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The Role of Boundary Layer Mass Transfer in Partial Oxidation Selectivity[1]

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Simple models predict that mass transfer in the boundary layer over a catalyst surface should have a large influence on reactor selectivity for any fast series reaction, but few experimental cases demonstrate this explicitly. In this paper, we show experimentally that selectivities of CH_4 oxidation to CO and H_2 over Pt–Rh gauzes and HCN synthesis from CH_4, NH_3, and air over Pt-coated ceramic monoliths are strongly affected by the gas flow rate and the catalyst geometry. For any series reaction in which the desired product is an intermediate species, such as HCN synthesis, an optimal residence time exists where the production of the desired component is maximized, and the selectivity of formation of the intermediate product improves with increasing rates of mass transfer. For parallel and series–parallel reactions, mass transfer may improve or reduce selectivity of formation of the intermediate product, with the effect of mass transfer depending strongly on the reaction orders of the kinetics. However, typical series–parallel partial oxidation reactions such as the partial oxidation of CH_4 to synthesis gas require high rates of mass transfer for maximum reactor selectivity.

INTRODUCTION

In partial oxidation of a fuel F, the desired product B is often an intermediate in a series–parallel reaction scheme:

$$F + O_2 \rightarrow B \tag{1a}$$

$$B + O_2 \rightarrow C. \tag{1b}$$

Thus, it is important to design a partial oxidation reactor to maximize the yield of the desired product. Oxidation reactions are typically so fast that reaction occurs on or near the external surface of catalysts. In this situation, external mass transfer rates become significant in controlling reaction rates and the selectivity of the catalyst. Mass transfer limitations will obviously slow reactions, but relatively few analyses (*1*, *2*) have demonstrated the coupling between external mass transfer limitations and reaction selectivity, and little experimental verification exists.

Traditionally, descriptions of the effect of mass transfer on reactor selectivities have centered on the analysis of pore diffusion in packed-bed reactors. In classic papers, Wheeler (*3*, *4*) examined the influence of pore diffusion on catalytic reactor selectivity for three cases: (1) two independent parallel reactions of different reactant species, (2) two independent parallel reactions with the same reactant species, and (3) a series of reactions where the intermediate is the desired product. He showed that pore diffusion limitations may have a strong effect on reaction selectivity in all three cases.

Similar ideas have also been applied qualitatively to external mass transfer. These ideas were outlined by Frank-Kamenetskii (*2*) and summarized elegantly by Carberry (*1*). These authors considered the effect of external mass transfer (interphase diffusion) on the differential selectivity of formation of

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the desired product. The analyses included consecutive (series) and simultaneous (parallel) reactions.

Different catalyst geometries and reactor flow patterns will produce very different external mass transfer characteristics. As sketched in Fig. 1, many geometries, such as (a) flat plates, (b) hollow tubes (extruded monoliths), (c) gauzes and packed beds, and (d) pellets in a fluidized bed will all have boundary layers of thickness δ, with the mass transfer coefficient $k_m \cong D_i/\delta$, where D_i is the diffusion coefficient of the rate-limiting species i. Basically, it is important to facilitate both the migration of reactant A through the boundary layer to the surface and *the removal of the intermediate B from the boundary layer into the flowing stream.*

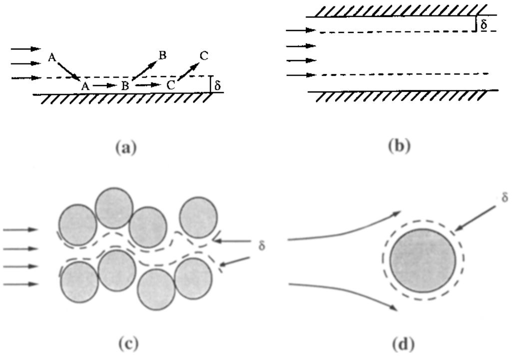

FIG. 1. Sketch of the boundary layer profiles for (a) a flat plate, (b) a hollow tube (extruded monoliths), (c) a gauze pack or packed bed, and (d) a pellet in a fluidized bed.

In this paper, we demonstrate the effect of mass transfer in two experimental examples using Pt gauze and monolith catalysts: HCN synthesis by partial oxidation of CH_4 and NH_3 mixtures over Pt using several types of monolithic supports and production of CO and H_2 by partial oxidation of CH_4 over a gauze in which selectivity varies strongly with flow velocity. Before presenting these experimental results, we discuss the influence of external mass transfer on selectivity in a tubular reactor for series, parallel, and series–parallel reactions. In this analysis, we extend and quantify the ideas of Frank-Kamenetskii and Carberry. We then use these simple models to qualitatively understand our experimental observations.

MODEL

We consider several possible reaction schemes using a simple one-dimensional plug flow model of an isothermal reactor that accounts for the transport of species by a lumped mass transfer coefficient as sketched in Fig. 1.

A species balance over a differential length of the reactor gives

$$v\frac{dc_i}{dz} = k_m a_s (c_{is} - c_i), \qquad (2)$$

where c_i is the bulk molar concentration of component i, c_{is} is the concentration in the gas phase near the surface, a_s is the catalytic surface area per unit volume, k_m is the mass transfer coefficient, and v is the linear flow velocity of the gases. The mass transfer coefficient (here assumed identical for all species) accounts for the transport of species to and from the catalytic surface.

For the general case involving R reactions, the net flux of species i from the wall must equal its net rate of formation or loss by reaction at the wall:

$$k_m (c_{is} - c_i) = \sum_{j=1}^{R} \nu_{ij} r_j(c_{is}), \qquad (3)$$

where ν_{ij} is the stoichiometric coefficient of species i in reaction j. This system of equations can be simply solved numerically or analytically by choosing initial concentrations for all of the reactant species and then integrating Eq. (2) while simultaneously satisfying Eq. (3).

Typically, surface reaction kinetics are correlated to gas partial pressures. Therefore, the rate expressions used in this model are a function of the species concentration ($c_{is} = P_{is}/R_gT$) in the gas phase near the catalyst surface. We have chosen to use molar concentrations rather than partial pressures to be consistent with the literature convention for similar reaction-diffusion problems. One should note that such rate expressions do not describe individual elementary surface reactions, but, rather, the expressions represent an overall reaction that is the result of several elementary steps.

Thus, these reaction kinetics do not explicitly include surface intermediates that are not observed as products in the gas phase. For example, for the series of reactions A → B → C, the actual physical situation being modeled would involve the following general steps: (1) the reactant A adsorbs on the surface (dissociatively or nondissociatively); (2) the surface species react, perhaps forming other surface intermediates, until B is formed, which then desorbs; (3) the gas phase species B adsorbs (dissociatively or nondissociatively); and (4) the surface species also react to form C, which then desorbs.

One should note that for this case, B is not merely a surface intermediate, but each B molecule that is formed is assumed to leave the surface. In general, any C formed via a surface intermediate B (which does not leave the surface) should be described by the overall reaction A → C, which is parallel to A → B. However, if B is in adsorption–desorption equilibrium at the catalyst surface, as usually assumed by Langmuir–Hinshelwood kinetics, the individual B molecules that are converted to C may or may not actually leave the catalyst surface after being formed from A. The important feature of this model is that, for this series reaction, the formation of C is a function of the partial pressure of only B at the catalyst surface. Of course, the partial pressure of B is affected by the concentration of A since B is formed from A, but the reaction B → C is otherwise independent of A.

In each of the three cases discussed in the following sections, the reaction systems will involve only three species (A, B, and C). In all cases, there is no net change in the number of moles, and the reactor (both gas and surface temperatures) is assumed to be isothermal. These simplifications have been chosen so that we may demonstrate qualitatively the influence of k_m on reaction selectivity independent of other factors.

Series Reactions

The first case is a series of surface reactions A → B → C, where B is the desired product. For an isothermal system with all reactions first order in the reactant species, the bulk concentrations for a plug flow reactor can be found analytically as

$$c_A = c_{A0} e^{-K_1\tau} \tag{4a}$$

$$c_B = \left[c_{B0} + \frac{K_3 c_{A0}}{K_2 - K_1} \left(e^{(K_2 - K_1)\tau} - 1 \right) \right] e^{-K_2\tau}, \tag{4b}$$

where

$$K_1 = \frac{k_m a_s k_1}{k_m + k_1}, \quad K_2 = \frac{k_m a_s k_2}{k_m + k_2}, \quad K_3 = \frac{k_m K_1}{k_m + k_2}. \tag{5}$$

The constants k_1 and k_2 are the reaction rate coefficients, and $\tau = z/v$ is the residence time. As for a homogeneous plug flow reactor, there is an optimal residence time at which the concentration of B reaches a maximum:

$$\tau_{opt} = \frac{\ln(K_2/K_1)}{(K_2 - K_1)} \quad (K_1 \neq K_2, c_{B0} = 0) \tag{6}$$

and

$$c_{B,max} = \frac{K_3 c_{A0}}{K_2} \left(\frac{K_1}{K_2} \right)^{K_1/(K_2 - K_1)} \quad (K_1 \neq K_2, c_{B0} = 0). \tag{7}$$

In the limit $k_m \to \infty$, the above equations of course become identical to those derived for a plug flow reactor with pseudo-homogeneous reactions having kinetics of the same form. Figure 2a shows typical concentration profiles as a function of residence time τ for an infinite mass transfer rate (equivalent to the plug flow reactor with pseudo-homogeneous reactions) and also for $k_m = k_1 = k_2$. As shown in Fig. 2b, for given rate constants, both selectivity $[c_{B,max}/(c_{A0} - c_A)]$ and conversion to B $[c_{B,max}/c_{A0}]$ increase as the mass transfer coefficient increases.

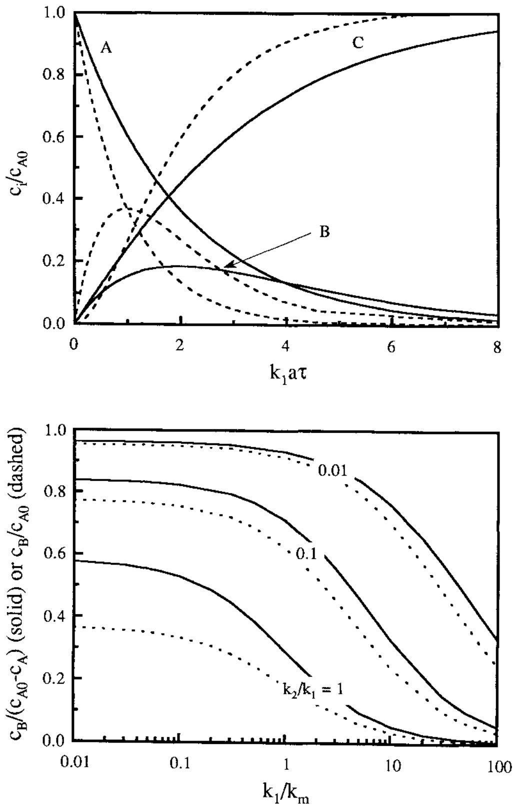

FIG. 2. (a) Dimensionless concentration profiles in a plug flow tubular reactor for the first-order reaction series A → B → C versus the dimensionless residence time $k_1a\tau$. For solid lines, $k_m = k_1 = k_2$; for dashed lines, $k_m \rightarrow \infty$ and $k_1 = k_2$. (b) Selectivities (solid lines) and conversions (dashed lines) to B versus k_1/k_m at the optimal residence time for maximum formation of B for two first-order reactions in series.

Parallel Reactions

The effect of mass transfer on selectivity for parallel surface reactions depends on the form of the reaction kinetics. For example, consider the two parallel reactions

$$A \rightarrow B, \quad r_1 = k_1 c_{As}^{m_{1A}} \tag{8a}$$

$$A \rightarrow C, \quad r_2 = k_2 c_{As}^{m_{2A}}. \tag{8b}$$

As discussed by Carberry, the ratio of B to C formed at a specific location (or residence time in a plug flow reactor) is

$$\frac{dc_B}{dc_C} = \frac{k_1}{k_2} c_{As}^{(m_{1A}-m_{2A})}. \tag{9}$$

Thus, if $m_{1A} = m_{2A}$, the selectivity is determined solely by the reaction kinetics and k_m *now only determines the residence time needed to achieve a given conversion.* However, if $m_{1A} \neq m_{2A}$, the mass transfer rate will also affect the overall reactor selectivity. For $m_{1A} > m_{2A}$, selectivity of B formation improves as the mass transfer coefficient increases, while the opposite is true for $m_{1A} < m_{2A}$. This is because increasing rates of mass transfer are accompanied by higher surface concentrations of the reactant, and, as shown in Eq. (9), the sign of $(m_{1A} + m_{2A})$ determines whether increasing c_{As} will increase or decrease the selectivity of B formation. In general, for $m_{1A} \neq m_{2A}$, the reactor selectivity depends strongly on k_m.

Series–Parallel Reactions

Most partial oxidation reactions are series–parallel (Eq. (1)) in that the reactions are parallel with respect to the oxidant and series with respect to the partially oxidized product. Consider the series–parallel surface reaction scheme

$$A \rightarrow B, \qquad r_1 = k_1 c_{As}^{m_{1A}} \tag{10}$$

$$A + B \rightarrow 2\,C, \quad r_2 = k_2 c_{As}^{m_{2A}} c_{Bs}^{m_{2B}}. \tag{11}$$

For this scheme, the ratio of B to C formed over a differential length (or time) is

$$\frac{dc_B}{dc_C} = \frac{k_1 c_{As}^{(m_{1A}-m_{2A})}}{2k_2 c_{Bs}^{m_{2B}}} - \frac{1}{2}. \tag{12}$$

Thus, the mass transfer coefficient influences the selectivity at a given point in the reactor by affecting the concentration of the reactants at the catalyst surface.

Figure 3 shows the variation of $c_{B,\max}$ in a plug flow reactor with mass transfer coefficient for various fixed rate constants and $m_{1A} = m_B = 1$. For $m_{2A} \geq m_{1A}$, $\tau_{\text{opt}} \rightarrow \infty$. Thus, the maximum selectivity and conversion to B are identical for these cases. As in the series case, selectivity and conversion to B increase as k_m increases for $m_{2A} = \frac{1}{2}$ and $m_{2A} = 1$; however, for $m_{2A} = 2$, higher rates of mass transfer

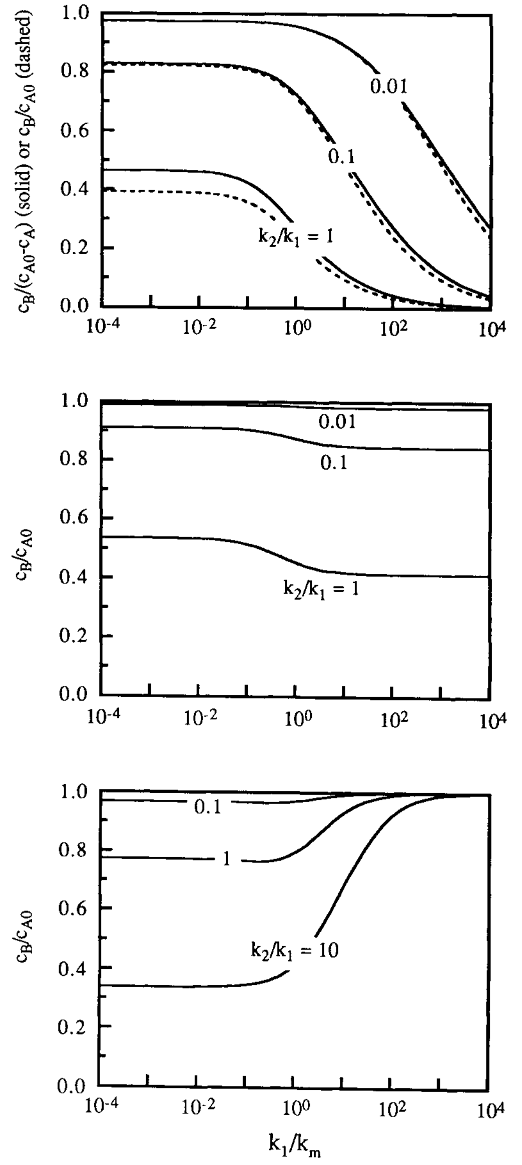

FIG. 3. Selectivities (solid lines) and conversions (dashed lines) to B versus k_1/k_m at the optimal residence time for the series-parallel scheme given by Eqs. (10) and (11). For all three plots, $m_{1A} = m_{2B} = 1$ and $c_{A0} = 1$. The reaction order m_{2A} is varied as follows: (a) ½, (b) 1, and (c) 2.

actually reduce the selectivity of formation of B. The effect of mass transfer is greater when $m_{1A} \neq m_{2A}$. On the other hand, similar calculations show that the reaction order m_{2B} does not strongly affect the role of the mass transfer coefficient in determining the selectivity of B formation. Thus, as for parallel reactions, the reaction orders (m_{1A}, m_{2A}) with respect to the feed component (the "parallel" species) determine the exact nature and magnitude of the effect of the mass transfer coefficient.

Typically, surface reactions of gas phase species are modeled using Langmuir–Hinshelwood kinetics that do not have the simple power law form of Eqs. (10) and (11), although, over limited temperature and pressure ranges, they reduce to a power law approximation. Also, since reaction orders can switch from positive to negative values as temperature varies, the influence of mass transfer is predicted to change dramatically with temperature. Nevertheless, Langmuir–Hinshelwood rate expressions will generally give reaction orders of ½ or 1 (for dissociative and nondissociative adsorption, respectively) with respect to individual species at the low coverages expected at high surface temperatures. Therefore, most series–parallel processes involving heterogeneous reactions of gas phase species at high temperatures will require $k_m \gg k_1$ for optimal selectivity of an intermediate.

EXPERIMENTAL RESULTS

HCN Synthesis: Effect of Catalyst Geometry

An example of a nearly series catalytic process is HCN synthesis by the Andrussow process. The formation of HCN can be described by the overall reaction

$$NH_3 + CH_4 + \tfrac{3}{2}\, O_2 \rightarrow HCN + 3H_2O. \quad (13)$$

Thus, the NH_3 + CH_4 mixture undergoes a partial oxidation to form HCN. While HCN could react with O_2, the reactor is operated with excess fuel, so this parallel reaction is not important. Another reaction, the hydrolysis of HCN, reduces the overall HCN conversion by consuming the products of the synthesis reaction:

$$HCN + H_2O \rightarrow NH_3 + CO. \quad (14)$$

Since both HCN and H_2O are products, this is truly a series reaction.

In the industrial process, the reactant gases are passed over a gauze pack consisting of several layers of woven Pt–10% Rh wires (*5*). Reactant and product concentration versus temperature in this process has been modeled successfully as a plug flow reactor (*6*). Hence, the above analysis suggests that the selectivity of formation of the intermediate product (HCN) should be maximized by increasing the rate of mass transfer and optimizing the residence time. Since the synthesis reaction is very fast at the typical industrial operating conditions (1400 K), high gas velocities (~1 m/s) and between 10 and 50 layers of gauzes are used for the best selectivity for HCN formation.

We have carried out experiments with gauzes and other catalyst geometries involving Pt films on ceramic monoliths that confirm the importance of mass transfer in this process. The experimental reactor is an insulated quartz tube with ~18 mm inner diameter into which the various catalysts with lengths in the axial direction ranging from 1 to 25 mm can be inserted. Mass flow controllers are used to set reactant gas flow rates, with linear gas velocities usually 0.1 to 1 m/s. The product gases are analyzed using gas chromatography. The details of the analytical procedure and the experimental results will be published later.

Table 1 shows the selectivities and NH_3 to HCN conversions for several different catalyst configurations. The monolithic catalysts were either an extruded honeycomb or foam ceramic substrate coated with a high loading of Pt. The Pt loadings were high enough that the ceramic substrates were completely covered by a relatively thick Pt film. Pure Pt coatings were used, although separate experiments showed that Rh does not enhance the HCN selectivity of the catalyst. The values shown correspond to the maximum conversion to HCN and the corresponding selectivity. In all cases, the reactant gases were fed at a velocity of 10 to 20 cm/s with the NH_3/air mole ratio fixed at 0.16 and the CH_4/NH_3 mole ratio optimized (between 1.1 and 1.2 for all of the catalysts). The lengths of the catalyst samples were chosen so that the conversion of NH_3 to HCN was optimized. For each sample, 85–95% of the CH_4 was consumed at this optimal length. For a given geometry and channel diameter, increasing the length beyond the optimum resulted in decreasing HCN conversions and increasing NH_3 and CO concentrations because of the hydrolysis reaction.

In Table 1, the characteristic channel dimensions d are the spacing between wires in the gauze, the average cell diameter in the foam monoliths, and the average distance between adjacent walls in the extruded monoliths. Thus, $d/2$ is an upper bound to the boundary layer thickness δ for any geometry. Of course, a flow pattern in the catalyst that improves the mixing of the gas phase will result in thinner boundary layers and higher k_m for a given characteristic channel dimension. Thus, a foam monolith should have a much higher k_m than an extruded monolith having the same characteristic channel dimension because the latter has essentially laminar flow while the former has better mixing within its cellular structure.

We interpret the results shown in Table 1 as follows. The extruded monoliths give the lowest selectivities because the laminar flow through the straight channels results in relatively thick mass transfer boundary layers and low k_m. However, the cellular (or sponge-like) geometry of the foam monoliths enhances the mixing of the gas stream, resulting in higher rates of mass transfer to and from the catalyst surface. In addition, for a given geometry, decreasing the average channel diameter markedly improves the reactor selectivity by decreasing the average boundary layer thickness.

As shown by the data, the woven mesh of the gauze is the best of these geometries for maximizing HCN production, and the small cell size foam monolith performs nearly as well. These and similar experiments all sug-

TABLE 1

Optimal Selectivity of HCN Synthesis for Gauze, Extruded Monolith, and Foam Monolith Catalysts at ~1400 K

Catalyst	Characteristic channel dimension d(mm)	Selectivity at optimum $\frac{HCN}{(NH_{3_0} - NH_3)}$	Optimal conversion $\left(\frac{HCN}{NH_{3_0}}\right)_{opt.}$
40-mesh Pt-10% Rh gauze	0.6	0.85	0.65
50 ppi[a] foam monolith (Pt coated)	0.5	0.70	0.28
30 ppi foam monolith (Pt coated)	0.8	0.50	0.29
2300 csi[b] extruded monolith (Pt coated)	0.5	0.37	0.15
1000 csi extruded monolith (Pt coated)	0.8	0.30	0.15
400 csi extruded monolith (Pt coated)	1.3	0.04	0.05

[a] ppi, pores per inch.

[b] csi, cells per square inch.

gest that HCN selectivity is directly related to how well a geometry minimizes the thickness of the mass transfer boundary layers. Clearly, the determining factor is not at all the total surface area of the catalyst because at sufficiently high area (longer residence time), hydrolysis of HCN dominates. Rather, an effective HCN synthesis reactor must have a geometry and flow rate that maximize k_m.

CH_4 Oxidation: Effect of Flow Velocity

Methane oxidation was also studied using the apparatus described above. The results described below were obtained by varying the flow velocity through 10 layers of Pt-Rh gauze at a fixed composition of CH_4 in air.

In CH_4 oxidation on Pt, CO and H_2 are the partial oxidation products, while CO_2 and H_2O are formed upon total oxidation of the fuel:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (15a)$$

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O. \qquad (15b)$$

Thus, methane oxidation can be regarded as a series–parallel process, where CO and H_2 are the intermediate species. The reaction can also be regarded as two partial oxidation processes, one giving either H_2 or H_2O and the other giving either CO or CO_2.

In the oxidation of 16% CH_4 in air over a Pt–10% Rh gauze catalyst (Fig. 4), the selectivity of formation of CO and H_2 (the partial oxidation products) increases strongly with increasing gas flow rates, approaching an upper limit at high flow rates. Stoichiometric compositions are 9.5% CH_4 in air for CO_2 + H_2O and 29.6% CH_4 in air for CO + H_2. For these experiments, almost

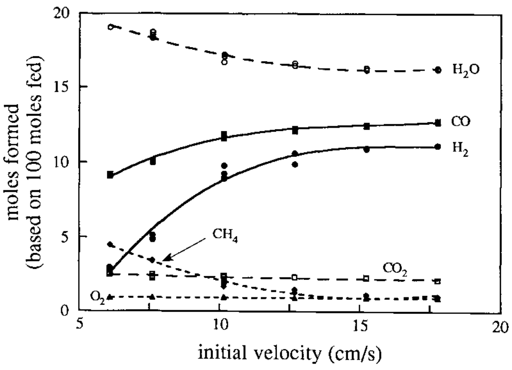

FIG. 4. Reaction products for oxidation of 16% CH_4 in air over 10 layers of 40-mesh Pt–10% Rh gauze. The molar composition of the product gases is based on 100 mol of gases fed (16 mol CH_4 and 84 mol of air).

all of the available O_2 is consumed, regardless of the flow rate used, so that for all flow rates, the reaction goes to completion. The gauze surface temperature is fixed at 1110 ± 10°C over this range of flow rates, so the effect of temperature on selectivity is not an important factor. Thus, at the lowest flow rates, the rate of mass transfer is so slow that the O_2 is presumably consumed by converting the partially oxidized products to CO_2 and H_2O before all of the CH_4 can react. As the flow rate (and k_m) increases, the selectivity of formation of the partial oxidation products increases and more CH_4 is consumed. At high enough flow rates, $k_m \gg k_1$, so further increase of the flow rate does not affect the reaction selectivity. In this "reaction-limited" regime, the reaction selectivity is apparently governed completely by the reaction stoichiometry and kinetics.

Also note that, in contrast to partial oxidation reactors, complete oxidation is desired in a catalytic combustor. Thus, one should design a combustion reactor so that $k_m \ll k_1$, the regime of low velocity in Fig. 4. This will reduce the selectivity of formation of the partial oxidation products by favoring total oxidation of the fuel to CO_2 and H_2O without requiring unnecessarily long residence times.

CONCLUSIONS

For a series process such as HCN synthesis, the selectivity of formation of the intermediate species is improved by increasing k_m, as shown by experiments in which catalyst geometries are varied from laminar flow to highly mixed flow between small wires or cells. There is an optimal length at which conversion to the intermediate species is maximized, and the upper limit to the maximum selectivity is determined by the reaction kinetics.

For a series–parallel reaction system such as CH_4 oxidation, the reaction order with respect to the "parallel" species (O_2) will determine the exact nature and magnitude of the effect of mass transfer on reactor selectivity. This is observed in experiments shown here where the selectivity over a given catalyst can be varied by a factor of ~5 by changing flow velocity under conditions where the reaction goes to completion in one reactant at all flow rates. The kinetics of most series–parallel reactions, such as the partial oxidation of CH_4, will generally require the maximization of k_m to obtain the best selectivity of formation of an intermediate allowed by the reaction kinetics.

These simple ideas show that mass transfer can play a dominant role in controlling reaction selectivity, although, even if a reaction is "mass transfer controlled" ($k_m \ll k_i$), values of reaction rate constants and orders of reaction are still important. Thus, in designing a reactor for maximum selectivity, the geometry and flow patterns must be chosen carefully. For a typical partial oxidation process, regions in the reactor of low k_m must be avoided, and the selectivity will improve as k_m increases until the reaction rate is governed solely by the reaction rate constants. Of course, in a real situation temperature variations, residence time distributions, pressure drops, and complex kinetics must be included in the design and analysis of a reactor. However, these effects all tend to enhance the influence of k_m on selectivity. In most practical situations, one should expect order of magnitude changes in selectivity for a given catalyst, depending on flow conditions and geometry.

APPENDIX: NOMENCLATURE

δ	(cm)	boundary layer thickness
τ	(s)	residence time
ν_{ij}		stoichiometric coefficient of species i in reaction j
a_s	(cm^{-1})	catalyst surface area per unit volume
c_i	(mol/cm^3)	bulk molar concentration of species i in the gas phase
c_{is}	(mol/cm^3)	molar concentration

		of species i in the gas phase at the surface
c_{i0}	(mol/cm^3)	initial molar concentration of species i
d	(cm)	characteristic channel dimensions
D_i	(cm^2/s)	diffusion coefficient of species i
k_i	(cm/s)	rate coefficient for reaction i (units shown are for first order)
k_{m}	(cm/s)	mass transfer coefficient
K_i	(cm/s)	defined in Eq. (5) (units shown are for first-order reactions)
m_{ji}		order of reaction j with respect to component i
P_{is}	(Torr)	partial pressure of component i near the surface
r_j	(mol/cm^2 s)	rate of reaction j
R		total number of reactions
R_{g}		gas constant
T		temperature
v	(cm/s)	gas flow velocity in reactor
z	(cm)	axial reactor position

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