

Kinetics and Characterization of Bismuth Molybdate Catalysts

I. A Gradientless Partial Oxidation Reactor

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A gradientless laboratory fixed bed reactor was designed for studying the partial oxidation of 1-butene to 1,3-butadiene over bismuth-molybdate catalysts. By dilution of the catalyst bed with inert silicon carbide, axial catalyst bed temperature gradients were routinely reduced to 2 K or less over the temperature range 650–740 K for the exothermic model reaction. A systematic experimental procedure was developed and used to show that potential transport “disguises” did not significantly influence the intrinsic rate of butadiene formation measured under both integral and differential conditions. For one Bi_2MoO_6 catalyst system, rate of butadiene formation data over the temperature range 700–740 K were fit to pseudo first-order (in butene) kinetics. Analytical solutions of the governing equations describing fixed bed reactor transport disguises for first-order catalytic reactions were used to confirm that the reactor operated in a near gradientless fashion, in agreement with experiment. © 1990 Academic Press, Inc.

INTRODUCTION

Selective oxidation of hydrocarbons via heterogeneous catalyst is currently practiced for the production of several commercial products, including acrylonitrile, ethylene oxide, and maleic anhydride (1). The industrial development of selective oxidation catalysts began in 1948 with Hearne and Adams (2), who reported that acrolein could be produced using a copper–cuprous oxide heterogeneous catalyst. Bismuth molybdate replaced this catalyst about ten years later as the more selective catalyst of choice (3), a discovery which initiated the development of supported multicomponent molybdates. It is generally accepted that bismuth molybdate forms the active phase in the multicomponent

molybdate catalysts (4). Although commercially obsolete now, unsupported bismuth molybdate provides sufficient similarity to modern molybdate catalysts for interpretation of their catalytic behavior.

The goal of our work was to study the oxidative dehydrogenation of 1-butene to 1,3-butadiene, a model reaction, over various compositions of unsupported bismuth molybdate catalysts in order to quantitatively compare their reactivities. A gradientless reactor was an essential requirement for meeting our goals. The influence of heat and mass transport rates for the exothermic reactions conducted over these catalysts, including our model reaction, could easily disguise the quantitative catalyst activity and selectivity rankings sought to be made. In a previous study by Matsuura *et al.* (5), a comparison of the activity of catalysts with different surface bismuth to molybdenum ratios using the same above model reaction was made using a fixed bed laboratory reactor packed solely with catalyst. However,

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the catalytic activity comparisons reported were significantly disguised by nonisothermal fixed bed operation, the so called "hot spots" (6). Hence, our efforts focused on designing a gradientless laboratory fixed bed reactor to investigate, in a more quantitative manner, the catalyst activity and selectivity ranking of unsupported Bi molybdates. This paper deals with the experimental approach used to achieve a gradientless fixed bed reactor design for measuring the differential rate of butadiene formation. In the companion paper (7), Part II, comparisons of Bi molybdate catalyst covering a wide range of surface compositions are given along with exploratory experiments aimed at looking more closely at the unique kinetic behavior of these catalysts.

EXPERIMENTAL

Several factors besides transport disguises, such as gas phase reactions, can mask a catalyst's performance when a fixed bed reactor is used. None of these factors were found to be important compared to the experimental catalytic rates of butadiene formation measured in this study (8).

Catalyst Preparation

The procedure of Basista (9) was followed in the preparation of 0.47 kg of Bi_2MoO_6 and 0.1 kg of $\text{Bi}_2\text{Mo}_3\text{O}_{12}$. For the synthesis of Bi_2MoO_6 , hot molybdenum solution (at 363 K) was dropwise added into a boiling bismuth nitrate solution under constant stirring over a period of 1.5 h and then refluxed for 30 h with constant stirring and adjustment to $\text{pH} = 5$. The solution was evaporated at 373 K for 10 h and then at 490 K for 8 h to concentrate the catalyst for subsequent calcination. Typically, 20-g catalyst samples were subjected to a stepwise calcination temperature protocol, ending at 743 K, which resulted in surface areas (measured with Kr) reproducible to $\pm 10\%$ (for example, for Bi_2MoO_6 , the surface area was $2.5 \pm 0.3 \text{ m}^2/\text{g}$).

Reactor System

A schematic of the atmospheric pressure reactor system and quartz fixed bed reactor is given in Fig. 1. The catalyst bed was diluted with silicon carbide (SiC) particles of equal diameter to the catalyst. Catalyst particle diameters used included 320, 460, and 540 μm . SiC particles were nitric acid washed, rinsed with deionized water, and calcined in air for 2 h at 773 K prior to use. The dilution ratio, defined as mass of SiC in the catalyst bed per mass of catalyst, required to obtain isothermicity ranged from 2.6 to 16 for the various catalyst loadings evaluated in this study. Quartz wool and additional SiC particles were used at the entrance and exit regions of the catalyst bed to prevent catalyst fluidization and to reduce the extent of gas phase reactions in the heated zones. A Techne TC4B PID temperature controller maintained the Tecam model SBL-2D fluidized sandbath isothermal. During the reaction studies, the observed radial temperature drop between the annular thermocouple and the sandbath was less than 1 K for reaction temperatures $T_{\text{rxn}} < 673 \text{ K}$ and less than 2 K for $T_{\text{rxn}} > 673 \text{ K}$. The actual total feed flowrate, F_T , used at a given temperature is reported here in sccm (standard cm^3/min referenced to 298 K and 101 kN m^{-2}).

Analytical System

Feed and product streams were analyzed on line using an Antek 300 gas chromatograph equipped with FID and TCD detectors. A 9 ft by $\frac{1}{8}$ in. stainless steel column packed with 80/100 mesh of 0.19% picric acid on Carbopack C was used for FID analysis of methane, 1-butene, *cis*- and *trans*-butene, 1,3-butadiene, and furan. A 10 ft by $\frac{1}{8}$ in. stainless steel column packed with 60/80 mesh Carbosieve B was used for TCD analysis of methane, oxygen, and carbon dioxide. Water was quantified using a cold trap. Methane, inert under the conditions studied, was used as an internal standard.

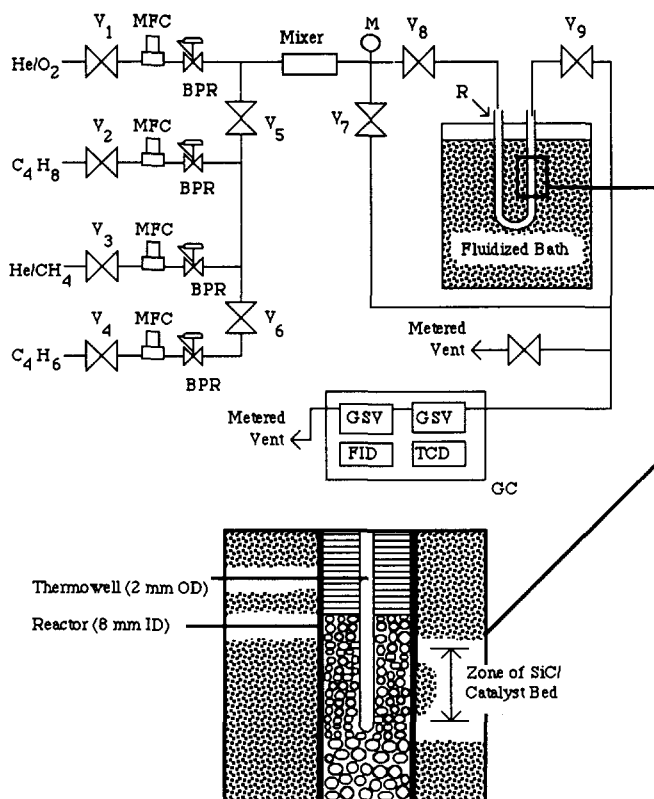


FIG. 1. Schematic diagram of the reactor apparatus: V, valves; MFC, mass flow controller (TylanTM); M, manometer; R, quartz reactor; GSV, gas sampling valve; GC, gas chromatograph; D, detector (FID or TCD); BPR, back pressure regulator.

Calculated mole fractions of reactants and products were accurate to $\pm 5\%$ of the value or better for both FID and TCD analyses; certified cylinder standards were used for calibration. The major products were butadiene and water; furan was detected at < 10 ppm. Selectivity was defined (in percent) as the ratio of butene conversion to butadiene divided by the total butene conversion to diene plus carbon dioxide.

Transport Processes in Fixed Bed Reactors

Several criteria have been developed to assess whether or not transport processes, inherent to fixed bed reactors, mask experimental heterogeneous catalyst performance (see (10, 11) for a review). One advantage

of fixed bed reactors over recirculating (e.g., Berty or Carberry) gradientless reactors is that the flow pattern approaches ideal plug flow and the calculation of reaction rates is straightforward; in addition, the large ratio of void volume to packed volume in recirculating reactors is not desirable for partial oxidation studies since significant homogeneous and wall reactions would occur, making data interpretation (of blank and catalyst loaded reactors, as a function of operating conditions, etc.) difficult. Criteria listed in Table 1 represent the general guidelines for estimating whether transport effects will be important in a given study. For the reactor conditions in our study, these criteria were in general satisfied: $44 > L/d_p > 200$ and $11 > D/d_p > 16$. In our study, for a typical Pe_m

TABLE 1
Criteria For Transport Processes in Fixed Beds

Criterion	Condition: to neglect	Reference
$D/d_p > 10$	gas bypassing and flow maldistribution	(17)
$1/[1 + Bi_w/e] < 0.7$	radial temperature gradients	(17)
$L/d_p > 150$	axial heat and mass effects	(23)
$L/d_p > 20 \ln[1/(1-x)]/Pe_m$	axial mass transfer, first order isothermal reactions	(24)
$D/d_p > 250 b/\text{del}$	gas bypassing and flow maldistribution	(25)

Note. Variables are defined as follows: L = length of catalyst bed; d_p = diameter of catalyst particle; Pe_m = axial Peclet number based on d_p , $d_p u_i / D_{ea}$; D_{ea} = effective axial diffusivity in packed bed; D = inner diameter of reactor; b = volumetric fraction of diluent; x = conversion of 1-butene to 1,3-butadiene; del = relative experimental % error in conversion; Bi_w = wall Biot number, $h_w D / (2\lambda_c)$; h_w = wall heat transfer coefficient; λ_c = effective radial bed thermal conductivity.

= 0.5, a catalyst particle size of 300 μm , and the largest measured conversion of 60% at 740 K, L/d_p was equal to 200, satisfying the criteria for pseudo first-order reactions. The reaction butene to butadiene was assumed to be pseudo first-order in the temperature range 700–740 K; results given in Part II as well as earlier studies (7, 12–14) support this assumption. The estimated Bi_w for the diluted catalyst bed was 3.7. Thus, approximately 45% of the heat transfer resistance was estimated to occur at the reactor wall. However, the exterior reactor wall temperature was essentially equal to the sandbath temperature and equal to the annular thermocouple reading (same axial location) for all cases when the catalyst bed was sufficiently diluted.

The methodology used to evaluate the effect of catalyst dilution on reactor is outlined in Table 2. Catalyst bed dilution was previously used by Lankhuijzen (15) and his results provided guidance for developing this methodology. The experiments conducted to confirm the usefulness of this methodology using Bi_2MoO_6 catalysts are presented below.

RESULTS

Reactivity of the Blank Reactor

As shown in Table 3, *cis*- and *trans*-butene production in the blank reactor loaded with SiC particles was negligible compared

to butadiene production. Using the same SiC, adding catalyst and running the reaction at identical conditions gave significantly larger conversions to butadiene. Adams had earlier reported (16) that the oxidative dehydrogenations of *cis*-, *trans*-, and 1-butene to butadiene were comparable. Thus, to simplify our analysis procedure, all butenes were lumped as a single reactant. In general, throughout the entire study it was found that blank reactions were negligible compared to reactions over the catalysts. Furthermore, for all of the Bi_2MoO_6 catalysts discussed in this paper, the selectivity for the butene reaction to butadiene was 95% or greater.

TABLE 2

Methodology for Using/Evaluating Catalyst Dilution To Eliminate Transport Disguise to Catalyst Performance

- I. Initial Reactor Considerations
 - a. Select L , d_p , D and u_i to satisfy criteria, Table 1
 - b. Select and evaluate materials for diluent and reactor with negligible reactivity
 - c. Experimentally identify dilution ratios for eliminating axial temperature gradients
 - d. Determine the effect of bypassing using dilution ratios \geq values identified in part c
- II. Isothermal Mass Transfer Experiments
 - a. Determine pore diffusion effects by varying catalyst particle size at identical conditions
 - b. Determine inter-particle effects on conversion at constant W/F_{B0} and feed conditions
 - c. If possible, measure the kinetics of the reactions and backcalculate transport effects

TABLE 3

A Comparison of Products Formed With and Without Bi_2MoO_6 Catalyst Loaded into the SiC Filled Reactor^a

X_{cis}	X_{trans}	X_{diene}	X_{CO_2}	$T(\text{in K})$
Reaction With Catalyst				
2.5	2.1	14.9	0.3	657
4.0	3.5	27.9	0.6	684
5.5	4.8	33.1	0.7	707
7.3	6.6	45.9	0.8	726
Reaction Without Catalyst				
0.6	0.6	0.4	0.0	677
1.1	1.0	0.6	0.1	713
1.9	1.6	0.9	1.0	723

Note. Conditions: 0.24 g catalyst, 2.2 g SiC, $d_p = 550 \mu\text{m}$, $F_T = 140 \text{ sccm}$, $15 \text{ C}_4\text{H}_8 : 15 \text{ O}_2 : 80 \text{ He (vol\%)}$.

^a The parameter X_i is the conversion of 1-butene to product "i" on a molar basis.

Catalyst Bed Dilution

An important step in catalyst dilution is to use diluent and catalyst particles equal in size to ensure a flat radial velocity profile and avoid excessive fluid bypassing, especially at the inner reactor wall (17, 18). If bypassing was pronounced in our experiments, a decrease in butene conversion would be expected as the dilution ratio was increased. The results of experiments conducted to check whether bypassing was important are shown in Fig. 2, where conversion to diene is plotted versus dilution ratio. Prior to the dilution experiments described

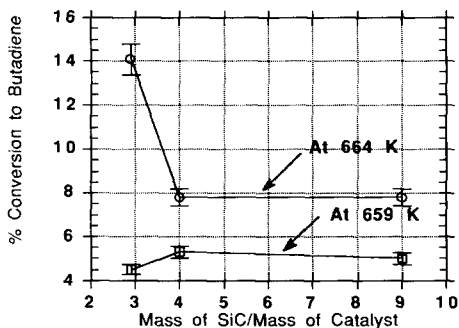


FIG. 2. Effect of catalyst bed dilution on conversion to butadiene at constant feed conditions: $10.3 \text{ C}_4\text{H}_8 : 14.7 \text{ O}_2 : 75 \text{ He}$; $F_T = 995 \text{ sccm}$; $0.4 \text{ g Bi}_2\text{MoO}_6$.

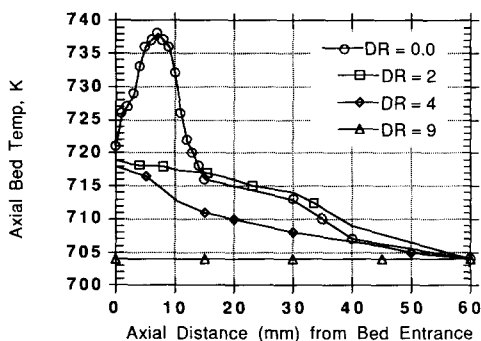


FIG. 3. Axial centerline temperature profiles for various catalyst bed dilutions at constant feed conditions; $10.3 \text{ C}_4\text{H}_8 : 14.7 \text{ O}_2 : 75 \text{ He}$; $0.4 \text{ g Bi}_2\text{MoO}_6$; feed preheated to 704 K ; $F_T = 995 \text{ sccm}$.

in Fig. 2, the same catalyst was loaded undiluted into the same reactor and, at a feed inlet temperature of 664 K , the maximum axial centerline temperature was 684 K at a butene conversion of 14% . Diluting the same catalyst at ratios of 2 and 4, holding all other reaction conditions constant, eliminated the 20 K hot spot with a concomitant reduction in the butene conversion to 7.9% for both dilution ratios. Isothermal conditions were also measured at a feed inlet temperature of 659 K for the same catalyst loading at dilution ratios of 3, 4, and 9, also shown in Fig. 2. Hence it was concluded that bypassing did not significantly mask the experimental butene conversions obtained as the dilution ratio was progressively increased once isothermicity was achieved. At a higher feed inlet temperature of 704 K , the hot spots were more pronounced, as shown in the temperature profiles plotted in Fig. 3. For the undiluted bed, the maximum axial centerline temperature increased to 738 K , a 34 K temperature rise; a dilution ratio of 9 was required to achieve an isothermal bed using the same catalyst loading. In Fig. 4, the conversion to diene is plotted versus dilution ratio for the same experiments of Fig. 3. It is clear that the conversion to butadiene is significantly larger (by 150%) for the undiluted bed as compared to the isothermal case. As the temperature

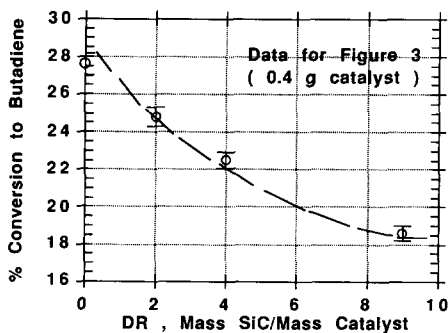


FIG. 4. Effect of catalyst bed dilution on conversion to butadiene at constant feed conditions; 10.3 C_4H_8 : 14.7 O_2 : 75 He; $F_T = 995$ sccm; 0.4 g Bi_2MoO_6 ; feed preheated to 704 K.

profiles in Fig. 3 flatten out going from dilution ratio 4 to 9, a concomitant flattening of the conversion of butadiene is presumed, as shown by the drawn-in dotted line in Fig. 4; however, experimental data between these two dilutions which would have conclusively shown this asymptotic behavior were unfortunately not obtained. Nevertheless, these results clearly show that dramatic hot spots would occur in an undiluted catalyst bed containing a selective Bi_2MoO_6 catalyst.

Mass Transfer Effects

Tests were performed to evaluate the effect of external "film" and internal catalyst pore diffusion rates on the measured rate of butadiene formation. First, a check was made for the effect of pore diffusion on the rate of butadiene formation at two temperatures, 659 and 704 K. In this test, the catalyst particle was varied by a factor of about 2, as shown in Fig. 5, while comparing the conversion to butadiene at a constant feed composition, and ratio catalyst surface area, S.A., times catalyst mass, W , divided by total feed volumetric flowrate, F_T . Since the conversion was constant for the two data sets plotted in Fig. 5, respectively, it can be concluded that the rate of internal mass transfer was fast compared to the rate of butadiene formation.

The results to test the influence of exter-

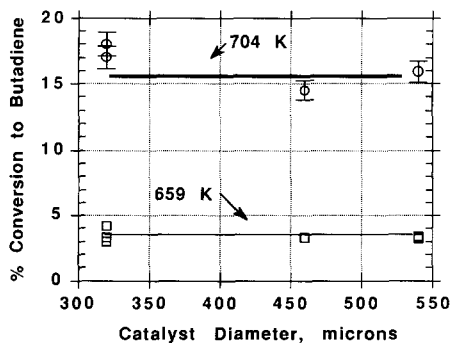


FIG. 5. Pore diffusion test: effect of catalyst particle diameter on conversion to butadiene for constant feed conditions and constant $W(S.A.)/F_T$: 15 C_4H_8 : 15 O_2 : 70 He; 0.4 g Bi_2MoO_6 .

nal mass transfer on the rate of butadiene production are shown in Fig. 6. In this test, the catalyst particle size and the ratio W/F_{B0} were held constant while W or F_{B0} , the molar feed flowrate of 1-butene, were varied independently. If the rate of butadiene formation is independent of F_{B0} but linearly dependent on W/F_{B0} , then the rate of external mass transfer is fast compared to the rate of butadiene formation. Two catalyst loadings, W equal to 0.20 and 0.34 g, respectively, were used. The volumetric flowrate was varied between 600 and 1000 sccm while the feed compositions were held constant. In Fig. 6, the conversion to butadiene is

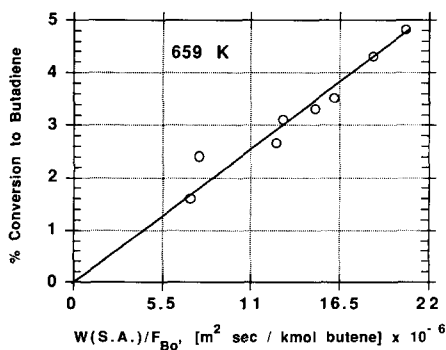


FIG. 6. External mass transfer resistance test: effect of $W(S.A.)/F_{B0}$ on conversion to butadiene over Bi_2MoO_6 at constant feed conditions: 10 C_4H_8 : 15 O_2 : 75 He.

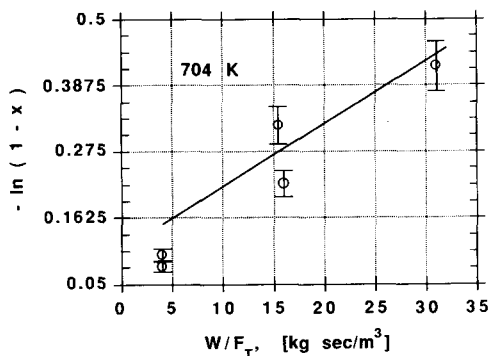


FIG. 7. Pseudo first-order plot for Bi_2MoO_6 at various W/F_T values for constant feed conditions: 10.3 C_4H_8 : 14.7 O_2 : 75 He.

plotted versus W/F_{B0} , showing that all the points fall on the straight line, intersecting the origin, indicating external mass transfer did not limit the rate of butadiene formation.

Butadiene Formation

Several researchers (12–14) have proposed that the rate of butadiene formation over Bi_2MoO_6 , r_D , is pseudo first-order in 1-butene partial pressure at temperatures >700 K,

$$r_D = kC_B = kC_{B0}(1-x) \\ = r_B = F_{B0}dx/dW, \quad (1)$$

where x is the conversion of butene and r_B is the rate of butene disappearance, equal to r_D assuming 100% selectivity. The integration of Eq. (1) gives the expression

$$k = (F_T/W)\ln\{1/(1-x)\} \\ = k_0 \exp(-E_a/RT), \quad (2)$$

where k_0 is the pre-exponential factor and E_a is the activation energy. In Fig. 7, a plot of $\ln\{1/(1-x)\}$ versus F_T/W is given using reaction data obtained using four individual Bi_2MoO_6 samples. The slope, equal to k at 704 K, was calculated to be $15 \text{ cm}^3/(\text{g sec})$, or using the catalyst packing density in the reactor of 150 kg/m^3 , $k = 2 \text{ sec}^{-1}$, and fit the data well (square of correl. coeff. = 0.97). The butene conversions over Bi_2MoO_6 were plotted versus $1/T$ (K^{-1}) in Fig.

8 to estimate E_a ; it is apparent that a distinct change in temperature dependence occurs at about 690 K. This behavior is discussed in detail in Part II. The value of E_a calculated over the temperature interval 700–715 K was equal to $40 \pm 4 \text{ kJ/gmol}$.

DISCUSSION

Using the Arrhenius rate parameters for butadiene formation, analytical solutions of the governing equations describing fixed bed reactor transport processes for first-order catalytic reactions were used to evaluate whether the reactor operated in a gradientless fashion at a feed inlet temperature of 704 K. The Bi_2MoO_6 catalyst discussed in this paper, for which the calculations were made, was the most active catalyst encountered in the entire study, including catalysts described in Part II (7). Table 4 lists the physicochemical properties used to evaluate the various transport disguise criteria.

For first-order kinetics, the analytical solution for the isothermal effectiveness factor for pore diffusion, η , in series with interphase mass transport yields an effectiveness factor, η_a (19):

$$1/\eta_a = 1/\eta + (k_v/k_g)(V_p/S_x) \quad (3)$$

The value of the second term in Eq. (3) was calculated to be 0.0003, indicating that external mass transfer resistance was negligible. The effective diffusivity for butene was

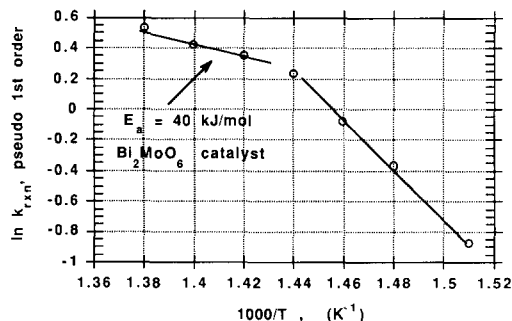


FIG. 8. Arrhenius plot of first-order rate constant versus $1/T$ For Bi_2MoO_6 feed conditions: 14 C_4H_8 : 13.5 O_2 : 72.5 He; $F_T = 596 \text{ sccm}$; 0.4 g catalyst.

TABLE 4

Physicochemical Properties Used to Evaluate Transport Disguises (10)

Catalyst:	$d_p = 500$ microns $D_c = 0.3$ cm ² /sec	$\rho_B = 150$ kg/m ² $k_{rxn} = 2$ sec ⁻¹ at 704 K, $E_a = 40$ kJ/mol	$\lambda_p = 0.4$ kJ/(m hr K)
SiC:	$\lambda_p = 4.2$ kJ/(m hr K)		
Transport:	$a_M = 30$ m ² /kg Sc = 1.2 $k_g = 0.9$ m/sec $h_f = 0.5$ kJ/(m ² sec K) $-\Delta H_{rxn} \approx 125$ kJ/mol at 673 K (for butadiene dehydrogenation)	$D_c \approx \frac{1}{8} D_{C_4H_6}$ in mixture Re _p = 8.5 $\beta_G = 0.02$ Pr = 3.5	$G = 0.5$ kg/(sec m ²) $\Phi_G \approx \phi$ $h_r \approx 0.1$ kJ/(m ² sec K)

calculated (8) to be 0.3 cm³/sec, and for 500 μ m catalyst particle diameter, the modulus, ϕ , ≈ 0.3 and $\eta_a \approx 1$. Even for a butene diffusivity of 0.007 cm²/sec, $\eta_a \approx 0.9$. The nonisothermal effectiveness factor derived by Weisz and Hicks (19) was also calculated and found to be equal to η_a (8). Thus, pore and gas phase mass transport resistances were calculated to be insignificant, in agreement with the experimental mass transfer tests described above.

One of the major heat transfer resistances is located in the gas "film" surrounding a catalyst particle, which can result in a temperature drop from the catalyst to the bulk gas phase. Carberry (20) derived the following expression for the maximum temperature difference between the external catalyst surface, T_s , and the bulk gas, T_b :

$$T_s - T_b = T_b(\beta_G \Phi_G / Nu') \quad (4)$$

This temperature difference was calculated to be less than 1 K (8). A similar analysis is possible for evaluating the temperature difference between the catalyst surface, T_{sc} , and the inert silicon carbide surface temperature, T_{si} :

$$(T_{sc} - T_{si})h_r = (-\Delta H_{rxn})r_B = q \quad (5)$$

where q is the maximum heat flux from the catalyst surface and h_r is the heat transfer coefficient due to radiation, the major heat transfer mechanism at the temperature range of interest. Assuming a view factor of one, $h_r \approx 4\Omega \langle T \rangle^3$, where $\langle T \rangle = (T_{sc} - T_{si})/2$ and Ω is the Stefan-Boltzmann constant

(21). The calculated temperature difference ($T_{sc} - T_{si}$) was less than 1 K (8).

Also important calculation is the estimate of the interparticle radial temperature gradients. Lapidus (22) obtained an approximate solution for the maximum radial temperature gradient at the hottest axial location in a fixed bed. At this location, the first derivative of the axial temperature profile is zero. Thus, the energy balance at the axial location of the hot spot is simplified to a balance of effective radial conduction of the catalyst bed to the exothermic rate of energy produced. A mean reaction rate was used, approximated as a linear function in temperature by a Taylor series expansion: average $r_B = a + bT$. The analytical solution obtained is

$$T(r) - T_w = \left(\frac{m}{n}\right) \left[\frac{J_0(r\sqrt{n})}{J_0(r_w\sqrt{n})} - 1 \right]$$

$$m = \frac{[(-\Delta H_{rxn})r_B]}{\lambda_{er}} \quad (6)$$

$$m/n = \frac{RT_0^2}{E_a} \quad T_w = T_0,$$

where J_0 is the zeroth order Bessel function. Using the correlations of Kunii, *et al.* (10), the effective thermal conductivity of the catalyst was estimated to be 0.4 kJ/m hr K (8). For silicon carbide, λ_{er} was calculated to be 4.2 (kJ/m hr K) (8). The maximum radial temperature difference was given by ($T_{max} - T_w$); for the undiluted bed this was equal to 2.6 K and for the diluted bed (characteristics of SiC) to 0.1 K.

As stated earlier, the Biot number for the diluted bed was estimated at 3.4. Finlayson's criterion, referenced earlier, required a Biot number of less than 3 for significant radial temperature to be absent. Thus, the Bi value of 3.7 estimated for the diluted bed agrees with the above calculation using Lapiduss' analysis.

In summary, the above calculations for estimating transport disguises have supported the experimental evidence that the observed rate of butadiene formation was not influenced by significant temperature and concentration gradients. The fixed bed reactor design and methodology developed herein are quite useful for systematic study of partial oxidation catalysts whereby significant transport disguises need to be eliminated for a more quantitative assessment of catalyst performance.

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