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Effect of pressure on three catalytic partial oxidation reactions at millisecond contact times [☆]

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The effects of pressure on reactant conversion and product selectivities in three catalytic oxidation systems have been examined at pressures between 1 and >5 atm. Reaction was sustained autothermally near adiabatic operating conditions at temperatures of ~1000°C with residence times over the noble metal catalysts between 10^{-4} and 10^{-2} s. The three systems investigated were (1) HCN synthesis over Pt–10% Rh gauze catalysts, (2) methane oxidation to synthesis gas (CO and H_2) over rhodium-coated monoliths, and (3) ethane conversion to ethylene over platinum-coated monoliths. We find that selectivities in all three reactions do not change dramatically with approximately a five-fold increase in pressure. This strongly suggests that free radical homogeneous chain reactions are not significant in these processes and that they can be operated reliably above atmospheric pressure. For the synthesis of HCN over Pt–10% Rh gauzes, the selectivity to HCN can be maintained above 0.75 at pressures up to 5.5 atm. Selectivities to synthesis gas (CO and H_2) from a methane–air mixture over a Rh-coated foam monolith at pressures up to 5.5 atm were maintained above 0.90. Over a Pt-coated foam monolith, the selectivity to ethylene from ethane–air and ethane–O_2 mixtures was independent of pressure up to 6.5 atm and conversion rose slightly although it was necessary to maintain constant velocity and residence time over the catalyst to avoid carbon formation.

Keywords: catalytic partial oxidation; pressure; millisecond reactors

1. Introduction

Catalytic partial oxidation can be used to convert alkanes and air or oxygen to useful chemicals with high selectivities and conversions. These reactions are very fast, exothermic, and autothermal (heat generated by the reaction is sufficient to sustain reaction). In order to understand mechanisms of complex catalytic oxidation processes, most studies have been at low pressures and low conversion of reactants [1–5]. However, industrial manufacturing conditions call for *high conversion* of reactants at *high pressures* in order to maximize throughput in a reactor.

Since homogeneous reactions become more likely at higher pressures, the role

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of homogeneous chemistry on a catalytic process may limit the pressures possible for these processes. The objective of this paper is to study three important catalytic partial oxidation processes at pressures from 1 to >5 atm to determine the effect of pressure and especially the role of homogeneous reactions.

1.1. METHANE AMMOXIDATION TO HCN

The Andrussow process for synthesis of HCN occurs by the catalytic partial oxidation reaction:

$$CH_4 + NH_3 + \tfrac{3}{2}O_2 \rightarrow HCN + 3H_2O \qquad (1)$$

The industrial catalyst consists of Pt–10% Rh wires woven into gauzes a few millimeters thick with bed diameters of several meters. Normally, 20 to 50 gauze layers are used for a commercial reactor, which usually operates at the adiabatic temperature of ~1100°C at pressures of 2 atm with a contact time over the catalyst of ~1 ms. The microstructure of the gauze pack changes during the first hours of operation accompanied by increasing selectivity to HCN. The Pt wires rearrange to increase surface area and roughness over the first 20 h, after which the catalyst activity and selectivity to HCN slowly decline [6]. Industrial yields of HCN on an NH_3 basis are 60–70% per pass.

The hydrolysis of HCN to CO and NH_3 reduces selectivity to HCN. If this reaction were allowed to reach equilibrium, the concentration of HCN present would be nearly zero. Other reactions on the catalyst that lower selectivity include ammonia oxidation,

$$2NH_3 + \tfrac{3}{2}O_2 \rightarrow N_2 + 3H_2O \qquad (2)$$

and methane oxidation reactions (eqs. (3) and (4) below).

In our laboratory, the synthesis of HCN over Pt–10% Rh gauze at industrial conditions was modeled by combining 13 simultaneous surface reactions [7]. With rate parameters determined from earlier low pressure studies using Langmuir–Hinshelwood kinetic expressions, the model successfully predicted HCN selectivities and optimum feed conditions. It also predicted that operation should be conducted at high temperatures and higher pressures to increase production of HCN. However, the model did not allow for any homogeneous reactions.

1.2. METHANE OXIDATION TO SYNTHESIS GAS

With recent concern about the availability of petrochemical fuel resources, much research has focused on natural gas utilization. In this laboratory we have shown that synthesis gas ($CO + H_2$) can be made with very high selectivity from the direct oxidation of methane [8],

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad (3)$$

This reaction is operated over Rh-coated alumina foam monoliths with contact times over the catalyst of $\sim 10^{-3}$ s in a steady-state flow reactor at temperatures $\sim 1000°C$ to yield $>90\%$ selectivities at $>90\%$ conversion. This process may be able to replace the energy intensive steam reforming process for methane conversion into syngas,

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{4}$$

Since processes for methanol synthesis or Fischer–Tropsch reactions currently operate at pressures of ~ 30 atm and other downstream applications call for high pressure, any new process to replace steam reforming also would have to operate at elevated pressures.

1.3. ETHANE OXIDATION TO ETHYLENE

Ethane and higher alkanes make up a significant fraction of natural gas, making it a major feedstock. Ethylene production from ethane is commonly carried out through homogeneous thermal dehydrogenation of ethane [9,10],

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{5}$$

This homogeneous pyrolysis reaction is run in a tube furnace at 750–900°C at 1.5–2 atm with a residence time of ~ 1 s. Since the reaction is strongly endothermic, a large amount of heat must be supplied to maintain the reaction, so several small diameter tubes (4″) containing the reactant mixture are surrounded by externally fired heaters. Since this is a free radical homogeneous process, coke readily forms in the tubes, especially as ethane pressure is increased. Operating pressures must be kept low to reduce carbon buildup, and water is added to the feed ($H_2O/C_2H_6 = 0.3$) in order to steam reform the carbon that does form,

$$C_s + H_2O \rightarrow CO + H_2 \tag{6}$$

Even with steam reforming, carbon will block tubes in several weeks, requiring coke to be periodically burned off.

Ethane can also be converted to ethylene by homogeneous or heterogeneous oxidative dehydrogenation,

$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \tag{7}$$

Previous studies on oxide catalysts with contact times of roughly 1 s have shown that at low conversions of ethane ($\sim 5\%$), selectivities to ethylene near 80% could be achieved [11–15].

Results from our laboratory show that ethane can be converted to ethylene over Pt-coated foam monolith catalysts with contact times over the monoliths from 10^{-3} to 10^{-2} seconds at temperatures of $\sim 900°C$ [16]. This reaction is run autothermally in a steady-state flow reactor with ethylene selectivity as high as 70% with a conversion of ethane over 80%. Contrary to the predictions of thermodynamics, solid carbon does not form at all at these conditions over Pt. Since the production of ethylene over Pt monoliths is believed to be surface catalyzed, higher pressure operation than is possible with homogeneous steam cracking should be feasible.

2. Experimental

An 18 inch long, 1/2 inch inner diameter, stainless steel reactor tube (1/4 inch wall thickness) fitted with multiple inlet and exit ports for gas feeds and product removal was built for these experiments. The reaction could be viewed through two quartz windows placed at the ends of the reactor tube and sealed with stainless steel flanges and high temperature viton o-rings.

At high pressures, special safety precautions were necessary. The flow control system network was configured so that the fuel and oxygen mixing point was close to the reactor. The reactor was also fitted with a pressure release valve upstream of the catalyst to prevent overpressure. Control of reactor operating pressure to within 1 psig was maintained with needle valves downstream from the reactor, and pressure to the gas chromatograph was kept constant at 6 psig. Temperatures at the catalyst surface were monitored with a Pt–Rh thermocouple.

Methane, oxygen, nitrogen, and ammonia flow were introduced into the system from high pressure cylinders and controlled using mass flow controllers. A fraction of the product gases was sent to a multiple column gas chromatograph for analysis through heated lines to prevent any water vapor formed in the reactor from condensing. The product gases were incinerated with a Bunsen burner.

Alumina supported catalysts were prepared by coating α-Al_2O_3 monoliths with saturated solutions of the appropriate metal as described previously [8,17,18]. Typical loadings for Rh-loaded monoliths were between 4 and 6% by weight, and 8 and 12% by weight for the Pt-loaded monoliths. Performance was quite insensitive to metal loading [18]. Monoliths with 45 pores per inch (ppi) were used for both Rh and Pt catalysts, and 80 ppi monoliths were also used for Rh catalysts.

Pt/10% Rh gauzes were used to catalyze methane ammoxidation to HCN. Three layers of 40 mesh (40 wires per inch) gauze were cut into 1/2 inch diameter circles and sandwiched between two uncoated extruded ceramic monoliths which acted as supports and radiation heat shields. New gauze catalysts had to be subjected to normal operating conditions for a period of hours for activation to increase activity and selectivity to HCN as will be described in a future publication.

2.1. STARTUP AND SHUTDOWN

The reactor was operated autothermally in that the heat generated by the reactions is large enough to maintain reaction on the catalyst after ignition. To light off the catalysts, a mixture of fuel, O_2, and N_2 in the tube was heated with a Bunsen burner to 200–250°C, at which ignition of the catalyst takes place. Ammonia was added to the CH_4 and air mixtures to ignite the catalyst because the lightoff temperature for pure CH_4 and air is $\sim$600°C. After the catalyst ignited, NH_3 flow was cut off for syngas experiments, and CH_4 flow was set to desired conditions.

The desired feed gas ratio was set with the mass flow controllers, and the reactor pressure was established by closing the leak valves. The reaction reached steady state operating conditions within 15 min of ignition. No significant transients were observed in these experiments over periods of at least several hours.

Since the feed gas ratios are in the fuel rich region, the reaction must be shut down by decreasing pressure in the reactor, turning off O_2 first, and then turning off fuel flow to prevent flames or explosions.

2.2. PRODUCT ANALYSIS

Product gases were analyzed by a Carle 510 gas chromatograph equipped with three columns as described previously [8,17,18]. Nitrogen was the calibration gas for mass balances in the methane and ethane oxidation processes since it is inert. The amount of water formed in the process was calculated from oxygen atom balances because of fluctuation of the size of this peak. Flow rates through the mass flow controllers were accurate to within ±0.05 standard liters per minute (slpm), carbon atom balances closed to within ±4%, and individual species concentrations were measured with a reproducibility of ±0.5%.

Since nitrogen is a product in Andrussow synthesis of HCN, it could not be used as a calibration gas to determine product gas flow rates. Instead, all carbon containing products were used as calibration by setting their sum equal to the methane flow into the reactor. Again, water production was determined from a mass balance. The hydrogen containing species mass balance closed to within ±3%.

3. Results

Conversions ($\Delta F_{\text{fuel}}/F_{\text{fuel,in}}$) and selectivities ($\nu F_{\text{product,out}}/\Delta F_{\text{fuel}}$, where F represents flow rate and ν is a stoichiometric factor) were determined from the molar flows into and exiting the reactor as described earlier [8,17,18]. Product yield is the product of conversion and selectivity.

3.1. METHANE AMMOXIDATION

Fig. 1 shows results for methane ammoxidation with increasing pressure at a constant mass flow rate of 5 slpm. Reaction was sustained autothermally at 1100°C over a Pt–10% Rh gauze catalyst consisting of three gauze layers. Superficial gas velocity at 1100°C and 1.4 atm with a 0.6 catalyst void fraction was 5.5 m/s. This

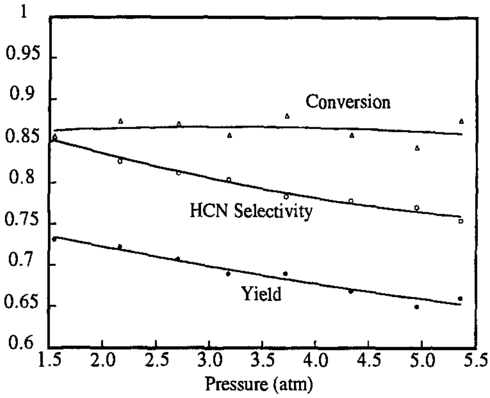

Fig. 1. Selectivity, conversion, and yield in methane ammoxidation to HCN versus pressure over a Pt/10% Rh gauze catalyst. In these experiments $CH_4/NH_3 = 1.6$, air/fuel = 3.25, and the flow rate was 5 slpm.

corresponds to a residence time across the catalyst of 1.8×10^{-4} s at 1.4 atm. Reactant gas ratios were maintained at $CH_4/NH_3 = 1.6$ and air/total fuel = 3.25, which were experimentally determined to give the largest yield of HCN.

As pressure was raised from 1.5 to 5.5 atm, selectivity to HCN decreased from 0.85 to 0.76. The conversion of NH_3 remained constant at 0.86 as pressure increased. Despite the decrease in HCN selectivity, the yield to HCN remained above 0.65 up to 5.5 atm. Because HCN is an unstable intermediate product, the downstream section of the reactor was not heated or insulated so that the partial oxidation reaction could be more quickly quenched. Since both methane and ammonia were fuels, each could be used to determine conversion and selectivity to HCN, although most industrial HCN processing sites use NH_3 conversion and HCN selectivity based on NH_3 as the standard for comparison. For these experiments, NH_3 conversion and HCN selectivity on an NH_3 basis were used.

3.2. METHANE OXIDATION

Fig. 2 compares the effects of pressure on methane oxidation in air with methane oxidation in oxygen (20% N_2 diluent). Methane was oxidized over Rh-coated 80 ppi foam monoliths at a constant mass flow rate of 5 slpm which corresponds to a gas velocity over the catalyst of 3.7 m/s and a residence time of 2.7×10^{-3} s (at 1000°C, 1.4 atm, 0.8 void fraction). For methane oxidation in air, the temperature on the catalyst surface remained near 915°C, which is about 50° below the calculated adiabatic temperature for the reaction. In these experiments, the methane to oxygen ratio was kept constant at 2 to 1 (the stoichiometric ratio to form syngas) with no preheat, and the effects of pressure on methane oxidation in air and in oxygen (20% N_2 diluent) were determined.

Fig. 2 shows that the H_2 selectivity remained constant at 0.86 as pressure

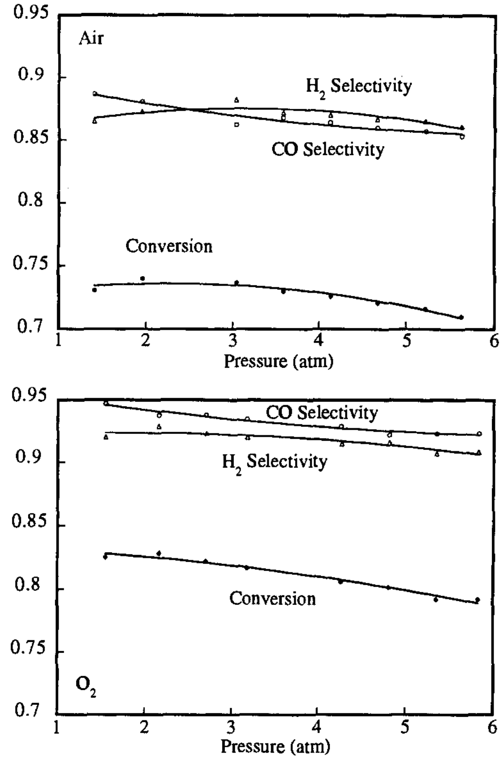

Fig. 2. Selectivity, conversion, and yield in methane oxidation in (a) air, and (b) in O_2 (with 20% N_2 diluent), versus pressure over a Rh-coated foam monolith (80 ppi). In these experiments, $CH_4/O_2 = 2$ and the flow rate was 5 slpm.

increased to 5.5 atm. The CO selectivity decreased from 0.89 to 0.85 over this pressure range, and methane conversion only changed 3% from 0.74 to 0.71 as pressure rose. The data shown was taken over a period of hours in which no signs of catalyst deactivation or carbon formation were evident.

The lower graph in fig. 2 shows results for methane oxidation in oxygen. (Nitrogen was fed at 1 slpm for calculation of a mole number change required for mass balances.) When the amount of N_2 diluent in the feed gases was reduced, selectivities to syngas increased to over 0.9, and conversion of methane increased to 0.83. The reaction temperature was only ~960°C (again about 50° below adiabatic) even though N_2 diluent was decreased substantially and methane conversion increased. This occurs because ~33% less CO_2 and H_2O formed at these conditions, so the heat evolved by these exothermic products was not felt. As pressure increased, the CO selectivity only decreased by 2% while the H_2 selectivity remained constant at 0.92. Again, after many hours of continuous operation, the catalyst did not show any signs of deactivation. Selectivities and conversions could be reproduced to within 3% for a given feed gas composition, which approaches the accuracy limit of the mass flow controllers.

3.3. ETHANE OXIDATION

Ethane was oxidized over Pt-coated 45 ppi foam monoliths at 5 slpm in the 1/2 inch i.d. stainless steel reactor with data shown in figs. 3 and 4. For this reaction, we conducted two types of experiments (1) at constant mass flow rate in air and in O_2, and (2) at constant superficial gas velocity in O_2. At 5 slpm, the gas velocity over the monolith was 5.4 m/s and the residence time was 1.9×10^{-3} s (at 1100 K, 1.4 atm, 0.4 void fraction). To maintain constant velocity, the mass flow rate was increased proportionately with pressure in order to maintain a constant velocity of 1.52 m/s over the catalyst. This velocity corresponds to a mass flow rate of 5 slpm at a pressure of 2.90 atm. The ethane to oxygen ratio was fixed at 1.7 to 1 since this has been found to give the highest selectivities to ethylene [16].

As shown in fig. 3, for ethane oxidation in air at a constant mass flow rate, the selectivity to ethylene did not change significantly with pressure. CO selectivity also remained constant while CO_2 selectivity decreased slightly. As pressure increased, the propensity to form higher molecular weight hydrocarbons increased slightly as well. The lower graph shows that conversion of ethane increased nearly

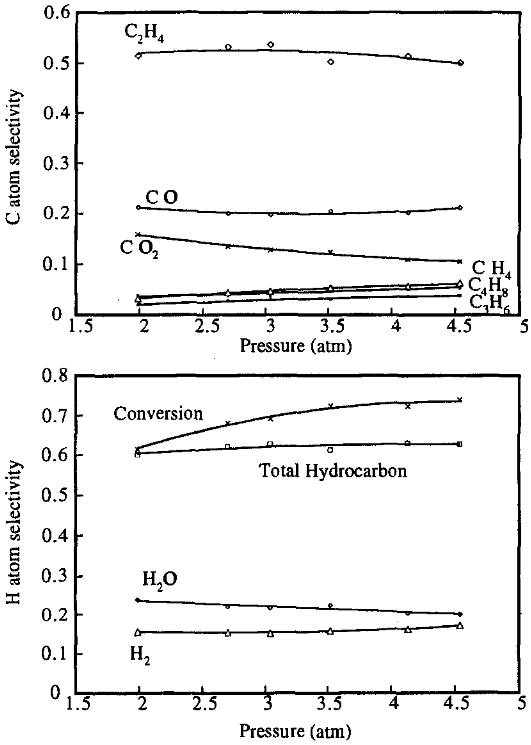

Fig. 3. Selectivity, conversion, and yield in ethane oxidation in air versus pressure over a Pt-coated foam monolith (45 ppi). In these experiments $C_2H_6/O_2 = 1.7$ and the flow rate was 5 slpm. The mass flow rate was held constant.

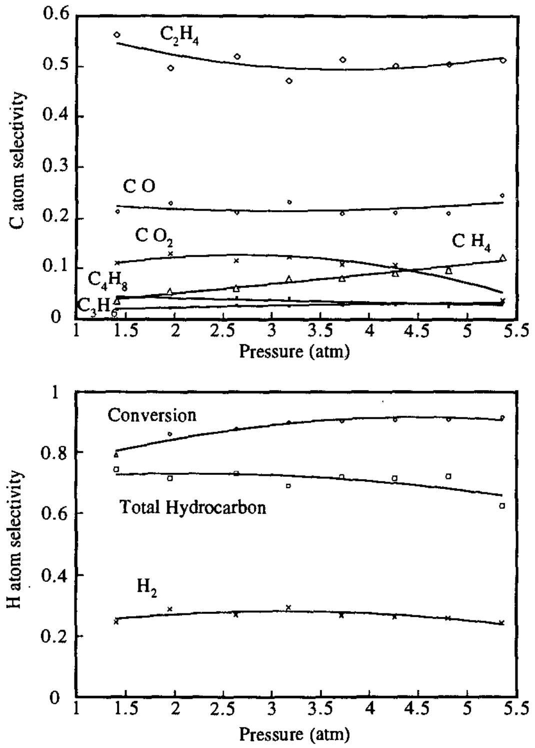

Fig. 4. Selectivity, conversion, and yield in ethane oxidation in O_2 (20% N_2 diluent) versus pressure over a Pt-coated foam monolith (45 ppi). In these experiments $C_2H_6/O_2 = 1.7$ and contact time was held constant at 6.7×10^{-3} s.

15% as pressure was raised, while selectivities to hydrocarbons, H_2, and H_2O all remained constant.

When the amount of N_2 was dropped to only 20% of the total flow, similar behavior with respect to increasing pressure occurred. Selectivity to C_2H_4 dropped slightly and then leveled around 0.54. Selectivities to other products behave as they did in the air oxidation case with the exception of CH_4 which rose more in the ethane/O_2 runs. The experiment at constant mass flow rate had to be halted, however, at 4.25 atm because of solid carbon formation blocking the pores of the catalyst causing subsequent deactivation.

From the results shown in fig. 4, C_2H_4 selectivity can be maintained above 0.50 *without any carbon formation* as pressure is increased if the superficial gas velocity and residence time over the catalyst is held constant. The conversion of C_2H_4 increases as pressure rises. At higher pressures CO_2 selectivity drops more sharply and CH_4 selectivity increases more prominently than in the constant mass flow rate cases. Selectivity to H_2 behaves as it did in the constant flow rate case, but H_2O selectivity is lower.

It is important to note that the ability to process ethane at these higher pressures is important for downstream applications. By maintaining constant velocity across the monolith, throughput of the reactor apparatus has increased by over 300% without any signs of carbon formation, catalyst deactivation or a drop in selectivity to C_2H_4.

4. Discussion

A summary of results from the three experimental systems is given in table 1.

At increased pressures, homogeneous reactions should become more prevalent, with carbon formation often as the result, especially in ethane dehydrogenation (both oxidatively and nonoxidatively). Lower velocities across the catalyst increase the thickness of the boundary layer and the residence time; both of which contribute to more chance for homogeneous reactions.

Varying pressure in a system reacting heterogeneously alters the process in several ways. Pressure affects heat and mass transfer to surfaces. It also affects contact time of gaseous species over the catalytic surfaces. Furthermore, entirely new reaction paths are possible if homogeneous reaction is allowed to occur. At low pressures and with dilution, homogeneous reactions are easily suppressed, but this becomes much more difficult as pressure is increased.

We shall consider these factors in the following sections.

Table 1
Summary of experiments

	Catalyst	Pressure (atm)	Results
methane ammoxidation	Pt–10% Rh gauze packs	1.4–5.5	HCN selectivity drops by 10%, industrially acceptable yields at higher pressures
methane oxidation	80 ppi Rh-coated foam monolith	1.4–6	no coking
	in air		CO and H_2 selectivities drop by 2%, CH_4 conversion high
	in O_2		CO and H_2 selectivities above 0.90, CH_4 conversion above 0.80
ethane oxidation	45 ppi Pt-coated foam monoliths		
	in air	1.4–4.5	no coking, C_2H_6 conversion increases, C_2H_4 selectivity constant
	in O_2 – constant mass flow rate	1.4–4.5	coking, catalyst clogged and deactivated
	in O_2 – constant gas velocity	1.4–5.5	no coking, C_2H_6 conversion increases, C_2H_4 selectivity constant

4.1. MASS AND HEAT TRANSFER

Changes in pressure affect the transport properties of gas species to the catalyst surfaces. For the catalytic systems described above, the flow through the porous monolith and gauze catalysts can be approximated as flow through small tubes. The Reynolds number for flow over these catalysts was calculated to be in a range from 5 to 20, which is well within the laminar flow region.

In foam monolith and wire gauze catalysts, the channels through the catalysts are small (450 μm for 45 ppi monoliths, 225 μm for 80 ppi monoliths, and ~100 μm for the wire gauzes) and have tortuous paths. It is important for these channels to be open ended so that desired products do not get trapped inside pores. Since the catalysts have many channels, flow through them can be approximated as flow through banks of tubes. Due to the high tortuosity in the monoliths, gases tend to see "entrance effects" over the entire catalyst, which leads to flat plate boundary layer analogies to describe molecular transport from gases in the center of channels (bulk) to the surface.

For laminar flow of gases within a tube, the mass transfer coefficient, k_m is given by the correlation

$$\frac{k_m d}{D} = 1.86\left(\frac{dv}{D}\right)^{0.8}, \tag{8}$$

where d is tube diameter, D is diffusion coefficient, and v is fluid velocity. Since both velocity over the catalyst at a constant mass flow rate and diffusion coefficient are inversely proportional to pressure, the correlation predicts that the mass transfer coefficient should vary inversely with pressure,

$$k_m = 1.86v^{0.8}\left(\frac{D}{d}\right)^{0.2} \propto \left(\frac{1}{P}\right)^{0.8}\left(\frac{1}{P}\right)^{0.2}. \tag{9}$$

When velocity is held constant, the mass transfer coefficient should therefore vary as $P^{-0.2}$.

For laminar flow in a pipe, the heat transfer coefficient, h, can be expressed as

$$\frac{hd}{k_T} = 1.86\left(\frac{\rho d v C_p}{k_T}\right)^{1/3}, \tag{10}$$

where d is pipe diameter, ρ is density, v is velocity, C_p is heat capacity, and k_T is the thermal conductivity of the fluid. At constant mass flow rate, only the gas density and velocity change appreciably with pressure (density as P, velocity as $1/P$), but their product removes any pressure dependence on the heat transfer coefficient. At constant velocity, h should vary as $P^{1/3}$.

The thickness of the boundary layer over a flat plate is proportional to the kinematic viscosity divided by the bulk fluid velocity. At constant mass flow rate, the thickness is independent of pressure. However, at constant velocity, the boundary layer thickness for this geometry should vary as $P^{-0.5}$. Thus, at these operating conditions, the transport coefficients go as $k_m \sim (1/P)^{0.2}$ and $h \sim P$, while the boundary layer thickness decreases.

At constant velocity over the catalyst, no carbon buildup was seen in ethane oxidation in oxygen over Pt. With constant velocity, the increase in mass and heat transfer to the surface across a thinner boundary layer may help inhibit carbon formation on the catalyst. Better mass transfer allows unstable products to desorb and exit the reactor, preventing surface carbon from forming. The increase in heat transfer coefficient allows better heat transfer from the surface to the gas. This increased cooling of the surface may help prevent thermodynamically stable solid carbon from forming at these high temperatures.

4.2. EFFECT OF HOMOGENEOUS REACTION

Homogeneous reactions (cracking, coking, total combustion) often plaque high pressure catalytic processes. For the three systems examined in this paper, significant homogeneous reaction would halt any high pressure processing because the catalyst would become rapidly covered with carbon and channels would be blocked. However, if homogeneous reaction were not occurring or if surface carbon removal rates are sufficiently fast, these catalytic processes show great promise for replacing current production methods.

For heterogeneous reaction inside a monolith or gauze catalyst operating at fuel rich conditions, the surface reaction rate is limited by the mass transfer rate of limiting reactant, O_2, to the surface [19,20],

$$r_s = k_M p_{O_2} \propto P^0 . \tag{11}$$

Since the mass transfer coefficient is inversely proportional to pressure and the O_2 partial pressure is directly proportional to pressure, the rate should be *independent of total pressure*. However, the reaction rate for all bimolecular homogeneous reactions is proportional to the partial pressure of each species,

$$r_h = k_r p_{fuel} p_{O_2} \propto P^2 . \tag{12}$$

An increase in pressure should cause any homogeneous reactions occurring at lower pressures to become much more important with $r_s/r_h \propto P^{-2}$. This is, of course, a simplification of the many free radical chain reactions in any homogeneous combustion process, but it should describe overall rates qualitatively.

Fig. 5a is a simplified sketch of a single monolith or gauze channel. The porous channel is drawn as a straight channel with geometry affecting mass and heat transfer rate across a boundary layer of thickness δ at the walls. Figs. 5b and 5c show likely concentration profiles of fuel, O_2, and free radicals, such as OH·, as a function of radial (r) and axial (z) position along the monolith or gauze channel. The figures depict a lumped model in which reactants at constant partial pressure must

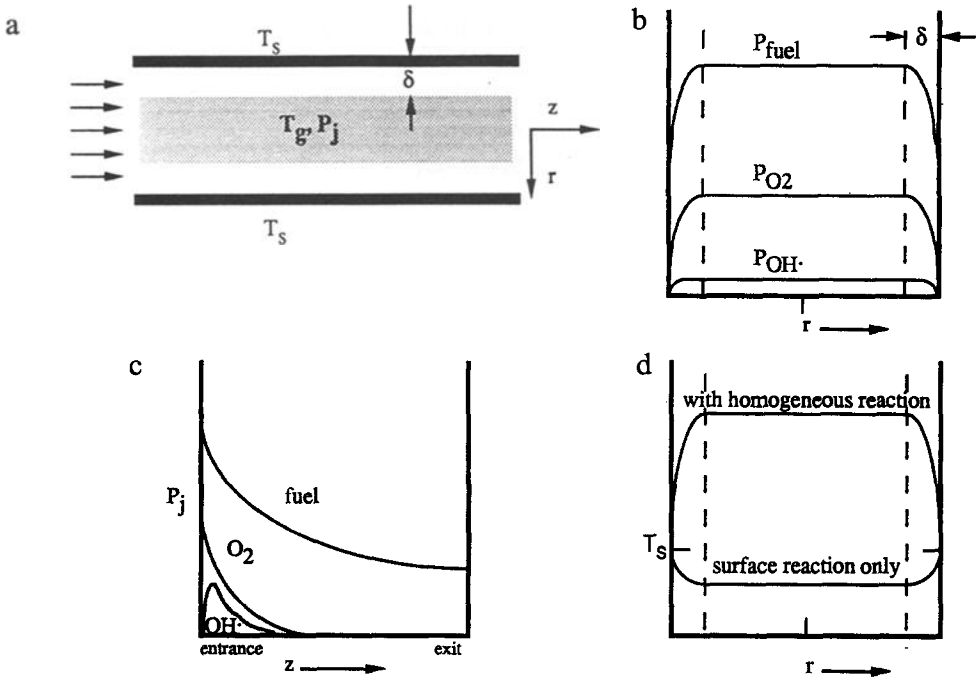

Fig. 5. (a) Simplified channel geometry. (b) Radial concentration profiles inside a monolith or gauze channel. (c) Axial concentration profiles inside a monolith or gauze channel. (d) Radial temperature profiles inside a monolith or gauze channel.

diffuse through a boundary layer of thickness δ above the surface for heterogeneous reaction to occur. The oxygen concentration falls to nearly zero very quickly ($<10^{-4}$ s) on the catalyst surface in a very short distance inside the catalyst due to fast reaction. Free radical concentrations (e.g. OH·) will be larger near the center of the channels since the walls serve as a sink for free radical species. Homogeneous reaction should only occur significantly when free radical species and the temperature in the center section are large enough to sustain chain reactions.

Fig. 5d shows likely temperature profiles for purely heterogeneous reaction and for heterogeneous plus homogeneous reaction as a function of radial position in the channel. When only surface reaction occurs, the temperature in the center of the channel would be lower than the surface temperature. However, homogeneous reaction increases the temperature in the center of the channel while the wall acts as a temperature sink.

As pressure is increased at a constant mass flow rate, the mass transfer coefficient decreases inversely with pressure, allowing free radical species to build up in the centers of catalyst channels, making homogeneous reaction more likely. The heat transfer coefficient does not change much with pressure, so any heat produced by increased homogeneous reactions will be transported away from the center less efficiently, again increasing the potential for homogeneous reaction.

As pressure is increased at constant velocity, the mass transfer coefficient decreases weakly with increasing pressure $P^{-0.2}$ causing a slower buildup of free radicals near the centers of the channels. Furthermore, the heat transfer coefficient increases with pressure as $P^{1/3}$ so heat can be removed from the centers of the channels more effectively. Both of these effects decrease the potential for homogeneous reactions.

For HCN production over the Pt/10% Rh gauze, the hydrolysis of HCN,

$$HCN + H_2O \rightarrow NH_3 + CO\,, \tag{13}$$

can occur homogeneously as well as heterogeneously, reducing selectivity to HCN. As the pressure is raised, the increased importance of this homogeneous reaction may explain the slight drop in HCN selectivity shown in fig. 1.

For the production of synthesis gas from methane, a mechanism has been proposed in which CH_4 first pyrolyzes on the catalyst surface to adsorbed C and H atoms [20]. Surface hydrogen atoms then combine and desorb. Next, surface carbon reacts with adsorbed O atoms to form CO, and the surface CO species readily desorb favoring CO over CO_2. This combined with a large activation energy barrier for formation of surface hydroxyl species on Rh inhibits the formation of H_2O and allows for very high selectivities to H_2 and CO [21]. Since product selectivities do not change significantly as pressure rises, homogeneous reactions do not interfere with the surface pyrolysis mechanism, allowing for high selectivities at high pressures.

The surface mechanism proposed for the production of ethylene consists of gaseous ethane reacting with adsorbed O atoms or with adsorbed OH groups to first form adsorbed ethyl (C_2H_5) and water. Next, the adsorbed C_2H_5 undergoes a β-hydrogen elimination to form gaseous C_2H_4. If the α-hydrogen were eliminated from C_2H_5, this would lead to adsorbed species that should preferentially form syngas ($CO + H_2$) or coke rather than C_2H_4. On metals other than Pt, such as Rh and Pd, syngas and coke formation occur.

As long as a high enough velocity is sustained, the fact that coking does not occur as pressure is increased is evidence that ethylene is not formed through a free radical homogeneous process. If it were, we should see carbon formation at higher pressures since homogeneous reaction rates are faster. These experiments show that on Pt-coated monoliths, C_2H_4 may be formed through the surface mechanism presented above.

5. Summary

High pressure catalytic partial oxidation at very short contact times over monolith and gauze catalysts is feasible for the three systems described above. These experiments show that high pressure operation is possible, but even higher pressure experiments are needed to fully test the processes to ensure that homogeneous reactions do not become important and selectivities to desired products do not drop substantially. Higher velocity conditions are probably essential to maintain short contact times and eliminate homogeneous reactions and carbon formation.

Since selectivities did not change dramatically with pressure, formation of partial oxidation products apparently proceeds primarily through heterogeneous paths. High velocities across the catalysts increase mass and heat transfer, which serves to decrease homogeneous reactions. Catalyst geometry may also be an important factor in preventing homogeneous reaction since the catalyst provides small channels with high heat and mass transfer and small boundary layers.

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