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Mass Transfer Effects in the Olefin Disproportionation Reaction

I. Promoter Concentration and Temperature Effects for Propylene on WO_3–Silica Catalysts

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Interphase mass transfer effects have been observed in propylene disproportionation with WO_3-silica catalysts, although calculations based on the external catalyst area predict the mass transfer rate to be several orders of magnitude greater than the observed rate of product formation. These diffusional effects were noted at all levels of conversion obtained by changes in WO_3 promoter concentration and reactor temperature. A reduction in the WO_3 concentration from 5.0 to 0.2 wt % reduced catalyst activity by a factor of ~120; however, the systematic dependence of conversion on linear velocity persisted. The reaction rate varied exponentially with temperature having an apparent activation energy of from 37-59 kcal/mole. These unexpected mass transfer limitations are, of course, difficult to resolve in the light of existing theory which predicts a weak temperature dependency and a constant rate of reaction with changing promoter concentration (on catalyst particles of the same size). These observed mass transfer effects may be accounted for by assuming that reaction occurs on a small number of very active sites which are widely separated on the catalyst surface. Hence, the reaction may be limited by site-localized diffusion effects which are a function of Reynolds number, WO_3 concentration, and temperature.

INTRODUCTION

Standard textbook, interphase mass transfer theory suggests that each catalyst particle is enclosed within a boundary layer across which both reactants and products must diffuse. If the catalyst is so active that the reactant cannot diffuse to the surface fast enough to keep pace with the reaction, then a concentration gradient will develop across the boundary layer and limit the surface reaction rate. When reactions are thus limited, an increase in the linear gas velocity reduces the boundary layer thickness and causes an increase in catalyst efficiency. Thus, when different weights of catalyst in the same reaction are compared at equal space velocity the larger catalyst bed will be the most efficient because of a higher linear gas velocity which in turn increases the rate of interphase mass transfer (*1*).

Preliminary propylene disproportionation studies on WO_3–silica catalysts were reported to show increased catalyst efficiency with increased flow rate (*2*) which is indicative of interphase diffusional effects in spite of calculations which predict that no limitation should exist (*3*). Calculations of this type use the total external, catalyst surface area in estimating interphase mass transfer rates. Since, with few exceptions, only a very limited fraction of the catalyst surface is active, there is reason to question a priori calculations which rule out interphase diffusional limitations on the basis of the total external surface area. Perhaps for widely separated, but very active sites one should use an effective external surface area which may be much smaller than the total external surface area.

NOMENCLATURE

A_d	Reactor cross-sectional area (0.66 cm^2)
a	External surface area or effective site area
D_{1m}	Multicomponent diffusion coefficient
d_p	Particle diameter
F	Volumetric flow rate
G	Mass flow rate/unit reactor area
k_G	Phenomenological mass transport coefficient
M_W	Reactant molecular weight
m	Catalyst weight (g)
N_{Re}	Reynolds number
N_{Sc}	Schmidt number
P_f	Film pressure (atm)
P_T	Total pressure (atm)
R	Gas constant
T	Absolute temperature (°K)
y	Reactant mole fraction in gas phase
y_s	Reactant mole fraction at the surface
y_{eq}	Reactant mole fraction at equilibrium
δ	Boundary layer thickness (cm)
ϵ	Void fraction
μ	Viscosity (poise)
ρ	Gas density (g/cm^3)

METHODS

Runs were made using a split-bed quartz reactor in which the propylene flow could be reversed, as shown in Fig. 1. Gas samples were withdrawn after full or one-half bed contact with the catalyst. Hence, two catalyst specimens were compared simultaneously under identical activation and reaction conditions. Comparisons were made between two different weights of catalyst as well as between two different particle sizes. In-line glc analyses were made using a Hewlett-Packard 5752B gas chromatograph. The relative response glc data of Messner *et al.* (*4*) were used in the treatment of data.

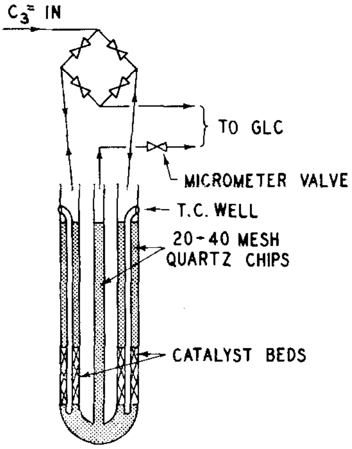

FIG. 1. Split bed reactor.

Phillips pure grade propylene was passed through activated mole sieve and magnesium oxide columns before use. The tungsten–silica catalysts used in this study (except for the 6.8% WO_3 catalyst) were prepared by impregnation of Davison grade 59 silica gel with ammonium meta tungstate. Each catalyst specimen was air activated for from 4 to 12 hr at ~600°C followed by a 2–3-hr helium purge at the same temperature. The activated catalyst was cooled in a static helium atmosphere to ~500°C where propylene was introduced and the temperature was then lowered to the desired temperature. The catalyst was conditioned with propylene for 12 to 24 hr to assure constant activity before data were collected. Catalyst activity normally increased for the first 12 to 20 hr, remaining reasonably constant for several days thereafter. Both air and helium used in catalyst activation were passed through mole sieve columns to remove traces of water.

RESULTS

Two of the more common disproportionation catalysts (cobalt molybdate on alumina and WO_3 on silica) were checked for interphase mass transfer effects. The disproportionation of propylene on the cobalt molybdate–alumina catalyst is shown in Fig. 2 where conversion is plotted against catalyst weight/flow rate (m/F) for two different weights of catalyst. Since the data for the two catalyst weights fall on the same curve, interphase diffusional effects are presumed to be absent (*5*). Two catalyst particle sizes 20–35 and 35–60 mesh were found to have the same activity per gram. Hence, it was concluded that propylene disproportionation on

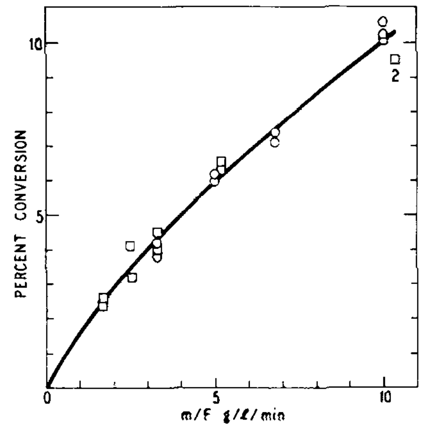

FIG. 2. Conversion vs m/F for the cobalt molybdate-alumina catalyst at 150°C; ○, 0.600 g of catalyst, □, 0.300 g of catalyst.

cobalt molybdate–alumina is neither limited by interphase nor pore diffusional effects. When similar studies were made using 6.8% WO_3–silica catalyst at 375, 400, and 425°C, the results shown in Fig. 3 were obtained which are indicative of interphase mass transfer limitations at all three temperatures.

Runs were made on catalysts with 5.0, 1.0, and 0.2% WO_3 to see the effect of promoter concentration on both the level of conversion and the mass transfer problem. Conversion vs. m/F data are listed in Table 1 for various temperatures. Interphase mass transfer effects were noted at all temperatures (Figs. 4, 5, and 6) and at all the promoter concentrations which were examined (Fig. 7). Two 1.0% WO_3 particle sizes (20–35 mesh and 35–60 mesh) were compared, and the 35–60-mesh catalyst was 1.5 times as active as the 20–35-mesh catalyst, which is indicative of a mass transfer problem.

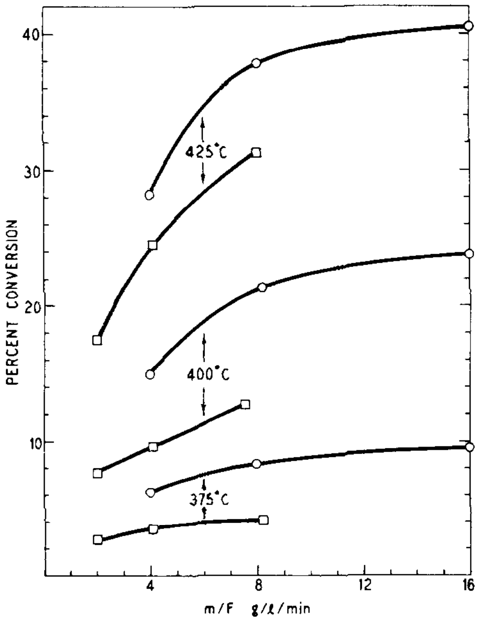

FIG. 3. Percent conversion vs m/F for 6.8% WO_3–silica catalyst at 375, 400, and 425°C; ○, 0.800 g of catalyst, □, 0.400 g of catalyst.

DISCUSSION

A. *Generalized Equations for Interphase Mass Transfer*

By the classical methods of Hougen and Watson (*6*), a material balance in a section of the catalyst bed under steady-state conditions equates the rate of disappearance of reacting gas to the rate of mass transfer across the interface per unit time:

$$\frac{FP_T}{RT}\left(\frac{dy}{dm}\right) = k_G a P_T (y - y_s),$$

$$\int_{y_{in}}^{y_{out}} \frac{dy}{y - y_s} = \frac{RTk_G am}{F} = \left(\frac{k_G P_T M_W}{G}\right)\frac{am}{A_d}. \quad (1)$$

By the Chilton–Colburn correlation (*7*), the term $(k_G P_T M_W/G)$ is a unique function of the Reynolds number $(d_p G/\mu)$ and Schmidt number $(\mu/\rho D_{1m})$ raised to experimentally determined exponents. Using the Reynolds and Schmidt number correlations of Petrovic and Thodos for low Reynolds numbers (*8*), the integrated form of Eq. (1) becomes

$$\ln\left(\frac{y_{in} - y_s}{y_{out} - y_s}\right) = \frac{k_G P_T am}{G_m A_d} = \frac{0.357 P_T am}{\epsilon A_d P_f (N_{Sc})^{2/3} (N_{Re})^{0.359}}, \quad (2)$$

which can be used to estimate when interphase mass transfer limitations should become important. For a reversible re-

TABLE 1
EFFECTIVE SITE AREA AS A FUNCTION OF TEMPERATURE AND PROMOTER CONCENTRATION

WO_3 (%)	Temperature (°C)	Flow rate (ml/min)	N_{Re}	Conversion[a] (%)	A_d/m (cm^2/g)	a_{avg} (cm^2/g)
6.8	375	200	3.36	6.2	0.826	
		100	1.68	8.3	0.826	0.155
		50	0.84	9.5	0.826	(1600)[b]
		199	3.34	2.6	1.65	
		98	1.65	3.5	1.65	0.123
		49	0.82	4.1	1.65	(2000)
6.8	400	200	3.26	15.0	0.826	
		98	1.60	21.4	0.826	0.451
		50	0.815	23.8	0.826	(554)
		198	3.23	7.6	1.65	
		98	1.60	9.6	1.65	0.377
		53	0.864	12.7	1.65	(663)
6.8	425	200	3.16	28.2	0.826	
		99	1.56	37.8	0.826	1.14
		50	0.79	40.5	0.826	(219)
		199	3.14	17.5	1.65	
		97	1.53	24.5	1.65	1.17
		50	0.79	31.3	1.65	(214)
5.0	350	240	4.15	3.5	0.66	
		120	2.08	5.4	0.66	
		60	1.04	7.3	0.66	0.107
		31	0.54	10.7	0.66	(2300)
		238	4.12	1.4	1.32	
		123	2.13	2.0	1.32	
		60	1.04	2.7	1.32	0.0799
		30	0.52	3.9	1.32	(3100)
5.0	375	241	4.05	11.0	0.66	
		120	2.02	17.3	0.66	
		59	0.99	23.0	0.66	0.413
		30	0.50	29.9	0.66	(605)
		240	4.03	4.4	1.32	
		119	2.00	7.0	1.32	
		58	0.97	10.1	1.32	0.299
		29	0.49	14.7	1.32	(836)
5.0	400	240	3.91	24.2	0.66	
		120	1.96	31.3	0.66	
		61	0.99	35.3	0.66	0.908
		30	0.49	40.5	0.66	(275)
		238	3.88	12.0	1.32	
		122	1.99	18.6	1.32	
		59	0.96	24.8	1.32	0.911
		29	0.47	32.6	1.32	(275)
1.0	375	240	4.03	0.70	0.66	
		121	2.03	0.97	0.66	
		60	1.01	1.28	0.66	0.0181
		30	0.50	1.61	0.66	(13 800)
		238	4.00	0.39	1.32	
		123	2.07	0.52	1.32	

TABLE 1 (*Continued*)

WO_3 (%)	Temperature (°C)	Flow rate (ml/min)	N_{Re}	Conversion[a] (%)	A_d/m (cm²/g)	a_{avg} (cm²/g)
		60	1.01	0.60	1.32	0.0181
		30	0.50	0.68	1.32	(13 800)
1.00	400	240	3.91	1.95	0.66	
		120	1.96	3.35	0.66	
		60	0.98	4.93	0.66	0.0680
		31	0.51	7.55	0.66	(3700)
		243	3.96	1.00	1.32	
		123	2.00	1.52	1.32	
		63	1.03	2.15	1.32	0.0624
		31	0.51	3.60	1.32	(4000)
0.2	400	240	3.91	0.30	0.66	
		121	1.97	0.43	0.66	
		60	0.98	0.58	0.66	0.00829
		30	0.49	0.90	0.66	(30 000)
		238	3.88	0.14	1.32	
		123	2.00	0.21	1.32	
		60	0.98	0.25	1.32	0.00709
		30	0.49	0.30	1.32	(35 000)
0.2	400	240	3.91	0.32	0.66	
		120	1.96	0.38	0.66	
		60	0.98	0.51	0.66	0.00787
		31	0.51	0.86	0.66	(32 000)
		238	3.88	0.16	1.32	
		120	1.96	0.19	1.32	
		59	0.96	0.22	1.32	0.00692
		30	0.49	0.30	1.32	(36 000)
0.2	450	240	3.70	5.15	0.66	
		120	1.85	8.16	0.66	
		61	0.94	11.9	0.66	0.173
		30	0.46	17.0	0.66	(1445)
		241	3.71	2.48	1.32	
		120	1.85	3.62	1.32	
		60	0.92	4.30	1.32	0.140
		30	0.46	6.61	1.32	(1785)

[a] The average of duplicates.

[b] (External surface area/a_{avg}) = (250 cm²/g/a_{avg}).

action, such as propylene disproportionation, which is markedly limited by interphase diffusion, the mole fraction of propylene at the catalyst surface (y_s) should approach the propylene equilibrium mole fraction (y_{eq}). Thus to simplify calculations, $y_{eq} \approx y_s$ was used. The void fraction (ϵ) was assumed to be 0.40; the film pressure (P_f) was taken to be equal to (or proportional to) the total pressure (P_T), which is in accord with the fact that equal molar counter-current diffusion occurs; and the external surface area (a) was estimated to be 250 cm²/g for 0.063 cm particles.

At 400°C using a viscosity of 1.67×10^{-4} poise, a gas density of 7.6×10^{-4} g/cm³ and a diffusion coefficient of 0.291 cm²/sec, the Schmidt number was estimated to be

$$N_{Sc} = \frac{\mu}{\rho D_{1m}} = \frac{1.67 \times 10^{-4}}{7.6 \times 10^{-4} \times 0.291} = 0.755.$$

D_{1m} was calculated as outlined by Satter-

TABLE 2

A Comparison of Calculated and Experimental $\ln[(y_{\text{in}} - y_{\text{eq}})/(y_{\text{out}} - y_{\text{eq}})]$ Values as a Function of Catalyst Weight and WO_3 Promoter Concentration

m (g)	$\ln[(y_{\text{in}} - y_{\text{eq}})/(y_{\text{out}} - y_{\text{eq}})]$				
		Experimental			
	Calculated	6.8% WO_3	5.0% WO_3	1.0% WO_3	0.2% WO_3
0.001	0.266	—	—	—	—
0.010	2.66	—	—	—	—
0.100	26.6	—	—	—	—
0.400	106.0	0.24	—	—	—
0.500	133.0	—	0.37	0.027	0.0037
0.800	213.0	0.41	—	—	—
1.000	266.0	—	0.86	0.053	0.0074

field (*9*), and Reynolds numbers were calculated from

$$N_{\text{Re}} = \frac{d_p G}{\mu}$$

Thus at 400°C with a 200 ml/min flow, Eq. (2) becomes

$$\ln\left(\frac{y_{\text{in}} - y_{\text{eq}}}{y_{\text{out}} - y_{\text{eq}}}\right) = 266m, \qquad (3)$$

where m is the catalyst weight in grams. Comparisons can be made between calculated and experimental $\ln[(y_{\text{in}} - y_{\text{eq}})/(y_{\text{out}} - y_{\text{eq}})]$ values as a function of both the promoter concentration and catalyst weight. The data in Table 2 show that the rate of mass transfer to the external catalyst surface should exceed the observed reaction rate by a factor of from ~ 275 for 5.0% WO_3 to $\sim 36\,000$ for 0.2% WO_3. Experimentally, however, there is abundant evidence, as shown in Figs. 3–7, for interphase mass transfer limitations.

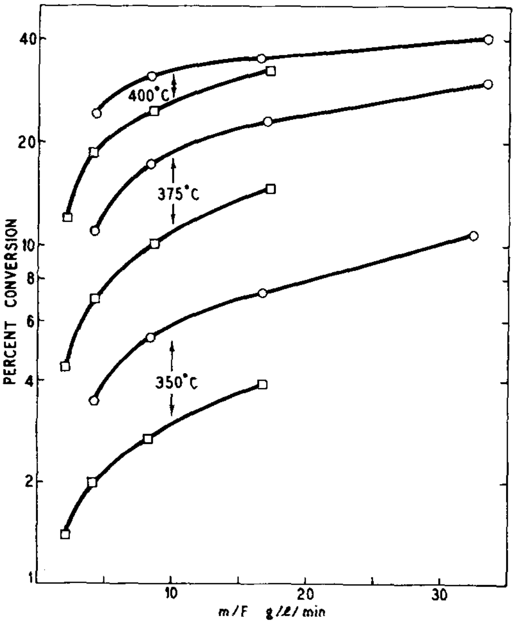

Fig. 4. Percent conversion vs m/F for 5% WO_3 at 400, 375, and 350°C; ○, 1.000 g of catalyst, □, 0.500 g of catalyst.

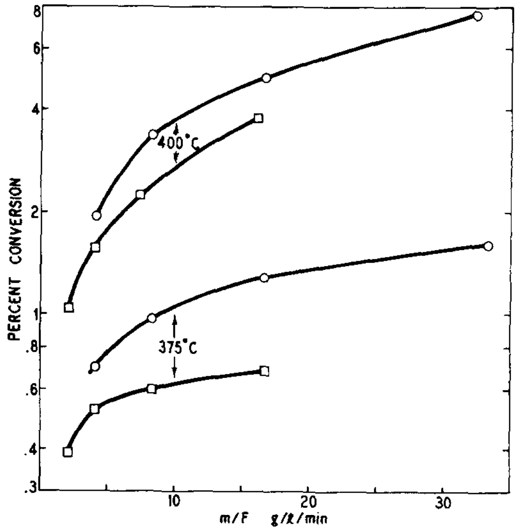

Fig. 5. Percent conversion vs m/F for 1.0% WO_3 on silica at 400 and 375°C; ○, 1.000 g of catalyst, □, 0.500 g of catalyst.

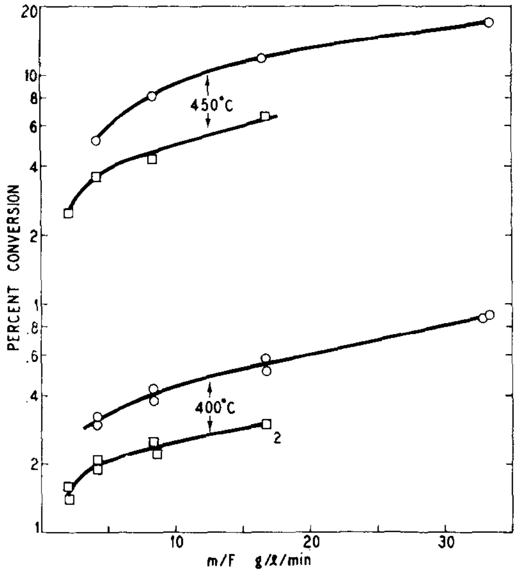

FIG. 6. Percent conversion vs m/F for 0.2% WO_3 on silica at 450 and 400°C; ○, 1.000 g of catalyst; □, 0.500 g of catalyst.

B. Temperature and Promoter Concentration Effects

Classical consideration of interphase mass transfer limited processes would suggest a very small temperature dependency (≈ 0 kcal) (*1*). If the temperature dependency is large, the linear velocity effect should rapidly disappear with decreasing temperature. Thus a large decrease in conversion with decreasing temperature should indicate a shift from interphase mass transfer limitation to surface reaction or pore diffusion limitation. The very marked dependency of conversion on temperature (37–59 kcal) shown in Figs. 3–6 is difficult to explain on the basis of classical theory. In addition to this large temperature dependency, there is no decline in the linear velocity effect with decreasing temperature. Even at the lowest levels of conversion and at all temperatures where a measureable level of conversion was obtained, these experimentally observable diffusion effects continued to persist.

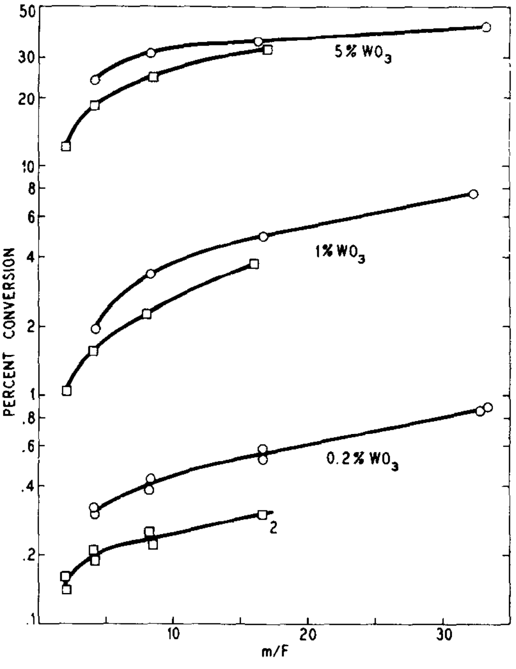

FIG. 7. Percent conversion vs m/F for 5, 1, and 0.2% WO_3 catalysts at 400°C; ○, 1.000 g of catalyst, □, 0.500 g of catalyst.

Similarly, on the basis of classical theory, a decrease in promoter concentration or a change in the number of active sites should have very little effect on the rate of a reaction which is already controlled by interphase diffusion unless the distance between sites approaches the boundary layer thickness. Figure 7 shows that a decrease in the WO_3 promoter concentration results in a large drop in conversion. However, the linear velocity effect remains and may even be enhanced at lower promoter concentrations.

C. Site-Localized Diffusional Effects

A catalyst having 6.8% WO_3 on silica with 345 m^2/g of surface would have on the order of only 5% or 17.3 m^2/g of the total surface area covered by a monolayer of WO_3. For 20–40-mesh particles with uniform promoter distribution as a monolayer only 12.5 cm^2/g of the external surface of 250 cm^2/g would be covered by promoter. Since perhaps only a very small percentage of the promoter is active, an even smaller fraction of the external surface is directly involved in the catalytic process. A decrease in promoter concentration would not be expected to have an effect on an interphase diffusion-limited reaction unless the promoter concentration is lowered to the point where the distance between active sites approaches the boundary layer thickness. Then catalyst activity should begin to be a function of the promoter concentration and should continue to show a Reynolds number dependency. For example, even though propylene may be transferred to the total, external catalyst surface 275 to 36 000 times faster than product is formed, widely separated and very active sites could have their inherent activities limited by site-localized film diffusional effects which provides a possible explanation for our experimental observations.

An estimate of laminar film thickness, using the data above and

$$\delta = \frac{D_{\mathrm{lm}}}{RTk_G} = 0.037 \text{ cm}, \tag{4}$$

predicts a film thickness (δ) of 0.037 cm for catalyst particles 0.063 cm in diameter. This large film thickness is perhaps realistic for one particle suspended in a flowing media. However, in a fixed bed where the catalyst particles are packed closely together, a film thickness much smaller than 0.037 cm would obviously be necessary. The channels or space between catalyst particles will be small (0.01–0.02 cm at most). Hence, the laminar layer around 0.063-cm particles in a packed bed would be smaller than the 0.01 to 0.02-cm channels through which the propylene is forced to flow. This suggests that one should not necessarily rule out site diffusional effects on the basis of boundary layer thickness calculations.

Where only a small fraction of the available tungsten oxide sites are active, the classical prediction of a low-temperature dependency (*1*) for interphase diffusional effects may also be in error. If the surface is heterogeneous, an increase in temperature could activate sites that are inactive or only moderately active at lower temperatures. The net result would be an increase in the total number of active sites and active site area for the diffusion-limited process with increasing temperature. The data plotted in Figs. 3 to 6 show a temperature dependency (37–59 kcal) which is greater than expected via classical considerations, but not inconsistent with the expected behavior of heterogeneous sites whose activities are limited by localized diffusional effects.

D. Active Site Area

The explanation offered above assumes that the number of widely separated and very active sites can be altered by changing temperature and promoter concentration. Assuming that Eq. (2) still applies, these changes should have little effect on the gross rate of mass transfer to the external surface, but should alter the *effective* external surface area. Hence a in Eq. (2) becomes an effective, active site area which can be expressed as

$$a = \frac{\epsilon A_d (N_{\mathrm{Sc}})^{2/3} (N_{\mathrm{Re}})^{0.359}}{0.357m} \ln\left(\frac{y_{\mathrm{in}} - y_{\mathrm{eq}}}{y_{\mathrm{out}} - y_{\mathrm{eq}}}\right). \tag{5}$$

Plots of all the data for 5.0, 1.0, and 0.2% WO_3 in Table 1 showed linear relationships between ln $\ln(y_{\mathrm{in}} - y_{\mathrm{eq}})/(y_{\mathrm{out}} - y_{\mathrm{eq}})$ and $\ln(N_{\mathrm{Re}})$ with an average slope (exponent of N_{Re}) of approximately $-\frac{1}{2}$. Since the calculated values of $\epsilon(N_{\mathrm{Sc}})^{2/3}/0.357$ are near unity, the effective site area can be approximated by

$$a = \left(\frac{A_d}{m}\right) (N_{\mathrm{Re}})^{1/2} \ln\left(\frac{0.48}{y_{\mathrm{out}} - 0.52}\right), \tag{6}$$

where $y_{\mathrm{eq}} \approx 0.52$ for propylene in the 350–450°C range. The last column in Table 1 lists average values for this calculated effective site area. A semilog plot of a vs 1/T°K in Fig. 8 shows that an Arrhenius-type relationship holds for the activation of sites in the 350–450°C range of this study. A rather large variation in site activation energy with WO_3 promoter concentration is observed (Table 3).

The 400°C data in both Tables 1 and 3 show a disproportionate decline in catalyst activity with decreasing WO_3 concentration. Initially one is tempted to interpret these data as being indicative of a dual site mechanism. If, for example, two adjacent WO_3 molecules were required before the 4-center intermediate could form,

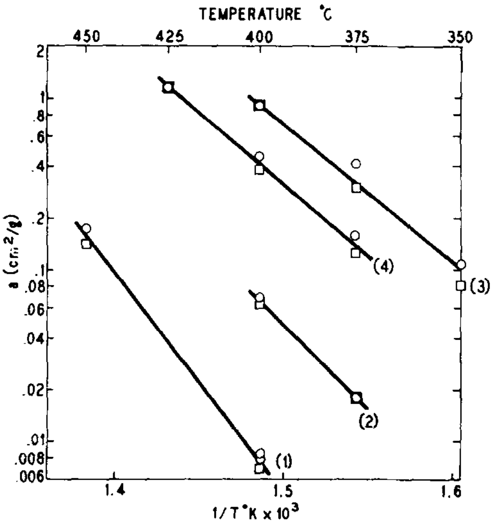

FIG. 8. The effects of temperature and WO_3 promoter concentration on effective site area (1) –0.2%, (2) –1.0%, (3) –5.0%, and (4) –6.8% WO_3.

then catalyst activity should decline with the square of the promoter concentration (assuming uniform promoter distribution, etc.). However, the large increase in site activation energy shown in Table 3 with decreasing WO_3 concentration is evidence for an increase in the WO_3–silica interactions (on a percentage basis) with decreasing WO_3 concentrations. These enhanced interactions could explain the observed relative rates in Table 3 and perhaps rule out the dual site mechanism. For example, these relative rates are a function of temperature and should decrease with increasing temperature. In fact, the activities per gram of WO_3 should, at some temperature higher than 400°C, become equal if the linear Arrhenius relationship continues to hold.

TABLE 3
RELATIVE ACTIVITY AND SITE ACTIVATION ENERGIES AS A FUNCTION OF WO_3 CONCENTRATION

WO_3 concn (wt %)	Relative concn	Relative activity 400°C	Site activation energy (kcal)
0.2	1.0	1.0	59
1.0	5.0	8.6	44
5.0	25.0	121.0	37
6.8[a]	—	—	38

[a] The 6.8% WO_3 catalyst is not included as part of the series because of a different method of preparation on a different silica support.

An alternate explanation for the observed temperature dependency has been proposed by Aris (*10*), who suggests that the observed rate of a reaction limited by interphase mass transfer may be a function of the surface diffusion coefficient, which can be more temperature dependent than bulk diffusion coefficients. Thus, the increased reaction rate, with temperature, could be caused by an increase in magnitude of the surface diffusion coefficient rather than an increase in the number of very active sites.

In either case and in spite of the surface reaction being masked by mass transfer effects, the large variation in apparent activation energy with WO_3 concentration is indicative of catalytic surface heterogeneity.

CONCLUSIONS

Observed interphase mass transfer effects, although unexpected via classical considerations, are explanable by assuming that very active sites are widely separated and, hence, the reaction is limited by site-localized diffusional effects. Calculations made on the basis of generalized diffusion equations, which use the total external, particle surface area instead of an effective site area, can be misleading. High apparent activation energies can exist for reactions limited by interphase diffusion in spite of classical considerations which suggest values near zero. It is concluded that perhaps the only sure way to determine the importance of interphase mass transfer effects is an experimental one. And even experimental methods may be open to question (*5*).

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