$$\Phi = \frac{2}{3}\Delta^3 - \frac{1}{2}\Delta^2 - \frac{1}{6}$$

$$= \frac{2}{3}\left[\frac{1 + (1 + 4\xi)^{1/2}}{2}\right]^3 - \frac{1}{2}\left[\frac{1 + (1 + 4\xi)^{1/2}}{2}\right]^2 - \frac{1}{6} \quad \text{(see Figure 3)}$$

$$G = \frac{1}{3}\Delta^3 - \frac{1}{2}\Delta^2 + \frac{1}{6}$$

$$= \frac{1}{3}\left[\frac{1 + (1 + 4\xi)^{1/2}}{2}\right]^3 - \frac{1}{2}\left[\frac{1 + (1 + 4\xi)^{1/2}}{2}\right]^2 + \frac{1}{6} \quad \text{(see Figure 4)}$$

(III) Cassonian model (Kooijman and Van Zanten, 1972):

$$f(\tau_{xz}) = \left\{\begin{matrix} 0, & \tau_{xz} \leqq \tau_C \\ (\tau_{xz}^{1/2} - \tau_C^{1/2})^2/\eta_C, & \tau_{xz} \geqq \tau_C \end{matrix}\right\}, \quad \eta_C > 0, \quad \tau_C \geqq 0$$

$$\eta_C = \mu^*, \quad \tau_C = \tau^*$$

$$F(\Delta) = (\Delta^{1/2} - 1)^2$$

$$\Delta(\Delta^{1/2} - 1)^2 = \xi \qquad \text{(see Figure 2)}$$

$$\Phi = \frac{2}{3}\Delta^3 - \frac{6}{5}\Delta^{5/2} + \frac{1}{2}\Delta^2 + \frac{1}{30} \qquad \text{(see Figure 3)}$$

$$G = \frac{1}{3}\Delta^3 - \frac{4}{5}\Delta^{5/2} + \frac{1}{2}\Delta^2 - \frac{1}{30} \qquad \text{(see Figure 4)}$$

(IV) Eyring hyperbolic sine model (Bird et al., 1960):

$$f(\tau_{xz}) = B\sinh(\tau_{xz}/A), \quad A > 0, \quad B > 0$$

$A = \tau^*$, B interpreted as τ^*/μ^*

$$F(\Delta) = \sinh(\Delta)$$

$$\Delta\sinh(\Delta) = \xi \qquad \text{(see Figure 2)}$$

$$\Phi = \Delta^2\sinh(\Delta) - \Delta\cosh(\Delta) + \sinh(\Delta) \qquad \text{(see Figure 3)}$$

$$G = \Delta\cosh(\Delta) - \sinh(\Delta) \qquad \text{(see Figure 4)}$$

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Effects of Nonseparable Kinetics in Alcohol Dehydration over Poisoned Silica-Alumina

Methanol and ethanol dehydration over fresh and poisoned silica-alumina have been used as a model system to demonstrate experimentally certain effects of nonseparable kinetics including the change in product distribution upon flow reversal in a reactor with a poisoning gradient. The rate expression $r = kK_Ac_A^{1/2}/(1 + K_Ac_A^{1/2} + K_Wc_W)$ describes the experimental data for all reactions although the constants for ether and olefin formation are entirely different and vary between fresh and poisoned catalysts. The nonseparability of kinetics and the concomitant variation of K_A, K_W with poisoning are briefly discussed in terms of interactions between poison molecules and surface acid-base sites.

K. R. BAKSHI

and

G. R. GAVALAS

Division of Chemistry and Chemical Engineering
California Institute of Technology
Pasadena, California 91125

SCOPE

A variety of deactivation processes including sintering, coking, and poisoning necessitate periodic catalyst replacement or regeneration. Between regenerations the catalyst is subject to continuous change inducing a change in the product distribution and posing problems of optimal operation and regeneration. Such optimization problems require models describing the kinetics on partially poisoned catalysts. For the sake of simplicity and due to the lack of detailed information, the kinetic models employed heretofore have been of the separable type. A separable kinetic model has the form $r = \phi r_i$, where r_i is an intrinsic rate, independent of poison adsorption, and ϕ is a factor accounting for the effect of the poison. Although separable kinetics does not explain changes in selectivity, it has been considered suitable for engineering calculations.

In a previous paper Gavalas (1971) has shown by computer simulation that separable kinetics fails to describe some important effects, such as the dependence of product distribution upon the direction of flow through a reactor with a poisoning gradient. This flow-directional effect and other related effects can be exploited in actual reactor operation to optimize the overall product distribution between successive regenerations. The purpose of this paper is to give an experimental demonstration of the flow-directional effect and other implications of nonseparable kinetics, using alcohol dehydration on acidic catalysts as a model system.

Correspondence concerning this paper should be addressed to G. R. Gavalas. K. R. Bakshi is with Chevron Research Company, Richmond, California 94802.

CONCLUSIONS AND SIGNIFICANCE

Methanol and ethanol dehydration over fresh and poisoned silica alumina exhibit the following effects of nonseparable kinetics:

1. The ratio $\rho = r(c, i)/r(c, j)$, where i and j represent two different poisoning states, varies as much as 40% over the concentration range investigated.

2. The selectivity $\sigma = 100 \times$ (ethylene formation) (ethanol consumption) increases by as much as two-fold upon poisoning by butylamine.

3. Ether and ethanol formation rates change by about 10 to 30% each upon flow reversal in a reactor with a poisoning gradient, while the corresponding change in the selectivity σ is as high as 17%. Such flow-directional effects can be utilized to optimize the product distribution in a commercial reactor subject to catalyst poisoning.

The empirical rate expression

$$r = \frac{kK_A c_A^{1/2}}{1 + K_A c_A^{1/2} + K_W c_W}$$

describes well fresh and poisoned catalysts, and the constants, k, K_A, K_W vary significantly with the poisoning level. The variation of K_A and K_W with poisoning can be interpreted as a result of the interaction between poison molecules and the acid-base surface sites consistent with a previously proposed mechanism (Figueras, 1971).

Chemical engineering studies of catalyst poisoning have been concerned mainly with problems of reactor analysis and optimization and have thus focused on the effects of deactivation on conversion and selectivity for a single catalyst pellet or for a fixed-bed reactor, see for example the comprehensive review of Butt (1972). In all such studies, for example, Bischoff (1969), Butt (1968), and Levenspiel (1972), it has been assumed that the reaction rate may be approximated by

$$r(c, T) = \phi r_i(c, T) \qquad (1)$$

where the factor ϕ fully accounts for the effect of poisoning while r_i is the rate of the fresh catalyst.

The rate expression (1) corresponds to an ideal surface, characterized by uniform noninteracting sites, the latter term indicating that a chemisorbed molecule does not modify the properties of neighboring free or occupied sites. There exists extensive chemical evidence indicating that nonuniform sites and surface interactions are the rule rather than the exception in catalytic systems. Such evidence includes, for example, the change in the heat of adsorption with coverage, the change in selectivity due to poisoning, and the distribution of site strengths of acidic catalysts obtained by various titration techniques. In spite of this evidence, the separable model, Equation (1), has been widely used for engineering analysis and design because of its simplicity and the lack of more detailed models. However, in addition to being at variance with the aforementioned chemical evidence, the separable model fails to predict certain effects which are directly connected with reactor operation and optimization. For example, in a computer simulation study of naptha reforming, Gavalas (1971) has pointed out the possibility of significant flow-directional effects solely attributable to nonseparable kinetics. These effects have not been experimentally investigated heretofore. Hence, the objective of the present study is an experimental demonstration of the following effects of nonseparable kinetics, attendant upon catalyst poisoning:

1. A ratio $\rho(c, T)$ may be defined for a catalyst at two poisoning levels i and j

$$\rho(c, T) = \frac{r(c, T;\ \text{poisoning level } i)}{r(c, T;\ \text{poisoning level } j)} \qquad (2)$$

For the separable model, Equation (1), ρ is constant so that variation in a range of c and T is a measure of deviations from separable kinetics. The quantity ρ is of no direct significance to reactor operation.

2. Flow-directional effect, that is, the changes in conversion and product distribution resulting from reversing the direction of flow through a reactor with a poisoning gradient. This effect can be exploited in reactor operation by providing a facility for flow reversal. After poisoning has advanced to a given level, a flow reversal, alone or accompanied by a variation in the feed temperature, may provide a better product distribution than that attained by maintaining the same flow direction throughout the life of the catalyst. More complex flow arrangements and switchings are conceivable in reactors consisting of adiabatic sections with intermediate heat exchangers as for example in naptha reforming reactors.

In the present work the experimental demonstration of the aforementioned effects (1) and (2) has been conducted using alcohol dehydration on silica alumina as a model system:

$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad (3)$$

$$2C_2H_5OH \rightarrow C_2H_5OC_2H_5 + H_2O \qquad (4a)$$

$$C_2H_5OH \rightarrow C_2H_4 + H_2O \qquad (4b)$$

The reactions are of little industrial importance but are very convenient experimentally due to the mild conditions of temperature and pressure, lack of coking, and other side reactions, etc. The dehydration of alcohols by alumina catalysts has been studied extensively, as reviewed by Winfield (1960) and Pines and Manassen (1966). Figueras et al. (1971) have investigated the kinetics of dehydration over silica alumina, including the qualitative effects of a variety of poisons and have presented a mechanistic interpretation of their results. The present work is mainly devoted to a demonstration of the effects (1) and (2) above. A quantitative correlation of the reaction kinetics on fresh and poisoned catalysts with the catalysts' acidity and basicity distributions is reported elsewhere (Bakshi, 1974).

EXPERIMENT

Reagents

Reagent grade methanol and ethanol were used without further purification. Reagent grade n-butylamine was distilled over sodium and percolated over a molecular sieve before use.

TABLE 1. COMMERCIAL CATALYSTS FOR ALCOHOL DEHYDRATION STUDY

Catalyst code	Supplier	Chemical composition
KSFO	Chemetron Corporation	Montmorillonite clay acid activated
F49	Filtrol Corporation	74% SiO_2 17.5% Al_2O_3 4.5% MgO
AHC	American Cyanamid Company	76% SiO_2 24% Al_2O_3
T-126	Chemetron Corporation	Activated γ-alumina
F-1	Aluminum Company of America	γ-alumina support

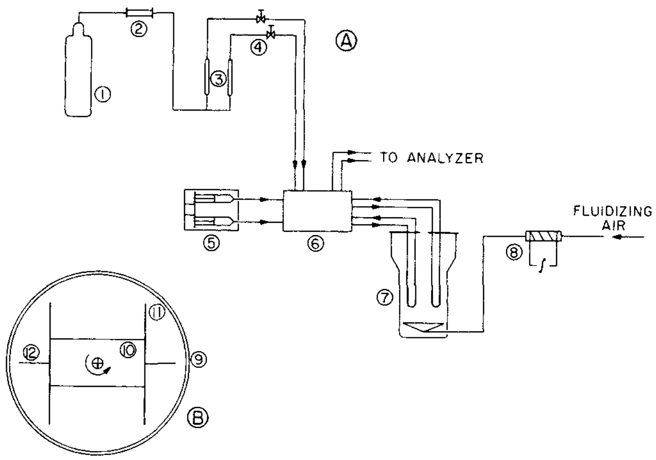

Fig. 1. Schematic diagram of experimental apparatus: (1) Nitrogen cylinder; (2) Gas dryer; (3) Rotameters; (4) Micrometer needle valves; (5) Volumetric infusion pump; (6) Vaporizer; (7) Fluidized sand bath with microreactors; (8) Air preheater; (9) Heated chamber; (10) Tumbling reactor; (11) Heat transfer disks; and (12) Capillary.

High purity grade nitrogen and helium were used as diluent and carrier gas, respectively, after drying over a molecular sieve bed.

Catalysts

Various commercial catalysts used in the present investigations are listed in Table 1. Most of the poisoning studies were conducted on F49 catalyst. The pelleted catalysts obtained from the suppliers were crushed and fractionated under dry nitrogen to prevent contamination. All the catalysts were stored under dry conditions after a five-hour preheating at 250°C under dry nitrogen.

Experimental Apparatus and Kinetic Experiments

The general layout of the experimental apparatus is shown in Figure 1A. The kinetic study was carried out in two micro flow reactors immersed in an isothermal fluidized sand bath. The temperatures of both the reactors were maintained within ±0.3°C of the reported values. The reagents were fed by a dual syringe volumetric infusion pump with flow controlled to within 0.5% deviation.

Alcohol was vaporized, mixed with the diluent N_2, and fed to the reactor. A valve matrix preceding the two reactors enabled the use of the reactors in series or in parallel and allowed the reversal of the direction of flow. Identical flow and thermal conditions within the two microreactors, when operated in parallel, enabled simultaneous evaluation of fresh and poisoned catalysts under comparable conditions. The tubes and valves were heated to prevent condensation of the reactant. The analysis of the products was carried out as follows:

Methanol dehydration: Detector—thermal conductivity, He flow rate—30 cm³/min, Column—10′ poropak T at 190°C, Sample volume—1 cm³.

2. Ethanol dehydration: Detector—flame ionization, He flow rate—20 cm³/min., Column—14′ of 10% Carbowax 20 M on chromasorb P at 110°C.

In Situ Poisoning

Dry N_2 was passed through the catalyst at the reaction temperature until no water or alcohol could be detected chromatographically. The N_2 flow rate was then reduced and a measured volume of *n*-butylamine solution in benzene was introduced through a mixing tee situated in the vaporizer. The reactor exhaust was monitored chromatographically to detect amine elution, if any. For sufficiently low amine/catalyst weight ratio, no amine eluted, indicating irreversible adsorption. After benzene could no longer be detected in the exhaust, the reactor was ready for resuming the kinetic experiments. The above procedure was repeated when it was desired to increase the level of poisoning.

Uniform Poisoning

The poisoning was carried out in a tumbling batch reactor consisting of a 1½-in. O.D. × 3-in. long stainless steel cylinder tumbling inside a larger, 6-in. I.D. × 6¾-in. long stainless steel chamber heated by an externally wound heater, as shown in Figure 1B. The entire assembly was controlled at 230°C ± 0.3°C. Two thin detachable disks covering the ends of the internal cylinder were used to increase the heat transfer area. A weighed amount of fresh catalyst was placed in the internal cylinder which could communicate with the gas in the external cylinder only through two fine capillary tubes attached on the side disks. The capillary tubes were designed to attain a controlled and slow poisoning rate. By tumbling the internal cylinder at a sufficiently high rate, for example, 50 rev./min., the catalyst particles were uniformly exposed to a low poison concentration. The procedure for poisoning consisted in first exposing the catalyst to pure N_2 at 230°C and 6 lb./sq.in.gauge. The N_2 was repeatedly flushed and replaced for a period of 5 hours which was sufficient to stabilize the water adsorbed on the catalyst. A measured solution of *n*-butylamine in dry benzene was then injected through a septum in the external cylinder. After overnight exposure, no amine could be detected chromatographically. The reactor was then cooled to room temperature and a weighed sample of the catalyst was transferred to the microreactor for kinetic studies.

Experimental Conditions

The kinetic experiments were carried out with feed alcohol concentrations in the range 0.001 to 0.024 moles/liter, feed water concentration in the range 0 to 0.0025 moles/liter, and temperatures 150° to 225°C. The total pressure in the reactor was somewhat higher than atmospheric and the pressure drop along the reactor was negligible under all flow conditions. No reaction was observed with an empty reactor at the highest temperatures employed. Low conversions ($<6\%$) were maintained to attain nearly differential conditions, and the measured reaction rates were assigned to the arithmetic average of reactor inlet and outlet concentrations.

Possible mass transfer limitations were tested experimentally and theoretically. Thus, a change of flow rate at constant space velocity and a change of catalyst particle size were found not to affect the rates. Mass transfer coefficients estimated by an appropriate correlation showed film diffusion not to be rate limiting. Similarly, using an effective diffusivity of 10^{-3} cm²/s, estimated by the procedure of Satterfield (1970), resulted in a value of the modulus $\Phi \sim 10^{-3}$ assuring the absence of pore diffusional limitations according to the criterion of Weisz (1954).

The adsorption capacity of F49 for *n*-butylamine at 200°C was estimated thermogravimetrically at 420 μmoles/g. All poisoning experiments employed poison amounts considerably lower than this capacity. The irreversibility of poison adsorption in the presence of alcohol and water was ascertained chromatographically by the absence of amine in the reactor outlet and more stringently by the reproducibility of kinetic results over a period of several days of operation.

RESULTS FOR METHANOL DEHYDRATION

In Situ Poisoning

Some preliminary kinetic runs were conducted at two methanol concentrations with a fresh and an in situ poisoned catalyst. As shown in Figure 2, the ratio of the rates ρ decreased steeply with initial amine chemisorption but more slowly on further poisoning, indicating that sites with higher activity towards amine chemisorption have also higher activity towards methanol condensation. An alternative explanation could be advanced in terms of interactions rather than nonuniformities of sites. Figure 2 also shows that the ratio ρ depends on methanol concentration, the difference being larger at higher poison levels. Note that the two curves would coincide for separable kinetics.

Uniform Poisoning

The results reported in Figure 2 do not correspond to any single catalyst state because in situ poisoning results in a gradient of poison concentration along the reactor. To study a catalyst at a single poison level, the catalyst was poisoned uniformly as described in the previous section, and the kinetic results obtained with this catalyst are as follows:

Flow-Directional Effects. A series combination of the two reactors, one filled with fresh catalyst, the other with a uniformly poisoned catalyst, establishes a variation of the catalyst state along the flow path. Low space velocities were used to attain high conversions under which the directional effects are significant. As shown in Table 2, as much as 10% difference is observed between the two directions of flow. The difference is more pronounced at low feed concentrations and higher conversions as predicted theoretically by Gavalas (1971). The directional effects are relatively modest in the case of single reactions, especially in cases of strong product inhibition, but are expected to be more pronounced in the case of competitive reactions.

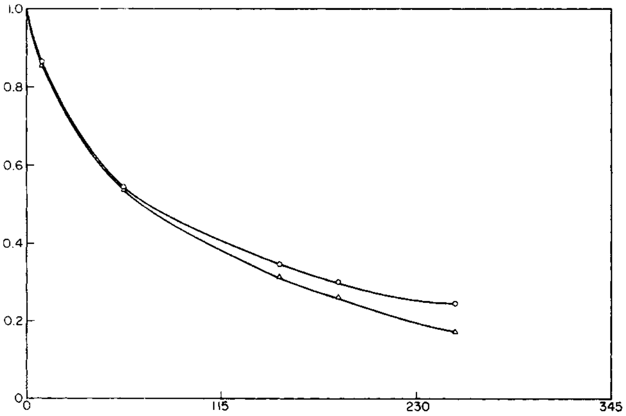

Fig. 2. Effect of in situ poisoning on methanol dehydration. Run conditions: weight of catalyst 4.3 g.; temperature 170°C; (○) $c_A = 0.006$; (△) $c_A = 0.022$.

TABLE 2. FLOW-DIRECTIONAL EFFECTS IN DEHYDRATION OF METHANOL

	c_A ($\times 10^3$)	Percentage conversion Forward*	Percentage conversion Reverse	Ratio (Reverse/forward)
A.	0.68	56.36	53.00	0.9404
	1.47	43.53	41.10	0.9442
	2.21	37.47	34.54	0.9218
	3.95	30.68	27.70	0.9029
B.	1.04	57.42	52.44	0.9129
	1.98	49.87	47.28	0.9481
	3.99	37.50	34.45	0.9187
	7.48	27.35	24.77	0.9057

Conditions: A. Catalyst weight = 3.64 g $T = 190°C$
Total feed rate = 0.237 moles/hr.
B. Catalyst weight = 3.64 g $T = 190°C$
Total feed rate = 0.142 moles/hr.

* Forward direction implies fresh catalyst bed followed by poisoned catalyst bed along the flow path.

TABLE 3. MODEL CONSTANTS FOR DEHYDRATION OF METHANOL

Product: Dimethyl ether

A. Fresh Catalyst

Temperature, °C	k ($\times 10^3$)	K_A	K_W
160	3.8	4.8	770
170	9.3	3.3	660
182	25.2	2.0	580

B. Poisoned catalyst

Temperature, °C	k	K_A	K_W
160	2.1	7.1	2,100
170	5.2	4.7	1,900
182	14.8	3.0	1,500

Kinetic Experiments and Model Fitting. To investigate the effect of poisoning on the reaction rate, kinetic experiments were carried out on fresh and uniformly poisoned catalysts. Since a strong product inhibition has been reported for alcohol dehydration (Figueras, 1971), the following types of experimental runs were conducted: (1) variation of alcohol concentration at fixed water concentration; (2) variation of water concentration at fixed alcohol concentration. A previous kinetic model of Figueras et al. (1971),

$$r = \frac{kK_Ac_A^{1/2}}{1 + K_Ac_A^{1/2} + K_Wc_W} \tag{5}$$

has been found to fit the data well for both the fresh and the poisoned catalyst. The constants k, K_A, K_W were determined by nonlinear regression using Marquadt's algorithm and the results are listed in Table 3. Various other models were derived by Knozinger (1973) from a series of reaction mechanisms differing by one or more elementary steps. At the lower temperature, some of these models were found to fit the present data equally well as Eq. (5), in the sense of yielding very similar residuals. At the higher temperatures, however, Equation (5) gives substantially lower residuals, for both the fresh and the poisoned catalyst, and hence it was chosen for data fitting in the whole range of conditions. The details of the model fitting are presented by Bakshi (1974).

Temperature Effects. The values of the constants k, K_A, K_W, appearing in the kinetic model Equation (5), are reported in Table 3 for various temperatures. If k is interpreted as the constant of the rate determining step, an estimate of the activation energy can be obtained from a least square fit of the data. Similarly, if K_A and K_W are interpreted as adsorption constants for alcohol and water, then the slopes obtained from their Arrhenius plots can be used to estimate the corresponding heats of adsorption, provided the entropies of adsorption are independent of temperature. The values of activation energies and heats

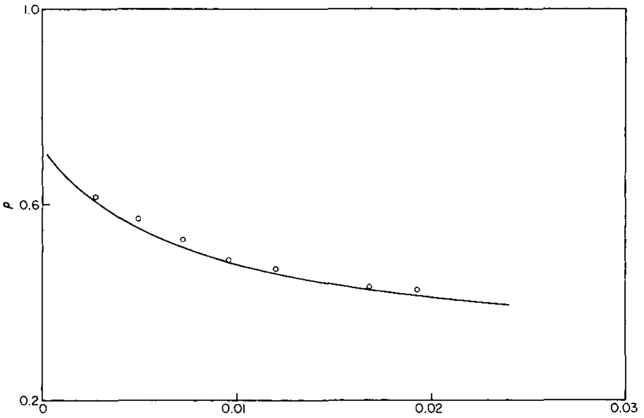

Fig. 3. Effect of water on ρ for methanol dehydration. Run conditions: $c_A = 0.0102$; $T = 170°C$.

TABLE 4. TEMPERATURE DEPENDENCE OF MODEL CONSTANTS FOR DEHYDRATION OF METHANOL

Catalyst	E_A[1]	Q_A[2]	Q_W[3]
Fresh	33	30	5
Poisoned	35	31	6

[1] $E_A = -R\dfrac{d\ln k}{d(1/T)}$

[2] $Q_A = R\dfrac{d\ln K_A}{d(1/T)}$

[3] $Q_W = R\dfrac{d\ln K_W}{d(1/T)}$

of adsorption so obtained are shown in Table 4. The activation energy for the fresh catalyst is 33 kcal/mole, in good agreement with the values reported by Winfield (1960); however, the amount of data is insufficient for the specification of confidence intervals.

Comparison Between Fresh and Poisoned Catalyst. The kinetic model, Equation (5), has been found to fit the data with both the fresh and the poisoned catalyst although (Table 3) the constants k, K_A, K_W are in each case different. In particular, the constants K_A and K_W, as well as the temperature coefficients for k, K_A, K_W are larger for the poisoned catalyst. The trend for the variation of ρ with c_A as observed during in situ poisoning experiments is in agreement with the effect of larger K_A due to poisoning. The effect of nonseparable kinetics in terms of the ratio ρ is exhibited in Figure 3 where the solid line represents the ρ predicted from the model, Equation (5), while the points represent the measurements. The ratio ρ, which is constant in separable kinetics, is seen in Figure 3 to be subject to significant variations. Additional data of this type are presented by Bakshi (1974).

RESULTS FOR ETHANOL DEHYDRATION

Flow-Directional Effects

The directional effects in competitive reactions with nonseparable kinetics are expected to affect the conversion and selectivity upon flow reversal. Two types of experiments were conducted to investigate these effects in ethanol dehydration.

A series combination of two reactors, one filled with fresh F49 catalyst and the other with a uniformly poisoned F49 catalyst, were used to obtain an activity gradient along the flow path. As in methanol dehydration, low space velocities were used to attain high conversions. As shown in Figure 4, as much as 10% change occurs in both ether and ethylene formation rates. The flow reversal has maximum effect at low concentrations and high conversions. The changes in conversions due to flow reversal are in opposite directions for ether and ethylene; hence the selectivity changes by as much as 17% in favor of ethylene upon reversal of flow.

Directional effects were also studied in a reactor consisting of a section containing F49 followed by a section containing T126. As shown in Table 5, the rates of ethylene and ether formation are changed by as much as 28% and 17% respectively, upon flow reversal. Since both changes are in the same direction, the selectivity change is of smaller magnitude.

Kinetic Experiments and Model Fitting

Experiments similar to methanol dehydration were carried out to study the kinetic effects of poisoning. Ethylene and diethyl ether were the only products and the rate of ether formation was observed to be considerably higher than that of olefin formation at 155°C.

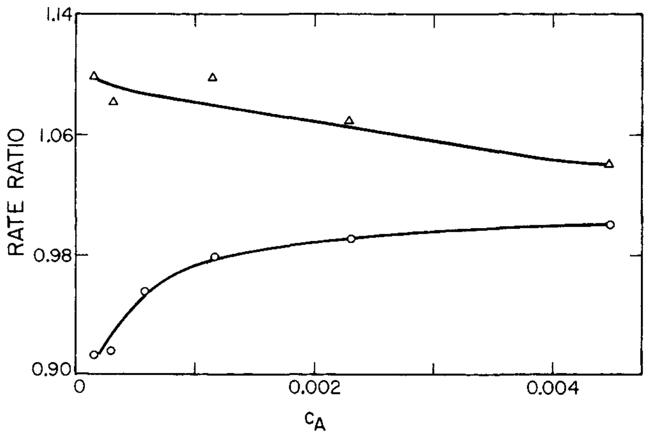

Fig. 4. Directional effects in dehydration of ethanol. Run conditions: $T = 170°C$; c_W (feed) = 0. Rate ratio = (reverse rate)/(forward rate).

TABLE 5. FLOW-DIRECTIONAL EFFECTS IN A GRADED REACTOR

Experimental conditions:

1. Catalysts:	0.61g F49; 4g T126
2. Temperature:	200°C
3. Feed concentration c_A:	1.45×10^{-2} moles/liter
4. Forward flow direction:	T126 followed by F49
5. Reverse flow direction:	F49 followed by T126

Rate of ethylene formation:

a. Forward:	7.03×10^{-4} moles/hr. g catalyst bed
b. Reverse:	9×10^{-4} moles/hr. g catalyst bed

Percentage increase upon flow reversal: 28.02%

Rate of ether formation:

a. Forward:	1.15×10^{-2} moles/hr. g catalyst bed
b. Reverse:	1.35×10^{-2} moles/hr. g catalyst bed

Percentage increase upon flow reversal: 17.39%

Kinetics of Ether Formation. The dependence of the rate of ether formation on the concentrations of alcohol and water was found to be very similar to that of methanol dehydration. Thus the same model, Equation (5), was used to fit the data and the constants obtained from a linear regression analysis are reported in Table 6 for the two catalyst states, fresh and poisoned. The ratio of the rates of poisoned and fresh catalyst ρ is observed to increase with the concentration of water and the change is less pronounced than in the case of methanol formation.

Kinetics of Ethylene Formation. Although the mechanism of ethylene formation is believed to involve different surface species from that of ether formation (Figueras et al., 1971), its rate can still be described by Equation (5) although the constants K_A, K_W have entirely different values as shown in Table 6. Figure 5 shows that the ratio ρ increases with water concentration in contrast to the case of ether production shown in Figure 4.

Effect of Poisoning on Selectivity. An important measure of deviation from separable kinetics is the variation in product distribution or selectivity with poisoning. Figures 6 and 7 show the experimentally measured selectivity

$$\sigma = 100 \times \frac{\text{alcohol converted to ethylene}}{\text{total alcohol reacted}} \tag{6}$$

as a function of alcohol and water concentration for the fresh and the poisoned catalyst. At all concentrations the poisoned catalyst has significantly higher selectivity towards ethylene production.

Kinetics on Various Commercial Catalysts. Four different commercial catalysts were investigated relative to the kinetics for ethylene and ether formation. These catalysts varied in method of preparation as well as chemical composition. The rate-concentration data for all catalysts were analyzed in a similar manner as described above. The model of Equation (5) was found to describe the data well and the constants obtained from a linear regression analysis are reported in Table 7 for the four catalysts. The model constants were found to vary considerably for both ethylene and ether formation among the various catalysts. The effect of alcohol concentration on the selectivity σ for these catalysts is shown in Figure 8. The selectivity is seen to vary as much as twenty-fold among the various catalysts tested.

TABLE 6. MODEL CONSTANTS FOR DEHYDRATION OF ETHANOL AT 155°C

Product: Diethyl ether

Catalyst	k ($\times 10^3$)	K_A	K_W
Fresh	3.5	6.2	550
Poisoned	0.87	9.1	650

Product: Ethylene

Catalyst	k ($\times 10^3$)	K_A	K_W
Fresh	0.085	280	77,000
Poisoned	0.042	70	18,000

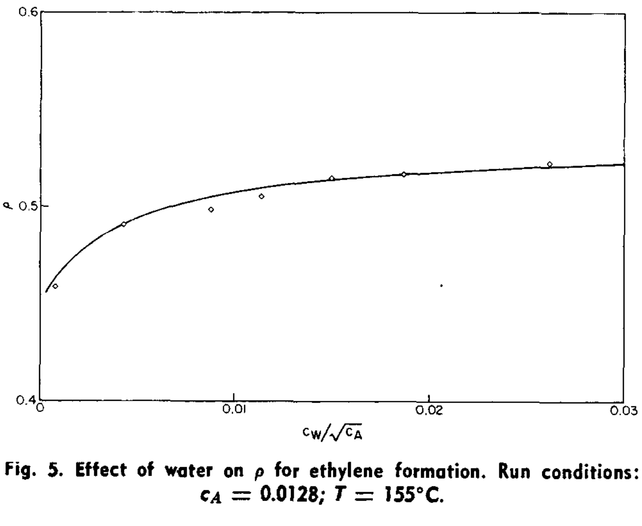

Fig. 5. Effect of water on ρ for ethylene formation. Run conditions: $c_A = 0.0128$; $T = 155°C$.

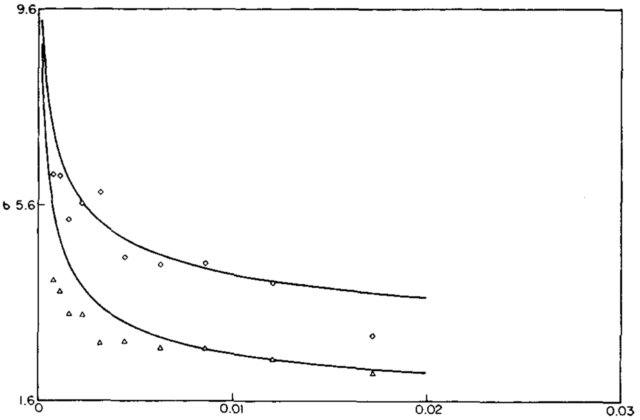

Fig. 6. Effect of alcohol on selectivity σ. Run conditions: c_W (feed) $= 0$; $T = 155°C$; (△) fresh catalyst: (◇) poisoned catalyst.

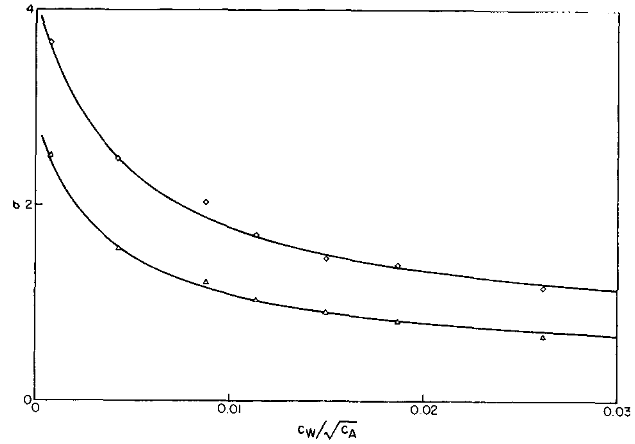

Fig. 7. Effect of water on selectivity σ. Run conditions: $c_A = 0.0128$; $T = 155°C$; (△) fresh catalyst; (◇) poisoned catalyst.

DISCUSSION

The magnitude and industrial significance of the variations in ρ, σ, and of the flow-directional effects have been already discussed. Although this study does not attempt to investigate the reaction mechanism, a few comments may be in order regarding the chemical significance of the rate Equation (5). First of all, it must be emphasized that K_A and K_W, although related to adsorption-desorption equilibria, should not be interpreted as equilibrium constants of Langmuir type isotherms in view of the strong interaction effects of adsorbed methanol and water. The adsorption of water, in fact, is known to directly affect the acidity of the catalyst in general (Matsuzaki and Fukuda, 1969), and hence its activity with re-

Table 7. Model Constants for Various Commercial Catalysts at 225°C

	Ethylene			Diethyl ether		
Catalyst	k ($\times 10^3$)	K_A	K_W	k ($\times 10^3$)	K_A	K_W
KSFO	16.0	81	4,000	260	2.3	220
F49	4.6	97	3,000	160	2.0	130
AHC	0.68	49	6,500	5.6	14	2,200
FI	0.007	130	46,000	0.24	78	23,000

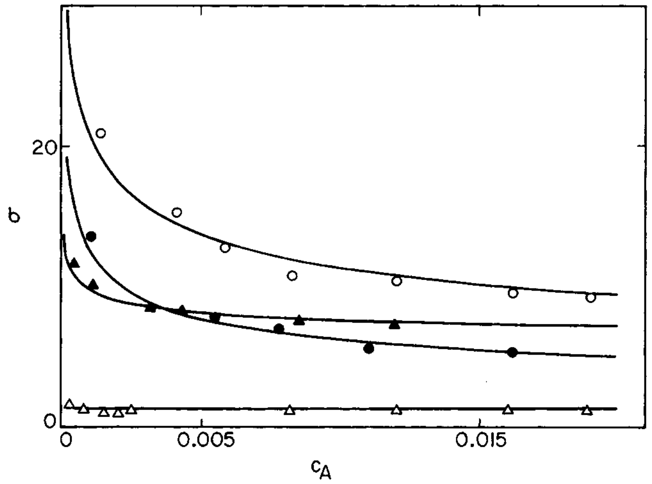

Fig. 8. Effect of alcohol concentration on σ for various catalysts. Run conditions: c_W (feed) = 0; T = 225°C. (○) KSFO; (●) F49. (▲) AHC; (△) FI.

spect to the alcohol dehydration reactions (Butt, 1970).

The comparison of K_W and K_A for fresh and poisoned catalysts presents some interesting evidence regarding the active sites. In the formation of methyl and ethyl ether, the constants K_A and K_W are larger on the poisoned catalyst. This can be explained by the assumption that chemisorption of both alcohol and water involves a strongly basic site (Figueras et al., 1971). Amine chemisorption on acidic sites would increase the strength of the neighboring basic sites resulting in stronger chemisorption as compared to the fresh catalyst. This induction effect may thus result in an increase in overall model constants K_A and K_W.

In ethylene production on the other hand, the two constants K_A and K_W substantially decrease with poisoning, consistent with the view that the reaction requires a strongly acidic site and a weakly basic one (Figueras et al., 1971). Another piece of evidence for the different type of sites involved in ether and ethylene production is the relative magnitude of the constants K_A, K_W. In the case of ether production, the constants K_A and K_W for methanol are quite close to those for ethanol, considering the difference in the chemisorbed species. In contrast, these constants differ by orders of magnitude compared to the constants for the ethylene formation reaction. These interpretations are also in agreement with Figueras et al. (1968) who observed two different types of chemisorption of ethanol on fresh silica-alumina.

The changes in K_A and K_W with poisoning are, of course, a manifestation of surface sites nonuniformity and interactions. A detailed investigation of the site strength distribution and its relation to the rates of dehydration is given in Bakshi (1974).

NOTATION

c = concentration vector
c_A = alcohol concentration in gas phase, moles/liter
c_W = water concentration in gas phase, moles liter
c_P = poison concentration in adsorbed phase, moles/g catalyst
E_A = activation energy for rate determining step, kcal/mole
k, K_A, K_W = nonlinear model constants as in Equation (5)
Q_A = heat of adsorption for alcohol, kcal/mole
Q_W = heat of adsorption for water, kcal/mole
R = universal gas constant
r = rate of product formation, mole of product/hr.-g catalyst

Greek Letters

ρ = rate ratio defined by Equation (2)
σ = selectivity defined by Equation (6)
ϕ = poisoning factor
Φ = Thiele modulus

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