

Two remarkable effects of steam dilution should be emphasized:

1. The first is the fact that a small amount of steam, 0.07 mol ratio, leads to an increase in the overall rate of conversion at 400°C and, by an extrapolation from our results, at temperatures below 400°C. The exact amount of steam addition required to maximize this effect at 400°C is not known. The effect may well be greater than that reported here.

2. We also suspect that, at higher temperatures, lower levels of steam addition (i.e., $\beta < 0.07$) may lead to a maximum in the "steam effect." At lower temperatures an extrapolation of our results suggests that an even larger promotion of isomerization reactions may be achieved, albeit at a lower rate of reaction and at higher dilutions. There may well be an optimum combination of dilution ratio and temperature at which isomerisation is maximized in both rate and selectivity. This condition will no doubt be a function of the catalyst used.

Perhaps, in the limit, there is very little isomerization or cracking under bone-dry conditions. This is not a realistic condition for commercial operations, but purposeful control of steam in a commercial cracker can be an important process variable.

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